# JOURNAL AND PROCEEDINGS

OF THE

# ROYAL SOCIETY

## OF NEW SOUTH WALES

FOR

**1952**

(INCORPORATED 1881)

---



## VOLUME LXXXVI

**Parts I-IV**

---

EDITED BY

IDA A. BROWNE, D.Sc.

*Honorary Editorial Secretary*

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THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN

SYDNEY
PUBLISHED BY THE SOCIETY, SCIENCE HOUSE
GLOUCESTER AND ESSEX STREETS

Issued as a complete volume, April, 14 1953

CONTENTS

# VOLUME LXXXVI

## Part I*


| | Page |
|---|---|
| Title Page .. .. .. .. .. .. .. .. .. .. .. | i |
| Officers for 1952–1953 .. .. .. .. .. .. .. .. .. | iii |
| Notices .. .. .. .. .. .. .. .. .. .. .. .. | iv |
| List of Members .. .. .. .. .. .. .. .. .. .. | v |
| Awards .. .. .. .. .. .. .. .. .. .. .. .. | vi |
| Annual Report of Council .. .. .. .. .. .. .. .. .. | vii |
| Balance Sheet .. .. .. .. .. .. .. .. .. .. .. | x |
| Report of Section of Geology .. .. .. .. .. .. .. .. | xiii |
| Obituary .. .. .. .. .. .. .. .. .. .. .. .. | xv |
| Art. I.—Presidential Address. By R. C. L. Bosworth— | |
| General .. .. .. .. .. .. .. .. .. .. .. | 1 |
| Transport Problems in Applied Chemistry .. .. .. .. .. .. | 3 |
| Art. II.—A Geological Account of Heard Island. By A. J. Lambeth .. .. .. | 14 |
| Art. III.—Occultations Observed at Sydney Observatory during 1951. By W. H. Robertson and K. P. Sims .. .. .. .. .. .. .. .. | 20 |


## Part II†


| | |
|---|---|
| Art. IV.—Climate and Maize Yields on the Atherton Tableland. By D. S. Simonett and N. T. Drane .. .. .. .. .. .. .. .. .. .. | 22 |
| Art. V.—Palladium Complexes. Part V. Reactions of Palladium Compounds with 2 : 2′ Dipyridyl. By S. E. Livingstone .. .. .. .. .. .. .. | 32 |
| Art. VI.—Liversidge Lecture. Electron Diffraction in the Chemistry of the Solid State. By A. L. G. Rees .. .. .. .. .. .. .. .. .. | 38 |
| Art. VII.—Permian Spirifers from Tasmania. By Ida A. Brown .. .. .. | 55 |



* Published October 10, 1952.
† Published January 21, 1953.

CONTENTS

## Part III*

ART. VIII.—Induced Optical Activity of the Tris-1 : 10-Phenanthroline and Tris-2 : 2′-Dipyridyl Copper II Ion. By N. R. Davies and F. P. Dwyer .. .. .. 64

ART. IX.—Soil Horizons and Marine Bands in the Coastal Limestones of Western Australia. By R. W. Fairbridge and C. Teichert .. .. .. .. .. 68

## Part IV†

ART. X.—A Contribution to the Geology and Glaciology of the Snowy Mountains. By A. S. Ritchie .. .. .. .. .. .. .. .. .. .. 88

ART. XI.—Graptolite Zones and Associated Stratigraphy at Four-Mile Creek, South-west of Orange, N.S.W. By N. C. Stevens and G. H. Packham .. .. .. 94

ART. XII.—Martiniopsis Waagen from the Salt Range, India. By Ida A. Brown .. 100

ART. XIII.—Contributions to a Study of the Marulan Batholith. Part II. The Granodiorite-Quartz Porphyrite Hybrids. By G. D. Osborne and J. S. Lovering .. 108

ART. XIV.—The Replacement of Crinoid Stems and Gastropods by Cassiterite at Emmaville, New South Wales. By L. J. Lawrence .. .. .. .. .. .. 119

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*ISSUED OCTOBER 10, 1952*

VOL. LXXXVI PART I

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## OF NEW SOUTH WALES

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1952

(INCORPORATED 1881)

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## PART I

OF

## VOL. LXXXVI

**Containing Report of Council, Balance Sheet, Presidential Address and Papers read in April and May, 1952.**

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EDITED BY

IDA A. BROWNE, D.Sc.

*Honorary Editorial Secretary*

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SYDNEY
PUBLISHED BY THE SOCIETY, SCIENCE HOUSE
GLOUCESTER AND ESSEX STREETS

1952

CONTENTS

# VOLUME LXXXVI

## Part I


| | Page |
|---|---|
| Title Page .. .. .. .. .. .. .. .. .. .. .. | i |
| Officers for 1952–1953 .. .. .. .. .. .. .. .. .. | iii |
| Notices .. .. .. .. .. .. .. .. .. .. .. .. | iv |
| List of Members .. .. .. .. .. .. .. .. .. .. | v |
| Awards .. .. .. .. .. .. .. .. .. .. .. .. | vi |
| Annual Report of Council .. .. .. .. .. .. .. .. .. | vii |
| Balance Sheet .. .. .. .. .. .. .. .. .. .. .. | x |
| Report of Section of Geology .. .. .. .. .. .. .. .. | xiii |
| Obituary .. .. .. .. .. .. .. .. .. .. .. .. | xv |
| Art. I.—Presidential Address. By R. C. L. Bosworth— | |
| General .. .. .. .. .. .. .. .. .. .. .. | 1 |
| Transport Problems in Applied Chemistry .. .. .. .. .. .. | 3 |
| Art. II.—A Geological Account of Heard Island. By A. J. Lambeth .. .. | 14 |
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A

# Royal Society of New South Wales

## OFFICERS FOR 1952-1953

**Patrons:**

His Excellency the Governor-General of the Commonwealth of Australia
The Rt. Hon. Sir William J. McKELL, G.C.M.G., P.C., Q.C., LL.D.

His Excellency the Governor of New South Wales,
Lieutenant-General Sir JOHN NORTHCOTT, K.C.M.G., C.B., M.V.O., D.Litt.

**President:**

C. J. MAGEE, D.Sc.Agr. (*Syd.*), M.Sc. (*Wis.*).

**Vice-Presidents:**

R. C. L. BOSWORTH, M.Sc., D.Sc. (*Adel.*), Ph.D. (*Camb.*), F.A.C.I., F.Inst.P.
D. J. K. O'CONNELL, S.J., D.Sc., Ph.D., F.R.A.S.
PHYLLIS M. ROUNTREE, D.Sc. (*Melb.*), Dip.Bact. (*Lond.*).
W. B. SMITH-WHITE, M.A. (*Cantab.*), B.Sc. (*Syd.*).

**Honorary Secretaries:**

IDA A. BROWNE, D.Sc.
K. E. BULLEN, M.A., Sc.D., F.R.S.

**Honorary Treasurer:**

H. A. J. DONEGAN, A.S.T.C., A.A.C.I.

**Members of Council:**

J. P. BAXTER, B.Sc., Ph.D., A.M.I.Chem.E.
G. BOSSON, M.Sc. (*Lond.*).
H. B. CARTER, B.V.Sc.
N. A. GIBSON, M.Sc., A.R.I.C.
T. IREDALE, D.Sc., F.R.I.C.
A. V. JOPLING, B.Sc., B.E.
F. D. McCARTHY, Dip.Anthr.
P. R. McMAHON, M.Agr.Sc. (*N.Z.*), Ph.D. (*Leeds*), A.R.I.C., A.N.Z.I.C.
C. E. MARSHALL, Ph.D., D.Sc.
G. D. OSBORNE, D.Sc. (*Syd.*), Ph.D. (*Camb.*), F.G.S.

## NOTICE.

The Royal Society of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society", by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

## TO AUTHORS.

Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the "Guide to Authors", which is obtainable on application to the Honorary Secretaries of the Society.

## FORM OF BEQUEST.

**I bequeath** the sum of £ to the Royal Society of New South Wales, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[*Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies are recommended to instruct their Solicitors to adopt the above Form of Bequest.*]

The volumes of the *Journal and Proceedings* may be obtained at the Society's Rooms, Science House, Gloucester Street, Sydney.

| | | | | |
|---|---|---|---|---|
| Volumes | XI | to | LIII | (that is to 1919) |
| ,, | LIV | ,, | LXVI | (1920 to 1932) |
| ,, | LXVIII | | | (1936) |
| ,, | LXX | ,, | LXXXII | (1938 to 1948) |
| ,, | LXXXIII | and | LXXXIV | |

Volumes I to X (to 1876) and LXVII and LXIX (1935 and 1937) are out of print.

Reprints of papers are available.

## LIST OF MEMBERS.

A list of members of the Royal Society of New South Wales up to 1st April, 1951, is included in Volume LXXXV.

During the year ended 31st March, 1952, the following have been elected to membership of the Society :

Banks, Maxwell Robert, B.Sc.(Hons.), Lecturer in Geology, University of Tasmania, Hobart, Tas.
Basden, Kenneth Spencer, A.S.T.C., Technical Officer, Department of Mining and Applied Geology, N.S.W. University of Technology, Broadway, Sydney.
Booker, Frederick William, M.Sc., c/o Geological Survey of New South Wales, Mines Department Sydney.
Bosson, Geoffrey, M.Sc. (*Lond.*), Professor of Mathematics, N.S.W. University of Technology, Broadway, Sydney.
Charlwood, Joan Marie, B.Sc., Biochemist, 184 Queen-street, Concord West.
Crane, Roslyn Ann, B.Sc., Librarian, Australian Leather Research ; p.r. 6 Chesterfield-road, Epping.
Darvall, Anthony Roger, M.B., B.S., D.O., Medical Practitioner, Royal Prince Alfred Hospital, Missenden-road, Camperdown.
Dunn, Thomas Melanby, B.Sc.(Hons.), Chemistry Department, University of Sydney, Sydney.
French, Oswald Raymond, Research Assistant, University of Sydney ; p.r. 66 Nottinghill-road, Lidcombe.
Goldstone, Charles Lillington, B.Agr.Sc. (*N.Z.*), Lecturer in Sheep Husbandry, N.S.W. University of Technology, c/o East Sydney Technical College, Darlinghurst.
Heard, George Douglas, B.Sc., Maitland Boys' High School, East Maitland, N.S.W.
Holmes, Robert Francis, 15 Baden-street, Coogee.
Jamieson, Helen Campbell, A.S.T.C. ; p.r. 3 Hamilton-street, Coogee.
Johnson, William, Geologist, c/o The Supervising Engineer, Warragamba Dam, N.S.W.
Jones, Roger M., Laboratory Assistant, Sydney Technical College ; p.r. 69 Moore Park-road, Centennial Park.
Lawrence, Laurence James, B.Sc.(Hons.), Lecturer in Geology, N.S.W. University of Technology ; p.r. 28 Church-street, Ashfield.
Livingstone, Stanley Edward, A.S.T.C.(Hons.), A.A.C.I., Lecturer in Inorganic Chemistry, N.S.W. University of Technology ; p.r. 5 Parker-street, Rockdale.
Lovering, John Francis, B.Sc., Assistant Curator, Department of Mineralogy and Petrology, Australian Museum, College-street, Sydney.
Mallaby, Hedley Arnold, B.Sc.(For.), Dip.For. (*Canberra*), 114 Kurrajong-avenue, Leeton.
Males, Pamela Ann, 81 Frederick-street, St. Peters.
Minty, Edward James, B.Sc., 2 Drayton Court, Mosman-street, Mosman Bay.
Murray, James Kenneth, B.Sc., 237 South-road, Broken Hill, N.S.W.
O'Dea, Daryl Robert, A.S.T.C. ; p.r. 123 Perouse-road, Randwick.
Packham, Gordon Howard, 61 Earlwood-avenue, Earlwood.
Rector, John, B.Sc., 46 Sir Thomas Mitchell-road, Bondi Beach.
Robinson, David Hugh, A.S.T.C., Chemist, 21 Dudley-avenue, Roseville.
Sellgren, Elise Evelyn, B.Sc., Teaching Fellow, Department of Geology, The University of Sydney ; p.r. 76 Bream-street, Coogee.
Stevens, Robert Denzil, 32 Menangle-road, Camden.
Stuntz, John, B.Sc., 511 Burwood-road, Belmore.
Weatherhead, Albert Victor, F.R.M.S., F.R.P.S., Technical Officer, Geology Department, N.S.W. University of Technology ; p.r. 3 Kennedy-avenue, Belmore.
Whitley, Alice, B.Sc., Teacher, 39 Belmore-street, Burwood.
Whitworth, Horace Francis, M.Sc., Mining Museum, Sydney.

### *Honorary Member.*

Fairley, Sir Neil Hamilton, C.B.E., M.D., D.Sc., F.R.S., 73 Harley-street, London, W.1.

### *Obituary.*

1916 Septimus Birrell.
1913 Edwin Cheel.
1916 Henry James Hoggan.
1909 Thomas Harvey Johnston (Corresponding member since 1912).
1930 William Percy Judd.
1915 Andrew Gibb Maitland (an Honorary member).

## AWARDS.

*The Clarke Medal.*

1951 Stillwell, Frank L., D.SC., C.S.I.R.O., Melbourne.

*The James Cook Medal.*

1951 Gregg, Norman McAlister, M.B., B.S., Macquarie Street, Sydney.

*The Edgeworth David Medal.*

1951 Bolton, John Gatenby, B.A., Division of Radiophysics, C.S.I.R.O., Sydney.

*The Society's Medal.*

1951 Penfold, Arthur Ramon, F.R.A.C.I., F.C.S., Director, Museum of Applied Arts and Sciences, Sydney.

# Royal Society of New South Wales

REPORT OF THE COUNCIL FOR THE YEAR ENDING 31st MARCH, 1952.
Presented at the Annual and General Monthly Meeting of the Society, 2nd April, 1952, in accordance with Rule XXVI.

The membership of the Society at the end of the period under review stood at 385, an increase of 16. Thirty-five new members were elected during the year and 13 members were lost by resignation. Six members have been lost to the Society by death during the year 1951 :

Septimus Birrell (elected 1916),
Edwin Cheel (elected 1913),
Henry James Hoggan (elected 1916),
Thomas Harvey Johnston (elected 1909) (Corresponding member since 1912),
William Percy Judd (elected 1930), and
Andrew Gibb Maitland (elected 1915), an Honorary member, died in January, 1951.

During the year nine General Monthly Meetings were held, at which the average attendance was thirty-six. Nineteen papers were accepted for reading and publication by the Society, twelve less than the previous year.

An Exhibit, " Bananas containing Seeds ", was discussed by Dr. C. J. Magee at the meeting on 6th June, 1951.

Lecturettes given during the year were as follow :

2nd May, 1951 : " Colloids ", by Prof. A. E. Alexander.

4th July, 1951 : " Polyploiedy and Evolution ", by Mr. S. Smith-White.

Addresses of general interest were given at several meetings.

6th June, 1951 : The evening was devoted to a discussion on " Fluorine ", and the following speakers gave addresses :

Prof. J. P. Baxter : " New Derivatives of Fluorine."

Mr. H. R. Sulliven : " Some Biological Aspects of Fluorine."

Dr. D. L. Ingles : " Defluorination of Artesian Waters."

5th December, 1951 : Mr. G. G. Blake spoke on " Xerographic Processes " and Dr. G. D. Osborne and Mr. J. S. Proud showed " Coloured Slides of Central Australia, mostly of a Geological Interest ".

*Question.*—At the meeting held on the 4th July, 1951, Mr. H. W. Wood answered the question " How many Star Systems are known ? "

The meeting held on the 1st August, 1951, was devoted to a Symposium on " Temperature ", at which the following addresses were given :

" The International Temperature Scale in Science and Industry ", by Mr. W. R. G. Kemp.

" Some Physiological Aspects of Temperature ", by Prof. F. S. Cotton.

" Vulcanological Aspects ", by Dr. G. D. Osborne.

" The Temperature of the Earth's Interior ", by Prof. K. E. Bullen.

A Film Evening was held on 3rd October, 1951, and, through the courtesy of the Australian Museum, Prof. A. P. Elkin and the Motion Picture Division of the U.S. Information Service, three films were shown :

(*a*) " Two Hundred and Fifty Million Years Ago."

(*b*) " Arnhem Land Dances."

(*c*) " The Story of Palomar."

The meeting devoted to the commemoration of great scientists was held on 7th November, 1951. The following addresses were given :

" William Harvey and the Circulation of the Blood ", by Prof. E. Ford.

" Linnæus ", by Prof. L. G. M. Baas Becking.

" What Science Owes to the 1851 Exhibition ", by Dr. T. Iredale.

Five Popular Science Lectures were delivered during the year, and were appreciated by members of the Society and the public :

17th May : " Wool ", by Dr. P. R. McMahon.

19th July : " Science, Medicine and Health in the Twentieth Century ", by Prof. Harvey Sutton.

16th August : " Shore Fluctuations : Their Causes and Effects ", by Dr. W. R. Browne.

20th September : " Chemical Discovery and Invention through the Last Half Century ", by Prof. R. J. W. Le Fevre.

18th October : " Seismology ", by Rev. D. J. K. O'Connell.

*Jubilee Conversazione.*—To commemorate the Jubilee of the Commonwealth of Australia, our Society, collaborating with other scientific bodies, organized a conversazione, which was held in the Great Hall of the University of Sydney on 18th April, 1951. This successful and well attended function was arranged to illustrate the scientific achievements of Australia during the last fifty years.

The Annual Dinner of the Society was held in the Withdrawing Room of the Union, University of Sydney, on the 27th March, 1952. There were present fifty-five members and friends.

The Section of Geology, whose Chairman was Mr. R. O. Chalmers and Hon. Secretary Mr. N. C. Stevens, held eight meetings during the year, at which the average attendance was eighteen members and six visitors. The activities included the showing of films, exhibits, notes and lecturettes.

The Council of the Society held eleven ordinary meetings during the year, at which the average attendance was twelve.

On Science House Management Committee the Society was represented by Mr. F. R. Morrison and Mr. H. O. Fletcher ; substitute representatives, Dr. R. L. Aston and Mr. H. H. Thorne.

On Science House Extension Committee the Society was represented by Dr. R. C. L. Bosworth and Dr. C. J. Magee.

Sir Neil Hamilton Fairley was elected an Honorary Member of the Society at the Annual and General Monthly Meeting held on the 4th April, 1951.

The Clarke Memorial Lecture for 1951 was delivered by Dr. A. B. Edwards on the 21st June, 1951, the title being " The Ore Minerals and their Textures ".

The Clarke Memorial Medal for 1952 was awarded to Professor J. G. Wood, of the University of Adelaide, for his distinguished work both on the vegetation of arid Australia and on mineral nutrition and metabolism in plants.

The Medal of the Royal Society of New South Wales for 1951 was awarded to Mr. A. R. Penfold in recognition of his outstanding services to the Society and his valuable researches in the chemistry of essential oils.

The Edgeworth David Medal for 1951 was awarded to Mr. J. G. Bolton for his outstanding researches in the field of radio-astronomy.

The James Cook Medal for 1951 was awarded to Dr. N. McAlister Gregg for distinguished contributions to medical science, particularly the discovery of, and work on, the connection between congenital defects in children and the occurrence of Rubella in the mother during pregnancy.

During the year overseas visiting scientists entertained by the Council were :

Sir Edward and Lady Mellanby, on 21st September.

The scientific members of the Danish " Galathea " Deep Sea Expedition, on 22nd November.

Sir Neil Hamilton Fairley, F.R.S., on 22nd November.

The financial position of the Society, as disclosed by the annual audit, is not a satisfactory one. The deficit for the year is £736, as compared with the previous year of £687. The largest increase in a single item of expenditure was £203 for salaries.

Although the Council has been applying rigid standards and fewer papers are being accepted for publication, the cost per page of printing the Journal and Proceedings has increased still further, and meeting this charge must remain one of our most serious problems.

At the General Monthly Meeting of 3rd October, 1951, Rule IX was altered to read : " The Annual Subscription shall be three guineas payable in advance, but members who are under twenty-eight years of age shall be required to pay only one and a half guineas.

" The amount of thirty-five guineas may be paid at any one time by a financial member as a life composition for the ordinary annual payment."

The Society's share of the profits from Science House for the year was £430, a decrease of £20 on the previous year.

The grant from the Government of New South Wales of £400 has been received. The continued interest of the Government in the work of the Society is much appreciated.

*The Library.*—The amount of £60 16s. 6d. has been spent on the purchase of periodicals, and £17 8s. 6d. on binding.

Exchange of publications is maintained with 417 societies and institutions, an increase of 11.

The number of accessions entered in the catalogue during the year ended 29th February, 1952, was 3,392 parts of periodicals.

The number of books, periodicals, etc., borrowed by members, institutions and accredited readers was 316.

Among the institutions which made use of the library through the inter-library borrowing scheme were : National Standards and Radiophysics Laboratories ; Waite Agricultural Research Institute ; Royal Society of Tasmania ; Fisher Library ; Colonial Sugar Refinery ; McMaster Laboratory ; Sydney Technical College ; Public Library of Victoria ; Forestry Commission, N.S.W. ; Sydney Hospital Library ; Department of Mines, Victoria ; Department of Health, N.S.W. ; Department of Public Works, N.S.W. ; University of Adelaide ; Department of Wood Technology ; Food Preservation Laboratory, Homebush ; New England University College ; C.S.I.R.O. Irrigation Research Station ; Standard Telephones and Cables ; Department of Agriculture, N.S.W. ; Bureau of Mineral Resources ; M.W.S. and D. Board, N.S.W. ; Institution of Engineers, Australia ; C.S.I.R.O. Division of Industrial Chemistry ; C.S.I.R.O. Division of Fisheries ; Geological Museum and Library, Melbourne ; Snowy Mountains Hydro-Electric Authority ; Taubman's Ltd. ; C.S.I.R.O. Division of Entomology ; State Fisheries Laboratory ; University of Melbourne ; Standards Association of Australia ; Granville Technical College ; Australian Museum ; Botanic Gardens, Sydney ; Queensland Institute of Medical Research ; Glenfield Veterinary Research Station ; Commonwealth Observatory ; Newcastle Technical College.

R. C. L. BOSWORTH,
President.

## THE ROYAL SOCIETY OF NEW SOUTH WALES.

## BALANCE SHEET AS AT 29th FEBRUARY, 1952.

LIABILITIES.

| 1951. | | 1952. | | | | | |
|---|---|---|---|---|---|---|---|
| £ | | £ | s. | d. | £ | s. | d. |
| 275 | Accrued Expenses .. .. .. .. .. | | | | 269 | 11 | 9 |
| 36 | Subscriptions Paid in Advance .. .. .. | | | | 22 | 11 | 6 |
| 98 | Life Members' Subscriptions — Amount carried forward .. .. .. .. .. .. | | | | 113 | 11 | 0 |
| | Trust and Monograph Capital Funds (detailed below)— | | | | | | |
| | Clarke Memorial .. .. .. .. .. | 1,941 | 16 | 9 | | | |
| | Walter Burfitt Prize .. .. .. .. | 1,081 | 16 | 8 | | | |
| | Liversidge Bequest .. .. .. .. .. | 744 | 5 | 1 | | | |
| | Monograph Capital Fund .. .. .. .. | 3,659 | 18 | 4 | | | |
| 7,507 | | | | | 7,427 | 16 | 10 |
| 24,886 | ACCUMULATED FUNDS .. .. .. .. .. | | | | 24,088 | 1 | 2 |
| £32,802 | | | | | £31,921 | 12 | 3 |

ASSETS.

| 1951. | | 1952. | | | | | |
|---|---|---|---|---|---|---|---|
| £ | | £ | s. | d. | £ | s. | d. |
| 634 | Cash at Bank and in Hand .. .. .. .. .. .. | | | | 572 | 9 | 11 |
| | Investments—Commonwealth Bonds and Inscribed Stock, etc.—at Face Value— | | | | | | |
| | Held for— | | | | | | |
| | Clarke Memorial Fund .. .. .. .. | 1,800 | 0 | 0 | | | |
| | Walter Burfitt Prize Fund .. .. .. .. | 1,000 | 0 | 0 | | | |
| | Liversidge Bequest .. .. .. .. .. | 700 | 0 | 0 | | | |
| | Monograph Capital Fund .. .. .. .. | 3,000 | 0 | 0 | | | |
| | General Purposes .. .. .. .. .. | 2,860 | 0 | 0 | | | |
| 10,160 | | | | | 9,360 | 0 | 0 |
| | Debtors for Subscriptions .. .. .. .. .. | 102 | 7 | 6 | | | |
| — | *Deduct* Reserve for Bad Debts .. .. .. | 102 | 7 | 6 | | | |
| | | | | | — | | |
| 14,835 | Science House—One-third Capital Cost .. .. .. | | | | 14,835 | 4 | 4 |
| 6,800 | Library—At Valuation .. .. .. .. .. | | | | 6,800 | 0 | 0 |
| 342 | Furniture—At Cost—*less* Depreciation .. .. .. | | | | 324 | 18 | 0 |
| 25 | Pictures—At Cost—*less* Depreciation .. .. .. | | | | 24 | 0 | 0 |
| 6 | Lantern—At Cost—*less* Depreciation .. .. .. | | | | 5 | 0 | 0 |
| £32,802 | | | | | £31,921 | 12 | 3 |

## TRUST AND MONOGRAPH CAPITAL FUNDS.

| | Clarke Memorial. £ s. d. | Walter Burfitt Prize. £ s. d. | Liversidge Bequest. £ s. d. | Monograph Capital Fund. £ s. d. |
|---|---|---|---|---|
| Capital at 28th February, 1951 .. | 1,800 0 0 | 1,000 0 0 | 700 0 0 | 3,000 0 0 |
| Revenue— | | | | |
| Balance at 28th February, 1951 | 126 2 10 | 126 10 11 | 21 18 9 | 733 0 6 |
| Interest for Twelve Months .. | 57 7 10 | 31 17 4 | 22 6 4 | 95 12 10 |
| | 183 10 8 | 158 8 3 | 44 5 1 | 828 13 4 |
| *Deduct* Expenditure .. .. | 41 13 11 | 76 11 7 | — | 168 15 0 |
| Balance at 29th February, 1952 .. | £141 16 9 | £81 16 8 | £44 5 1 | £659 18 4 |

## ACCUMULATED FUNDS.

| | | £ s. d. |
|---|---|---|
| Balance at 28th February, 1951 .. .. .. | | 24,886 2 9 |
| *Less*— | | |
| Increase in Reserve for Bad Debts .. .. .. .. | £44 1 0 | |
| Loss on Sale of Inscribed Stock | 15 17 6 | |
| Deficit for twelve months (as shown by Income and Expenditure Account) .. | 736 1 1 | |
| Bad Debts written off .. | 2 2 0 | |
| | | 798 1 7 |
| | | £24,088 1 2 |

The above Balance Sheet has been prepared from the Books of Account, Accounts and Vouchers of the Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 29th February, 1952, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,
Chartered Accountants.

Prudential Building,
39 Martin Place,
Sydney, 18th March, 1952.

## INCOME AND EXPENDITURE ACCOUNT,

### 1st March, 1951, to 25th February, 1952.

| 1950-1. | | 1951-52. | | | | | |
|---|---|---|---|---|---|---|---|
| £ | | £ | s. | d. | £ | s. | d. |
| | To Annual Dinner— | | | | | | |
| | Expenditure .. .. .. .. .. .. | 83 | 6 | 3 | | | |
| 13 | *Less* Received .. .. .. .. .. | 63 | 8 | 6 | | | |
| | | | | | 19 | 17 | 9 |
| 31 | ,, Audit.. .. .. .. .. .. .. .. | | | | 31 | 10 | 0 |
| 36 | ,, Cleaning .. .. .. .. .. .. .. | | | | 41 | 7 | 8 |
| 20 | ,, Depreciation .. .. .. .. .. .. | | | | 19 | 2 | 0 |
| 13 | ,, Electricity .. .. .. .. .. .. .. | | | | 11 | 3 | 3 |
| 4 | ,, Entertainment Expenses .. .. .. .. .. | | | | 6 | 4 | 8 |
| 24 | ,, Insurance .. .. .. .. .. .. .. | | | | 12 | 9 | 6 |
| 199 | ,, Library Purchases and Binding .. .. .. .. | | | | 65 | 10 | 7 |
| 109 | ,, Miscellaneous .. .. .. .. .. .. | | | | 100 | 4 | 2 |
| 78 | ,, Postage and Telegrams .. .. .. .. .. | | | | 75 | 16 | 3 |
| | ,, Printing and Binding Journal—Vol. 84 .. .. | 829 | 14 | 9 | | | |
| 921 | *Less* Received .. .. .. .. .. .. | 75 | 0 | 0 | | | |
| | | | | | 754 | 14 | 9 |
| 117 | ,, Printing—General .. .. .. .. .. .. | | | | 145 | 3 | 0 |
| 59 | ,, Rent—Science House Management Committee .. | | | | 107 | 8 | 8 |
| | ,, Reprints— | | | | | | |
| | Expenditure .. .. .. .. .. .. | 380 | 12 | 0 | | | |
| 141 | *Less* Received .. .. .. .. .. | 252 | 9 | 4 | | | |
| | | | | | 128 | 2 | 8 |
| 579 | ,, Salaries .. .. .. .. .. .. .. | | | | 782 | 9 | 7 |
| 21 | ,, Telephone .. .. .. .. .. .. .. | | | | 24 | 12 | 0 |
| £2,365 | | | | | £2,325 | 16 | 6 |

| 1950-1. | | 1951-52. | | |
|---|---|---|---|---|
| £ | | £ | s. | d. |
| 624 | By Membership Subscriptions .. .. .. .. .. .. .. | 632 | 12 | 6 |
| 9 | ,, Proportion of Life Members' Subscriptions .. .. .. .. | 10 | 10 | 0 |
| 400 | ,, Government Subsidy .. .. .. .. .. .. .. | 400 | 0 | 0 |
| 450 | ,, Science House—Share of Surplus .. .. .. .. .. | 430 | 0 | 0 |
| 183 | ,, Interest on General Investments .. .. .. .. .. | 116 | 12 | 11 |
| 12 | ,, Other Receipts .. .. .. .. .. .. .. .. | — | | |
| 1,678 | | 1,589 | 15 | 5 |
| 687 | ,, Deficit for Twelve Months .. .. .. .. .. .. | 736 | 1 | 1 |
| £2,365 | | £2,325 | 16 | 6 |

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

# GEOLOGY

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*Chairman:* R. O. Chalmers, A.S.T.C.

*Honorary Secretary:* N. C. Stevens, B.Sc.

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*Meetings.*—Eight meetings were held during the year 1951, the average attendance being eighteen members and six visitors.

April 20th.—Annual Meeting. Election of Office-bearers for 1951: Chairman, Mr. R. O. Chalmers; Honorary Secretary, Mr. N. C. Stevens.

Films: Colour slides were shown by Mr. A. V. Jopling (Broken Hill), Mr. G. E. McInnes (Warrumbungle Mtns. and the A.C.T.), Mr. N. C. Stevens (Belubula River district), and Mr. T. G. Vallance (New England and North Coast).

Exhibit: By Mrs. K. M. Sherrard, of Upper Ordovician graptolites from Carboona Gap, near Jingellic.

May 11th.—Lecturettes: Wallabadah District, by Mr. J. Hallinan; Bungonia District, by Mr. B. H. Flinter and Mr. N. O. Jones; Wollongong District, by Mr. C. T. McElroy.

June 15th.—Address: " Some Aspects of a Trip to Great Britain and America ", by Dr. G. D. Osborne.

July 20th.—Notes and Exhibits: By Mr. A. S. Ritchie: Glacial features near Mt. Kosciusko. By Mr. G. E. McInnes: Magnetic Is. and Townsville. By Mr. N. C. Stevens: Geophysical survey of bathyliths in N.S.W. By Mr. T. G. Vallance: Pleistocene glacial banded clays from Trapyard Ck., Kosciusko. By Mr. J. M. Hallinan: Tertiary volcanic rocks from Lamington National Park, Q. By Mr. G. Packham: Silurian plant remains from west of Sofala, N.S.W. By Mr. W. H. Williamson: Very porous sandstone from Eumungerie, N.S.W. By Mr. Chalmers: Photographs of parabolic current bedding in sandstone at Glenorie and Eastwood; and curved crystals of prehnite from Prospect, N.S.W.

August 17th.—Discussion: " Contributions to the Geology of the Marulan-Wombeyan-Yerranderie District." By Mr. L. Lawrence (Yerranderie), Mr. J. Lovering (Tallong-Marulan) and Dr. G. D. Osborne (who presented the work of Mr. C. V. Phipps in the Wombeyan-Taralga area).

September 21st.—Lecturettes: " On the Work of the Geological Survey during the Past Year ", by Officers of the Survey, including a general account by Mr. C. St. J. Mulholland; investigations in the Western Coalfield, by Mr. E. O. Rayner, and Contour Trench formations in upland plains of N.S.W., by Mr. C. T. McElroy.

Exhibit: By Mrs. Sherrard: Upper Ordovician graptolites (zone of *Nemagraptus gracilis*) from two localities north and north-east of Walli, N.S.W.

October 19th.—Addresses, illustrated by colour slides: " On N.W. Queensland and Central Australia ", by Miss F. M. Quodling and Dr. H. Narain.

November 16th.—Notes and Exhibits: By Dr. C. J. Magee: Mt. Lamington, N.G. By Dr. W. R. Browne: Deuteric alteration of South Coast lavas. By Dr. G. D. Osborne: Dunite with phlogopite xenoliths from Mt. Strangways, Central Australia; reaction rims with humite, chondrodite, cummingtonite and anthophyllite. By Miss F. M. Quodling: Kyanite from Harz Ra., Central Australia. By Mr. N. C. Stevens: Crinoidal limestone from Borenore, N.S.W. By Mr. Chalmers: Copper and coalfield material from Long Reef, Narrabeen, N.S.W.

# Obituary

SEPTIMUS BIRRELL, who died on 17th July, 1951, had been a member of this Society since 1916. In his early days he vacated a position in the Physiology School in the University of Sydney to join the newly-established Bureau of Microbiology of the Department of Public Health, where he worked on matters related to pathology and dairy bacteriology.

He became Dairy Bacteriologist under Dr. Darnell Smith in the Biological Branch of the Department of Agriculture, N.S.W., in 1913, and was directly associated with the establishment of the course in Dairy Bacteriology for Diploma Students at Hawkesbury Agricultural College. In 1915 he became a commercial biochemist, and was recognized as an authority on the bacteriology and chemistry of fats and oils. He took an active part in the Australian Society of Dairy Technology, of which he was a foundation member.

EDWIN CHEEL, who was born in England on 14th January, 1872, and died in Sydney on 19th September, 1951, had been a member of this Society since 1913.

On his arrival in Australia as a young man he worked as a gardener in Queensland and in Sydney. In 1897 he was appointed to the staff of Centennial Park, Sydney, and later transferred to the gardening staff of the Sydney Botanic Gardens, where he was entrusted with the care and maintenance of the Cryptogam collections of the Herbarium. His keen interest in the knowledge of his work led to his appointment to the botanical staff in the National Herbarium in 1908, and to his appointment in 1933 to the position of Chief Botanist and Curator, which he held until his retirement in 1936.

He had a wide knowledge of many groups of Australian plants, but his greatest interest was in the Myrtaceæ, many species of which he cultivated and observed at his home at Ashfield and on private ground at Hill Top, south of Picton. His plant collections added much to the resources of the National Herbarium.

He contributed many botanical papers and articles to scientific journals in N.S.W., including 21 to This Society. He took an active part in the work of the scientific societies in Sydney and was President of the Naturalists' Society of N.S.W. in 1924, of the Linnean Society of N.S.W. in 1930, of This Society in 1931, and of the Botany Section of A.N.Z.A.A.S. in 1937. He was a delegate of the A.N.R.C. to the Fifth Pacific Science Congress in Canada in 1933.

He was a warm supporter of the Friendly Society movement, and served in the highest position in the Manchester Unity Order of Oddfellows.

In 1943 This Society awarded its Bronze Medal to Edwin Cheel " in recognition of his contributions in the field of botanical research and to the advancement of science in general ".

HENRY JAMES HOGGAN, a member of This Society since 1916, died on 25th December, 1951, at the age of 74. Born in Scotland, he came to Australia at an early age, and received his schooling in Australia.

For nearly thirty years he was a teacher of Engineering Trades Drawing at St. George Technical College (1910–1939) and from 1934 to 1939 also taught at the Sydney Technical College.

As Consulting Engineer to St. George County Council Electricity Supply Undertaking, he was responsible for the planning and construction of the distribution system during the period from 1920 to 1923.

He was a foundation member of The Institution of Engineers, Australia, and was formerly a member of the Engineering Association of Australia.

WILLIAM PERCY JUDD, who died on 27th November, 1951, at the age of 77 years, had been a member of This Society since 1930.

THOMAS HARVEY JOHNSTON was born and educated in Sydney and died at Adelaide on 30th August, 1951, aged 70. He became a member of the Society in 1909, and a Corresponding member in 1912. He graduated in Arts at the Sydney University in 1904 and in Science in 1906. He obtained his M.A. in 1907 and D.Sc. in 1911. He was Lecturer in Zoology and Physiology at the Sydney Technical College (1907–1909) and Assistant Microbiologist in the Bureau of Microbiology, N.S.W. (1909–1911), in which State he was responsible for the revival of plant pathology after the departure, in 1905, of Dr. N. A. Cobb to take up a post in Hawaii. Among his early studies of note in this field were those associated with first outbreaks of Irish blight of potatoes in Australia. He was Lecturer, and later Professor, of Biology in the University of Queensland (1911–1922), and Professor of Zoology in the University of Adelaide (1922–1951).

Professor Johnston has been one of the leading Australian zoologists for many years and was Honorary Zoologist to the Australian, Queensland and South Australian Museums.

In the course of his work he travelled widely: as a member of the Prickly Pear Travelling Commission, which visited many countries of the world in search of a means of controlling prickly pear (and it was on his recommendation that the Commission introduced the cochineal parasite to control the pest); on several anthropological expeditions from Adelaide into Central Australia; and twice to the Antarctic with the British, Australian and New Zealand Antarctic Research Expeditions.

He published more than 200 scientific papers, chiefly on Australian parasitology. He was President of the Royal Society of Queensland, Queensland Field Naturalists' Club, Royal Society of South Australia, Entomological Club of South Australia, Anthropological Society of South Australia, and Zoological Section of the Australian Association for the Advancement of Science. In recognition of the excellence of his work he was awarded the David Syme Memorial Medal (1913), the Polar Medal (1934), the Sir Joseph Verco Medal (1935), and the Mueller Memorial Medal (1939).

Andrew Gibb Maitland, who was elected an Honorary Member of This Society in 1915 and died on 27th January, 1951, was the last of the pioneer geologists of Australia. Born in Huddersfield, Yorkshire, on 30th November, 1864, he studied geology at Yorkshire College, Leeds, under Professors A. H. Green, W. W. Watts and J. E. Marr.

At the age of twenty-four, he was appointed Assistant Geologist to the Geological Survey of Queensland, where, under the direction of the late Dr. R. L. Jack, he spent eight years, some of his most important work being connected with the survey of the north-eastern intake beds of the Great Artesian Basin. During his period of service in Queensland, he was seconded in 1891 to accompany Sir William Macgregor in his explorations in New Guinea, and produced the first systematic account of the geology of Papua as known at that time.

In 1896 he went to Western Australia as Government Geologist and Director of the Geological Survey, a position in which he laboured for thirty years. Apart from administrative achievements, which included the organization and enlargement of the Geological Survey and the determination and implementation of its policy, he made important and far-reaching contributions to the general and economic geology of the State. Outstanding among these were the discovery of artesian water and the elucidation and mapping of the geology of the Pilbara area in the "north-west".

It was due to his careful field work that he was able to predict the occurrence of valuable supplies of artesian water in the country between Shark Bay and North-West Cape (an area of pastoral possibilities but poorly provided with surface water), and later in the West Kimberley region, around Perth and in the Nullarbor Plain.

He initiated a geological survey of the Pilbara region (which became noted as a producer of gold, tin, tantalum and the rare-earth metals) and was responsible for the publication of several important Bulletins of the Geological Survey dealing with the geology of various mineral fields in the State. The extensive knowledge of the geology of the State gained by himself and his staff was epitomized in his "Summary of the Geology of Western Australia", published in 1919, accompanied by a coloured geological map.

Maitland took an active interest in the advancement of Science. He played an important part in the foundation of the Royal Society of Western Australia, of which he was twice President, and was for twenty-five years Local Secretary of A.N.Z.A.A.S. and President of Section C (Geology) in 1907.

He was awarded the Mueller Medal of A.N.Z.A.A.S. in 1924, the Clarke Memorial Medal of This Society in 1927, and the Kelvin Memorial Medal of the Royal Society of Western Australia in 1937.

# PRESIDENTIAL ADDRESS

By R. C. L. Bosworth, Ph.D., D.Sc.

*Delivered before the Royal Society of New South Wales, April 2, 1952.*

## Part I.

## THE SOCIETY'S ACTIVITIES DURING THE PAST YEAR.

The year under review will long be remembered for two important events : the Jubilee of the Commonwealth of Australia, followed shortly afterwards by the tragic news of the death of His Well-Beloved Majesty King George VI. I was among one of the many millions who were shocked by the solemn news, which came through so unexpectedly just eight weeks ago. On behalf of the Members and Council I sent a letter to Her Majesty Queen Elizabeth expressing our respectful sympathy.

In the Jubilee celebrations, your Society played its part as the leading organizer in the Jubilee Conversazione held in the Great Hall of the University of Sydney. Other scientific and professional bodies co-operating with the Royal Society in this event were : The Institution of Engineers, Australia ; The Royal Australian Chemical Institute ; The Institute of Physics, N.S.W. Division ; The Institute of Mining and Metallurgy ; and the Linnean Society of N.S.W. The Conversazione provided a brilliant display on the evening of Wednesday, April 18th, and was much appreciated when the exhibition was thrown open to the general public on the following day. I think it is only fit at this stage that we should express our appreciation of the pioneer organizational work done for this function by your last year's Council, and in particular by my immediate predecessor in office, Mr. F. R. Morrison.

As another fitting mark of the Jubilee year, the Society arranged to cover, in its normal course of popular science lectures, representative scientific achievements of the last half century, with special reference to Australia. Lectures were given on the following subjects :

On May 7th Dr. P. R. McMahon spoke on " Wool ".

On July 18th Prof. Harvey Sutton spoke on " Science, Medicine and Health in the 20th Century ".

On August 16th Dr. W. R. Browne spoke on " Shore Fluctuations, Their Causes and Effects ".

On September 20th Prof. R. J. W. Le Fevre spoke on " Chemical Discovery and Invention Through the Last Half Century ".

On October 18th Rev. J. L. K. O'Connell spoke on " Seismology ".

While in some instances a combination of inclement weather and electricity blackouts resulted in audiences of a disappointing size, their enthusiasm invariably paid tribute to the lecturer, and I would like again to express to our popular science lecturers the appreciation of the Society.

The general meetings of the Society have, this year, been somewhat more varied than usual. Fewer papers have been read before the Society, and in their place lecturettes and exhibitions have been given. Two symposia were arranged and one evening was devoted to the showing of scientific films. The subject matter at the meetings generally was well balanced and was appreciated by the audiences.

On Monday, June 18th, your President and Secretary waited on His Excellency the Governor, Sir John Northcott. His Excellency expressed keen interest in the affairs of the Society and was looking forward to an occasion when he might be present at one of our functions.

The Council, to whose report you have listened earlier this evening, has been untiring in applying itself to the business of the Society and in giving me, as your President, unstinted co-operation. In a year of financial stringency, there have been many controversial matters brought before the governing body of the Society, and while initial opinions held by Councillors were often very varied, yet when the matter in question had been thoroughly discussed and the time had come to take the vote it was frequently an unanimous one. I repeat, your Council has been one which it has been a pleasure to lead, and I am grateful to each and every one of them. Particularly, however, am I indebted to the members of your Executive Committee. I was fortunate in that this body contained two past Presidents of the Society, who were able to give me valued advice as well as co-operation, namely Mr. Morrison as the immediate past President, and Mr. Wood who was President in 1949 and who, in spite of the fact that he has already served the Society for many years, yet accepted again the responsibilities of Business Secretary, responsibilities which he shouldered so willingly and so well that the task of your President was made so much the lighter. Dr. Ida Browne has again acted as Editorial Secretary, and in that position she has done, I assure you, more than any other single person in restoring our Journal to a position where it appears reasonably on time. In addition, Dr. Browne has been tireless in exploring all possibilities of saving costs by efficient editorship.

And now to our Honorary Treasurer, Dr. C. J. Magee, there is due a special word of appreciation. Under present conditions the position of treasurer in any society such as ours is a most unenviable one, and while, as you have heard, we have recorded a large deficit, I can assure you that, had it not been for the efficient management of Dr. Magee, the deficit would have been a far larger one.

Among the other functions performed for the Society by Dr. Magee has been that of placing our financial position before persons and bodies likely to be interested. Not long ago he visited officers of the Rural Development Branch of the Commonwealth Bank, and shortly afterwards we heard that the Society had been made a grant of £400 from the fund administered by this branch of the Bank. The grant arrived too late for inclusion in this year's balance sheet but will provide a very favourable starting point for the new financial year under our new President, Dr. C. J. Magee. Let me here express our deep appreciation of the action of the Bank in making this grant.

I must also at this stage refer to the valuable work done by our Honorary Librarian, Mr. F. N. Hanlon. The duties which he has performed have largely relieved the Secretary of responsibility for library matters, permitting that officer to devote himself more fully to the other business of the Society. I, as President, the Council and every member are indebted to Mr. Hanlon in this matter.

Lastly, I must refer to the work of our Assistant Secretaries, Miss M. Ogle and Mrs. M. Golding, who have managed the office and library of the Society in a most efficient and courteous manner. Few members are aware that the smooth running of these general meetings of ours, and likewise our Council meetings, are due to the very complete and orderly agenda prepared in advance by our Assistant Secretaries.

And now it is my regretful duty to refer to the balance sheet. We are passing through a period when the cost of every service we offer to members is growing, and in many cases growing at an alarming rate. While our Society can still claim to be a comparatively wealthy one, we cannot continue to sustain such deficits and must either contract our services or seek additional sources of revenue. For some little time your Executive has been pressing the State Government for an increase in our grant—so far unsuccessfully. However, you have already heard of one successful venture in this field by our President-elect, and it will be one of the most urgent tasks of the new Council you have just elected to continue to explore all other possible lines of action in this matter of securing additional revenue from those bodies who, directly or indirectly, derive benefit from the activities of the Society.

During the year we have had somewhat fewer papers accepted for publication than in the immediately previous years. Not only have there been fewer papers offered, but, in addition, your Council has adopted a more stringent editorial policy. The world standing of the Society is judged, primarily, on the contents of its Journal, and if the rising costs of publication are to enforce restriction of our output it is doubly imperative to ensure that those papers which are accepted are of the highest possible quality.

I might, at this stage, be permitted a word to the authors of our papers. I have gained the impression, both from the chair, and, in earlier days, in the audience, that authors, and particularly young authors, when reading a paper are very much on the defensive and are attempting to justify their methods and conclusions before the audience in this hall. I would remind these authors that before their papers are even accepted by the Council for reading and/or publication that these papers have been submitted to the highest authorities in the appropriate subject which your Editor and Council could find, and found acceptable. When it comes to reading to the persons present in this hall, the author is usually by far the highest authority on the subject matter of his paper and the audience are interested primarily in comprehending sufficient of the subject matter to be able to judge what relation new facts brought forward by the author bear to the structure of science as a whole and each to their own little field in particular. As I said at the dinner six days ago, one of the most pressing problems facing scientists as a class is that of breaking down the growing barrier of incomprehensibility between experts in different fields, and I believe that the author who is reading an abstruse paper before the body of this Society and attempting to make the contents comprehensive to the audience is making a genuine effort in that regard.

The translation of scientific achievement to improved standards of living usually demands the co-ordination of the experts in many different fields, not only scientific—a fact recently observed by Meier (1951)—and the Royal Society would serve an end valuable not only to scientists themselves but to the industrial world as well, if it could promote better understanding between scientists in different fields.

## Part II.

## TRANSPORT PROCESSES IN APPLIED CHEMISTRY.

### (I) Introduction.

While a presidential address has to be acceptable to an audience of mixed scientific interests, it is also traditionally expected to deal with some of the more recent developments in one particular branch of science. In an attempt to make some kind of a bridge between the requirements of generalization on one hand and close specialization on the other, I shall follow the course of first defining the relation between the subject matter of this address and the better known physical sciences.

The translation of a chemical reaction or synthesis from a primary gain in chemical knowledge made in the laboratory to an industrial achievement involves the co-ordination of chemical developments with those gained in other fields. This has now been known for a considerable time and has frequently formed the bases of discussions, especially in the last decade. An important member of these allied studies is that of Physics, concerned as that subject is with the measurement, control and co-ordination of the properties of reactants, intermediates, resultants and equipment and with the balance of the forces acting between these bodies (Bosworth, 1950).

While physicists in general would agree that their subject finds important application in the field of chemical industry, there appears to be a fertile field for discussion in considering just what branches of physics are of major importance in such an application. There is fairly general agreement, for example, that methods of measurement of the physical properties of materials of construction and process materials form an important section of such a study. It is more difficult to get agreement as to the value of the other less direct applications, and it is on one of these applications that I have elected to speak this evening.

Many of the engineering operations of the chemical and other industries involve the transport of matter and/or physical properties from one point to another in a material assembly. The chemical engineering unit operation of drying, for example, involves the transfer of water molecules from one medium (the material to be dried) to another (the drying agent), and simultaneously and necessarily the transfer of heat in the opposite direction. The study of this and other allied unit operations is of subject matter proper to chemical engineering, but the study of the transport processes in themselves is, I claim, an aspect of physics as applied principally, but by no means exclusively, to the chemical industry.

## (II) The Two Ways of Studying Transport Processes.

In the discussion of the transport of physical properties such as heat, momentum and the electric current, it is convenient to consider the property concerned as transported by the movement of certain mobile parts of the assembly which, in moving, carry the property concerned with them. Heat and electric current in metals, for example, are conducted by the movement of the so-called free electrons. In gases, both heat and momentum may be transported by the random movement of the molecules, whereas electric current may only be transported by ionized particles. In other systems, non-material entities—electromagnetic or acoustical waves—can act as carriers. It is convenient to extend the concept of carrier from physical properties to material particles. Oxygen diffusing through air, for example, can be transported by the movement of oxygen molecules, which thus constitute the carriers. Carbon dioxide diffusing through, for example, a limed sugar solution, can be carried as carbon dioxide molecules or in the form of carbonate or bicarbonate ions.

One particular class of carrier, as we have seen in the example above, may often transport two or more properties, and there necessarily arises a certain degree of parallelism between the different transport processes so that it is frequently possible and often desirable to argue from one process to another by analogy.

There are two ways in which transport processes may be studied. We may take a mechanical picture and consider the different carriers operative and the mechanism of their movement. On the other hand the flow involved in a transport process may be considered as a physical property in its own right and related to other properties of the system. The best known example of this, the phenomenological approach, is of course the study of current electricity. The study of heat transfer is, of course, also well known, as in the possibility of arguing from electric current to heat flow by means of setting up the equivalent electric circuit. The use of such devices for studying complicated heat (and incidentally also mass) transfer by analogy with an electrical circuit has recently been considered in detail by Paschkis and his co-workers (1942, 1946).

## (III) Recent Developments.

The mechanical study of transport phenomena on the molecular basis was first encountered in the Kinetic Theory of gas as developed by Joule, Clausius, Maxwell, Crookes, Jeans, Loeb, Knudsen (1934), Chapman and Cowling (1939) and others. Here the movement of individual molecules in a molecular assembly results in a scattering of local differences in composition or in the concentration of such physical properties as momentum and energy ; and also, if the gas is ionized, of the electric charge.

Fundamental study on the molecular basis in condensed phases has not proved as easy as in gaseous systems, but we have recently seen the development of an embryo Kinetic Theory of Liquid by Born and Green (1949) and also by Eisenschitz (1950).

The study of transport phenomena on the molar as distinct from the molecular bases has been developed in the theory of turbulence by Prandtl, von Karman, G. I. Taylor, E. G. Richardson and others. Similarly, transport produced by convective mechanism has been studied in connection with the flow of heat, evaporation processes and, more recently, in the corrosion of metals (Bosworth, 1950*a*, 1951).

On the basis of the phenemological approach to transport processes a major development has occurred in the growth of the thermodynamics of irreversible phenomena developed by Onsager (1931), Prigogine (1949), Cox (1950), de Groot (1951) and others, and in the recent publication of a book on this subject by de Groot.

Just what significance the ultimate development of theory in this field may have for the more humble practising chemist may be appreciated by reference to a very old physico-chemical principle. I refer to the principle of Le Chatelier, which says in effect that any chemical reaction gives rise to physical conditions which tend to stop and ultimately to reverse the reaction. Thus conditions for a reaction which is exothermic are rendered less favourable by a rise in temperature. Continuation of any reaction is thus ultimately contingent on the transport processes which dissipate the unfavourable conditions produced by the reaction. Further, the dissipation of any changed physical property is usually rendered more difficult by an increase in the size of the containing vessels. The large scale manufacturer of a chemical product is usually much more dependent on the transport processes than the laboratory worker. Where one or more transport processes become rate determining factors for any particular reaction, some knowledge of these processes is imperative if the chemical engineer is to face his design problem with intelligence.

## (IV) Type of Transport Process.

A flow process is characterized by the occurrence of a flux or current of some particular substance or property. This current may always be expressed as the temporal derivative of a particular parameter of the system. The current further proceeds under the influence of a driving force or potential which takes different values in different parts of the assembly.

As examples of such flow processes we may cite :

(*a*) Hydraulic or mechanical flow.
(*b*) The electric current.
(*c*) The flow of heat.
(*d*) Chemical diffusion.
(*e*) Momentum flow or fluid friction.
(*f*) Magnetic displacement.
(*g*) Elastic and plastic deformation.
(*h*) Relaxational phenomena.
(*i*) Chemical reaction.

This list of processes may be divided into three classes, depending on the tensor rank of the flux. In the first four processes the flux is a directed vector quantity. In the next three the flux is a tensor of the second rank. In the last two processes the flux is that of a change between two co-existing and spatially superimposed distinct states of the assembly and as such is a scalar quantity.

Again, magnetic displacement differs from the other processes listed above in that continual magnetic flux can only occur in a magnetic system in which the driving force is continually changing. The flow in such a system is referred to as a displacement current. Pure displacement currents also occur in ideally elastic bodies—*i.e.* those not subject to plastic deformation, and in electric phenomena in dielectric bodies.

## (V) General Properties of Transport Systems.

While the properties of transport systems differ according to whether the flux is a scalar, vector or tensor quantity, and to whether it constitutes a real or a displacement current, there are certain general properties shown by all such systems.

Every transport process, as we have seen, consists of a flux produced by the influence of a potential difference and carried by the movement of mobile carriers. The types of carrier operative differ both with the properties carried and with the systems concerned. A table of some of the important carriers with the properties for which they may be effective in maintaining flow is given below (Table I).

Table I.

*Carrier Operative for the Different Transport Systems.*

| Carrier. | Effective in the Flow of. |
|---|---|
| Steady electromagnetic field .. | Electric current, magnetic flux. |
| Alternating electromagnetic field | Electric current, magnetic flux, heat flux, momentum flow. |
| Steady elastic field .. .. | Elastic deformation. |
| Alternating elastic field .. .. | Elastic deformation, heat flux, momentum flow. |
| Electrons .. .. .. .. | Electric current, heat flux. |
| Ions .. .. .. .. | Electric current, heat flux, chemical diffusion, momentum flow. |
| Molecules .. .. .. .. | Heat flux, chemical diffusion, momentum flow. |
| Molar aggregates .. .. .. | Heat flux, hydraulic flow, chemical diffusion, momentum flow. |
| Convection currents .. .. | Heat flux, hydraulic flow, chemical diffusion, momentum flow. |
| Metastable molecules .. .. | Heat flux, chemical diffusion. |

In any transport system the flux may be regarded as proceeding from an initial point or source to a final point or sink. The possibility of endless flux lines (or toroidal fluxes), however, is not excluded. Given a distribution of carriers continuous along some path or paths from the source to the sink, flux will only occur if there exists a potential difference between the source and the sink and, usually, if there is a continuous potential fall along the " conducting path " joining these two points. Current or flux is the time rate of change of some physical parameter of the system which we may call the change ($Q$). In classical transport systems we may define the potential difference between any two points (say $A$ and $B$) as the work done in taking unit charge from $B$ to $A$. In considering the thermodynamics of irreversible processes, it has been found more convenient to take a definition of the potential difference as the entropy generated when unit charge is taken in the reverse direction, namely from $A$ to $B$. If $\triangle S$ is the entropy of the system measured with respect to a state of equilibrium, and if $Q_i$ is the charge, $X_i$ the potential and $J_i$ the flow, all measured with respect to the $i^{\text{th}}$ property, then we have as a definition of $X_i$ and $J_i$

$$X_i = -\frac{\partial(\triangle S)}{\partial Q_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$J_i = \frac{dQ_i}{dt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

It is, as a matter of observation, frequently noted that, at least for a limited range of $X_i$ over a conducting path, the flux is directly proportional to the potential difference

$$J_i = L_i X_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where the property(ies) $L_i$ may be known as the conductance or phenomenological constants. Applied to current electricity, equation (3) becomes a statement of Ohm's law ; to chemical diffusion, Fick's law ; to heat flow, Fourier's law ; to the transport of momentum, a definition of Newtonian behaviour ; and to hydraulic flow, a statement of the Poiseuille equation.

In any transport process proceeding from a source $A$ to a sink $B$ under a potential difference which is maintained at some fixed value, the flux at all points along the conducting path eventually settles down to a condition in which just as much charge flows into any and every elementary volume of that path in unit time as flows out of that same volume. Such a transport process is said to have attained steady flow conditions and is associated with a steady potential fall along the conducting path. If now, however, the potential difference between source and sink were suddenly altered, the current would not immediately settle down to conditions of steady flow. Before such is attained, a certain time must elapse, during which the current flows into local sources and sinks all along the conducting path until such points are brought up to the new operating local potential. While charge is thus going into storage along the path, the flow is said to be in the unsteady state. The magnitude of the charge required to raise any volume of the conducting path by unity is referred to as the capacity of that volume. For a path having a capacity $C$ and conductance $L$, the condition of unsteady flow persists for a time proportional to $C/L$.

For some transport processes, particularly current electricity and hydraulic flow in pipes, it is often permissible to regard the conducting path as a linear one. With other processes, particularly heat flow and chemical diffusion, the conducting path is often very diffuse and we may prefer to have local measures of the intensity of the current and potential properties. The most convenient of such local measures are the field and the flux or current density. By the field ($E$), we mean the local measure of the gradient of the potential, and by the flux density ($j$) we mean the quantity of charge crossing unit area normal to the direction of flow

$$E = \text{grad } X \quad \ldots \quad (4)$$

and

$$j = J/a \quad \ldots \quad (5)$$

If we choose the $x$ direction to be locally the line of steepest descent of the potential, then

$$E = \frac{dX}{dx}$$

$$j = \frac{J}{yz}$$

Applied to the localized system the Ohm-Fourier-Fick-Newton law becomes

$$E = \sigma j \quad \ldots \quad (6)$$

where $\sigma$, the specific conductance or conductivity, is related to the conductance $L$ by

$$\sigma = \frac{Lyz}{x}.$$

When dealing with local unsteady state flow the capacity of the path as a whole may be replaced by the concept of the specific capacity ($\gamma$) or capacity per unit volume

$$\gamma = \frac{c}{xyz} \quad \ldots \quad (7)$$

Both $\sigma$ and $\gamma$ are properties of the medium constituting the conducting path. The flow, while in the unsteady state, proceeds by a diffusive mechanism with a diffusivity $D = \frac{\sigma}{\gamma}$ (Bosworth, 1949). This diffusivity has the physical dimension of $\frac{l^2}{t}$ for every type of transport process. On the other hand, the physical dimensions of conductivities (and specific capacities) in general differ with each different transport process.

## (VI) The Entropy Source.

Whenever a flow process takes place work is dissipated or entropy generated. For any single transport process, the rate of generation of entropy is equal to the product of the flux by the potential, namely

$$\frac{dS}{dt} = J_i X_i = L x_i^2 \quad \ldots \quad (8)$$

The local entropy generated per unit volume per unit time in a large conducting path is likewise given by the product $j \times E$. Entropy is generated only by the flowing in conductances. Entropy is not generated by the flow of charge into capacities. Such a process is reversible while the flow in conductances is not.

## (VII) Cross Potential Differences. The Onsager Relationships.

The single transport process discussed above is comparatively rare. Frequently a single potential difference gives rise to two or more fluxes. Thus a temperature difference in a circuit involving two different metals gives rise not only to a heat current but also to an electric current—the so-called thermoelectric effect. In a mixture of two different chemical substances, a temperature can give rise both to a heat flow and to the differential migration of one of the chemical constituents in the phenomena of thermal diffusion. When coupled transport processes of this nature occur we must modify equation (3) to the form

$$J_i = \sum_k L_{ik} X_k \quad \ldots\ldots\ldots\ldots \quad (9)$$

where the current now depends on a whole number of different potentials and the potential conversely depends on a whole number of different currents. The phenemological coefficients $L_{ik}$ with $i \neq k$ now represent the effect of cross potential differences such as the thermoelectric and Peltier coefficients, electro-osmosis and the streaming potential and so on. The fundamental equation to these phenemological constants for cross fluxes is given by the Onsager reciprocal relations (Onsager, 1931 ; de Groot, 1951) which state that, for all $i$'s and $k$'s

$$L_{ik} = L_{ki} \quad \ldots\ldots\ldots\ldots \quad (10)$$

provided the fluxes and potentials have been defined in a proper manner. A proper choice of these quantities demands that the fluxes should be the time derivative of the state parameters $A_i, \ldots. A_k$, and that the entropy change produced in the system by a departure of these state parameters by amounts $Q_i, \ldots. Q_k$, etc., from their equilibrium value should be a quadratic expression of these quantities, namely

$$\triangle S = \tfrac{1}{2} \sum_{jk} J_{ik} Q_i Q_k \quad \ldots\ldots\ldots\ldots \quad (11)$$

Since the $Q_i$'s commute, the quantities $J_{ik}$ also may be taken as symmetric

$$J_{ik} = J_{ki} \quad \ldots\ldots\ldots\ldots \quad (12)$$

Since the potentials $X_i$ are defined by

$$X_i = \frac{\partial(\triangle S)}{\partial Q_i} \quad \ldots\ldots\ldots\ldots \quad (13)$$

It follows that

$$X_i = -\sum_k J_{ik} Q_k \quad \ldots\ldots\ldots\ldots \quad (14)$$

and that the $J_{ik}$'s are the capacity factors.

The Onsager reciprocal relationship may be proved on the basis of the principle of detailed balancing, and provides a basis for the theoretical treatment of all examples of coupled transport processes.

Particular examples occur in electric and thermal conduction in anisotropic media. In such media the resultant flux density is not necessarily co-directional with the applied potential field. In a field with components $E_x, E_y, E_z$ the resultant flows are $j_x, j_y, j_z$ given by the equation

$$j_x = k_{xx}E_x + k_{xy}E_y + k_{xy}E_z$$
$$j_y = k_{yx}E_x + k_{yy}E_y + k_{yz}E_z$$
$$j_z = k_{zx}E_x + k_{zy}E_z + k_{zz}E_z.$$

The $k_{ij}$'s are subject to the Onsager reciprocal relationship

$$k_{xy} = k_{yx}, \text{ etc.}$$

This particular symmetry with regard to the thermal and electric conductivity tensors, even when the crystal order did not demand such symmetry, has been known for a long time.

A limitation on the possible degrees of coupling between different transport processes is provided by the principle referred to as Curie's law (Curie, 1908), which states that coupling is only possible between transport processes of the same rank. In other words, coupling is not possible between scalar chemical reaction and vector mass diffusion or between vector heat conduction and tensor momentum flow.

## (VIII) Inductive Phenomena.

In certain types of coupled transport processes it is possible to trace a cyclic relationship between the flow of the properties concerned. This condition arises when the second p.d. in the circuit is produced as a result of the first current and conversely the first p.d. is produced by the second current. Thus in an appropriate circuit a magneto-motive force may be set up by an electric current and an electromotive force as the result of a (displacement) magnetic current. Again, when a fluid flows in a pipe, the hydraulic current gives rise to velocity differences across any one sectional area. These velocity differences constitute potential differences for the transport of momentum and thus tend to drive a momentum current across these sectional areas. The momentum flow in turn constitutes a stress and as such provides the potential for an hydraulic flow. Other examples of this type of cyclic coupling could be given.

Pairs of transport processes coupled in such a way that the $X_2$ depends on the $J_1$ and the $X_1$ on the $J_2$ have some interesting properties concerned with the transient state. Any sudden increase in $X_1$ gives rise to transient processes resulting in a storage of charge in the capacities associated with circuit 1. The effect of these capacities alone results in the change in flux $J_1$ lagging behind the change in potential $X_1$. On the other hand, change in $J_1$ results in an instantaneous change in $X_2$ which leads to storage of charge 2 in the capacities associated with circuit 2. The action of these capacities alone results in the change of flux $J_2$ and thus the potential $X_1$ lagging behind the change in $J_1$. The capacities for circuit 2 thus act as the inductances for circuit 1 (and *vice versa*). Again, any increase in the resistance of circuit 2 acts as an increase in the conductance of circuit 1 (and again *vice versa*). If, however, one of the coupled transport processes is of a pure displacement type, this process will make no contribution to the steady state conductance of the other process, but, by adding inductances to the capacities may profoundly effect the transient phenomena.

Inductive phenomena are, of course, best known in electrical and mechanical transport systems but other coupled transport processes also give rise to these phenomena. Examples connected with heat flow by natural convection have been given by the author (Bosworth, 1946, 1948).

## (IX) Treatment of Coupled Transport Processes.

Some of the most complicated examples of coupled transport phenomena occur in the field of chemical industry. Even comparatively simple chemical engineering operations involve consideration of several transport processes. In the process of fractional distillation, for example, there occurs, at each stage, an exchange of two or more chemical components as well as the associated latent heats between the two interacting streams. At the same time the two streams, one liquid and one vapour, are flowing in opposite directions under driving forces ultimately provided by the overall temperature difference across the still. An interesting discussion of the performance of a fractionating column, from the point of view of thermostatic equilibrium rather than in terms of the irreversible transport processes, has been given by Rossini (1950).

A continuous chemical reaction provides a still more complicated example of coupled and interlocked transport processes. In any typical reactor in which reagents flow into the reaction zone under prescribed physical conditions, react there with resultant change in heat content and volume, and then flow out again, there occurs simultaneously the following transport processes :

(*a*) Flow of heat.

(*b*) Flow of momentum.

(*c*) Flow of each of the chemical reagents and resultants.

(*d*) Chemical reaction or reactions. And possibly there may occur

(*e*) Relaxational phenomena.

Progress of each flow process depends not only on its own phenemological constants and storage capacities, but also on the degree of coupling with other transport processes. In each process too there may be several carriers operative.

Attempts at a theoretical treatment of these coupled processes have been made in several different manners :

(*a*) By using the thermodynamics of irreversible processes.

(*b*) By dimensional analysis.

(*c*) By using model methods.

A comprehensive discussion of the application of the first method has been given by de Groot (1951). The second (the method of dimensions) has been discussed by a number of authors. An early paper by Greenewalt (1926) discussed application of dimensional methods to the problem of the absorption of water by sulphuric acid. The application of the same method to a continuous chemical reactor has been discussed by Damkohler (1936), by Edgeworth-Johnstone (1939) and by Bosworth (1946), all of whom were concerned with laying down conditions of similarity between reactors of different sizes. The conditions, however, are so stringent that the method is only applicable in certain special instances.

The application of model methods to heat and mass flow problems has become a tool of power and importance in the hands of Paschkis and his co-workers. A similar comprehensive attempt to apply such methods to all the transport processes occurring in a chemical reaction has not been reported, although Wilhelm, Johnson, Wynhoop and Collier (1948) have applied this method to the transport processes occurring in fixed-bed catalyst converters.

### (X) Grand Transport Processes.

The concept of an irreversible transport process or flow occurring under the influence of a potential or driving force at a rate dependent upon conductance terms when in the steady state, and on combined conductance and capacity terms when in the transient state, is by no means restricted to phenomena on the molecular scale. On the contrary, many industrial and other operations involving the irreversible generation of entropy may be regarded as examples of transport processes. The distribution of steam from boiler house to the various thermal sinks of a factory is a typical example. Because, however, such a process, while involving an overall transport under a driving force, may also be resolved into a series of microscopic and molecular transport processes—

heat flow, chemical diffusion, etc., it is perhaps appropriate to refer to the aggregate process as a Grand Transport Process. The operation of the fractiona-tion column considered in the section above constitutes another example of such a grand transport process.

## (XI) Feedback.

A type of flow circuit which is involved in many different forms of engineering equipment causes the main stream of the grand transport process to divide at some point or points in the conducting path. Part of the stream then goes on and another part is fed back to an earlier stage in the system. Circuits with feedback of this nature are particularly well known in radio physics, but the general effect of similar feedback in hydraulic and chemical systems is not at all well understood and would appear to offer a particularly apt subject for study by the method of models mentioned above. A heat exchanger is a particularly simple example of an engineering equipment based on a transport process with feedback. The performance of a factory as a whole, considered as a flow from sources (raw materials) to sinks (scrap heaps, sewers, chimney stacks and sales departments), could also usually be represented as that of a grand transport process with multiple feedback. The influence of this feedback on the time of the transient period—or the time taken to settle down after a break—is frequently sensed by factory personnel but has never received the detailed study it undoubtedly merits.

## (XII) Efficiency.

In the study of thermodynamics we are familiar with the concept of efficiency of operation as an inverse measure of the useful energy wasted in carrying out the operation; and also with the fact that certain classes of operation are inherently more efficient than others. Such a concept has yet to develop with respect to industrial chemical operations. The efficiency, just like the efficiency of a prime mover, could be judged on the balance of the entropy of the raw material coming in through the various sources—including fuel, power and services—and on the finished materials going out through all sinks. The difference is a measure of the entropy generated when the irreversible process constituted by the factory operation takes place and is minimized when that factory reaction is carried out in the most efficient manner. As far as I know, no attempt to carry out such a balance has yet been made. A very rough preliminary survey of a particularly simple industrial chemical operation has, however, indicated a very low overall efficiency.

The present industrial index of efficiency is cost. A process is judged good if of low cost, and there is probably some truth in such a judgment, but the correlation between cost and thermodynamical efficiency is by no means perfect. Examples could be given of operations judged desirable on a cost basis which to future generations appeared disastrous. Witness, for example, the profligate waste of potential organic chemicals in coal, and, as a simpler example, the direct-acting steam-reciprocating pump, which while praised by old hands for its reliability, has a thermodynamical efficiency of 2% or under and is a source of profligate waste of power.

Again, analysis on the cost basis gives little real indication as to what benefits, if any, may be expected from more concentrated industrial research, whereas analysis of the factory operations into steps with the efficiency shown for each would indicate at once where intensive research would not likely result in improved performance.

I do not think I am being fanciful here. Analysis of prime movers thermo-dynamically has provided just such information and has resulted in a steady improvement in efficiency. Further, while the science of thermodynamics was developed over 100 years ago from a fundamental study of the performance of heat engines it has, particularly in the last half century, increasingly been applied to chemical phenomena and now provides the theoretical basis of chemical energetics. The concerted use of thermodynamical principles to the improvement of the efficiency of thermally operated equipment is much more recent. A similar application to improve the efficiency of industrial chemical operations has yet to begin. Most of the fundamental information necessary for finding, for example, the relative rates of entropy generation in the different steps of the grand transport process constituting a factory operation, or for choosing the most efficient (*i.e.* the least wasteful) way of preparing a given product, are now available. Perhaps some day in the not too distant future we shall hear that sufficient data has accumulated to enable these applications to be made.

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# A GEOLOGICAL ACCOUNT OF HEARD ISLAND.

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With Plate I and one Text-figure.

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CONTENTS.


| | Page |
|---|---|
| I. Introduction | 14 |
| II. Stratigraphy— | |
| (*a*) Laurens Peninsula Limestones | 14 |
| (*b*) Drygalski Agglomerates | 15 |
| (*c*) Lavas— | 16 |
| (i) The Mt. Olsen Lavas | 16 |
| (ii) The Coast Lavas | 16 |
| (iii) The High Lavas | 17 |
| III. Tectonics and Structure | 17 |
| IV. Correlation with the Kerguelen Archipelago | 18 |
| V. Summary | 18 |
| Acknowledgments | 18 |
| References | 19 |


## I. INTRODUCTION.

A general account of the geographical features of Heard Island together with notes on the glaciology has already been given (Lambeth, 1951).

Prior to 1947 only four scientific expeditions had called at Heard Island, and little is recorded of the stratigraphical and tectonic features. The observations contained herein were made by the first party of the Australian National Antarctic Research Expedition during 1947–49.

Heard Island is glaciated throughout the year and because of the scarcity and discontinuity of outcrops much reliance has been placed on collections made from moraines.

As far as is known, three formations exist, as follows :

Uppermost : Lavas.

Intermediate : Drygalski Agglomerates.

Basal : Laurens Peninsula Limestones.

## II. STRATIGRAPHY.

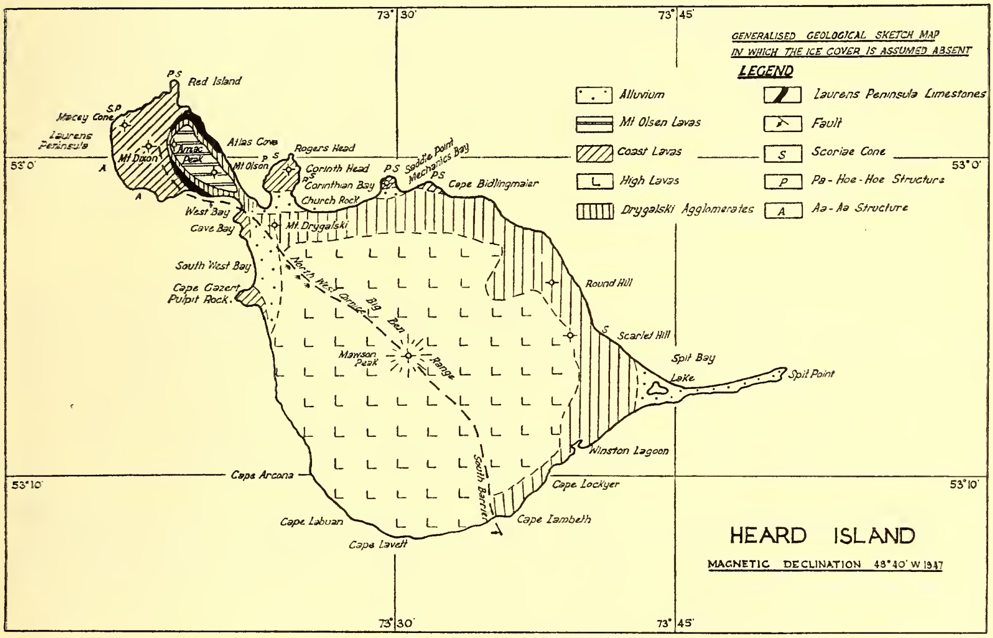
### (*a*) *Laurens Peninsula Limestones.*

The lowest formation, here called Laurens Peninsula Limestones, outcrops on both the south and north-east coasts of Laurens Peninsula, in latitude 53° 01′ S., longitude 73° 20′ E. The existence of this underlying pelagic limestone was suspected in 1908, but it is believed that the outcrops reported above are the first observed *in situ.*

The limestones are thinly bedded and intercalated with thin soft tuffaceous shales, and are folded about an E.-W. magnetic axis with north and south dips varying between 25° and 35°. The colour varies from white or grey to blue or brown, the texture being even and fine-grained with conchoidal fracture. There are abundant foraminifera which indicate a Palæogene age.*

The upper surface of the formation is plane and sub-horizontal, the greatest elevation being approximately 250 ft. above sea level on the south coast of Laurens Peninsula. From here it dips gently southwards to below sea level. The attitude indicates that the formation is not very far below sea level throughout the north-eastern part of the island.

On the south coast of Laurens Peninsula the formation has been intruded, prior to folding, by concordant sills of fine-grained, non-porphyritic, holocrystalline trachybasalt, varying in thickness from a few inches to five feet. These are the only igneous rocks observed.




*(b) Drygalski Agglomerates.*

These were first reported by Phillipi from the flanks of Mt. Drygalski near Atlas Cove, and as the widespread nature was not realized the occurrence was described as a crater ruin. They occur over most of Laurens Peninsula and the east and south coasts of the island. Their threefold nature is apparent at Mt. Drygalski and the southern and north-eastern parts of Laurens Peninsula, which may be taken as the type area. (Mt. Drygalski, lat. 53° 02′ S., long. 73° 23′ E.)

The agglomerates are sub-horizontal in attitude, overlying the Laurens Peninsula Limestones with an angular unconformity of approximately 35°, the maximum thickness on the Laurens Peninsula being 1100–1200 ft.

Their lower division consists largely of agglomerates, but near the top of the division local thinly-bedded tuffaceous shales are developed. Volcanic bombs are recognizable, while the variable-sized, angular to sub-angular, and rounded agglomerate pebbles are mainly porphyritic olivine-basalt, limburgite and limburgitic scoriæ. The bond is tuffaceous, shaly, palagonite and occasionally

* Glaessner, M. F., personal communication, 8th September, 1950, *Globigerina* sp. and *Gumbelina* sp. were determined.

calcareous. Much of the material was deposited under water. Locally there is little sorting, but broadly there are significant differences in grainsize, the grainsize diminishing towards the top. The maximum thickness of this division on the Laurens Peninsula is about 350 ft.

The igneous rocks are of three types: minor gabbroic stocks and bosses, contemporaneous trachytic necks, and the feeder dykes of the middle division.

The middle division overlies the lowest on an approximately even erosional surface, some of the trachytic necks being truncated. It is entirely igneous and, unlike the other divisions, is not continuous but is a series of volcanic outpourings within the Drygalski Agglomerate. Thin flows emanating from small dykes have produced local thicknesses of up to 300 feet. Columnar structure is common, the rock types being olivine-basalts and feldspar-basalts.

The upper division, thickness approximately 400 ft., shows a return to the agglomeratic facies of the lowest, with a finer grainsize in the agglomeratic particles, whilst tuffaceous shales and grits are more common than elsewhere. Their presence assists in the differentiation of the lower and upper divisions, where the middle is not developed. Contemporaneous brecciated plugs are the only igneous rocks.

The upper surface of the Drygalski Agglomerates is roughly plane, conforming to the general attitude of the formation.

(*c*) *Lavas.*

These are known mainly from moraines, although those near sea level can be examined in detail. Geographically, the lavas fall into three groups; these, however, are not necessarily in sequence and may be contemporaneous.

(i) *The Mt. Olsen Lavas*: Situated on the heights of Laurens Peninsula.

(ii) *The Coast Lavas*: Parasitic cones adjacent to sea level.

(iii) *The High Lavas*: Situated on the main mass of the island.

(i) *The Mt. Olsen Lavas.* These are situated on the heights of Laurens Peninsula about Mt. Olsen and Mt. Anzac, and are mostly glaciated (Mt. Olsen, lat. 53° 01′ S., long. 73° 20′ E.). They overlie the Drygalski Agglomerates with disconformity, and stratigraphically are in a situation similar to the High Lavas, although they may not be contemporaneous.

The basal beds are trachyandesites, approximately 100 ft. maximum thickness, with traces of columnar structure, overlain by an accumulation of trachyte, up to 1300 ft. thick, which forms the various peaks. Moraine material does not suggest that any other rock type is present.

(ii) *The Coast Lavas.* These are diverse. The limburgite of Rogers Headland is noteworthy. This is a crater floor-relic, remnants of the sides occurring in the limburgitic tuff relics of Rogers Head, portion of Corinth Head and Church Rock. This cavernous lava issued from many centres in the floor and is similar to occurrences at Saddle Point, Cape Bidlingmaier, Scarlet Hill, Red Island and Mt. Macey. At these places, Mt. Macey and Cape Bidlingmaier excepted, the containing walls are absent. They all show *pa-hoe-hoe* structure, and columnar structure on a small scale, while tumuli are common. The conspicuous and almost linear scoria-cones developed at these places with their abundant lapilli ejecta, are of an earlier date than the surrounding limburgites.

The lavas on the northern and western coasts of Laurens Peninsula centre about Mt. Dixon. This mound-like structure is completely glaciated and outcrops can be seen only at the base. They are trachyte, overlain by massive basalts, followed by vesicular *aa-aa* basalts. The accumulation of cinders probably represents the final outburst.

The Cave Bay trachytes with the overlying scoriaceous lavas appear to be allied to this Mt. Dixon suite, both forming part of a former widespread occurrence extending to the islands (*e.g.* Pulpit Rock) lying off Cape Gazert, where the *aa-aa* type overlies a massive basalt.

(iii) *The High Lavas.* The high lavas appear to extend upwards from the top of the Drygalski Agglomerate to the culminating peak Mt. Mawson. Consequently they represent a piling up of nearly 8000 ft. of volcanic material. They are known almost entirely from moraines, as those few outcrops which do exist are either difficult of access or unapproachable.

The lavas appear to have built up Big Ben Range by emanating from vents situated about the centre of the island. Seen from the air, the plateau-like upper surface of this mass resembles an infilled crater, in which case Mt. Mawson is a cone-in-cone structure, a feature commonly developed in the vents of the Laurens Peninsula coast lavas. The great height of this mountain mass developed in the narrow island area suggests lavas of high viscosity. In the samples collected limburgites, olivine-augite-basalts and trachybasalts predominate, with some subordinate plagioclase-basalts and trachytes, whilst more coarsely grained olivine-augite-types probably represent local intrusions into the lavas.

## III. Tectonics and Structure.

Three distinct formations are superimposed in a simple structure. The elevation and folding of the Laurens Peninsula Limestones indicates movements of great magnitude and, since these sediments are Palæogene in age, the movement may have been contemporaneous with the Alpine of the Northern Hemisphere. Only minor trachybasalt sills occur.

After a period of erosion, widespread explosive volcanic activity occurred from many centres, the ejecta being mostly limburgite and basalt, but some trachyte necks were formed. These formed the lowest division of the Drygalski Agglomerate. A hiatus followed during which thin fissure basalts formed discontinuous local accumulations. Explosive vulcanism followed, the average grainsize of the ejecta being finer than previously.

So far there was no sign of glaciation, it being inferred that the glacial epochs of the Pleistocene had not yet intervened. Consequently the Drygalski Agglomerates are probably late Tertiary, when this formation was undoubtedly of much greater extent than at present.

During the break in deposition which followed, the upper surface of the Drygalski Agglomerates was eroded to a roughly plane surface.

Igneous activity on a grand scale then commenced, localized about Big Ben. Other centres probably existed and may be represented by the various neighbouring islands. Lavas of high viscosity rapidly built up the mass of Big Ben. The main island fault may have had its beginnings here, providing a fissure through which the lavas were extruded. Most of the vulcanism appears to have finished before the Pleistocene glaciation, but its recurring and diminishing nature is clearly indicated in the numerous cone-in-cone structures. Some of the more recent flows overwhelmed the eroded edges of the Drygalski Agglomerates, indicating a general erosion of this formation. Fumaroles and hot springs do not occur on Heard Island.

The main island fault appears to have been most active after glaciation. It has truncated and destroyed the old trunk glacier flowing down Atlas Cove, as well as the headlands of the Jacka Glacier. The downthrow side was on the south-west and the throw could not be determined. Evidence of its existence is the non-occurrence of the Drygalski Agglomerates on the downthrow side either *in situ* or in moraines, as well as the truncation of the glaciers. It is represented physiographically by the escarpments of South Barrier and North West Cornice, which appear to represent the eroded scarps, at the latter place slickensided pebbles being found. The movement of the fault was associated in the Laurens area with trachytic vulcanism followed by basalts of increasing viscosity, culminating in *aa-aa* lavas, ashes and cinders.

The east coast may have been influenced by faulting. The almost linear arrangement of centres of eruption of limburgitic tuff, limburgite with *pa-hoe-hoe* structure, and scoriæ, extending from Mt. Macey to Scarlet Hill is significant. The tuff of Rogers Head contains fragments which, judging from their *in situ* position in the Drygalski Agglomerate and the attitude of this formation, could not have been brought from below if this area were not downfaulted. No other evidence was apparent, but the existence of such a fault would account for the absence of the eastern wall of the old Atlas Cove Glacier, which would have been downfaulted. The island appears to have had its origin in a tectogene in the early Tertiary, and is now a horst with downthrows to the north-east and south-west.

## IV. Correlation with the Kerguelen Archipelago.

A threefold division of the strata on the Kerguelen Archipelago has been indicated by Mawson (1933). A basal series of early Tertiary age is overlain by fluviatile conglomerates, which are in turn overlain by a great thickness of volcanics, the ash beds of which contain molluscan fauna of Pliocene age.

The centrally situated conglomerates are of basalts and trachytes, in which tuffceous beds are common. Contemporaneous trachyte plugs occur as well as scoriæ and agglomerate. Thin intercallated lignites contain Araucarian flora indicating a late Oligocene age (Mawson, 1933 ; Crié, 1869 ; de la Rue, 1929). The section displayed in the ravine of the Port Jeanne D'Arc rivulet through the heights dominating the old whaling station there is the best known, and must for the time being be considered the type. (Port Jeanne D'Arc, lat. 49° 34′ S., long. 69° 51′ E.)

The presence of globigerina limestone in the basement rocks has been indicated by Roth (1875) and Mawson, and detrital material was found in the central conglomerates. Consequently both islands stand on pelagic sediments. While the Port Jeanne D'Arc conglomerates are not directly comparable with the Drygalski Agglomerates, the two formations appear to be coeval. It is clear that explosive volcanic activity was happening in both places, but whilst it was dominant at Heard Island, it was of a lesser degree at Kerguelen Land and the products are mingled with erosion débris. As these places are approximately two hundred miles apart topographical differences at the time are to be expected.

Other points of correlation may be revealed by petrological methods.

## V. Summary.

Three formations were recognized on Heard Island. The basal pelagic limestones of early Tertiary age are unconformably overlain by agglomerates, which in turn are overlain by an immense thickness of lavas. The area has characteristics similar to those of a tectogene. Faulting has occurred and the island now appears to stand as a horst.

## Acknowledgements.

The writer wishes to thank Mr. George S. Compton, of Kalgoorlie, for unfailing help throughout the duration of the expedition, and to whom the observations in the vicinity of Round Hill are due ; and E. O'Driscoll, B.E., of Sydney, for many helpful discussions.

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## Explanation of Plate I.

Fig. 1.—Laurens Peninsula seen from Mt. Drygalski. West Bay on the left, Atlas Cove on the right with the moraine-strewn plain of Atlas Cove. Top centre is Mt. Olsen (2080 ft.). The glaciated heights about Mt. Olsen are composed of Mt. Olsen Lavas, the cliffs below are of Drygalski Agglomerate. The Laurens Peninsula Limestones outcrop at sea level on West Bay below the cliffs. Left distance, the slopes of Mt. Dixon composed of Coast Lavas.

Fig. 2.—The culminating point, Mt. Mawson (9005 ft.), surmounting the plateau-like top of Big Ben Range (approx. 8000 ft.) suggesting a cone-in-cone structure. The rib-like outcrops are of High Lavas. Air photo from the south.

These photographs are reproduced by kind permission of the Department of External Affairs, Antarctic Division.

# OCCULTATIONS OBSERVED AT SYDNEY OBSERVATORY DURING 1951.

By W. H. Robertson, B.Sc.
and K. P. Sims, B.Sc.

*Manuscript received, February 8, 1952. Read, April 2, 1952.*

The following observations of occultations were made at Sydney Observatory with the 11½-inch telescope. A tapping key was used to record the times on a chronograph. The reduction elements were computed by the method given in the Occultation Supplement to the Nautical Almanac for 1938 and the reduction completed by the method given there. The necessary data were taken from the Nautical Almanac for 1951, the Moon's right ascension and declination (hourly table) and parallax (semi-diurnal table) being interpolated therefrom. No correction was applied to the observed times for personal effect but a correction of $-0 \cdot 00076$ hour was applied before entering the ephemeris of the Moon. This corresponds to a correction of $-1'' \cdot 5$ to the Moon's mean longitude.

Table I gives the observational material. The serial numbers follow on from those of the previous report (Robertson, 1951). The observers were H. W. Wood (W), W. H. Robertson (R) and K. P. Sims (S). In all cases the phase observed was disappearance at the dark limb. Table II gives the results

Table I.

| Serial No. | N.Z.C. No. | Mag. | Date. | U.T. | Observer. |
|---|---|---|---|---|---|
| | | | | h m s | |
| 216 | 855 | 6·8 | Feb. 16 | 11 23 26·8 | W |
| 217 | — | 7·4 | Feb. 16 | 11 24 38·6 | W |
| 218 | 864 | 6·7 | Feb. 16 | 12 42 28·6 | W |
| 219 | 1018 | 5·5 | Feb. 17 | 12 47 08·0 | W |
| 220 | — | 7·9 | May 16 | 14 17 59·9 | W |
| 221 | 1676 | 6·7 | May 16 | 14 22 40·0 | W |
| 222 | 1888 | 6·2 | May 18 | 13 03 36·7 | W |
| 223 | 1907 | 6·7 | July 12 | 9 45 01·6 | W |
| 224 | 1913 | 7·1 | July 12 | 11 32 52·2 | W |
| 225 | 2039 | 5·6 | July 13 | 13 49 51·4 | W |
| 226 | 2157 | 6·1 | July 14 | 9 49 03·1 | W |
| 227 | 2470 | 6·1 | July 16 | 7 55 09·7 | R |
| 228 | 2505 | 5·4 | July 16 | 13 30 37·5 | W |
| 229 | 2108 | 6·4 | Aug. 10 | 9 08 37·1 | R |
| 230 | 2268 | 4·8 | Aug. 11 | 13 04 04·9 | W |
| 231 | 2273 | 5·9 | Aug. 11 | 13 33 57·2 | W |
| 232 | 2536 | 7·4 | Sept. 9 | 10 30 20·4 | W |
| 233 | 2545 | 6·4 | Sept. 9 | 12 55 31·1 | W |
| 234 | 2554 | 5·4 | Sept. 9 | 14 23 35·8 | W |
| 235 | 2723 | 6·7 | Sept. 10 | 11 19 24·6 | S |
| 236 | 2735 | 7·2 | Sept. 10 | 14 03 51·4 | W |
| 237 | 2740 | 6·3 | Sept. 10 | 14 46 27·8 | W |
| 238 | 2907 | 6·3 | Sept. 11 | 14 06 04·9 | W |
| 239 | 2852 | 7·4 | Oct. 8 | 10 24 08·2 | R |
| 240 | 2864 | 4·7 | Oct. 8 | 13 05 26·4 | W |
| 241 | 3416 | 5·6 | Oct. 12 | 13 36 04·1 | W |
| 242 | 2804 | 5·9 | Nov. 4 | 9 23 08·7 | W |
| 243 | 68 | 5·7 | Nov. 10 | 9 53 12·8 | W |

TABLE II.

| Serial No. | Luna-tion. | p | q | p² | pq | q² | Δσ | pΔσ | qΔσ | Coefficient of | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Δα | Δδ |
| 216 | 348 | + 88 | +48 | 77 | +42 | 23 | —1·1 | —1·0 | —0·5 | +11·3 | +0·50 |
| 217 | 348 | + 86 | +51 | 74 | +44 | 26 | —1·8 | —1·5 | —0·9 | +11·1 | +0·53 |
| 218 | 348 | + 89 | —46 | 79 | —41 | 21 | —1·0 | —0·9 | +0·5 | +11·7 | —0·44 |
| 219 | 348 | + 83 | +56 | 69 | +46 | 31 | —1·4 | —1·2 | —0·8 | +11·5 | +0·48 |
| 220 | 351 | +100 | — 3 | 100 | — 3 | 0 | —0·2 | —0·2 | 0·0 | +13·0 | —0·50 |
| 221 | 351 | + 98 | +20 | 96 | +20 | 4 | —0·3 | —0·3 | —0·1 | +14·4 | —0·29 |
| 222 | 351 | + 79 | —62 | 62 | —49 | 38 | —0·2 | —0·2 | +0·1 | + 6·3 | —0·90 |
| 223 | 353 | + 96 | +29 | 92 | +28 | 8 | —0·5 | —0·5 | —0·1 | +14·5 | —0·16 |
| 224 | 353 | + 98 | —22 | 95 | —22 | 5 | —0·7 | —0·7 | +0·2 | +11·4 | —0·63 |
| 225 | 353 | + 49 | —87 | 24 | —43 | 76 | +2·2 | +1·1 | —1·9 | + 1·8 | —0·99 |
| 226 | 353 | + 53 | +85 | 28 | +45 | 72 | 0·0 | 0·0 | 0·0 | +10·7 | +0·64 |
| 227 | 353 | +100 | + 3 | 100 | + 3 | 0 | —1·2 | —1·2 | 0·0 | +13·3 | —0·05 |
| 228 | 353 | + 99 | —13 | 98 | —13 | 2 | —0·8 | —0·8 | +0·1 | +13·0 | —0·18 |
| 229 | 354 | + 27 | —96 | 7 | —26 | 93 | +2·5 | +0·7 | —2·4 | — 0·8 | —1·00 |
| 230 | 354 | + 98 | +19 | 96 | +19 | 4 | —0·5 | —0·5 | —0·1 | +13·6 | —0·03 |
| 231 | 354 | + 83 | +56 | 69 | +46 | 31 | —1·6 | —1·3 | —0·9 | +12·7 | +0·36 |
| 232 | 355 | + 94 | —34 | 88 | —32 | 12 | —2·0 | —1·9 | +0·7 | +12·3 | —0·35 |
| 233 | 355 | + 31 | +95 | 10 | +29 | 90 | —0·6 | —0·2 | —0·6 | + 4·1 | +0·95 |
| 234 | 355 | + 79 | +61 | 63 | +48 | 37 | —1·0 | —0·8 | —0·6 | +10·5 | +0·61 |
| 235 | 355 | + 96 | —28 | 92 | —27 | 8 | —1·1 | —1·1 | +0·3 | +13·1 | —0·16 |
| 236 | 355 | + 24 | +97 | 6 | +23 | 94 | —0·8 | —0·2 | —0·8 | + 1·5 | +0·99 |
| 237 | 355 | + 36 | +93 | 13 | +34 | 87 | —1·0 | —0·4 | —0·9 | + 2·9 | +0·97 |
| 238 | 355 | + 64 | +77 | 41 | +49 | 59 | —1·6 | —1·0 | —1·2 | + 5·7 | +0·91 |
| 239 | 356 | + 61 | —79 | 37 | —48 | 63 | +1·2 | +0·7 | —0·9 | +10·3 | —0·65 |
| 240 | 356 | + 95 | +31 | 90 | +29 | 10 | —0·7 | —0·7 | —0·2 | +11·7 | +0·51 |
| 241 | 356 | + 73 | —69 | 53 | —50 | 47 | +0·5 | +0·4 | —0·3 | +14·5 | —0·27 |
| 242 | 357 | + 87 | +50 | 75 | +43 | 25 | —1·1 | —1·0 | —0·6 | +10·3 | +0·65 |
| 243 | 357 | + 96 | +29 | 92 | +28 | 8 | —2·0 | —1·9 | —0·6 | +10·6 | +0·70 |

of the reductions which were carried out in duplicate. The N.Z.C. numbers given are those of the Catalog of 3539 Zodiacal Stars for the Equinox 1950·0 (Robertson, 1940), as recorded in the Nautical Almanac.

The stars involved in occultations 217 and 220 were not included in the Nautical Almanac list. Their apparent places were as follows:

| No. | Star. | R.A. | Dec. | Catalogue. |
|---|---|---|---|---|
| 217 | G.C. 7088 | $5^h\ 38^m\ 15^s{\cdot}34$ | +29° 28′ 25″·8 | G.C. |
| 220 | B.D. +3°2518 | 11 30 53·57 | + 2 43 52·1 | Yale Vol. 20 |

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## OF NEW SOUTH WALES

FOR

1952

(INCORPORATED 1881)

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## PART II

OF

## VOL. LXXXVI

Containing Liversidge Lecture and Papers read in July and August, 1952

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EDITED BY

IDA A. BROWNE, D.Sc.

*Honorary Editorial Secretary*

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THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN



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CONTENTS

# VOLUME LXXXVI

## Part II


Page

Art. IV.—Climate and Maize Yields on the Atherton Tableland. By D. S. Simonett and N. T. Drane .. .. .. .. .. .. .. .. .. .. 22

Art. V.—Palladium Complexes. Part V. Reactions of Palladium Compounds with 2 : 2′ Dipyridyl. By S. E. Livingstone .. .. .. .. .. .. .. 32

Art. VI.—Liversidge Lecture. Electron Diffraction in the Chemistry of the Solid State. By A. L. G. Rees .. .. .. .. .. .. .. .. .. 38

Art. VII.—Permian Spirifers from Tasmania. By Ida A. Brown .. .. .. 55

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D

# CLIMATE AND MAIZE YIELDS ON THE ATHERTON TABLELAND.

By D. S. Simonett, M.Sc.,
and N. T. Drane, B.Ec.
*Department of Geography and Faculty of Economics, University of Sydney.*

With one Text-figure.

*Manuscript received, May 13, 1952. Read, July 2, 1952.*

The Atherton Tableland, situated in the coastal ranges of north Queensland near Cairns, virtually lies in the cloud zone of the north-west monsoon and the south-east trade winds for the greater part of the year. Due to this, as much as to its height, it experiences an equable temperature and humidity regime, very like that of the northern rivers of N.S.W., and its rainfall pattern shows less of the rigid wet-dry division so characteristic of tropical Australia. The wet season opens earlier with storms in November, rainfall intensities are lower, the proportion of cloudy days significantly higher, and the end of the wet season is blurred by the " drizzle " season of April, May, and occasionally June, the dry season being limited to July to October in the maize area centred on Atherton. Add to the above a major wet season cyclone every four or five years, and the combination is peculiar to the Atherton Tableland.

In land use the Tableland falls into three distinct divisions (see Skerman, 1947). In the hilly, high rainfall area south of Malanda (65″) there is no cultivation and dairying is based entirely on introduced pastures. Between Malanda and the Barron River (*c.* 55″) is a rolling fragmented maize belt, the small cultivated plots forming an integral part of a dairy-maize economy. North and west of the Barron River is the major maize producing area, almost 85 per cent. being grown on undulating land within a three-mile radius of Atherton and the two small silo townships of Tolga, three miles north, and Kairi, six miles north-east of Atherton. Rainfalls here are the lowest on the Tableland, Atherton obtaining 54 inches per annum, Tolga and Kairi 48 inches.

## Relationship between Climate and Maize Yields.

With relatively few exceptions, and these mainly in the intermediate maize-dairy belt between Malanda and the Barron River, maize production on the Tableland is a monoculture, neither animals nor subsidiary crops entering the economy. No moisture conserving practices are employed, indeed they are unnecessary, fertilizers are used only to an insignificant degree, the soils are extremely uniform kraznosems on basalt, cultivation practices are sensibly uniform throughout, and the varietal composition of the crop has not undergone serious changes during the last three decades.[1]

Night temperatures are never a limiting factor in growth, and both moisture and temperature conditions are usually very favourable, and it is doubtful if adverse effects from high temperatures and low moisture during tasseling have been experienced in more than two seasons since 1900.

[1] W. R. Straughan, Manager, Atherton Tableland Maize Marketing Board, personal communication on the varietal composition of the maize crop.

With so many factors constant or inapplicable, since they are not limiting in this area, two appear to outweigh all others in influencing ultimate yields, namely the growing season rainfalls from December to February, including the tasseling period, and the rainfalls of the cob-development stage during March and April, when the maize is severely affected by ear-rots. These relationships, together with the influence of time (hypothetical declining soil-fertility) form the basis of the following study.

## DATA.

*Rainfalls.* Monthly rainfalls at Atherton were used for they provided the only reliable, unbroken figures covering the last 35 years. Rainfalls within the maize area vary from 65 inches at Malanda on the southern boundary to *c.* 45 inches at Rocky Creek on the northern limits of cultivation. Atherton is centrally placed, and moreover, since this pattern persists in most years, rainfall at Atherton is a good guide to totals elsewhere in the maize area.

*Maize Yields.* The Petty Sessions District of Atherton covers all the Tableland, and up to 1940 formed the unit of collection for production data. Since that date collection has been by shires, the two shires Atherton and Eacham covering the area of the former P.S.D. Post 1940 figures are for the two shires ; this introduces no change in the area involved.

*The Period.* Maize production on the Tableland commenced over 70 years ago. The shorter period 1913–14 to 1948–49 was used to keep as many factors constant as possible. Prior to 1914 acreages were below 15,000 acres. After 1914 acreages fell below 15,000 in only four years. From the little that is known of the composition of the crop prior to 1913–14 it appears that numerous varieties were introduced and the varietal picture probably fluctuated considerably from year to year. Since then, however, it has not appreciably changed. Until November, 1907, when a large area was thrown open for selection, and to a lesser extent after the First World War, when the area under cultivation was expanded for soldier settlement, maize growing was widely spread over the Tableland and hand cultivation was generally practised following " scrub " burns. The present methods of cultivation did not become really widely used until about 1915–1920.

In Table 1 for the period 1913–14 to 1948–49 are given the growing season rainfalls (December-February) for Atherton, the totals of the ear-development stage (March-April), and the yield of maize in bushels per acre for Atherton Petty Sessions District. Those years in which gales accompanying cyclones in the Coral Sea caused destruction of a considerable portion of the crop are marked by an asterisk.

For the analysis of the influence of time and the two rainfall periods on maize yields certain seasons have been rejected :

(1) Those in which excessive damage to maize resulted from cyclones. In addition to bringing heavy rains, cyclones frequently flatten portion of the maize crop.

(2) Seasons in which the December-February rainfall was below 22 inches. The choice of a 22-inch rainfall in December-February as a rejection level was based on the fact that preliminary inspection of the data (see Table 3) indicated that below this level of rainfall maize yields ranged widely and showed little relation to the actual rainfalls received. In other words factors such as the incidence of rainfalls within the growing season, as well as the amount, are apparently important. Since the present analysis is concerned with the influence of *heavy* rainfalls on maize yields, it was considered advisable to exclude these

seasons as they would only weaken the relation being studied. While this rejection level was thus arbitrarily chosen, inspection of the data of Table 3 in the light of the following analysis appears to confirm such rejection.

TABLE 1.

*Rainfalls at Atherton During the Different Stages of Crop Growth for Maize, and Seasonal Yields of Maize for the Atherton Tableland during* 1914–1919.

| | Rainfall. Dec.-Apr. | Yield Maize. Bushels/Acre. | Rainfall. Dec.-Feb. | Rainfall. Mar.-Apr. |
|---|---|---|---|---|
| 1944–45 .. .. | 81·7 | 12·98 | 51·61 | 30·06* |
| 1948–49 .. .. | 71·3 | 32·75 | 47·0 | 24·3 |
| 1933–34 .. .. | 69·1 | 13·22 | 48·7 | 20·4* |
| 1938–39 .. .. | 65·3 | 25·79 | 41·7 | 23·6 |
| 1920–21 .. .. | 60·4 | 29·64 | 22·6 | 37·8 |
| 1928–29 .. .. | 59·0 | 29·51 | 44·6 | 14·4 |
| 1926–27 .. .. | 57·0 | 29·24 | 44·5 | 12·5* |
| 1939–40 .. .. | 52·9 | 22·44 | 29·1 | 23·8* |
| 1945–46 .. .. | 52·8 | 23·34 | 40·0 | 12·8* |
| 1932–33 .. .. | 51·0 | 43·33 | 37·2 | 13·9 |
| 1924–25 .. .. | 48·4 | 37·79 | 28·0 | 20·4 |
| 1929–30 .. .. | 48·2 | 38·34 | 44·7 | 3·6 |
| 1921–22 .. .. | 46·4 | 35·46 | 38·4 | 8·0 |
| 1942–43 .. .. | 43·3 | 34·40 | 41·2 | 2·1 |
| 1916–17 .. .. | 42·0 | 37·28 | 31·3 | 11·4 |
| 1927–28 .. .. | 41·6 | 42·11 | 33·6 | 9·0 |
| 1917–18 .. .. | 40·2 | 30·23 | 26·0 | 14·2* |
| 1935–36 .. .. | 39·5 | 34·16 | 24·7 | 14·8* |
| 1913–14 .. .. | 39·2 | 47·46 | 23·1 | 16·1 |
| 1931–32 .. .. | 38·6 | 42·45 | 31·3 | 7·3 |
| 1936–37 .. .. | 38·5 | 42·87 | 29·4 | 9·1 |
| 1922–23 .. .. | 37·1 | 43·35 | 23·0 | 14·1 |
| 1937–38 .. .. | 35·9 | 40·80 | 33·6 | 2·3 |
| 1947–48 .. .. | 33·7 | 29·68 | 19·5 | 14·2 |
| 1934–35 .. .. | 33·2 | 23·26 | 13·4 | 19·8* |
| 1946–47 .. .. | 31·7 | 37·34 | 18·8 | 12·9 |
| 1943–44 .. .. | 31·2 | 36·23 | 22·1 | 9·2 |
| 1925–26 .. .. | 30·9 | 49·64 | 23·1 | 7·8 |
| 1915–16 .. .. | 29·6 | 50·28 | 23·8 | 6·0 |
| 1941–42 .. .. | 29·2 | 24·73 | 20·0 | 9·2 |
| 1930–31 .. .. | 26·7 | 35·31 | 19·8 | 6·9 |
| 1923–24 .. .. | 26·7 | 27·52 | 18·4 | 8·3 |
| 1919–20 .. .. | 26·3 | 43·12 | 21·2 | 5·1 |
| 1918–19 .. .. | 21·8 | 42·58 | 10·0 | 11·8 |
| 1914–15 .. .. | 10·7 | 21·49 | 9·4 | 1·3 |

* Years in which considerable damage to maize resulted from cyclonic storms.

Eighteen seasons were then available for study, covering the 36-year period 1913–14 to 1948–49. The results of the simple correlations are given below.

$r_{12} = -0\cdot5044$ $x_1$=Yield of maize in bushels per acre.
$r_{13} = -0\cdot5581$ $x_2$=March-April rainfall.
$r_{14} = -0\cdot4314$ $x_3$=December-February rainfalls.
$r_{23} = -0\cdot0837$ $x_4$=Time.
$r_{34} = +0\cdot5060$
$r_{24} = -0\cdot0328$

We then applied a confluence analysis to these simple correlations, following Frisch (1934), in order to test the usefulness of including all three independent variables in the explanation of yields. In the circumstances, we think this is a more useful technique to use than the standard method of applying significance tests to the partial correlation coefficients. These tests of significance are, we feel, suspect in this case, for it is difficult to justify the assumption that our data constitute a " sample "—and a random sample at that. Our methods of selection are not designed to preserve randomness, and in any case our data cover *all* (suitable) available observations, and hence seem nearer to the concept of " population ". Even if this is no objection, however, it would seem that the inter-correlation between $x_3$ and $x_4$ must make the significance tests for these variables of doubtful validity.

### The Confluence Analysis, and Interpretation of the Bunch Maps.

The confluence analysis is designed to help overcome some of the difficulties which arise in interpretation of the results of multiple regression analysis when more than one relation might be present among the explanatory variables. This problem is particularly present in economic data since most economic quantities are the results of simultaneous activities in different sectors of the market, *e.g.*, prices are determined by simultaneous behaviour of both buyers *and* sellers. Thus if we were to construct a relation between price and quantity sold (or quantity bought), we would have difficulty, after confronting this with the data, in saying whether this was a demand or a supply equation, since the same factors enter largely into both. (See J. R. N. Stone, 1945, for a more detailed explanation of these problems, and for practical applications of the confluence technique.) But the problem is a more general one, and arises whenever we have more than one relation between the determining variables, so that the influence of the second (or other) relation(s) tends to distort the " true " influence of the first relation, which we assume to be the significant one for the purpose in hand.

The method developed by Frisch for determining where such multicollinearity exists consists in plotting the complete sets of regression coefficients in the form

$$\beta^{(i)}_{ij(1\cdot\cdot\cdot\cdot n)} = -\frac{R_{ji(1\cdot\cdot\cdot\cdot n)}}{R_{ii(1\cdot\cdot\cdot\cdot n)}}$$

where $R_{ij}$, $R_{ii}$ are co-factors of the matrix of zero-order correlation coefficients,

$$\begin{vmatrix} r_{11} & \cdots\cdots\cdots & r_{1n} \\ \vdots & & \vdots \\ \vdots & & \vdots \\ \vdots & & \vdots \\ r_{n1} & \cdots\cdots\cdots & r_{nn} \end{vmatrix}$$

and the β's are in terms of " normalized " variates which can be transformed to the regression coefficients in terms of the original variables by the formulæ

$$b^{(i)}_{ij(1\cdot\cdot\cdot\cdot n)} = \beta^{(i)}_{ij(1\cdot\cdot\cdot\cdot n)}\sqrt{\frac{\Sigma x_i^2}{\Sigma x_j^2}}$$

Thus, he starts from the theorem that if perfect correlation is present without multicollinearity, all regression equations lead to the same result. This is the familiar result from simple regression analysis that if $r_{12}=I=r_{21}$ then the two regression coefficients $1/r_{12}$, $r_{21}/1$ will be identical. This holds too in the general case.

The first step, then, is to plot the bunch map for the two-sets . . . 12, 13, 14, 23, 24, 34 from which a general idea of the relations can be obtained. Then by systematic inclusion of additional variables it is possible to deduce from the bunch map whether or not the relation is " improved " by this new explanatory factor. In the present example, since there is no difficulty in determining the dependent variable, we are only concerned with the various combinations of the explanatory variables with this dependent variable.

In interpreting the bunch maps, we must consider the possibility of the new variable being useful, superfluous, or detrimental to the analysis. Frisch provides several criteria, given below, for interpreting these cases, but they must be used with care, since they are highly subjective. Outside, or *a priori* theoretical considerations may have to be relied upon to make the final decision, particularly where the criteria appear to be contradictory.

Indeed, if theoretical considerations indicate that the variable is very important, whilst our statistical analysis shows it to be detrimental, then it is the statistical analysis, at least in this linear form, which must be discarded. All we can deduce, then, is that we cannot measure the influence of that variable by this method. There will remain, of course, the possibility that the data might fit some non-linear function.

Frisch states that a variate is *useful* if the bunch is tightened by its inclusion ; if the beam representing this variate falls inside the sector of the other beams ; and if the general direction of the bunch is changed (p. 100). A variate is *superfluous* if " (1) the bunch does not tighten by the inclusion of the new variate ; (2) the general slope of the bunch does not change (or more specifically, each of the beams in the bunch remains unchanged) ; (3) the beam of the new variate falls outside the sector of the other beams ; (4) the beam of the new variate is much shorter than the other beams in the new bunch ; (5) the beams of the other variates are not appreciably shortened by the inclusion of the new variate ".

" If all these criteria are simultaneously fulfilled, the variate in question is decidedly superfluous. The variate must, however, be considered superfluous even if only some of the above criteria are fulfilled, particular importance must then be attached to the criteria (1)-(3) " (p. 102).

Finally, " if the bunch explodes by the inclusion of the new variate, that is to say, if it becomes much less tight than before, the new variate must be considered as *detrimental* " (p. 103).

In the present application (Figure 1), we see from the *two-sets* that time (4), December-February rainfalls (3), and March-April rainfalls (2), all show a moderate correlation with yields (1), whilst (23), (24) are non-correlated. (34) however, does reveal some positive correlation. This appears to be an accidental bias introduced because of the several criteria of selection. It does serve, however, to impair the reliability of our regression coefficients for both (3) and (4) when we include time as a separate explanatory variable in the four-set, even though some decline in yields due to fertility deterioration over time is to be expected from general considerations. This is already evident in the *three-sets*, which reveal considerable improvement in the relations, following the inclusion of the third variable, in the bunches (12·3), (13·2), (12·4), (14·2), whilst (13·4) and (14·3) are " exploded ". This is because (3) and (4) are intercorrelated, and are therefore to some extent incompatible variables. In the *four-sets*, the (12·34) bunch shows a slight further improvement, whilst the (13·24) and (14·23) plots are exploded. This seems to indicate that in our four variable multiple regression analysis, if we hold (3) and (4) constant together we can get a somewhat better relation than by using simply (12·3) or (12·4) alone. Whilst (3) and (4) are intercorrelated, when taken together the result is as if we were to use a third variable z compounded of $x_3$ and $x_4$ by some such relation as

$$z = Ax_3 + BU$$

where (U) represents the residual time element which is required to give full effect to the influence of time, part of which is contained in $x_3$. Since, however, we cannot separate this residual in practice, we use another variable, time ($x_4$), which is already partly contained in $x_3$, and this then explodes the relation for any but the (12·34) case. We feel, however, that since the (12·34) bunch map is a slight improvement over the (12·3) bunch as a result of including (4) (the bunch is tightened slightly ; all beams are slightly shortened ; and beam (4) lies very nearly along the (1) and (3) beams), we are justified in regarding time

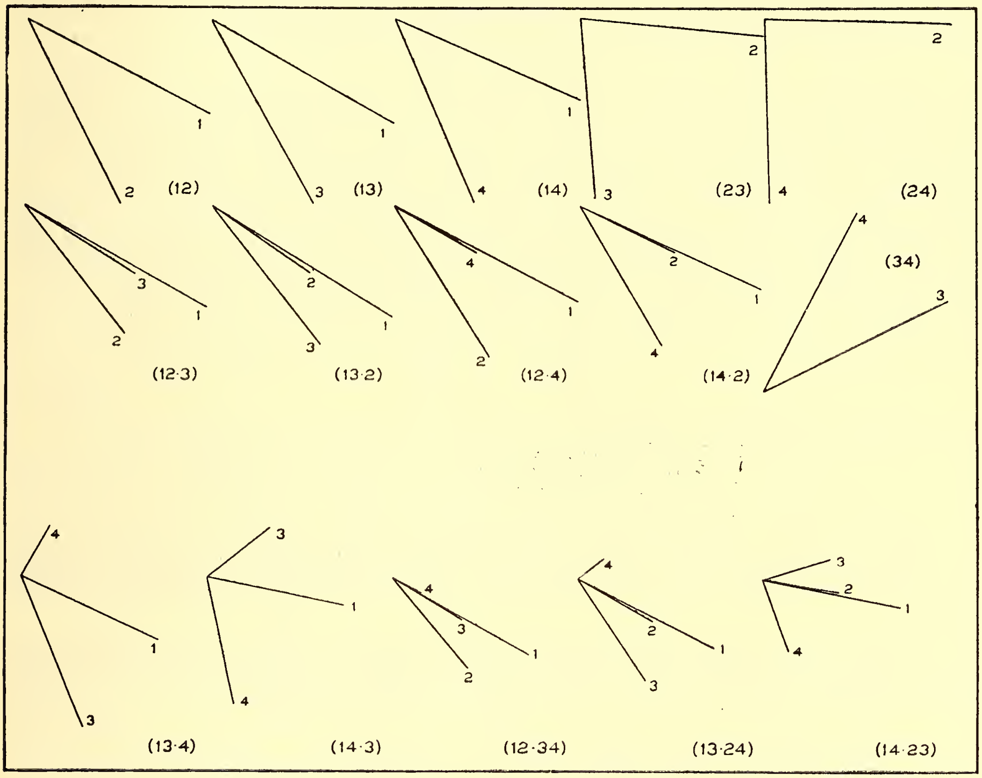


Fig. 1.—Confluence analysis bunch maps.
1=Yield of maize in bushels per acre.
2=March-April rainfalls.
3=December-February rainfalls.
4=Time.

as a useful variable—a conclusion we could not arrive at from the ordinary partial correlation coefficients, without confluence analysis.

$r_{12\cdot34} = -0\cdot6791$ Significant at 1% level.
$r_{13\cdot24} = -0\cdot5902$ Significant at 1% level.
$r_{14\cdot23} = -0\cdot2693$ Not significant at 5% level.

This is reinforced to some extent by consideration of the multiple correlation coefficients, and standard errors of estimate.

| | |
|---|---|
| $R_{1\cdot234} = 0\cdot8031$ | $S_{1\cdot234} = 4\cdot0269$ |
| $R_{1\cdot23} = 0\cdot7856$ | $S_{1\cdot23} = 4\cdot1816$ |
| $R_{1\cdot24} = 0\cdot6747$ | $S_{1\cdot24} = 4\cdot9893$ |

The fact that $R_{1 \cdot 23}$ is considerably better than $R_{1 \cdot 24}$ indicates that (4) has only a fairly small influence on the regression, but nevertheless $R_{1 \cdot 234}$ is still better than $R_{1 \cdot 23}$, reducing the S.E.E. by the amount of some 3%. This is small but does indicate that the *residual* amount of time does have some effect, lending some support to our argument that if the time-element in $x_3$ could be removed in some way, then the additional variable time ($x_4$) (not now intercorrelated with $x_3$) would be significant. We conclude, then, that the influence of time is a " useful " one.

By including (4) then we are able to get a better estimate of the influence of March-April rainfalls on yields. This regression coefficient is

$$b_{12 \cdot 34} = -0 \cdot 4380.$$

When we come to the other regression coefficients, however, between yields and December-February rainfalls, and between yields and time, the results obtained from the four-set are biassed due to intercorrelation between December-February rainfalls and time, hence we cannot measure the " true " influence of each of these variables. The nature of this interrelation is difficult to unravel, but for our purposes—prediction—we may tentatively use the estimates from the four-set, provided that the interrelation persists in its present form, and with the reservation that they are probably somewhat lower than the " true " regression coefficients, because of this intercorrelation. The estimates are

$$b_{13 \cdot 24} = -0 \cdot 4021$$

$$b_{14 \cdot 23} = -0 \cdot 1335.$$

The full regression equation is

$$X_1 = -0 \cdot 4380 x_2 - 0 \cdot 4021 x_3 - 0 \cdot 1335 x_4 + 59 \cdot 7493.$$

## Results and Discussion.

From a study of Table 1, the regression analysis, and a close inspection of the monthly rainfall distribution for the 35 years studied, the following points emerge :

1. The maximum mean yield of maize on the Atherton Tableland was 50·28 bushels per acre in the 1915–16 season, when rainfalls at Atherton were 29·6 inches from December to April, distributed as follows :

| Dec. | Jan. | Feb. | Mar. | Apr. | |
|---|---|---|---|---|---|
| 9·1 | 7·6 | 7·0 | 3·7 | 2·2 | Total, 29·6 inches. |

Inspection of the distribution of rainfall for years with yields close to the maximum suggests that the highest yields would be obtained with the following rainfall distribution at Atherton :

| Dec. | Jan. | Feb. | Mar. | Apr. | |
|---|---|---|---|---|---|
| 7 | 8 | 7 | 3 | 2 | Total, 27 inches. |

This is not strictly the " optimum " rainfall for the crop since portions of the maize lands would receive some inches more or less depending on their position. Effectively, however, it represents the optimum rainfall for the area as a whole.

2. In slightly less than 80 per cent. of the years under review, rainfalls during the December-February period were in excess of the optimum of 22 inches.

3. In slightly less than 90 per cent. of seasons, rainfalls during the March-April period were in excess of the optimum of five inches. The analysis of the rainfall-yields relationship for these two critical periods thus devolves largely into an assessment of the influence of excessive rainfalls on maize yields.

4. Cyclones caused major damage to the maize crop in 8 of the 35 years studied, depressing yields by an average of the order of 10 bushels per acre below the expected yield for the various rainfall levels.

5. In years either not affected, or only slightly affected, by cyclonic storms, and with a December-February rainfall exceeding 22 inches :

(i) Rainfalls greater than 22 inches during the growing period December-February significantly depress yields, each additional inch reducing the crop by approximately 0·402 bushel per acre. This may be due to weed competition for nitrogen in excessively wet seasons when inter-row cultivation is abandoned earlier than in more favourable seasons, or it may be due to excessive leaching of nitrates, or it may be partly a function of the decreased light intensity during cloudy, rainy weather. Whatever the reason, or reasons, the net effect of the factors associated with very heavy rainfalls during this period is to reduce the growth rate of the maize plant and hence both the number and size of the cobs.

(ii) Rainfalls above five inches during cob-development in March-April significantly depress yields, each additional inch by 0·438 bushel per acre below the level produced by the December-February rainfall. The high humidities and the moist state of the cobs which are a natural corollary of high rainfalls during this season, together with almost perfect incubation temperatures—average day temperatures of 80° F., night temperatures of 60° F.—favour cob diseases, particularly *Diplodia* ear rot. At present no economic control of cob rots is available, and in almost every season some loss is experienced from these diseases.

In addition to causing large-scale rejection of *Diplodia*—infested, dead grain at the harvest—inclusion would reduce the sale-value of the crop, as well as increasing the silo-storage difficulties—high rainfalls in March and April result in a high moisture content in the grain, particularly in that pulled in late May or June. Consequently, before storage in the nests of silos at Atherton, Tolga and Kairi, most of the early harvest must be artificially dried to a moisture content of 14 per cent. (Straughan, 1949).

6. During the period under review, yields declined to a slight but significant degree—probably of the order of 0·1335 bushel per acre per annum—and present-day yields would appear to be at least five bushels per acre below those obtaining in the beginning of the period.

No precise data are available as to the exact causes of this decline, but on general grounds we may reasonably expect that there would be a time-nitrogen regression (in the absence of fertilizers and nitrogen-building rotations), a soil-structure deterioration, and erosion loss similar to those noted by Cornish (1949) in his study of yield trends in the wheat belt of South Australia.

A suggestion of such a nitrogen decline in the maize lands is found in the following figures (Table 2), taken from Teakle (1950).

If the nitrogen-loss of the maize area north of Tolga, which was originally under *Eucalyptus* woodland, parallels that of the rain forest soils to the south (Atherton, Table 2), there is every reason to suspect a nitrogen-deficiency in them at least, for even under the virgin woodlands (Mapee *et seq.*, Table 2) they were only of moderate to low nitrogen content.

Teakle further notes that " under paspalum (pasture) or cultivation the crumb structure is greatly reduced and there is some sub-surface compaction ".

Sheet erosion, though masked by the uniform red colour of the soils, is evident on long gentle slopes where drifting against fences is characteristic.

It appears likely, then, that all three factors are contributory to the diminishing maize yields.

7. The suggested March-April optimum rainfall of five inches at the 22-inch level almost certainly does not apply through the whole range of December-February rainfalls. Logically, we would expect that stored soil moisture from heavy rains in the first period, and the residual effect of the higher humidities attending these heavy rains would reduce the requirements during ear-development. Unfortunately, no data are available on this point. The converse is probably not true, except when the distribution in the preceding months is irregular.

TABLE 2.

*Nitrogen Content of Selected Red Loams on Basalt, Atherton Tableland.* (*After* Teakle.)

| District. | Approx. Rainfall. | Depth, Ins. | Condition. | N%. |
|---|---|---|---|---|
| Atherton .. .. | 50 | 0–6 | Rain forest. | 0·613 |
| Yungaburra .. .. | 55 | 0–6 | Cleared and under Wild Tobacco and regrowth. | 0·559 |
| Atherton .. .. | 52 | 0–7 | Maize. | 0·235 |
| Sth. Mapee .. .. | <50 | 0·6 | Eucalyptus woodland. | 0·257 |
| Mapee .. .. | <50 | 0·6 | | 0·202 |
| Sth. Carbeen .. | 40 | 0–6 | | 0·155 |
| Carbeen .. .. | 40 | 0–2 | | 0·194 |
| Nth. Carbeen .. | 40 | 0–6 | | 0·113 |
| Nth. Carbeen .. | 40 | 0–6 | | 0·114 |

8. Seasons little affected by cyclones, and in which the December-February rainfalls were below 22 inches, ranged widely in yields from 21·50 to 43·12 bushels per acre (Table 3).

TABLE 3.

*Maize Yields and Rainfalls in Low-rainfall Years, Atherton Tableland.*

| Season. | Dec. | Jan. | Feb. | Mar. | Apr. | Growing Season Total. | Yield, Bushels/ Acre. |
|---|---|---|---|---|---|---|---|
| 1914–15 .. | 386 | 256 | 294 | 69 | 59 | 10·64 | 21·50 |
| 1918–19 .. | 412 | 410 | 181 | 599 | 591 | 21·93 | 42·56 |
| 1919–20 .. | 113 | 1,299 | 711 | 102 | 408 | 26·33 | 43·12 |
| 1923–24 .. | 651 | 576 | 610 | 671 | 156 | 26·64 | 27·52 |
| 1930–31 .. | 450 | 1,042 | 487 | 287 | 403 | 26·69 | 35·31 |
| 1941–42 .. | 333 | 164 | 1,498 | 187 | 734 | 29·16 | 24·73 |
| 1946–47 .. | 202 | 442 | 1,239 | 1,089 | 200 | 31·72 | 37·34 |
| 1947–48 .. | 380 | 1,200 | 365 | 1,107 | 319 | 33·71 | 29·68 |

From the information in Table 3 it is clear that growing season rainfalls alone are not a good indicator of crop success when rainfalls are below the optimum. Nor are the pre-seeding rainfalls of September to November which in the above cases bear no relation to yields. The important factors are probably rainfall incidence and (possibly) heat wave spells in relation to critical stages in growth.

## Summary.

Maize yields on the Atherton Tableland in north Queensland are significantly depressed by rainfalls exceeding 22 inches in the growing season of December-February (including the tasseling period), each additional inch reducing yields by approximately 0·402 bushel per acre. Rainfalls above five inches during cob-development in March-April also reduce yields, each inch by 0·438 bushel per acre. During the period 1913–14 to 1948–49 maize yields declined to a slight but significant degree and present day totals are at least five bushels per acre below those of the early years. The factors responsible for the time-yields decline, and the factors associated with rainfall which appear to be responsible for the rainfall-yield suppression were discussed. The statistical technique used was that of confluence analysis.

## Acknowledgements.

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# PALLADIUM COMPLEXES.

## Part V. Reactions of Palladium Compounds with 2 : 2′ Dipyridyl.

By S. E. Livingstone, A.S.T.C., B.Sc.

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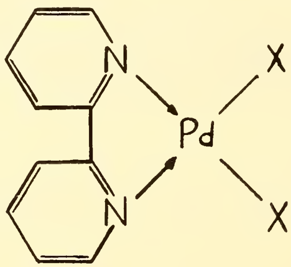
An investigation of the types of compounds formed by palladium with 2 : 2′ dipyridyl has been carried out similar to that describing the reactions of palladium compounds with 1 : 10 phenanthroline (Livingstone, 1951).

Some complexes of palladium containing 2 : 2′ dipyridyl (dipy) have been previously reported : viz. Pd dipy $Cl_2$ (Morgan and Burstall, 1933) ; Pd dipy $(NO_2)_2$ and Pd dipy $C_2O_4$ (Mann and Purdie, 1936). Compounds of the type Pd dipy $X_2$, similar to these, are described here (X=Br, I, CNS, $NO_3$). These compounds are all insoluble in water and organic solvents—except Pd dipy $(NO_3)_2$, which is moderately soluble in water—and are precipitated when a solution of $PdX_2$ or $K_2PdX_4$ is treated with an aqueous solution of 2 : 2′ dipyridyl. These compounds probably have the structure



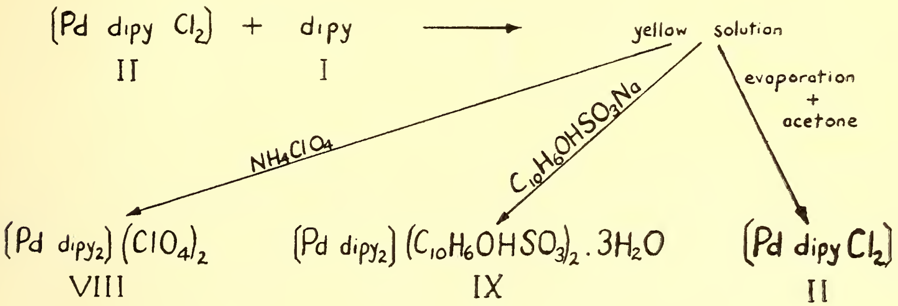

the dipyridyl acting as a bidentate ligand and thus giving the palladium atom a coordination number of four, which is usual for divalent palladium. Precipitates are not formed when dipyridyl is added to solutions of (i) $PdSO_4$, (ii) $PdSO_4$+NaF, (iii) $K_2Pd(CN)_4$. All the above compounds of general formula Pd dipy $X_2$ dissolve in cold aqueous solutions of KCN to give colourless solutions liberating 2 : 2′ dipyridyl, in analogy with Pd[phen]$X_2$ (where phen=1 : 10 phenanthroline) (Livingstone, 1951).

A tetravalent palladium complex *tetrachloro-2 : 2′ dipyridyl palladium (IV) chloride* is formed as reddish-orange crystals by the oxidation of Pd dipy $Cl_2$ with chlorine.

$$\underset{\text{II.}}{[\text{Pd dipy Cl}_2]} + \text{Cl}_2 \xrightarrow{\text{CHCl}_3} \underset{\text{VII.}}{[\text{Pd dipy Cl}_4]}$$

This compound VII, unlike its phenanthroline analogue (Livingstone, 1951), does not liberate chlorine in moist air, nor on boiling with water, and is stable on heating to 160° C. It appears to have much greater stability than other tetrachlorodiammine palladium (IV) type compounds previously reported (Rosenheim and Maass, 1898; Drew *et alii*, 1932).

The reactions of [Pd dipy $Cl_2$] (II) with different amines were investigated. II dissolves in excess aqueous 2 : 2′ dipyridyl to give a yellow solution. Concentration and precipitation with acetone yields the original [Pd dipy $Cl_2$]. However, salts of the ion [Pd $dipy_2$]$^{++}$ can be obtained with the anions perchlorate and 2-naphthol-6-sulphonate.




Existence of the equilibrium

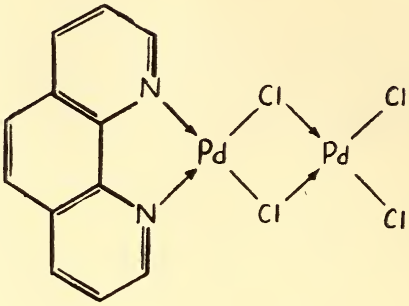
$$[\text{Pd dipy Cl}_2] + \text{dipy} \rightleftarrows [\text{Pd dipy}_2]^{++} + 2\text{Cl}^-$$

is demonstrated by the fact that addition of a large excess of NaCl to an aqueous solution of [Pd $dipy_2$] $(ClO_4)_2$ immediately precipitates [Pd dipy $Cl_2$].

Solutions of mixed tetrammines of the type [Pd dipy $Am_2$]$^{++}$ (where Am = ammonia, pyridine, 2Am = ethylenediamine, propylenediamine) are obtained by treating II with an excess of amine in dilute aqueous solution. Addition of $NH_4ClO_4$ to the pale green solution precipitates [Pd dipy $Am_2$]$(ClO_4)_2$. These perchlorates, surprisingly, are fairly soluble in cold water, but all excepting [Pd dipy en]$(ClO_4)_2$ could be recrystallized from water. A considerable excess of 1 : 10 phenenthroline must be added to [Pd dipy $Cl_2$] and the mixture boiled to effect solution; addition of $NH_4ClO_4$ precipitates [Pd $phen_2$]$(ClO_4)_2$. This is probably due to the fact that 2 : 2′ dipyridyl is appreciably volatile under these conditions.

Comparison of the results obtained with palladium and 2 : 2′ dipyridyl with those for palladium and 1 : 10 phenanthroline (Livingstone, 1951) and for platinum and 2 : 2′ dipyridyl (Morgan and Burstall, 1934) shows that there is a considerable similarity between them. Failure was experienced in all cases to isolate $[M(chel)_2]Cl_2$ (where M = Pt, Pd and chel = dipy or phen), [M chel $Cl_2$] being obtained in each case. However, the perchlorates and 2-naphthol-6 sulphonates of [Pd $phen_2$]$^{++}$ and [Pd $dipy_2$]$^{++}$ could be prepared. Morgan and Burstall (1934) claimed to have isolated (i) [Pd $dipy_2$]$PtCl_4$ and (ii) [Pt dipy $py_2$]$PtCl_4$, but this seems unlikely since their products were yellow and one would expect these compounds to be pink or possibly green (Drew *et alii*, 1932) and hence the substances obtained were probably (i) [Pt dipy $Cl_2$] and (ii) a mixture of [Pt dipy $Cl_2$] and [Pt $py_2Cl_2$]. Using similar procedures with the palladium phenanthroline complex, the author obtained yellow [Pd phen $Cl_2$]. However, by altering the conditions, *viz.* addition of a solution of [Pd $phen_2$]$(ClO_4)_2$ to excess of concentrated ice-cold solution of $K_2PdCl_4$, salmon pink products resulted, which were undoubtedly impure [Pd $phen_2$]$PdCl_4$. However, this latter compound could not be prepared in the pure condition.

It is possible that it may have been contaminated with a bridged compound having the structure




Support for this is given by the fact that if the solutions are mixed at the boiling point, which usually favours formation of bridged compounds, the palladium content of the resulting product is increased. A similar result was obtained using $K_2PdBr_4$, but no pure compounds could be isolated. Chatt and Mann (1939) attempted to prepare bridged palladium complexes of this particular type (*i.e.* having four halogen atoms attached to one palladium atom) but reported negative results. The matter is being further investigated as part of a study of the formation of bridged compounds of palladium.

## Experimental.

(III) *Dibromo-2 : 2′ dipyridyl palladium (II).*

A hot aqueous solution (50 ml.) of $K_2PdBr_4$ (0·5 g.) was mixed with a warm solution of 0·16 g. of 2 : 2′ dipyridyl—I— in water (30 ml.) containing 3 ml. of alcohol. Orange prisms of III separated immediately ; the product was insoluble in water and organic solvents, but readily soluble in aqueous KCN to a colourless solution. Yield 0·385 g.

Found : Pd, 25·6% ; Br, 38·4%.

$PdC_{10}H_8N_2Br_2$ requires : Pd, 25·24% ; Br, 37·82%.

(IV) *Diido-2 :2′ dipyridyl palladium (II).*

(i) A solution of $K_2PdI_4$ was treated with a hot aqueous solution of I. A pinkish brown precipitate resulted.

Found : Pd, 20·7%.

(ii) Dichloro-2 : 2′ dipyridyl palladium (II)—compound II—(0·45 g.) and 0·35 g. of I were dissolved in hot water containing a few drops of alcohol. The yellow-brown solution was poured into 20 ml. of water containing KI (5 g.). 0·63 g. of pinkish brown crystals of IV were precipitated.

Found : Pd, 20·6% ; I, 48·1%.

$PdC_{10}H_8N_2I_2$ requires : Pd, 20·65% ; I, 49·12%.

(V) *Dithiocyanato-2 : 2′ dipyridyl palladium (II).*

$K_2PdCl_4$ (0·3 g.) was dissolved in water (30 ml.) and KCNS (2·5 g.) added. On addition of an aqueous solution containing I (0·14 g.), pale yellow crystals were thrown down. Yield, 0·33 g.

Found : Pd, 28·1% ; C, 37·8% ; H, 2·0%.

$PdC_{10}H_8N_2(CNS)_2$ requires : Pd, 28·15% ; C, 37·92% ; H, 2·13%.

(VI) *Dinitrato-2 : 2′ dipyridyl palladium (II).*

I (0·15 g.) dissolved in hot water (30 ml.) was added to a solution of $Pd(NO_3)_2$ (excess) in dilute $HNO_3$ and the mixture heated to boiling. On cooling, pale yellow crystals, appreciably soluble in water, were deposited. Yield, 0·20 g.

Found: Pd, 27·3%.

$PdCO_{10}H_8N_2(NO_3)_2$ requires: Pd, 27·58%.

(VII) *Tetrachloro-2 : 2′ dipyridyl palladium (IV).*

II (0·4 g.) was suspended in chloroform and chlorine passed into the suspension for 40 minutes. On filtering, the product was washed with chloroform, then dry ether, and dried *in vacuo* over $P_2O_5$. Yield, 0·43 g. The reddish orange crystals had no smell of chlorine and were not decomposed by heating to 160° C., nor by boiling with water.

Found: Pd, 26·5%; Cl, 35·1%.

$PdC_{10}H_8N_2Cl_4$ requires: Pd, 26·36%; Cl, 35·05%.

*Reactions of II with Amines.*

(A) *2 : 2′ Dipyridyl.*

II (0·2 g.) and I (0·2 g.) were heated to boiling in water (15 ml.) to give a deep yellow solution. On concentration to 5 ml., acetone was added. Pale cream needles were precipitated.

Found: Pd, 32·0%.

Calculated for $PdC_{10}H_8N_2Cl_2$: Pd, 31·96%.

(VIII) *Bis (2 : 2′ dipyridyl) palladium (II) perchlorate.*

II (0·2 g.) and I (0·2 g.) were warmed with water (25 ml.) and alcohol (3 ml.). On addition of an aqueous solution of $NH_4ClO_4$ 0·35 g. of deep yellow dentritic crystals of VIII separated. On recrystallization from water (150 ml.) 0·3 g. of deep yellow prisms were obtained.

Found: Pd, 17·3%.

$Pd(C_{10}H_8N_2)_2(ClO_4)_2$ requires: Pd, 17·29%.

0·15 g. of VIII were dissolved in boiling water (100 ml.) and NaCl (3 g.) added; pale yellow needles were deposited while the solution smelt strongly of 2 : 2′ dipyridyl.

Found: Pd, 32·0%.

Calculated for $PdC_{10}H_8N_2Cl_2$: Pd, 31·96%.

(IX) *Bis (2 : 2′ dipyridyl) palladium (II) 2-naphthol-6-sulphonate trihydrate.*

II (0·1 g.) and I (0·1 g.) were warmed with water to give a yellow solution and excess of a solution of sodium 2-naphthol-6-sulphonate was added. Deep yellow crystals (0·25 g.) separated; these were washed with hot water, then acetone and dried *in vacuo* over $P_2O_5$. On heating in a closed tube, water was evolved at a temperature just below decomposition.

Found: Pd, 11·9%; C, 51·9%; H, 3·8%.

$Pd(C_{10}H_8N_2)_2(C_{10}H_6OHSO_3)_2.3H_2O$ requires: Pd, 11·60%; C, 52·24%; H, 3·95%.

(B) *Ammonia.*

(X) *Diammino-2 : 2′ dipyridyl palladium (II) perchlorate.*

II (0·35 g.) was treated with water (30 ml.) and 1N $NH_4OH$ (4 ml.) and the mixture warmed to 40° C. After 15 minutes a pale greenish yellow solution resulted. On addition of $NH_4ClO_4$ thin needles of X were slowly precipitated. Recrystallization from water (8 ml.) yielded 0·14 g. of colourless prisms.

Found: Pd, 21·4%.

$PdC_{10}H_8N_2(NH_3)_2(ClO_4)_2$ requires: Pd, 21·52%.

(C) *Pyridine.*

(XI) *Dipyridine-2 : 2′ dipyridyl palladium (II) perchlorate.*

II (0·35 g.) was placed in water (40 ml.) and treated with drops of pyridine in the cold to give a pale greenish yellow solution. Addition of $NH_4ClO_4$ caused acicular prisms of XI (0·51 g.) to slowly separate. Recrystallization from water gave very pale green elongated prisms (0·43 g.).

Found: Pd, 17·1%.

$PdC_{10}H_8N_2(C_5H_5N)_2(ClO_4)_2$ requires: Pd, 17·21%.

(D) *Ethylenediamine.*

(XII) *Ethylenediamine-2 : 2′ dipyridyl palladium (II) perchlorate.*

II (0·3 g.) was treated with water (10 ml.) and 3% aqueous ethylenediamine (3 ml.). After 10 minutes at room temperature a clear pale green solution was obtained. Addition of $NH_4ClO_4$ caused slow crystallization of thin needles (0·10 g.) of XII, very soluble in water.

Found: Pd, 20·1%.

$Pd(C_{10}H_8N_2(C_2H_8N_2)(ClO_4)_2$ requires: Pd, 20·44%.

(E) *Propylenediamine.*

(XIII) *Propylenediamine-2 : 2′ dipyridyl palladium (II) perchlorate.*

II (0·3 g.) was treated with water (7 ml.) and 3% aqueous propylenediamine (3 ml.). To the resulting pale yellow green solution, $NH_4ClO_4$ was added, precipitating colourless needles (0·23 g.). These were recrystallized from water (8 ml.).

Found: Pd, 19·9%.

$Pd(C_{10}H_8N_2)(C_3H_{10}N_2)(ClO_4)_2$ requires: Pd, 19·91%.

(F) *1 : 10 Phenanthroline.*

II (0·3 g.) and 1 : 10 phenanthroline (0·2 g.) were heated in water (30 ml.); an extra 0·2 g. of 1 : 10 phenanthroline was required to achieve a clear solution. $NH_4ClO_4$ precipitated yellow prisms of (Pd $phen_2$)$(ClO_4)_2$, which were recrystallized from water (300 ml.). Yield, 0·37 g.

Found: Pd, 15·8%, 15·8%.

Calculated for $Pd(C_{12}H_8N_2)_2(ClO_4)_2$: Pd, 16·02%.

*Attempted preparation of bis (1 : 10 phenanthroline) palladium (II) chloropalladate (II).*

(i) Bis (1 : 10 phenanthroline) palladium (II) perchlorate—compound XIV—(0·14 g.) dissolved in boiling water (80 ml.) was added slowly to a solution of $K_2PdCl_4$ (0·45 g.) in ice cold water (100 ml.). The salmon pink product was filtered, washed with cold water, then acetone.

Found: Pd, 33·8%.

(ii) XIV (0·25 g.) in boiling water (100 ml.) was slowly added to a solution of $K_2PdCl_4$ (1 g.) in ice cold water (80 ml.). Yield of salmon pink crystals, 0·30 g.

Found: Pd, 33·6%; Cl, 22·2%, *i.e.* Pd : Cl = 1·00 : 1·99.

$Pd(C_{12}H_8N_2)_2PdCl_4$ requires: Pd, 29·82%; Cl, 19·83%.

$Pd_2C_{12}H_8N_2Cl_4$ requires: Pd, 39·86%; Cl, 26·49%.

*Attempted Preparation of bridged chloro compound.*

A solution of XIV (0·25 g.) in boiling water (100 ml.) was slowly poured into a boiling aqueous solution (100 ml.) of $K_2PdCl_4$ (0·7 g.). The solution was kept boiling for a further 30 minutes. The orange brown product (0·33 g.) was filtered, washed well with hot water, then acetone, and dried over $P_2O_5$.

Found: Pd, 35·6%.

*Attempted preparation of bridged bromo compound.*

XIV (0·15 g.) dissolved in boiling water (80 ml.) was added to a solution of $K_2PdBr_4$ (0·7 g.) in boiling water (50 ml.) over a period of 20 minutes and the mixture kept at the boil for a further 20 minutes. The precipitate of reddish-brown crystals was filtered, washed with hot water, then acetone, and dried over $P_2O_5$.

Found: Pd, 28·2%.

$Pd_2C_{12}H_8N_2Br_4$ requires: Pd, 29·91%.

$Pd(C_{12}H_8N_2)_2PdBr_4$ requires: 23·88%.


## Summary.

An investigation of compounds formed by palladium with 2 : 2′ dipyridyl (compound I) acting as a chelating group, has been described. I reacts with $PdX_2$ and $K_2PdX_4$ to form [Pd dipy $X_2$] (where dipy=2 : 2′ dipyridyl and X=Br, I, CNS, $NO_3$). Similar compounds (where X=Cl, $NO_2$ and $2X=C_2O_4$) have been previously reported. [Pd dipy $Cl_2$] (compound II) is oxidized to the orange-red compound [Pd dipy $Cl_4$] by passing chlorine through a suspension of II in chloroform. II dissolves in excess of aqueous solution of I to form a solution of the tetramine chloride [Pd $dipy_2$]$Cl_2$, which could not be isolated from solution, but addition of ammonium perchlorate and sodium 2-naphthol-6-sulphonate yields VIII, [Pd $dipy_2$]$(ClO_4)_2$, and IX, [Pd $dipy_2$]$(C_{10}H_8OHSO_3)_2.3H_2O$ respectively. II also dissolves in aqueous ammonia, pyridine (py), ethylenediamine (en) and propylenediamine (pn) to give pale yellow green solutions which upon addition of $NH_4ClO_4$ yields X, [Pd dipy $(NH_3)_2$]$(ClO_4)_2$, XI, [Pd dipy $py_2$]$(ClO_4)_2$, XII, [Pd dipy en]$(ClO_4)_2$. XIII, [Pd dipy pn]$(ClO_4)_2$. Attempts to prepare [Pd $phen_2$]$PdCl_4$ (phen=1 : 10 phenanthroline) gave salmon pink products with high Pd and Cl content, possibly due to contamination with a bridged compound, which could be isolated in the pure state.



## Acknowledgement.

The author is indebted to Dr. F. P. J. Dwyer for his generous gift of 2 : 2′ dipyridyl used in this investigation and also to Dr. E. Challen for the carbon and hydrogen analyses.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# LIVERSIDGE RESEARCH LECTURE*

## ELECTRON DIFFRACTION IN THE CHEMISTRY OF THE SOLID STATE.

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With 17 Text-figures and Plates II-IV.

Technical rather than scientific progress over the last 20 years has been largely responsible for the useful application of physics to the problems of chemistry. Naturally enough physical methods find immediate application in the identification and analysis of chemical species ; later, as a proper understanding of the physical phenomenon is acquired, application to the more fundamental problems of structure, energetics and dynamics becomes possible. Electron diffraction has been understood fairly completely, in a formal way at least, from a time shortly after the establishment of wave mechanics, but recent experimental advances have only now permitted some realization of its full potential in chemistry.

The terms of the Liversidge Bequest require that the subject of this lecture should be such as to encourage research and stimulate interest in some aspect of chemistry. The importance of the chemistry of the solid state, both in academic and technological spheres, the relevance and uniqueness of the information on the solid state provided by electron diffraction and the prospect of exciting experimental and theoretical development constitute a topic which, I venture to submit, satisfies these terms.

### The Electron Diffraction Method.

Electrons, of mass $m$ and charge $e$, accelerated by a potential $V$ of the order of 50 kV., have, from the relation $\lambda = h/(2meV)^{\frac{1}{2}}$, an equivalent wave-length $\lambda$ of $\sim 0 \cdot 06$ Å, somewhat smaller than the normal X-ray wave-lengths used in diffraction studies, but still of the right order of magnitude for diffraction by regular arrangements of atoms or molecules. One would expect an electron diffraction pattern to have a formal resemblance to an X-ray diffraction pattern ; this is so, but there are important differences. Indeed, it is these differences which represent the value of electron diffraction in chemistry. By reason of its charge a 50 kV. electron can penetrate only some hundred or so atomic planes without suffering considerable inelastic scattering (*i.e.*, scattering in which kinetic energy of translation is not conserved). Moreover, electrons are scattered elastically by atoms some $10^7$ times more efficiently than are X-rays. Electron diffraction is restricted then to the study of solid surfaces and of extremely small crystals, for both of which X-ray diffraction is of indifferent value.

Those refinements to the technique of electron diffraction responsible for widening its scope have been largely electron-optical in character. An electron diffraction camera is simply an instrument for producing a narrow beam of

* Delivered to the Royal Society of New South Wales, July 17, 1952.

high-velocity electrons by means of a system of electromagnetic lenses and small apertures, and recording on a photographic plate held normal to the beam direction the beams diffracted by the specimen. Figure 1 is a diagrammatic representation of the principle of a high-resolution electron diffraction camera.

For high resolution in single-crystal reflections, with which we shall be particularly concerned here, the electrons in the narrow pencil impinging on the specimen must be of uniform velocity, as this determines their wave length, and must have small angular spread. To fulfil these conditions stability in

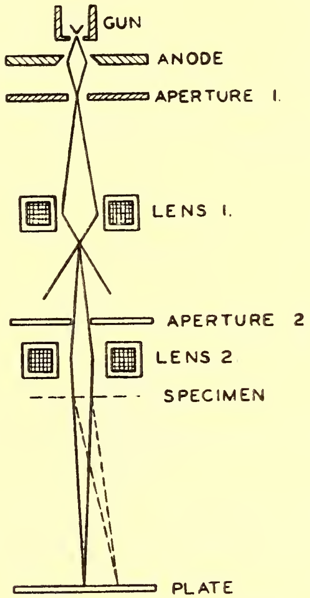


Fig. 1.—Principle of high-resolution electron diffraction camera.

accelerating voltage (determining the electron velocity) and in lens current (determining the focal length of the lens) and freedom from external perturbations, either electrical, magnetic or mechanical, are required. For a given resolution, the tolerable fluctuations in any of these may be calculated. This problem was analysed before construction of the diffraction camera in Melbourne (Cowley and Rees, 1952), which is shown in Plate II, Fig. 2.

Many of the applications of electron diffraction to solid state studies require high resolution, since it is the fine structural detail of these patterns which provides the relevant information. Recent work indicates that experimental conditions must be controlled even more rigorously if all useful information is to be extracted from the method.

Diffraction patterns obtained from specimens in which the crystallites are in random orientation, either by transmission through a powder specimen or by reflection from the surface of a polycrystalline solid, consist of circles centred on the undeflected beam. The radii of the rings give the diffraction angle $2\theta_{hkl}$, related to the lattice spacings $d_{hkl}$ by the Bragg law

$$(2/\lambda)\sin\theta_{hkl}=1/d_{hkl}.$$

Patterns from a single crystal or from a number of crystals in identical orientation consist of single reflection spots or, in special cases, an array of spots, which has become known as a cross-grating pattern owing to its resemblance to the diffraction pattern from a two-dimensional grating.

It is convenient to discuss diffraction from single crystals in terms of a concept introduced by Ewald, that of the *reciprocal lattice.* This concept is one

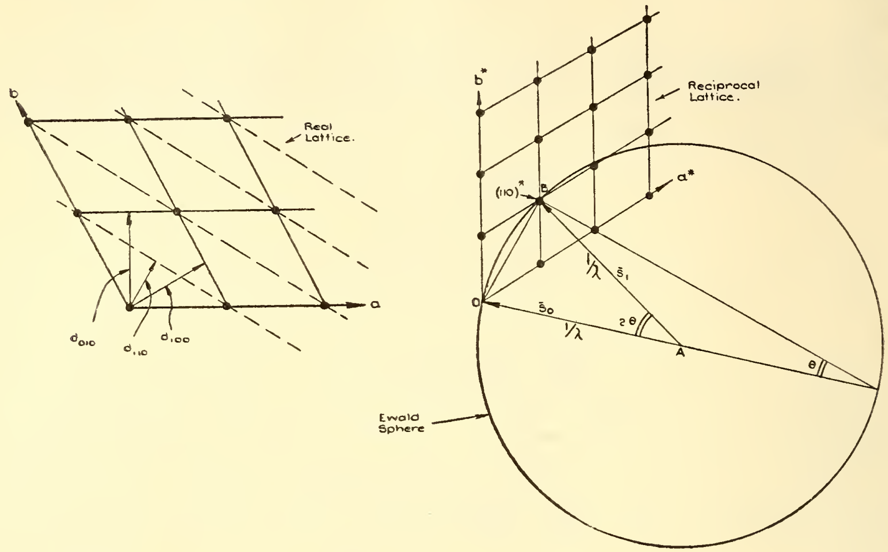


Fig. 3.—Ewald's reciprocal-lattice construction for diffraction conditions.

of the most useful in diffraction studies ; as it is necessary for subsequent discussion it will be outlined briefly here. The vector equivalent of Bragg's law is given by a construction wherein the incident beam is represented by a vector

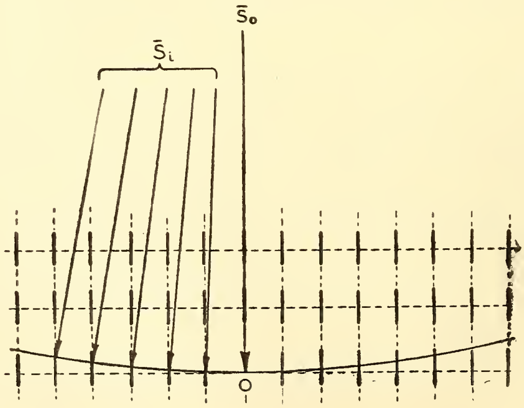


Fig. 4.—Reciprocal-lattice construction for diffraction by a thin crystal plate. Electron beam parallel to short dimension of crystal.

$\bar{S}_0$ of magnitude $1/\lambda$ and the diffracted beam by a vector $\bar{S}_1$, of identical magnitude but making an angle $2\theta$ with the incident beam. The difference between the vectors $\bar{S}_1$ and $\bar{S}_0$ is a vector of magnitude $1/d_{hkl}$ if the diffraction condition is satisfied. All diffracted beam vectors must terminate on the surface of a sphere centred on the origin of the beam vectors and of radius $1/\lambda$. If $d_{hkl}$ is a proper lattice spacing then it is obvious from Figure 3 that Bragg's law is implicit in this construction. The vector $\overrightarrow{OB}$, having the direction of a normal to the diffracting planes and of magnitude $1/d_{hkl}$ is termed a *reciprocal lattice vector*. For any given crystal lattice, a reciprocal lattice of terminal points of vectors $1/d_{hkl}$ may be constructed. The directions of the permitted diffracted beams for a specific orientation of the crystal to the incident beam vector $\overrightarrow{AO}$ will then

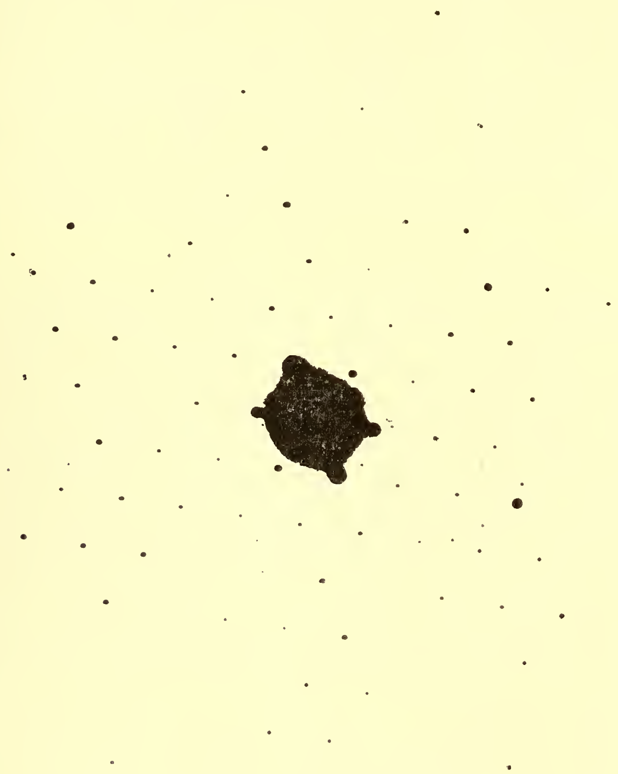

Fig. 5.—Cross-grating pattern from crystal of boric acid.

be given by the vectors $\overrightarrow{AB}$ terminated at the intersections of the Ewald sphere and the integer points of the reciprocal lattice. A change in orientation of the real crystal leads to a rotation of the reciprocal lattice about its origin O through the same angle. In this way different integer points of the reciprocal lattice intersect the surface of the Ewald sphere and diffracted beams are permitted. Reflections for which $1/d_{hkl}$ is greater than $2/\lambda$ will not be permitted as the corresponding reciprocal lattice points lie outside the volume swept out by the Ewald sphere pivoted on O.

In the same way that the resolving power of an optical diffraction grating is determined by the total number of lines, the angular breadth of a reflection from a three-dimensional crystal grating is greater the smaller the number of scattering points in the crystal. For an *infinite crystal* the reciprocal lattice is a lattice of points and the angular range of any reflection is infinitesimal; for a *finite crystal* the deterioration in resolution appears in the reciprocal lattice as a spreading of each reciprocal lattice point. This spread will be greatest in the direction of the smallest dimension of the crystal. The Ewald sphere will now pass through the region around a reciprocal lattice point for a range of directions of the incident beam vector. This is the origin of the dependence of breadth of reflections on crystal size.

The construction for the diffraction of fast electrons is simplified as $1/\lambda$ is much greater than the unit reciprocal lattice spacings and the Ewald sphere may be approximated by a plane or near-plane sectioning the reciprocal lattice. Moreover, since the small penetration of electrons limits the effective dimensions of the three-dimensional grating, it is to be expected that reciprocal lattice points will be invariably extended into the space between the integer points. For a thin crystal plate the diffraction conditions are as shown in Figure 4. The reciprocal lattice points are drawn out into spikes parallel to the short dimension of the crystal and the Ewald sphere of large radius can section many of these spikes simultaneously. The pattern resulting from such a diffraction experiment is a cross-grating pattern, a symmetry-true projection of a section of the reciprocal lattice. An example of such a pattern is given in Figure 5.

## The Structural Problem.

Application of electron diffraction to chemical problems followed its discovery very promptly; particularly successful application came from the laboratories of G. I. Finch, G. P. Thomson, S. Kikuchi, J. J. Trillat and L. H. Germer (Thompson and Cochrane, 1939; Finch and Wilman, 1937). Studies of the growth and structure of thin films, of the structure of metal oxides, particularly surface oxides, of surface films and lubrication were among the important fields of application to chemistry. The useful fundamental information extracted from these investigations was confined to cell dimensions, crystal symmetry, orientation and habit, and to some extent structure. No structural problems were attempted from single-crystal data and Fourier methods were not applied. The reason for this lay in the anomalies in observed electron diffraction intensities and in the presence of reflections forbidden on space-group grounds. These anomalies were ascribed to various causes, among them dynamic interaction, limitation of crystal dimensions and secondary scattering.

Over the last five years Pinsker and his colleagues (Vanchstein and Pinsker, 1949, 1950) have used intensity data from powder patterns to analyse crystal structures by Fourier methods. The disadvantage of using patterns of this type, from which only one parameter, the Bragg angle, is available for determining the geometry of the lattice and in which different reflections often appear in coincidence, is familiar to all crystallographers. The possible use of single-crystal data for structure analysis was examined in Melbourne several years ago as the result of the study of secondary scattering of electrons (Cowley *et al.*, 1951*a*).

The high efficiency of elastic scattering of electrons results in the appearance of a considerable proportion of the incident energy in the diffracted beams; strong primary reflections may therefore be rediffracted by underlying crystallites or mosaic elements of the same crystal as shown in Figure 6. This secondary scattering may lead to many unusual and anomalous features in patterns; in polycrystalline specimens extra spots, extra rings, groups of spots, diffuse bands with sharp edges and rings centred on primary spots may occur; in single-crystal patterns a redistribution of the intensity among the reflections in the pattern and the appearance of the forbidden reflections may result. These features are illustrated in the patterns as shown in Plate III, Figs. 7, 8, 9 and 10.

In the cross-grating pattern of Plate III, Fig. 10, there are superimposed secondary patterns identical with the primary pattern and of the same orientation, but centred on each of the primary reflections. The secondary reflections consequently coincide with primary reflections of different indices. This is illustrated in Figure 11. Each reflection in the pattern has lost intensity by contributing to all other reflections and has gained by secondary contributions from every other spot. This modification of the intensities is the obstacle to their use for structure analysis.

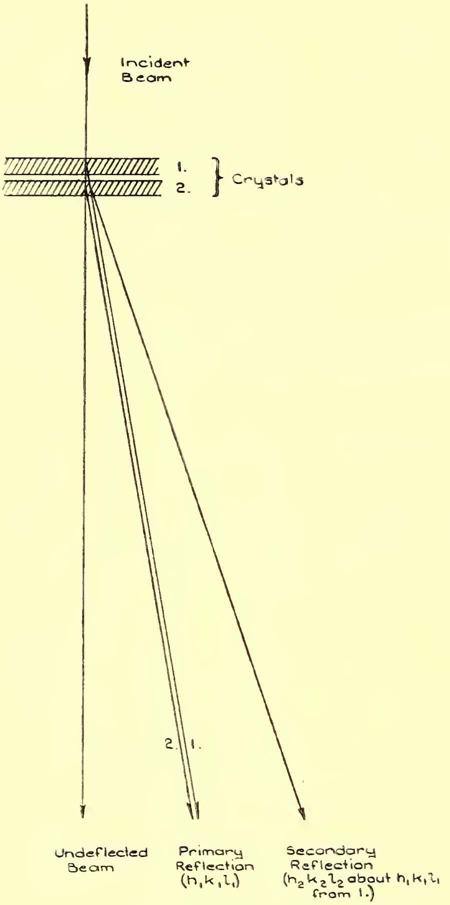


Fig. 6.—Diagrammatic representation of secondary elastic scattering of primary diffracted beams by underlying crystallites. See Plate III, Figs. 7-10.

The theoretical problem is relatively simple. The contribution by secondary scattering from a reflection $h_1k_10$ to another reflection $h_2k_20$ is proportional to the product of the theoretical intensities

$$I_{h_1k_10} \cdot I_{(h_2+\bar{h}_1)(k_2+\bar{k}_1)0}$$

and the total contribution from all primary reflections to this reflection is proportional to the sum of such products over all indices $h_1$ and $k_1$

$$\sum_{h_1}\sum_{k_1} I_{h_1k_10} \cdot I_{(h_2+\bar{h}_1)(k_2+\bar{k}_1)0}$$

A mathematical analysis on this basis leads to an expression for the correction of observed intensities for secondary scattering. The magnitude of the corrections and the way in which they account for the intensity anomaly is shown in Figure

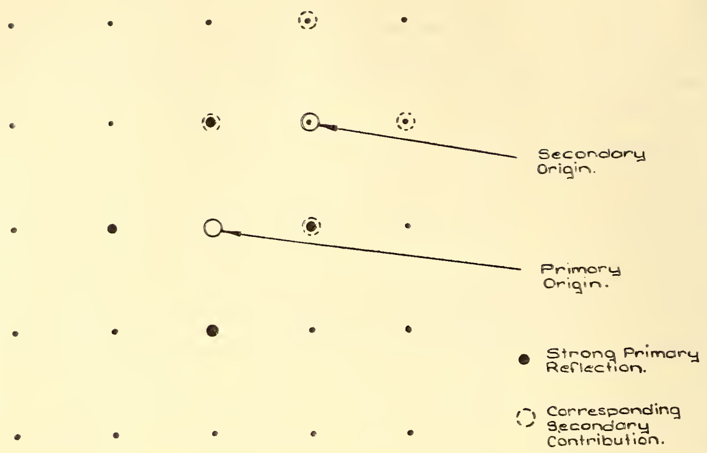


Fig. 11.—Diagram showing coincidence of secondary reflections with primary reflections of different indices in a cross-grating pattern.

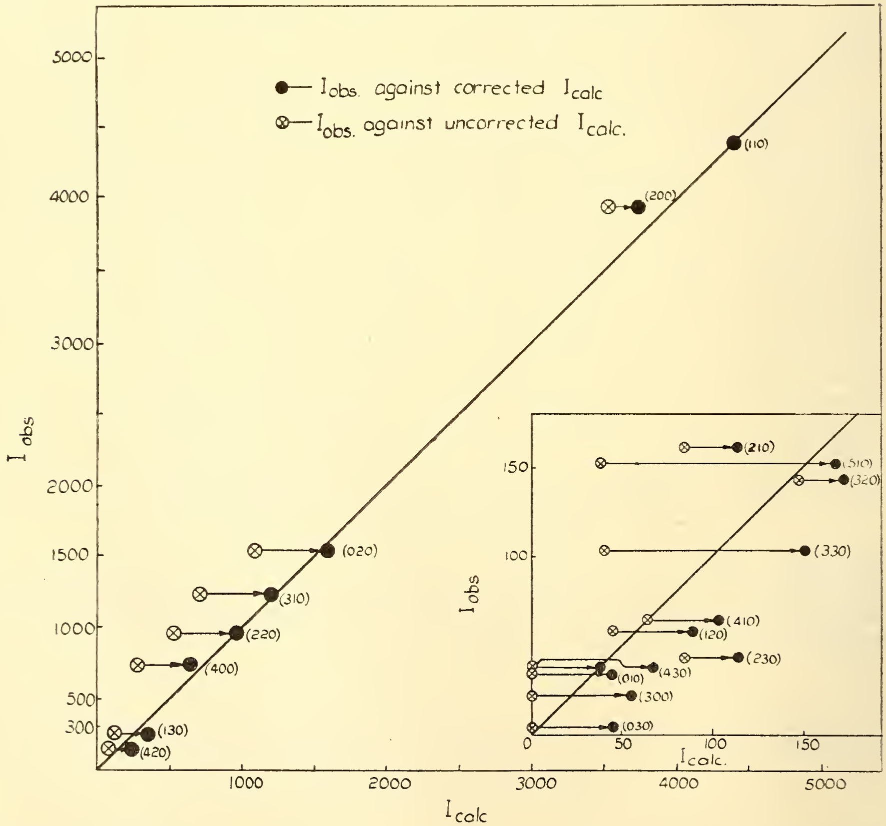


Fig. 12.—Comparison of observed and calculated intensities of reflections from dicetyl single-crystal. Satisfactory correspondence of observed and calculated intensities is obtained only when a correction for secondary scattering is introduced.

. 13.

. 14.

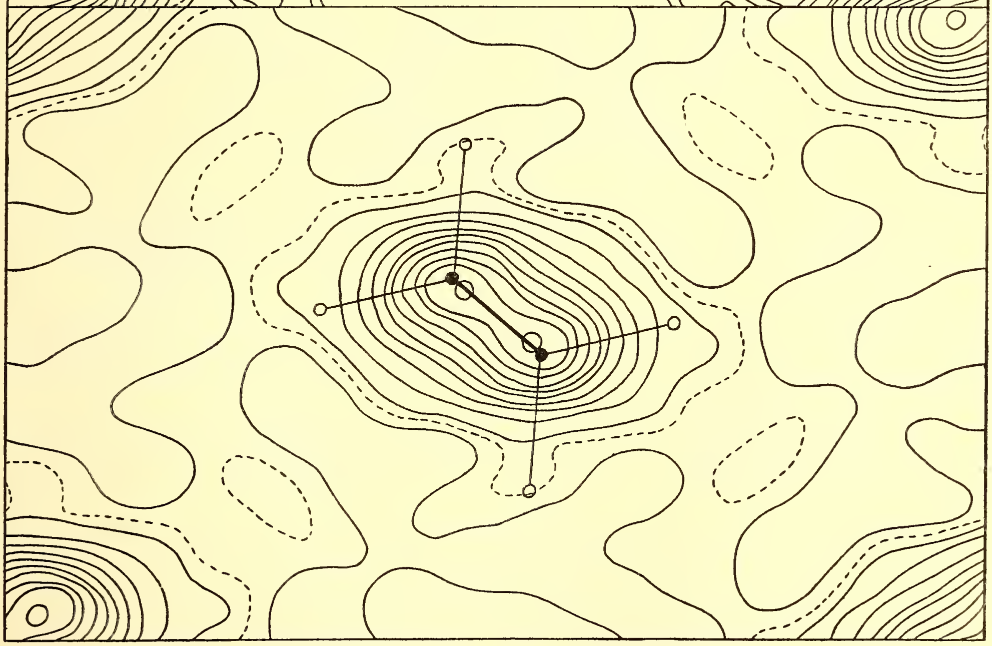

Fig. 13.—Basal-plane Fourier projection of potential distribution in dicetyl using intensity data uncorrected for secondary scattering.

Fig. 14.—Basal-plane Fourier projection of potential distribution in dicetyl using intensity data corrected for secondary scattering. Full circles denote carbon atom positions and open circles hydrogen atom positions deduced from data on bond lengths and angles. Note that the hydrogen atom positions are clearly indicated in the contour map.

12. The importance of this correction in structure analysis was tested by obtaining basal-plane Fourier projections of the hydrocarbon dicetyl ($C_{32}H_{66}$). The Fourier projections obtained from diffraction of electrons are projections of the distribution of potential in the lattice and not of the electron density, to which, however, they are closely related. In Figure 13 the contour map obtained from uncorrected intensities shows spurious and misleading detail ; in Figure 14 the contour map obtained from corrected intensities not only shows the carbon atom positions but also gives an indication of the hydrogen atom positions.

This particular test structure analysis made it clear that the application of electron diffraction to structural problems in chemistry had specific merit. Crystals of very small dimensions only are necessary and light atoms, notably hydrogen, can be located more readily than by X-ray methods owing to their

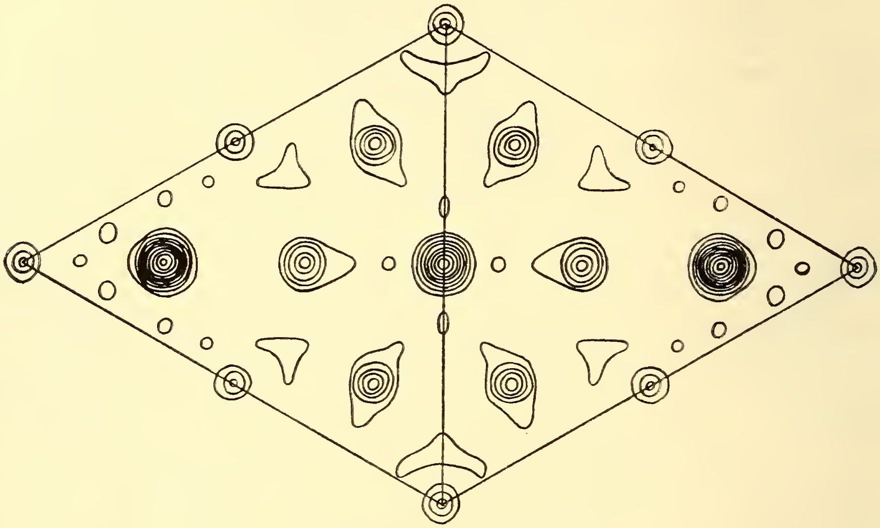

Fig. 15.—(111)-Fourier projection of $\gamma$-$Al_2O_3$ obtained from intensities in an electron diffraction cross-grating pattern. This projection must be interpreted in terms of a stacking disorder in the lattice.

higher relative scattering power for electrons than for X-rays. New problems are, however, introduced, a major one being the measurement of intensities. Intensities must be measured with greater accuracy than in the X-ray method, but this is not difficult to achieve.

The results of subsequent structural studies by Dr. J. M. Cowley and Mr. A. F. Moodie have justified development of this method and illustrate its value in chemistry.

It has been known for some time that the electron diffraction pattern of polycrystalline gold foil developed several extra reflections if the specimen was heated at $\sim$500° C. in air or oxygen. Nothing of this sort occurred if larger specimens treated in the same way were studied by X-ray methods. Moodie (unpublished work) succeeded in obtaining cross-grating patterns after protracted heating of gold films in oxygen and was able to identify several Au-O phases of different symmetry from these patterns. The intensity data were complete enough to obtain Fourier projections of two of these phases. The significant feature of this result is that gold dissolves oxygen to form well-characterized phases of low oxygen content, even though on a bulk specimen this may be confined to a surface layer less than 100 Å thick. This is, moreover, a problem which could not be investigated by X-ray methods as the low heat of formation of these phases and the high heat of activation of the diffusion of oxygen into

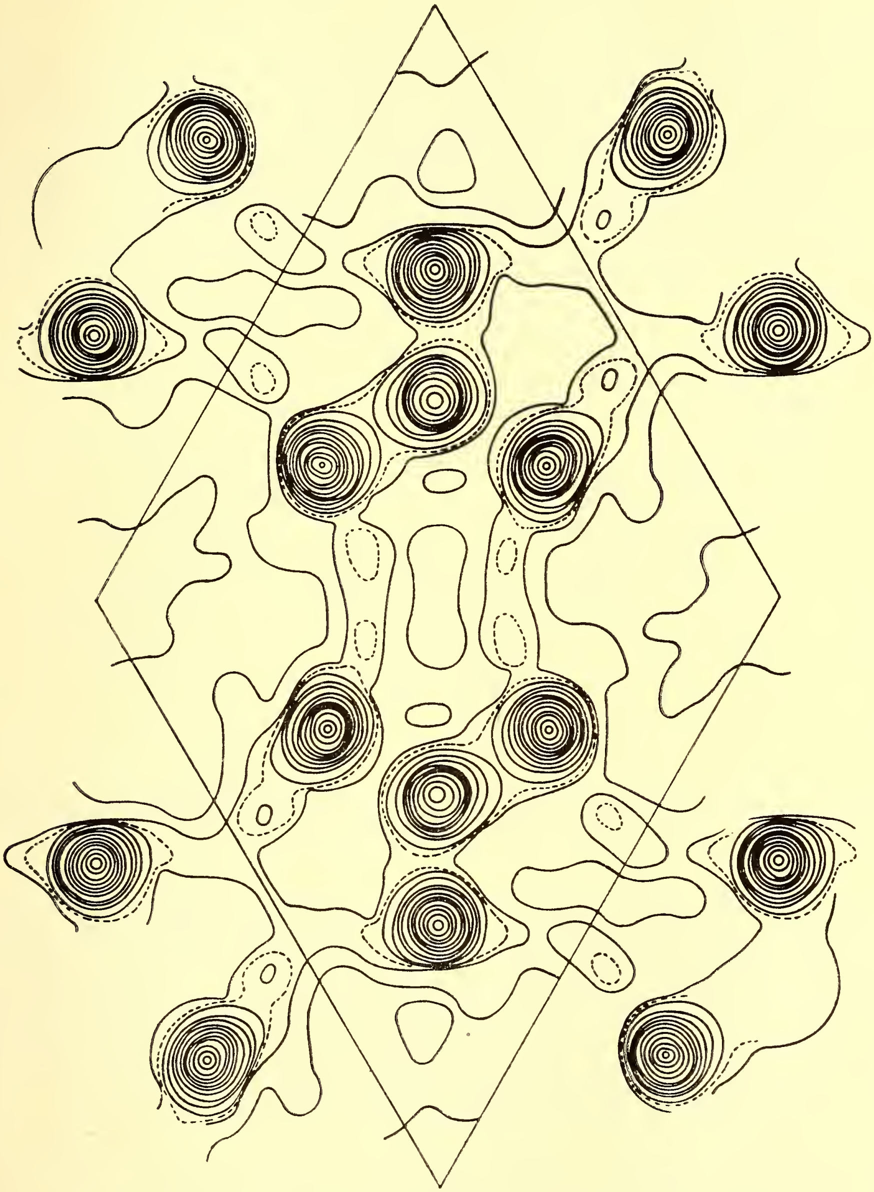

Fig. 16.—Basal-plane Fourier projection of boric acid crystal showing distribution of potential in single two-dimensional layer of the lattice. The trigonal groups are $BO_3^{3-}$, each forming three pairs of hydrogen bonds with the three neighbouring $BO_3^{3-}$ groups. Note the distribution of potential in the region of the hydrogen-bond pairs.

gold preclude the preparation of any but a small amount of the material in a reasonable time.

Cowley (unpublished work) has studied the structure of $\gamma$-alumina and related compounds. A (111) Fourier projection of a disordered $\gamma$-$Al_2O_3$ (cubic, spinel-type) is shown in Figure 15. The X-ray work on $\gamma$-$Al_2O_3$ has been confined to powder patterns largely because of the small crystal size and the extensive disorder.

The structure of boric acid has been determined by Zachariasen (1934) by X-ray methods in so far as the boron and oxygen locations are concerned, but no information on the location of the hydrogen atoms was obtained. It was inferred from the intermolecular O–O distances, however, that hydrogen-bonds occur extensively in the structure. Cowley (1952) has developed new methods of dealing with stacking disorder in layer-lattice structures and has been able to obtain a clear projection of a single two-dimensional atom layer showing

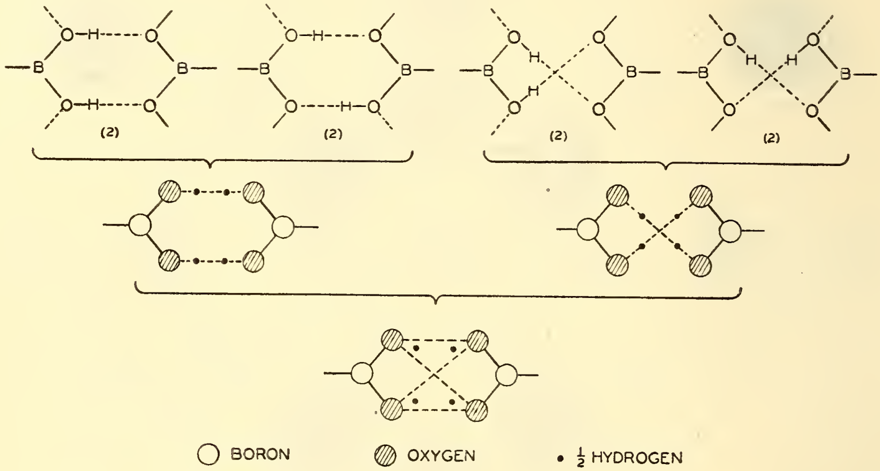


Fig. 17.—Diagram showing the eight possible canonical structures for a pair of hydrogen bonds in the boric acid structure and the resulting " resonance " structure.

trigonal $BO_3^{3-}$ groups and also the *hydrogen bonds* interlinking these groups. The projection is shown in Figure 16. It is to be noted that (i) the hydrogen atom in the bond tends to be near either one oxygen or the other and not symmetrically disposed between them, and (ii) hydrogen positions do not lie on the internuclear line between the hydrogen-bonded oxygens. Evidently the explanation is to be found in the interaction of the two parallel orthodox hydrogen bonds. There are, in fact, eight different canonical structures that may be written down showing different possible positions of the protons. These structures are given in Figure 17 together with the resultant distribution. This type of hydrogen-bond " resonance " must be common among oxyacids of the non-metals and probably occurs in protein structures also. This type of structural study would certainly be impossible by X-ray methods at present.

Of further chemical interest is the fact that structural disorder is common in small crystals. For layer-lattice structures it is invariably present. It is possible that the 3-dimensional structure of larger crystals is not the thermodynamically stable configuration when crystal dimensions are small. Moreover, there is evidence (Rees and Spink, 1950*a*) that the lattice parameters change significantly when crystal dimensions are reduced. Further study along these lines is desirable.

## Fine Structure in Electron Diffraction Patterns and the Size and Habit of Crystals.

High-resolution diffraction patterns show fine structure of the individual single-crystal reflections which is closely related to the size and habit of the crystal. The origin of this fine structure is to be found in two effects, namely (i) the deviation of an electron beam on crossing a crystal boundary (refraction) (Sturkey and Frevel, 1945 ; Hillier and Baker, 1945, 1946 ; Cowley and Rees, 1946, 1947 ; Honjo, 1947), and (ii) the extension of reciprocal lattice points arising from small crystal dimensions (Rees and Spink, 1950*b*). These effects may be discussed independently by means of a kinematic approximation, adequate for most purposes, or more rigorously by a dynamic treatment.

Since the potential inside a crystal is different from that of free space, the electron velocity is also different and a refraction phenomenon is to be expected. Actually the square root of the inner potential is the electron analogue of the refractive index for light. Angular deviation of an electron beam will occur at

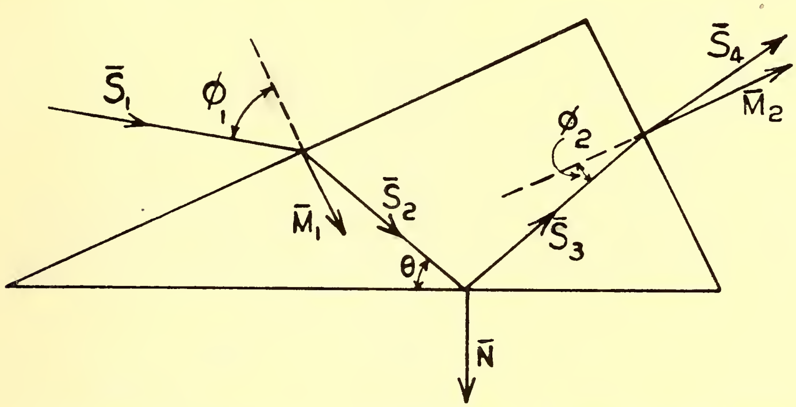


Fig. 18.—Diagram of deviation of an electron beam at entrant and exit faces of a crystal at diffraction plane. $\bar{S}_1$, $\bar{S}_2$, $\bar{S}_3$ and $\bar{S}_4$ are beam vectors ; $\bar{M}_1$ and $\bar{M}_2$ are crystal normals ; $\bar{N}$ is the diffracting plane normal ; θ is the Bragg angle.

the entrant and exit faces of a crystal and also, if the diffraction conditions are satisfied, at the diffracting planes inside the crystal, as shown in Figure 18. Since the deviations due to refraction are normally very small, electrons entering non-parallel faces of the crystal may still satisfy the somewhat relaxed diffraction conditions associated with small crystals. Each single reflection will consequently be broken up into a number of components corresponding to the number of possible entry and exit faces presented to the beam by the crystal in its given orientation. Typical spot groups attributable to refraction are shown in Plate IV, Fig. 19. The spot configuration is characteristic of the orientation and habit of the crystal.

The effect of crystal shape can be discussed only in terms of the reciprocal lattice. As we have seen earlier, the shape of the relevant reciprocal lattice region about an integer point depends on the external form of the crystal and in fact the distribution of scattering amplitude around each integer point of the reciprocal lattice is accurately described by the square of a function of the reciprocal lattice co-ordinates known as the shape transform. This amplitude is greatest along directions perpendicular to crystal faces and the transform is in fact a 3-dimensional periodic function. For a plain parallel slab the scattering amplitude is extended along the c*-direction and is of the form $\sin^2 N\pi u/(N\pi u)^2$, where $u$ is the reciprocal lattice co-ordinate measured from the integer point and $N$ is the number of scattering points in that direction. Referring now to Figure 20, in which the situation for refraction and diffraction at (110) planes of a small crystal of cubic habit is represented in real and reciprocal space, we see the way in which the more complicated spot groups originate. A contour map of the distribution of scattering amplitude around a reciprocal lattice point in a small crystal of cubic habit is shown in Figure 21. There is now a different Ewald sphere for each face of entry and each sphere makes a different section of the amplitude function. Each refraction spot is broken up into a configuration determined by the shape transform. In some instances the sphere sections the

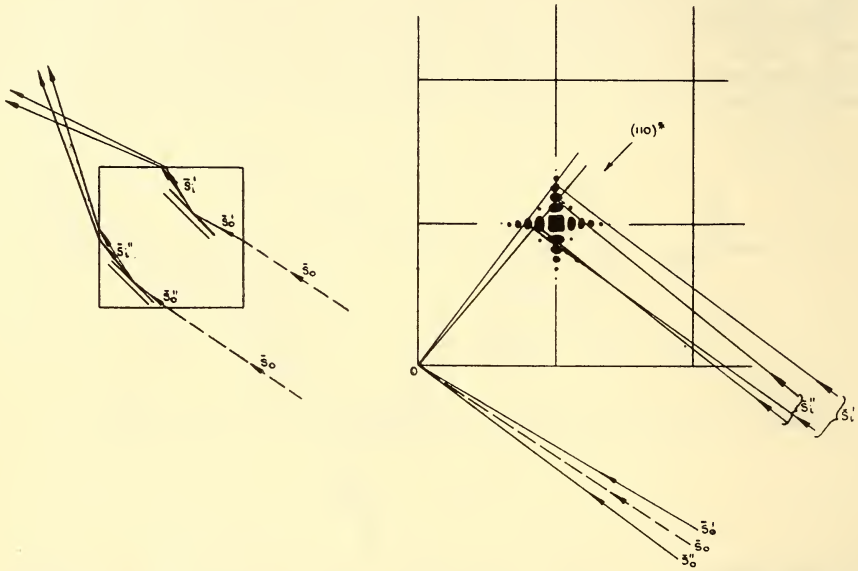


Fig. 20.—Diagram illustrating splitting of the 110 diffraction spot into group of reflections by a very small crystal of regular habit (cubic) in real and reciprocal space. The vectors $\bar{S}_0$ denote beams prior to diffraction, the vectors $\bar{S}_1$ denote beams after diffraction. The distribution of scattering amplitude (square of the shape transform) around the (110)* reciprocal-lattice point is shown on a considerably enlarged scale.

transform in such a way as to show the subsidiary maxima, from the positions of which the dimensions of the crystallite may be determined uniquely (Rees and Spink, unpublished). Examples of this are shown in Plate II, Fig. 22. Further development of this could provide one with a powerful method of studying crystal growth.

An interesting example is provided by zinc oxide prepared by burning zinc in air or oxygen. The particles grow as "fourlings", four elongated hexagonal prisms roughly in tetrahedral configuration. Often one finds thin sheets forming webs between one spine and each of the other three. Further spines may grow from these sheets. It has been possible to use electron diffraction methods to provide a complete morphological description of these crystals (Cowley *et al.*, 1951*b*). A drawing of an idealized crystal is shown in Figure 23 and an electron micrograph in Plate IV, Fig. 24. The reason for this fantastic habit is not known, but it does represent an interesting problem in the mechanism of crystal growth.

The possibility of deducing the shape of the molecules of crystalline proteins is within reach. These molecules are well ordered units of dimensions of the order of 50–100 Å and should give reflections from individual molecules in a dried molecular dispersion. The water necessary to preserve long-distance order in protein crystals is intermolecular and drying should not therefore interfere with the order in each individual molecule. Shape transform detail should allow a complete and unique description of the polyhedral shape of the molecule to be given, an important step in the structure analysis of large complex molecules.

The rigorous (dynamic) treatment of diffraction (Bethe, 1928 ; Heidenreich, 1950 ; and Kato, 1951) predicts a different effective inner potential for different

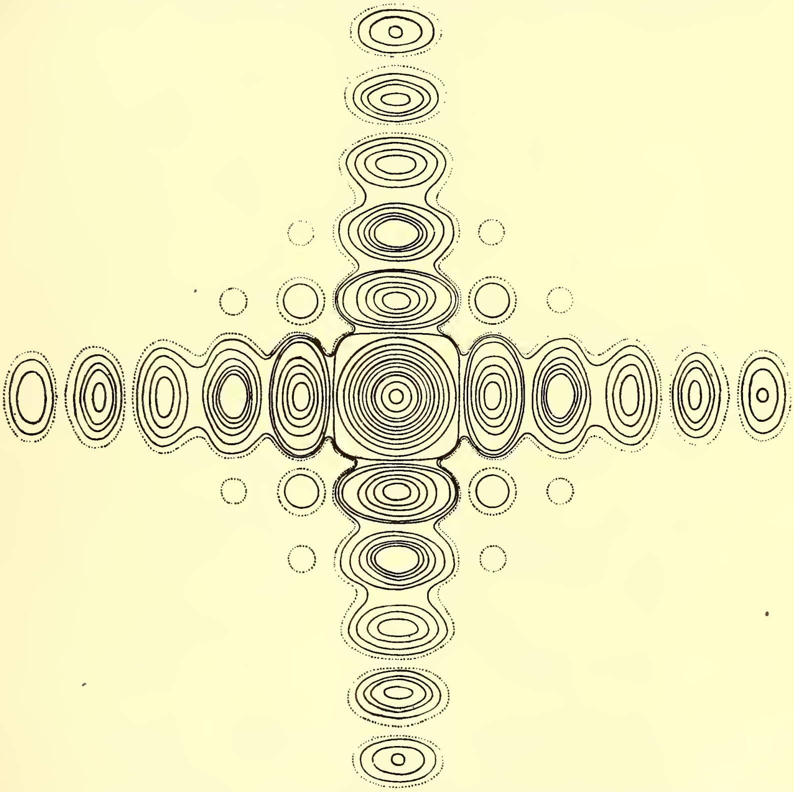

Fig. 21.—Contour map of scattering amplitude around a reciprocal lattice point for a crystal of cubic habit.

reflections, a prediction which is confirmed by experiment. Experimental data on the dimensions and configurations of spot groups such as those of Figure 19 may be used to deduce the Fourier coefficients $V_{hkl}$ of the three-dimensional potential distribution in the unit cell. Goodman (unpublished work) has been able to compute the $V_{hkl}$ values for several reflections in MgO from his experimental data and has shown that they are in good agreement with values obtained from the known structure of MgO. This provides us with a new approach to structure analysis. The Fourier coefficients may be determined for all observable reflections by measurements of spot group dimensions and the structure analysis performed in the usual way. This could be of considerable value for crystals for which intensity measurements are difficult to make. It is my opinion that this represents the most promising approach to the problem of structure analysis by electron diffraction.

## Reactions in the Solid State.

At some stage in a reaction involving the solid state a new solid phase must be formed from a solid reactant phase. The mechanism by which this is accomplished is a problem of some importance in chemistry. For simplicity we may examine two types of solid state reactions, namely

(i) *tarnish reactions*, in which an oxide, sulphide, halide, etc., film is formed on the surface of a metal by reaction with the corresponding non-metallic element ; and

(ii) *simple dissociation processes*, in which an ionic compound is decomposed by thermal or photo-chemical means into a gas and a solid product.

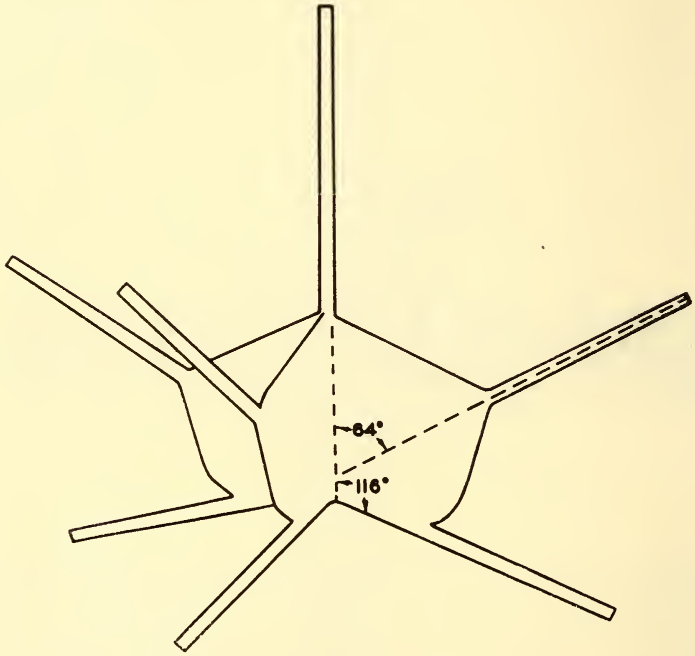


Fig. 23.—Diagram of ideal crystal form of "fourling" in ZnO smoke. Three needles of hexagonal section are twinned on (11$\bar{2}$2) with the fourth needle (vertical in the diagram) making an angle of 116° with it. The webs grow as continuations of the lattice of the vertical needle and have a twin relationship with the three lower needles.

The nucleation and growth steps are always the result of aggregation of defects in the crystal, *e.g.* in simple dissociation reactions the step may be either the aggregation of interstitial cations or of vacant anion lattice sites trapping electrons. A schematic representation of the aggregation of vacancy defects is given in Figure 25. The aggregate of defects is in fact simply a lattice of cations and electrons, that is, a small crystal of the metal with somewhat enlarged lattice dimensions and perhaps different symmetry. It is clear that the defect aggregate will at some point become thermodynamically unstable and break away from the parent lattice to form a small crystal of the metal of correct lattice dimensions. The metal lattice will have an orientational relationship to the parent lattice which will reflect the mechanism of nucleation and this can be established by electron diffraction studies. Moreover, the size and shape of the precipitated particles can be deduced from the fine structure.

An illustration of this type of study is Pashley's (1950, 1951) recent work on the photolytic and electron-induced decomposition of silver halides. Pashley was able to show that the lattice of silver produced from silver chloride is in parallel orientation to the silver chloride lattice, even though the cell dimensions of the two are such that no good atomic fit is to be expected. AgCl is a cubic crystal of the $NaCl^-$ type; the $Ag^+$ ions form a face-centred cubic lattice of side 5·55 Å. Removal of $Cl^-$ ions by aggregation of F-centre defects will leave a face-centred lattice of Ag of side 5·55 Å, which at some stage collapses to give the face-centred cubic lattice of silver metal of side 4·08 Å without change of orientation. This particular study is of importance in the mechanism of the

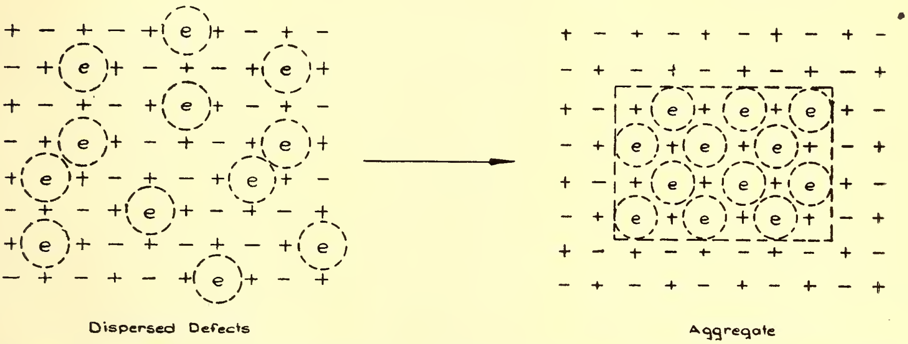


Fig. 25.—Illustration of the aggregation of F-centre defects in an ionic lattice to give a metallic nucleus.

photographic process. Reactions in the solid state are intimately associated with the existence of crystal defects, the structural consequences of which are almost unknown. In my opinion electron diffraction is capable of providing this information with little improvement on present experimental methods.

## Conclusion.

Our understanding of the chemistry of the solid state, particularly those aspects which concern small crystals and defect solids, is still elementary and any prospect of increasing this understanding is of no small consequence. Recent developments in electron diffraction show promise of improving this knowledge and point the way to undoubtedly fertile fields of scientific work.

The work we have done in Melbourne in an effort to pioneer some of these fields has been carried out by a small group, namely Dr. J. M. Cowley, Messrs. A. F. Moodie, P. Goodman and J. A. Spink. They are responsible for the diffraction patterns used for illustration here, and I gratefully acknowledge my indebtedness to them.

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Pashley, D. W., 1950. *Acta Crystallographica*, **3**, 163.
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Sturkey, L., and Frevel, L. K., 1945. *Phys. Rev.*, **68**, 56.
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Vanshstein, B. K., and Pinsker, Z. G., 1949. *J. Phys. Chem., U.S.S.R.*, **23**, 1058.
——— 1950. *Dokl. Akad. Nauk., S.S.S.R.*, **72**, 53.
Zachariasen, W., 1934. *Z. Krist.*, **88**, 150.

## Explanation of Plates.

### Plate II.

Fig. 2.—Electron difiraction camera in Chemical Physics Section, Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

Fig. 22.—Fine structure of single reflections in patterns from small crystals of ZnO of elongated hexagonal prismatic habit.

### Plate III.

Fig. 7.—Electron diffraction pattern from crystals of a long-chain paraffin hydrocarbon. Secondary scattering is responsible for diamond-shaped groups of reflections and extra spots inside first strong ring.

Fig. 8.—Electron diffraction pattern from dicetyl showing secondary rings centred on strong primary reflections. Secondary rings originate from diffraction by numerous small crystals in random orientation underlying a large crystal giving the strong primary spots.

Fig. 9.—Electron diffraction pattern from dicetyl illustrating the origin of "extra" rings. The envelope (distinguished by an arrow) of the numerous secondary rings, which originate from either (i) 200 secondaries around 110 primaries, or (ii) 110 secondaries around 200 primaries, forms a non-legitimate "extra" ring centred on the undeflected beam.

Fig. 10.—Cross-grating pattern from single-crystal of dicetyl showing effects attributable to secondary scattering. The odd orders on both axes are forbidden on space-group grounds, but appear in the pattern as a result of secondary scattering.

### Plate IV.

Fig. 19.—Typical spot groups in patterns from MgO crystals of cubic habit. These spot groups, which comprise the fine structure of ring patterns from specimens consisting of randomly oriented crystals of regular habit, are attributable in part to refraction effects.

Fig. 24.—An electron micrograph of an imperfect ZnO "fourling" showing webs. The dotted outline is a dark-field image of this crystal.

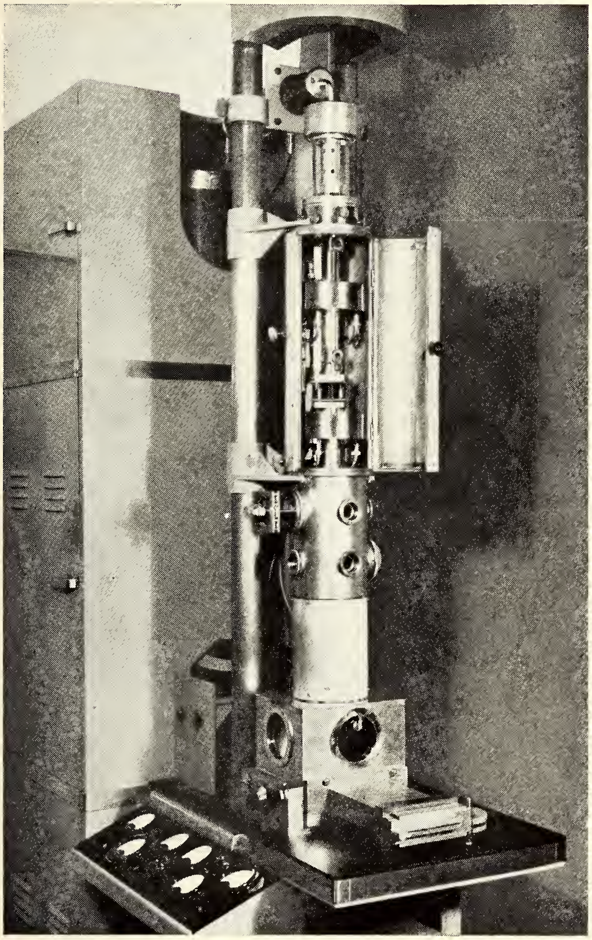
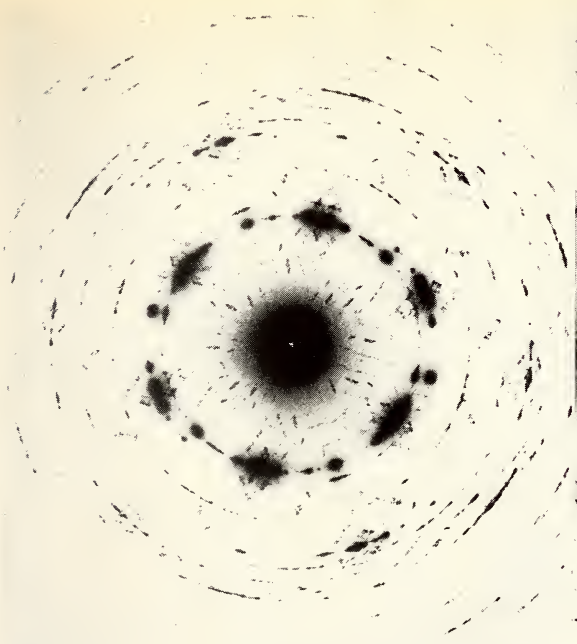


Fig. 2.

Fig. 22.



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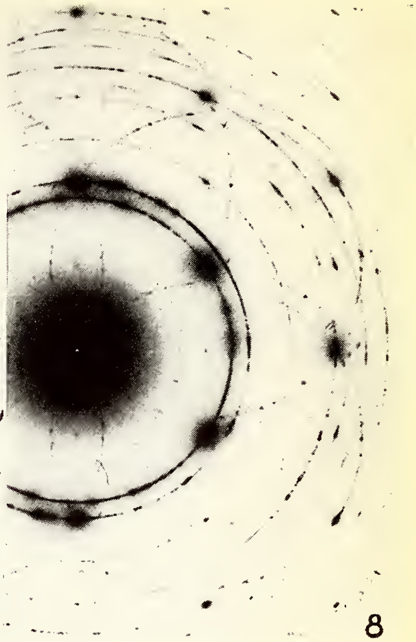

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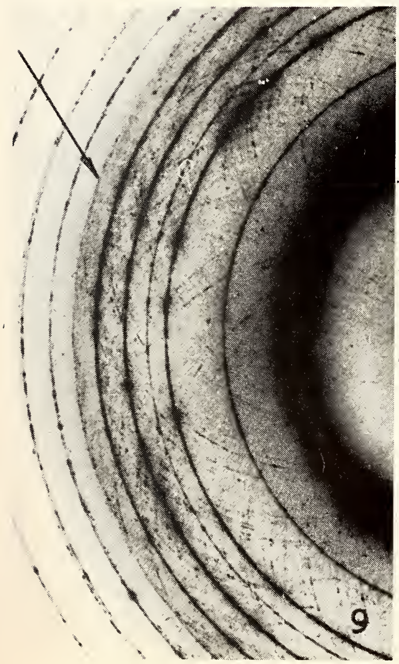

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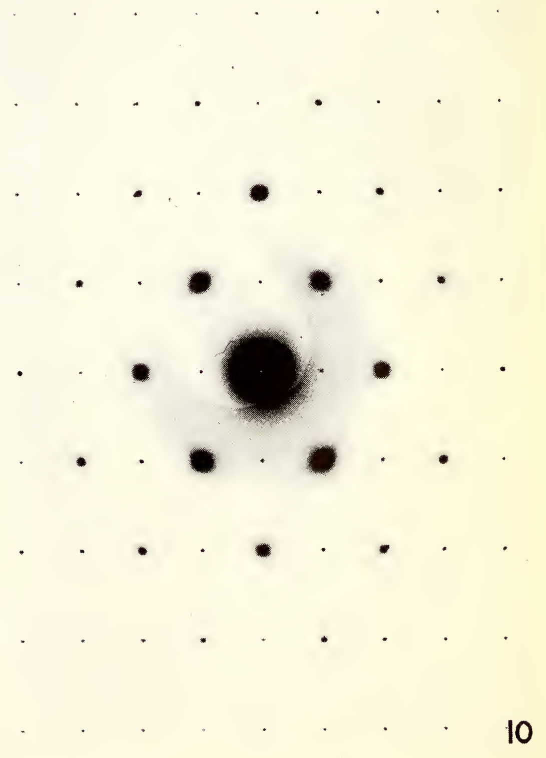

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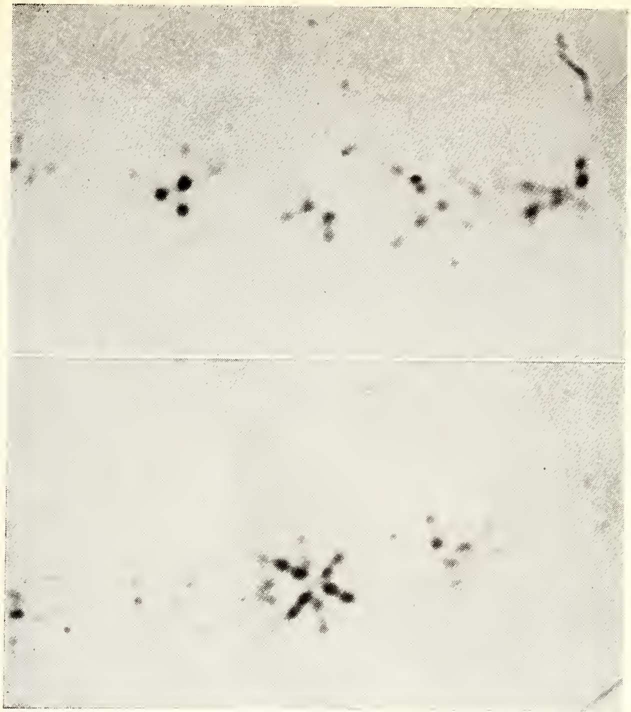

Fig. 19.

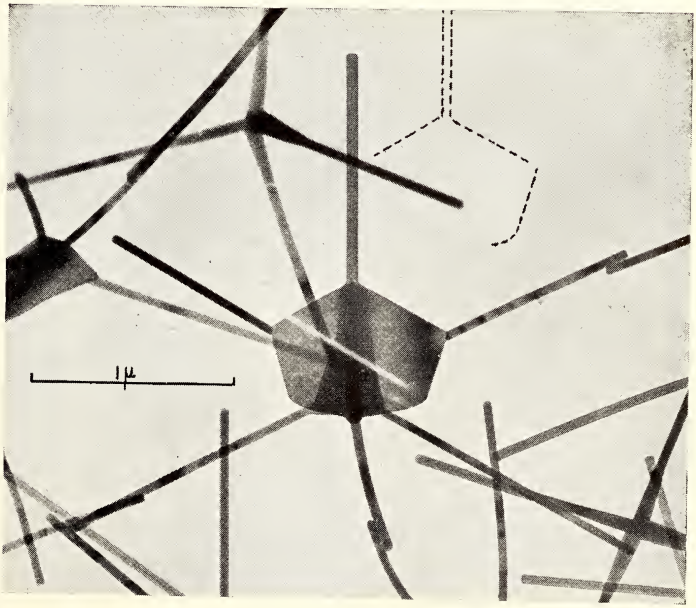


Fig. 24.

# PERMIAN SPIRIFERS FROM TASMANIA.

By Ida A. Brown, D.Sc.
[Mrs. W. R. Browne.]

With Plates V and VI.

*Manuscript received, July 14, 1952. Read, August 6, 1952.*

*Abstract.*—Descriptions are given of two species of Permian Spirifers (Brachiopoda) from the Berriedale (or Granton) Limestone near Hobart, Tasmania; one, *Trigonotreta stokesii* Koenig, 1825, based on the holotype and on topotype material collected by the writer, the other, *Trigonotreta stokesii* auctt. (*non* Koenig, 1825), for which the name *Grantonia hobartensis* gen. et spec. nov. is proposed. It is shown that *Spirifer tasmaniensis* Morris, 1845, is a synonym for *Trigonotreta stokesii* Koenig, 1825.

## Introduction.

The early collections of Australian Permian Spirifers made by Robert Brown, Darwin, Strzelecki, Dana, W. B. Clarke and others were sent to Europe or America for identification and description and most of them were retained in museums abroad. Thus the holotypes of many of the most common and important species of south-eastern Australian fossils have not been re-examined since their original descriptions, in some cases more than one hundred years ago.

In 1938 the writer examined all the known holotypes of eastern Australian Permian spirifers in museums in England, and during 1946 and 1947 studied the extensive brachiopod collections from all parts of the world in museums in U.S.A., particularly at the U.S. National Museum, Washington, D.C.; the American Museum of Natural History, New York; the Peabody Museum, Yale; and the Museum of Comparative Zoology, Harvard. Museum collections in Australia have supplemented the writer's own collections made in Tasmania in January, 1940, and in New South Wales over many years.

This work has revealed some rather unexpected misconceptions, two of which are discussed below. These concern specimens collected by R. Brown and P. E. de Strzelecki.

Robert Brown, naturalist to the Joseph Banks Expedition to New Holland (Australia) under Capt. Matthew Flinders (1798 to 1802), made a collection of fossils, which was described briefly by Buckland (1821, p. 481). Apparently the collection was acquired by Charles Stokes, a member of Council of the Geological Society of London, who donated it to the Society's Museum in 1821 (Stokes, 1821 : 1854, xxvi). It was transferred to the British Museum in 1911. The specimen of *Spirifer* in this collection was described by C. Koenig (1825) and named by him *Trigonotreta Stokesii*, " a supra laudato Carola Stokes nobiscum communicata ". A wax cast of the specimen was presented by Chas. Stokes to the British Museum (Nat. Hist.), specimen B4798, and a plaster cast of this is in the University of Sydney, by courtesy of the British Museum.

P. E. de Strzelecki collected a number of fossils during his visit to this country in 1839 to 1843 and the Permian spirifers in his collection were described by J. Morris (in Strzelecki, 1845). The specimens are in the British Museum, and plaster casts of them were presented to the University of Sydney and the Australian Museum in 1939.

Although frequent reference has been made to the genus *Trigonotreta*, no description of the genotype based on the type specimen has been published since Koenig's original identification. The misinterpretation of this species by Morris (1845) has been the cause of much confusion in the literature dealing with the affinities of the genus and also the recognition of the species.

The following description is based on an examination of the holotype, on a topotype collection made by the writer, and a study of comparative material in the U.S. National Museum, Washington, D.C. The two species concerned both occur in the Berriedale or Granton Limestone of the Granton Stage (Voisey. 1938) of the Permian, in the vicinity of Hobart, Tasmania.

No classification (other than generic) of the spirifers is offered at this stage, since the writer is of the opinion that such is futile in the present state of knowledge of the group. The " Classification of the Spiriferidæ " by Fredericks (1926) is admitted by him to be purely artificial and unnatural.

The terminology used in this paper is that defined by Cloud, 1942, except where otherwise stated.

## Acknowledgements.

The writer wishes to thank all those who have assisted in this work, particularly Dr. W. D. Lang and Dr. H. M. Muir-Wood of the British Museum ; Dr. G. A. Cooper of U.S. Nat. Museum ; Prof. C. O. Dunbar, Yale ; and Mr. H. O. Fletcher of the Australian Museum. The late Dr. A. N. Lewis gave valuable assistance in the field-work in Tasmania and Prof. L. A. Cotton arranged for the writer's leave of absence from teaching duties on two occasions for study abroad, for which she is deeply appreciative.

A grant from the Commonwealth Research Fund administered by the University of Sydney to cover portion of the field expenses in Tasmania is gratefully acknowledged.

### Genus **Trigonotreta** Koenig, 1825.

Plate V, figs. 1–5.

Koenig, C., 1825. *Icones Fossilium Sectiles*, p. 3, pl. 6, fig. 70.

Bronn, H. G., 1837. *Lethæa Geognostica*, Vol. I, p. 77, Tab. II.

King, W., 1850. The Permian Fossils of England, *Pal. Soc. of London*, Vol. 3, Pt. 1, pp. 81, 122, 126–134.

Davidson, T., 1854. British Fossil Brachiopoda, *Pal. Soc. of London*, Vol. VII (for 1853), p. 79.

Meek, F. B., and Hayden, F. V., 1865. Pal. of Upper Missouri, *Smiths. Cont.* No. 172, Wash., p. 19.

Schuchert, C., 1893. *American Geologist*, Vol. XI, p. 141.

Hall, J., and Clarke, J. M., 1894. Natural History of New York, *Palæontology*, Vol. VIII, Brachiopoda, Part II, p. 8.

Hall, J., and Clarke, J. M., 1894. 13th Annual Report of the State Geologist of New York (for 1893), Vol. II, p. 751.

Schuchert, C., 1897. Synopsis of American Fossil Brachiopoda, *Bull. U.S. Geol. Surv.*, No. 87, p. 127.

Buckman, S., 1908. Brachiopod Homœomorphy : *Spirifer glaber*, *Quart. Jour. Geol. Soc. London*, Vol. 64, p. 30.

Schuchert, C., 1913. In Zittel : Text-book of Palæontology, p. 410.

SCHUCHERT, C., and LE VENE, C. M., 1929. Fossilium Catalogus, Animalia, Pars. 42, Brachiopoda, p. 125. W. Junk, Berlin.
PAECKELMANN, W., 1932. Neues Jahrb. fur Min., *Geol. u. Pal.*, Ablandl. 67, BB. Abt. B, Erstes Heft, z. 9,36.

Genotype (by subsequent designation). (?) King, 1850, or Buckman, 1908.

*Trigonotreta stokesii* Koenig, 1825. Locality, Isle of Van Diemen, New Holland (=Tasmania).

*Diagnosis.* Impunctate, spiriferoid brachiopods ; biconvex, width greater than the length ; high ventral interarea, open delthyrium, strong medial fold in dorsal valve and corresponding sulcus in ventral valve. Anterior commissure parasulcate.

Surface ornamentation characteristic : coarsely costate, not fasciculate : four angular costæ on the dorsal fold interlock anteriorly with three strong costæ in the sulcus of the ventral valve ; six or seven primary costæ on both sides of fold and sulcus, the outer of which may bifurcate once only. Concentric growth lines.

In ventral valve receding dental plates do not reach the floor of the valve, but support pyramidal articulating processes or teeth, which fit into corresponding sockets in dorsal valve. Cardinal process of dorsal valve sessile, with myophore vertically striated for reception of diductor muscles.

Heavy deposit of callus in ventral posterior region.

*Discussion.* Koenig (1825) gave a generic description intended to distinguish *Trigonotreta* from *Spirifer* Sowerby, *Pentamerus* and other Brachiopoda, and illustrated his remarks by two figures, " Fig. 70. *TRIGONOTRETA Stokesii.* n." from the Permian of Tasmania, and " Fig. 71. *TRIGONOTRETA speciosa.* (*Terebratulites speciosus* Schloth.) " from the Eiffel, without designating a type species. The latter species has since been assigned to the genus *Hysterolites* Schlotheim.

Bronn (1837) accepted *Trigonotreta* as a genus distinct from *Spirifer* and described additional species.

King (1850) cited *Trigonotreta stokesii* Koenig as a Permian form in his tabular " Classification of the Various Groups constituting the Class Paliobranchiata ", and this was regarded by Hall and Clarke (1894, p. 8) and by Schuchert and Le Vene (1929, p. 125) as selection of the genotype, although it is not always accepted. King (1850, pp. 125–126) considered *Anomites cuspidatus* Martin to be the type of *Spirifer* Sowerby, and thus retained " for another group of *Spiriferidæ*, a name which many conchologists have considered a cancelled synonym. Genus *Trigonotreta* Koenig." He discussed the genus based on Koenig's diagnosis and described five other species as belonging to *Trigonotreta.*

Davidson (1854, p. 79) in England and Meek and Hayden (1865, pp. 17–19) and others in America have regarded *Trigonotreta* as a synonym for *Spirifer* ; however, Meek and Hayden indicated " *Spirifer cuspidatus* Sowerby " as the type of *Spirifer* Sowerby and recognized as a sub-genus " *Trigonotreta* Koenig = *Spirifer* of most authors . . . Example.—*Spirifer striatus,* Sowerby." Subsequent suspension of the Rules (Opinion 100) by the International Commission on Zoological Nomenclature has fixed the genotype of *Spirifer* Sowerby as *Anomia striata* Martin. (Smithsonian Misc. Coll., Vol. 73, no. 5.)

Buckman (1908, p. 30) recognized *Trigonotreta* as a valid genus, indicating *T. stokesii* Koenig as the type.

Schuchert's choice (1913, p. 410) of *Spirifer aperturatus* (Schloth.) as the genotype of *Trigonotreta* is invalid under International Rules of Zoological

Nomenclature, Article 30, *e*, *α*, as this species was not included under the generic name at the time of its original publication.

Schuchert and Le Vene (1929, p. 125) cite as " Genolectotype (King) *T. stokesii* Koenig, 1825 ", but place *Trigonotreta* as a synonym for *Spirifer* (s.s.) Sowerby, 1818.

In his discussion of the classification of the *Spiriferidæ* King, Paeckelmann (1932, pp. 36–37) recognizes *Trigonotreta* as a sub-genus of *Spirifer* (s.l.) in the sub-family Elythinæ Fredericks.

*Comparison.* *Trigonotreta* differs from *Spirifer* Sowerby [genotype *S. striatus* (Martin), Lower Carboniferous] in gross form, surface ornamentation of few coarse costæ, and probably in internal characters. It also differs in geological age. No recent study of *S. striatus* has been published to the writer's knowledge. Martin's specimen is supposedly lost, although the writer, in December, 1938, saw in the Department of Geology, Manchester University, England, a collection labelled " Types of (?) Martin . . . " containing a specimen which exactly matched in appearance and dimensions that illustrated by Martin (1809, T.23, figs. 1–2) from Castleton, Derbyshire. A small specimen collected by the writer from this locality is shown in Plate VI, fig. 6. As Martin states, the valves are " convex, semicircular, and longitudinally striated on every side. The striæ close, nearly equal, and prominent. In the smaller valve, a convex wave, which is answered by a concave one (scarcely distinguishable) in the larger valve ; both terminating in a small wave at the margin."

The specimen illustrated by Davidson (1857, Pl. II, figs. 19, 20) as *Spirifer striatus* var. *attenuatus* Sowerby is a much more alate form, often mistakenly called *S. striatus* in text-books ; it is in the Sedgwick Museum, Cambridge.

*Trigonotreta* Koenig differs from *Neospirifer* Fredericks, 1924 (genotype *Spirifer fasciger* Keyserling, 1846) by the coarseness of the costæ and the lack of fasciculation. Photographs of specimens of *Neospirifer fasciger* from the Upper Productus Limestone, Salt Range, India, and of *Neospirifer condor* from the Wolfcamp (Permian) of Texas, U.S.A., are reproduced on Plate V, figs. 7 and 8, for comparison with the Tasmanian spirifers.

### **Trigonotetra stokesii** Koenig, 1825.

Plate V, figs. 1–5.

*Trigonotreta Stokesii* Koenig, 1825. *Icones Fossilium Sectiles*, p. 3, Pl. 6, fig. 70. B.M. (N.H.) specimen B4798.

*Spirifer Tasmaniensis* Morris, 1845. In Strzelecki, 1845, p. 280, Pl. XV, fig. 3. B.M. (N.H.) BB6246.

non *Spirifer stokesii* Morris, 1845. In Strzelecki, " Physical Description of New South Wales and Van Diemen's Land ", p. 283, Pl. XV, figs. 1 and 1*a*. B.M. (N.H.) 96859.

non *Spirifer stokesii* d'Orbigny, 1846. In Dumont d'Urville, " Voy. au Pôle Sud ", Géologie, Atlas, t. 9, ff. 12–14.

non *Spirifer stokesii* Eth. fil., 1892. *Geol. and Pal. Queensland and New Guinea*, p. 232, Pl. 10, figs. 2, 3.

*Holotype.* Brit. Mus. (Nat. Hist.) specimen B4798. Plastotype : Univ. of Sydney, Spec. 8469.

*Locality.* " Isle of Van Diemen, New Holland " (Tasmania).

According to Buckland (*Trans. Geol. Soc.*, 1st Series, Vol. V, 1821, p. 481) this or a similar specimen came from " the south side of the Table Mountain, near Hobart's Town, Van Diemen's Land."

*Horizon.* Berriedale (Granton) Limestone, Granton Stage (Voisey, 1938). Permian.

*Description of Holotype.* The specimen is a somewhat crushed external cast of the dorsal valve and the cardinal area and beak of the ventral valve of a typical Spiriferoid shell (Plate V, fig. 1) embedded in rock.

The dorsal valve is 3·4 cm. in length and 5·0 cm. in greatest width, slightly below the hinge-line, which is long (4·5 cm.) and straight. The cardinal extremities are slightly rounded. There is a marked median fold, which is almost carinate posteriorly, but wide at the anterior margin; radiating costæ are superimposed on the median fold and six or seven folds occur on each side of it. At a distance of about 12 mm. from the beak smaller secondary ribs appear on one side of most of these lateral costæ. The alar portions of the shell show less pronounced folding. Concentric growth lines occur close together over the anterior and lateral parts of the shell and they indicate the existence of a pronounced broad sinus in the anterior commissure, otherwise obscured by rock matrix.

The ventral valve is shown by its sharply pointed and overhanging beak and the cardinal area, which reaches a height of 8 mm. in the centre. The features of the delthyrium are not clearly shown in this specimen: the sides and base of the triangular delthyrium are each about 9 mm. and its remarkable size evidently inspired the name *Trigonotreta.*

The writer has numerous specimens from various localities along the outcrop of the Berriedale Limestone including an almost perfect specimen from the slopes of Mt. Dromedary, on the north side of the Derwent River, three miles N.W. of Bridgewater, near Hobart (Plate V, figs. 2*a*-2*d*). This specimen is not crushed (as indeed the majority of specimens are), and the costæ of the dorsal valve can be matched exactly against those of the holotype (Plate V, fig. 1). The ventral valve of this specimen shows the presence of a deep sulcus containing three prominent costæ, each lateral part of the shell being ornamented by about seven costæ, the outer of which tend to bifurcate halfway to the margin; anterior commissure parasulcate. This valve can be matched exactly with the specimen (Brit. Mus. (N.H.) BB6246) of a ventral valve figured by J. Morris (1845, Pl. XV, fig. 3) as the type of *Spirifer Tasmaniensis* (see Plate V, fig. 5).

Thus *S. Tasmaniensis* Morris, 1845, becomes a synonym for *Trigonotreta stokesii* Koenig, 1825.

The identification of *S. tasmaniensis* auctt. is the subject of further investigation. A common species in the Lower Marine of New South Wales often referred to this species is not the same as the Tasmanian form.

Morris was in error therefore in the identification of a *Spirifer* showing fasciculate ornamentation, which occurred with *Trigonotreta stokesii*, and which he mistook for it. This form is described below as a new species.

The internal characters of *T. stokesii* have been studied by means of various preparations. Plate V, fig. 3, shows the interior of a typical ventral valve: the wide, open delthyrium is bounded on its inner surface by the dental plates which converge towards the inside of the valve, but they do not reach the floor of the valve. At the cardinal margin they produce small, pyramidal projections, which fit into the sockets of the dorsal valve. The old positions of these teeth form narrow triangular structures or false areas on each side of the delthyrium, but these are not true deltidial plates. No supporting or apical plates are present. The adductor muscle-scars are long and narrow and are placed slightly posteriorly; they are surrounded by the diductor scars, which are relatively large. The whole of the region below the palintrope is filled with a dense deposit of secondary shell, and the delthyrial cavity is almost half-filled with callus. This covers over the trace of the muscle-track, which appears as a dark line in sections of the shell (Plate V, fig. 4).

The interior of the dorsal valve shows widely divergent crural plates bounding the inner sides of the sockets. The crura give rise to descending lamellæ, thin ribbon-like structures supporting the spiralia, which are directed postero-laterally towards the ends of the hinge-line. There are about twenty turns in each spire. There is no jugum.

The cardinal process is sessile and the myophore is vertically striated for the reception of the diductors. The adductor scars are long and narrow, situated high inside the fold.

### Genus **Grantonia** Brown, gen. nov.

Plate VI, figs. 1–8.

*Genotype. Grantonia hobartensis* Brown, sp.n.

*Diagnosis.* Large spiriferoid shell; strongly biconvex, length about equal to the width, somewhat greater than the thickness; hinge-line sub-megathyroid, cardinal extremities obtuse; beak of the ventral valve prominent, incurved; wide ventral inter-area, striated parallel to the hinge-line, but curved in section at right angles to it; large open delthyrium, unmodified in adult. High, almost carinate, median fold in dorsal valve and deep broad sulcus in ventral valve. Multicostate over the entire shell, three prominent folds or plicæ each bearing three or five fasciculate costæ on each side of the sulcus, with corresponding ornamentation on the dorsal valve, giving the shell a rough appearance. Three primary plications in the sulcus. Concentric lamellæ most pronounced near the margin of the shell. Fine surface ornamentation, seldom preserved, of radiating costellæ and concentric filæ, producing a cancellated effect. Anterior commissure modified uniplicate, or parasulcate. Shell impunctate.

*Interior of the Ventral Valve.* Cardinal teeth supported by receding dental plates or delthyrial ridges, which do not reach the floor of the valve; no supporting accessory plates or apical lamellæ. Adductor muscle-scars centrally placed, long, narrow; diductor muscle-scars large, heart-shaped, situated slightly above the centre of the valve. Pallial markings, pittings in the posterior region.

*Interior of Dorsal Valve.* Cardinal process sessile, myophore vertically striated for the reception of diductor muscles; adductor muscle-scars long, narrow. Socket plates divergent, convex to the median plane of the shell, supported only by adventitious tissue below the palintrope. The crura give rise to parallel descending lamellæ, with no jugum, which support spiralia directed postero-laterally towards the ends of the hinge-line. Twenty to twenty-three turns in each spire.

*Discussion. Grantonia* is distinguished from *Trigonotreta* Koenig and *Spirifer* Sow. by major differences in gross form and surface ornamentation of fasciculate costæ. From *Neospirifer* Fredericks, 1924 (genotype *Spirifer fasciger* Keyserling, 1846) it is distinguished by the kind of fasciculation. The type of *Neospirifer* comes from Pechora Land, and the genus has a wide distribution over Eurasia, North America, Timor, Western Australia and Tasmania. The generic characters are discussed in some detail by Dunbar and Condra (1932), who give the diagnosis: "Shells differing from true *Spirifer* (*Spirifer striatus* stock) in having the ribs fasciculate." However, examination of specimens from Russia, and from the Salt Range, India, and the Permian of Texas, U.S.A., as illustrated on Plate VI, figs. 7, 8, shows that the fasciculation in the shells of the two genera is quite distinct. Whereas in *Neospirifer* the numerous costæ are finely and evenly distributed over the major folds of a thin shell, and may even be reflected on the inner surface of the shell, in *Grantonia* there are only one or two pairs of costæ about a central one, superimposed on the surface layers of the principal folds of a thick shell.

**Grantonia hobartensis** Brown, spec. nov.

Plate VI, figs. 1–9.

(?) *Spirifer trapezoidalis* G. Sowerby, 1844. In Darwin, " Geological Observations in Volcanic Islands . . . ", p. 159. (Specimen lost).

*Spirifer Stokesii* Morris, 1845. In Strzelecki, " Physical Description of New South Wales and Van Diemen's Land ", p. 283, Pl. XV, figs. 1, 1*a*, B.M. (N.H.) 96859.

*Spirifer stokesii* d'Orbigny, 1846. In Dumont d'Urville, " Voy. au Pôle Sud ", Géologie, Atlas, t. 9, ff. 12–14.

*Spirifer crassicostatus* Jukes, 1847. (Nomen nudum) *Quart. Journ. Geol. Soc. Lond.*, Vol. III, pp. 248, 249, B.M. (N.H.) 81606.

*Holotype.* Aust. Mus. specimen F44666, Coll. I.A.B. (Plate VI, figs. 1*a*, 1*b*).

*Locality.* Rathbone's Quarry, New Norfolk Road, near Granton, about 12 miles N.N.W. of Hobart, Tasmania. On aerial photo No. 9744, Run 1, Hobart (Land and Surveys Dept., Tasmania) appears about 5 cm. north of centre point.

*Horizon.* Berriedale or Granton Limestone, Granton Stage (Voisey, 1938), Permian.

*Description of Holotype.* The specimen is well-preserved shell consisting of a complete dorsal valve and the posterior half of the ventral valve (Plate VI, fig. 1).

The dorsal valve is 54 mm. wide and 34 mm. long. The hinge-line is the full width of the shell. There is a high median fold and there are three prominent folds on each side of it. There are four costæ on each flank of the median fold, and the lateral folds bear one pair of costæ on their flanks. Several minor costæ occur on the alar part of the shell, and the whole surface is ornamented by concentric growth lines.

The ventral valve, 45 mm. long, has a long, wide cardinal area, divided by a large open delthyrium. The beak is high and curved over that of the dorsal valve. A deep sulcus is flanked by three marked folds corresponding with those of the dorsal valve, and with similar ornamentation. The sulcus bears three primary costæ in addition to the pair belonging to the lateral folds.

Morris (1845) gave a brief description and illustrations (Pl. XV, figs. 1, 1*a*) of specimens of this species from Mt. Dromedary, Tas., under the title *Spirifer Stokesii* (p. 283). These specimens are both in one block of limestone (B.M. (N.H.) 96859), a plaster cast of which is in the Australian Museum, Sydney.

Etheridge (1892) followed Morris in identifying specimens of *Grantonia hobartensis* as *Spirifer stokesii*, and gave a good description of specimens from the Gympie Beds, Queensland; specimens in the Australian Museum from Mt. Britton, Q., appear to the present writer to show some variation from the Tasmanian material.

Preparations have been made from topotypes to show all the internal characters of the shell. The internal structures of the ventral beak (Plate VI, figs. 3*b*, 3*c*, 6, 7 and 8) and the cardinalia (Plate VI, figs. 4*a* and 5) are essentially similar to those already described for *Trigonotreta stokesii* Koenig, and are undoubtedly of family value in the classification of these forms (see Ulrich and Cooper, 1938, p. 6; Cloud, 1942). The receding dental plates (Plate VI, figs. 3*b*, 6) do not reach the floor of the valve, but heavy callus fills the umbonal cavities and part of the delthyrial cavity (Figs. 3*b* and 7). This is best shown in the thin section of the beak of a ventral valve (Fig. 8) ; the covered track of the muscle-scars appears as a horizontal dark band within the secondary shelly material. The cardinalia are shown in Fig. 4*a*, and Fig. 5 shows the natural mould of the striated myophore of the cardinal process.

Serial sections of an average uncrushed specimen revealed that the brachidium consists of two descending lamellæ about 5 mm. apart and 20 mm. in length from which arise two postero-laterally directed spiralia, each with twenty-three turns in the spire.

Internal moulds of *Grantonia hobartensis* show distinctly the three lateral folds on each side of the medial fold and the sulcus, and thus may be distinguished from internal moulds of *Trigonotreta stokesii*, which are relatively smooth.

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## Explanation of Plates.

All photographs were taken by the author, and are natural size, except Plate VI, figs. 5, 6 and 8, which are mag. ×3.

Tasmanian figured specimens are in the Australian Museum, Sydney.

### Plate V

Fig. 1.—*Trigonotreta stokesii* Koenig, 1825. Plaster cast of holotype, B.M. (N.H.) 4798. "Isle of Van Diemen, New Holland."

Fig. 2*a-d*.—*Trigonotreta stokesii*. Aust. Mus. (F44663). Coll. I.A.B. Near Old Lime Kiln, Upper Dromedary Rd., 3 mls. N.W. of Bridgewater, Derwent River, Tasmania. (*a*) Dorsal view. (*b*) ventral, (*c*) side, and (*d*) anterior views, showing anterior commissure.

Fig. 3.—*Trigonotreta stokesii*. Interior of the ventral valve, showing open delthyrium, dental plates and teeth, muscle scars and pallial markings. A.M. (F44664), Rathbone's Quarry, Granton.

Fig. 4.—*Trigonotetra stokesii*. Vertical median section of ventral valve to show callus in delthyrial cavity, also dental plate. A.M. (F44665), Rathbone's Quarry, Granton.

Fig. 5.—*Trigonotetra stokesii*. Plaster cast of ventral valve, B.M. (N.H.) 6246, figured by Morris as *Spirifer Tasmaniensis* on his Pl. XV, fig. 3.

Fig. 6.—*Spirifer striatus* (Martin). A.M. (F44669). Coll. I.A.B. Loc. Treak Cliff, near Castleton, Derbyshire, England. (Lower Carb.)

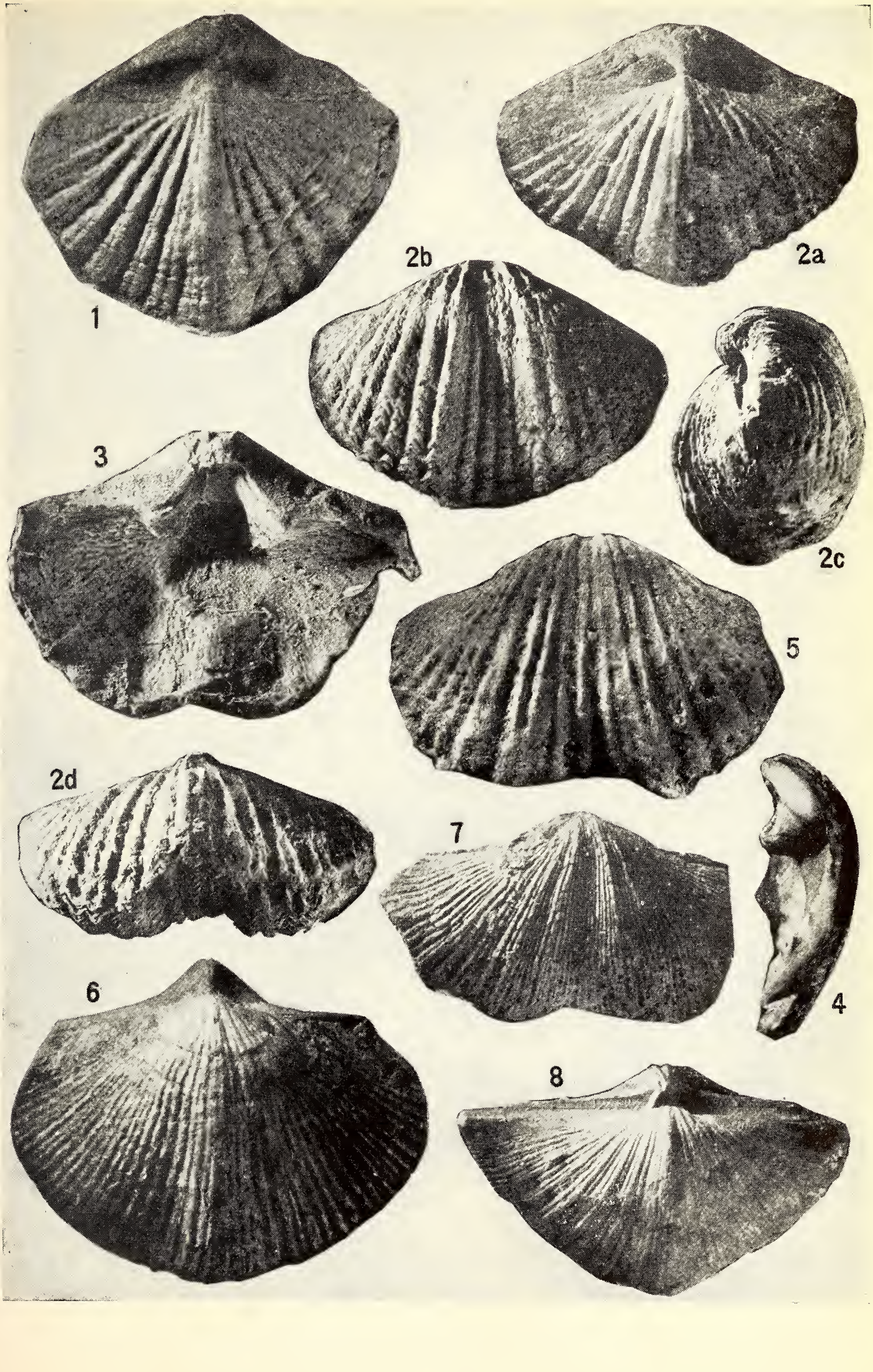
Fig. 7.—*Neospirifer fasciger* (Keyserling). Ventral valve. Syd. Univ. Coll. 9487. (Geol. Surv. Coll. K7/353). Loc. Warcha, Salt Range, India. (Upper Productus Limestone.)

Fig. 8.—*Neospirifer condor* (Orbigny). Loc. N.W. of Marion School, Texas, U.S.A. (Early Wolfcamp, Permian.)

### Plate VI.

*Grantonia hobartensis* gen. et spec. nov.

Figs. 1*a*, 1*b*.—Holotype. Aust. Mus. (F44666). Coll. I.A.B. Loc. Rathbone's Quarry New Norfolk Road, near Granton, about 12 miles N.N.W. of Hobart, Tasmania. ×1.


1
2a
2b
2c
3
5
2d
7
4
6
8


1a
1b
6
2
4a
5
3a
4b
7
3c
3b
8
3d

Fig. 2.—Rubber mould of portion of ventral valve showing details of external ornamentation. A.M. (F44670). Loc. 1,000 feet above s.l. on Huon Road from Hobart. Coll. I.A.B. Mag. ×1.

Figs. 3*a-d*.—Ventral valve showing (3*a*) exterior, (3*b*) interior, and (3*c*, 3*d*) posterior views. A.M. (F44671). Rathbone's Q. Mag. ×1.

Figs. 4*a*, 4*b*.—Dorsal valve showing (4*a*) interior, and (4*b*) exterior views. A.M. (F4466 ). Mag. ×1.

Fig. 5.—Natural mould of cardinal process, showing vertical striations. A.M. (F44668). Rathbone's Quarry. Mag. ×3.

Fig. 6.—Portion of beak of ventral valve (left) and dorsal valve (right) showing curved dental plate over callus fitting into socket behind crus of dorsal valve. Mag. ×3.

Fig. 7.—Vertical median section of ventral valve, showing callus in delthyrial cavity. A.M. (F44672). Mag. ×1.

Fig. 8.—Thin section through beak of ventral valve, showing folding and fasciculation of outer layers of shell, and microscopic structure of callus. Divergent receding dental plates and trace of muscle-track, sub-parallel to the sulcus. A.M. (F44673). Mag. ×3.

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FOR

1952

(INCORPORATED 1881)



PART III

OF

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Containing Papers read in October, 1952

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IDA A. BROWNE, D.Sc.

*Honorary Editorial Secretary*

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN

SYDNEY
PUBLISHED BY THE SOCIETY, SCIENCE HOUSE
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1953

CONTENTS

# VOLUME LXXXVI

## Part III

Page

ART. VIII.—Induced Optical Activity of the Tris-1 : 10-Phenanthroline and Tris-2 : 2′-Dipyridyl Copper II Ion. By N. R. Davies and F. P. Dwyer .. .. .. 64

ART. IX.—Soil Horizons and Marine Bands in the Coastal Limestones of Western Australia. By R. W. Fairbridge and C. Teichert .. .. .. .. .. 68

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# INDUCED OPTICAL ACTIVITY OF THE TRIS-1 : 10-PHENANTHROLINE AND TRIS-2 : 2′-DIPYRIDYL COPPER II ION.

By N. R. DAVIES, B.Sc., F.R.I.C.
and F. P. DWYER, D.Sc.

With one Text-figure.

*Manuscript received, August 21, 1952. Read, October 1, 1952.*

Hexacovalency is relatively rare among copper II compounds and with the exception of anhydrous copper II chloride and bromide, which in the solid state show a weak octahedral arrangement of the halogen atoms about the metal (Wells, 1947 ; Helmholtz, 1947), appears to be confined to complexes containing nitrogen, such as hexammine copper II iodide (Peyronel, 1941), and hexakis pyridine copper II nitrate (Pfeiffer and Pimmer, 1905), both of which are relatively unstable. Chelate derivatives with ethylene diamine have been prepared, but in solution appear to eliminate one molecule of the ligand and pass to the familiar 4-covalent planar bis-ethylene diamine ion (Dubsky and Tritilek, 1934). However, Rosenblatt (1932) concluded from absorption spectral curves that the ionic species $[Cu(en)_2(H_2O)_2]^{++}$ exists in aqueous solutions and Wahl (1927) claimed to have resolved this cation through the tartrate. This claim was not substantiated by later workers (Johnston and Bryant, 1934).

When 2 : 2′-dipyridyl or 1 : 10-phenanthroline are added to solutions of copper II salts, the deep blue colour of the bis chelate complex ion results, but with excess of the bases the colour then lightens and stable pale blue salts, $Cu(dipy)_3X_2$, $Cu(phenan)_3X_2$, can be isolated (Jaeger and van Digk, 1934).

The octahedral configuration of the metallic atom in these complexes could not be demonstrated by resolution through the tartrate, bromcamphor sulphonate or antimony tartrate. With the latter anion, which is particularly suitable for the resolution of phenanthroline metallic complexes (Dwyer and Gyarfas, 1950), antimony oxide rapidly precipitated, showing that extensive dissociation of the complex cation had occurred in solution.

Pfeiffer and co-workers (1932) noted considerable rotational changes when various optically active anions were added to solutions containing the ion $M.(A)_3^{++}$, (M=Zn, Cd, Ni, $Fe^{II}$, $Co^{II}$, $Mn^{II}$ ; A=dipy. phenan.) and ascribed the rotation to excess of either the dextro or lævo complex cation in the mixture. Recently, following the work of Turner and Harris (1948) on the phenomenon of asymmetric induction in organic compounds, the above changes in rotation have been related to the movement of the equilibrium $d^{++} \rightleftharpoons l^{++}$ consequent on differential activity changes on the enantiomeric ions with the added optically active anion (Dwyer, Gyarfas and O'Dwyer, 1951).

Since the iron and nickel compounds can be resolved, but are optically labile, as demanded by this theory, rotational changes of the kind observed by Pfeiffer can be regarded as diagnostic of potentially active complex salts that are too labile to be separated into discrete enantiomeric forms. The time required to reach the maximum rotation change after addition of the optically active anion can be used to determine whether resolution is practicable. Thus the zinc and cadmium compound, which showed the effect instantly, has resisted all efforts at resolution, whilst the nickel phenanthroline compound, which reaches the maximum rotation only after several days, has a half-life for the active forms of 16 hours at 25° C.

In the present work the equilibrium :

$$CuA_2^{++} + A \rightleftarrows d\,CuA_3^{++} \rightleftarrows l\,Cu(A_3)^{++}$$

(A=1 : 10-phenanthroline ; 2 : 2′-dipyridyl ; ethylene diamine) has been studied in the presence of ammonium *d* bromcamphor sulphonate, ammonium *d* camphor sulphonate and *d* trisethylene diamine cobalt III nitrate.

Addition of the phenanthroline and dipyridyl copper complexes to ammonium bromcamphor sulphonate solution led to marked increases in the rotation. The change was increased with increasing concentration of the free chelate bases or of the ammonium bromcamphor sulphonate. Since the effect was immediate, it can be concluded that the enantiometric forms of the copper compounds are too labile to be separated. No rotational change was observed in the presence of ammonium camphor sulphonate or tris-ethylene diamine cobalt III nitrate. Negative results were obtained in all experiments using the ethylenediamine copper complex. This could be due to the fact there was no appreciable concentration of the tris ethylenediamine copper II ion in solution or to the necessity of using very dilute solutions owing to the intense colour of the complex.

An appreciable lightening in colour was also observed when ammonium bromcamphor sulphonate was added to the phenanthroline and dipyridyl complexes. This effect did not occur when ammonium camphor sulphonate or the optically inactive ammonium β naphthalene sulphonate were added.

Absorption spectral curves of solutions containing various ratios of 1 : 10 phenanthroline to cupric ion were found to show the development of a pronounced maximum at 520μ and a weaker maximum of 475–480μ due to the tris-1 : 10 phenanthroline copper II ion. Ammonium bromcamphor sulphonate added to solutions containing both the bis and the tris phenanthroline complexes led to an appreciable enhancement of the maxima due to the tris phenanthroline complex ion.

## Experimental.

The observations were carried out at 17° C. in a 1 d.m. tube using either a sodium amp or a mercury lamp, with filter to isolate the green line 5461, as light sources. The copper complex solution was placed in a polarimeter tube, and in

Table I.

| Phenan. Added. Mols. | Conc. Brom. Camphor Sulphate. % | Change in Rotation. | |
|---|---|---|---|
| | | $Na_D$. | $Hg_{5461}$. |
| 3 | 0·5 | 0·03° | — |
| 6 | 0·5 | 0·05 | — |
| 6 | 1·0 | 0·09 | 0·11° |
| Dipyridyl added Mols. | | | |
| 3 | 0·5 | 0·02 | 0·03 |
| 3 | 2·0 | 0·04 | 0·09 |

Initial rotations of ammonium *d* bromcamphor sulphonate solutions : 0·5%, $\alpha_D$=0·43° ; 1%, $\alpha_D$=0·85° ; $\alpha_{5461}$=1·04° ; 2%, $\alpha_D$=1·70° ; $\alpha_{5461}$=2·00°.

a second tube the optically active salt solution, diluted with an equal volume of water. The rotation of the optically active salt was determined with both tubes in the polarimeter. In this way corrections were made for errors due to lack of uniformity in the illumination of the field of the polarimeter. Equal volumes of the copper complex and the optically active salt were then mixed and the rotation again measured. The difference between the readings was ascribed to the optical activity of the complex.

Copper sulphate solution, M/100 was used in all experiments and treated with solid 1 : 10 phenanthroline or 2 : 2′ dipyridyl in order to obtain various molecular proportions of salt and chelate groups. The results are shown in Table 1.

Transmission curves in the range 400–700μ are shown in Fig. I.

Absorption Curves of Copper Sulphate and 1 : 10 Phenanthroline.

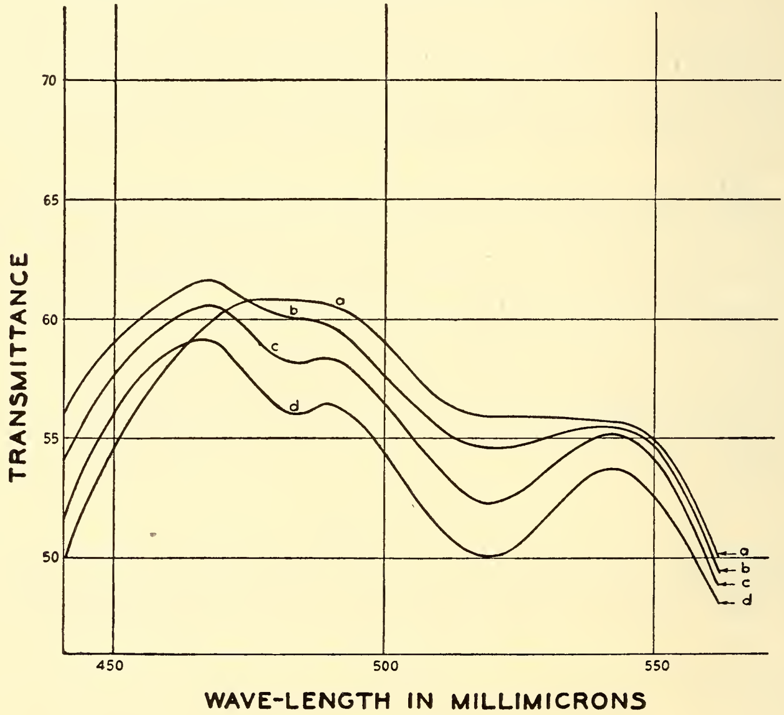


Fig. I.

(*a*) System $CuSO_4$+2 phenan.
(*b*) System $CuSO_4$+3 phenan.
(*c*) System $CuSO_4$+6 phenan.
(*d*) System $CuSO_4$+3 phenan+Ammonium-bromcamphorsulphonate.
All solutions were 0·01 molar with respect to copper.

## Summary.

Addition of solutions containing the tris-1 : 10-phenanthroline and tris-2 : 2′-dipyridyl copper II ions to ammonium *d* bromcamphor sulphonate solutions lead to appreciable increases in the rotation. The increases are roughly proportional to the concentration of the bromcamphor sulphonate and to the excess of the chelate bases. The rotational changes have been ascribed to the movement

of the equilibrium *d* complex$\rightleftarrows$*l* complex and to the existence of optically labile forms of an octahedral complex copper ion. This conclusion is supported by absorption spectral curves.

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# SOIL HORIZONS AND MARINE BANDS IN THE COASTAL LIMESTONES OF WESTERN AUSTRALIA.

By Rhodes W. Fairbridge
and Curt Teichert.

With Plates VII and VIII and five Text-figures.

*Manuscript received, July 29, 1952. Read, October 1, 1952.*

Contents.

| | | Page |
|---|---|---|
| I. | Introduction | 68 |
| II. | Soil Horizons | 71 |
| | (*a*) Hamelin Bay and Island | 71 |
| | (*b*) Other Fossil Soil Localities | 74 |
| III. | Marine Bands | 74 |
| | (*a*) Cowaramup Bay | 74 |
| | (*b*) Other Occurrences of Marine Members | 77 |
| IV. | Interpretation of the Æolianites and Their Soils | 78 |
| V. | Correlation with England and North Africa | 80 |
| | Conclusions | 82 |
| | Bibliography | 85 |

Abstract.

Formed under eustatic and climatic controls, a cyclic sequence of marine bands, æolianites, and travertine crusts in Western Australia correspond to the Riss/Würm interglacial, the three substages of the Würm, and the post-Glacial (Flandrian) transgression.

Dune building took place with periods of high eustatic sea level, each of which was relatively short and coincided with the beginning of each arid interstadial. During each succeeding eustatic low (corresponding to a glacial maximum) the base-level was lowered and rapid consolidation took place with travertine crust and karst formation. Thus conglomerates of the latter mark the following marine invasion. In the south, as at Cowaramup Bay, only the youngest marine band and æolianite are represented, resting with a conglomerate of granite-gneiss boulders on the pre-Cambrian basement.

Numerous horizons of immature soils intercalated in each æolianite, as at Hamelin Bay and elsewhere, do not represent interglacial pauses, as postulated for similar soils in Bermuda by Sayles, but merely minor oscillations in short periods of dune building.

## I. Introduction.

The " Coastal Limestone " of Western Australia is a formation of more than local interest. It is of Pleistocene age and includes marine and continental sediments which reflect the extraordinary changes of climate and the eustatic oscillations of sea level characteristic of that epoch. Since Western Australia is largely a great pre-Cambrian shield and suffered no glaciation whatever during the Pleistocene, its coasts are not unnaturally regarded as amongst the most stable in the world. It is here then that we may expect to find traces of Pleistocene eustatic events most faithfully recorded.

The Coastal Limestone is a rock essentially similar to that for which Sayles (1931) in Bermuda introduced the term " calcareous eolianite ", that is to say, a lithified dune-rock. For general descriptions of the Western Australian æolianites see Teichert (1947*a*, 1947*b*) and Fairbridge (1950). It is, as a rule, a medium-grained clastic sediment, in which the grains consist mainly of fragmental calcareous algæ, mollusca, foraminifera, and bryozoa, with varying amounts of inorganic constituents and a cement of secondary calcium carbonate. The $CaCO_3$ may vary as much as 10 to 90 per cent. Nevertheless, the rock reacts to weathering as a ragged limestone, almost regardless of the amounts of insolubles, which normally increase considerably in the proximity of the pre-Cambrian basement. Intercalated in the dune rock are found prominent bands of red and brown fossil soils (terra rossa and rendzina), and in the lower parts of the formation there are generally wedges of shallow-water marine beds in reef, beach or estuarine facies.

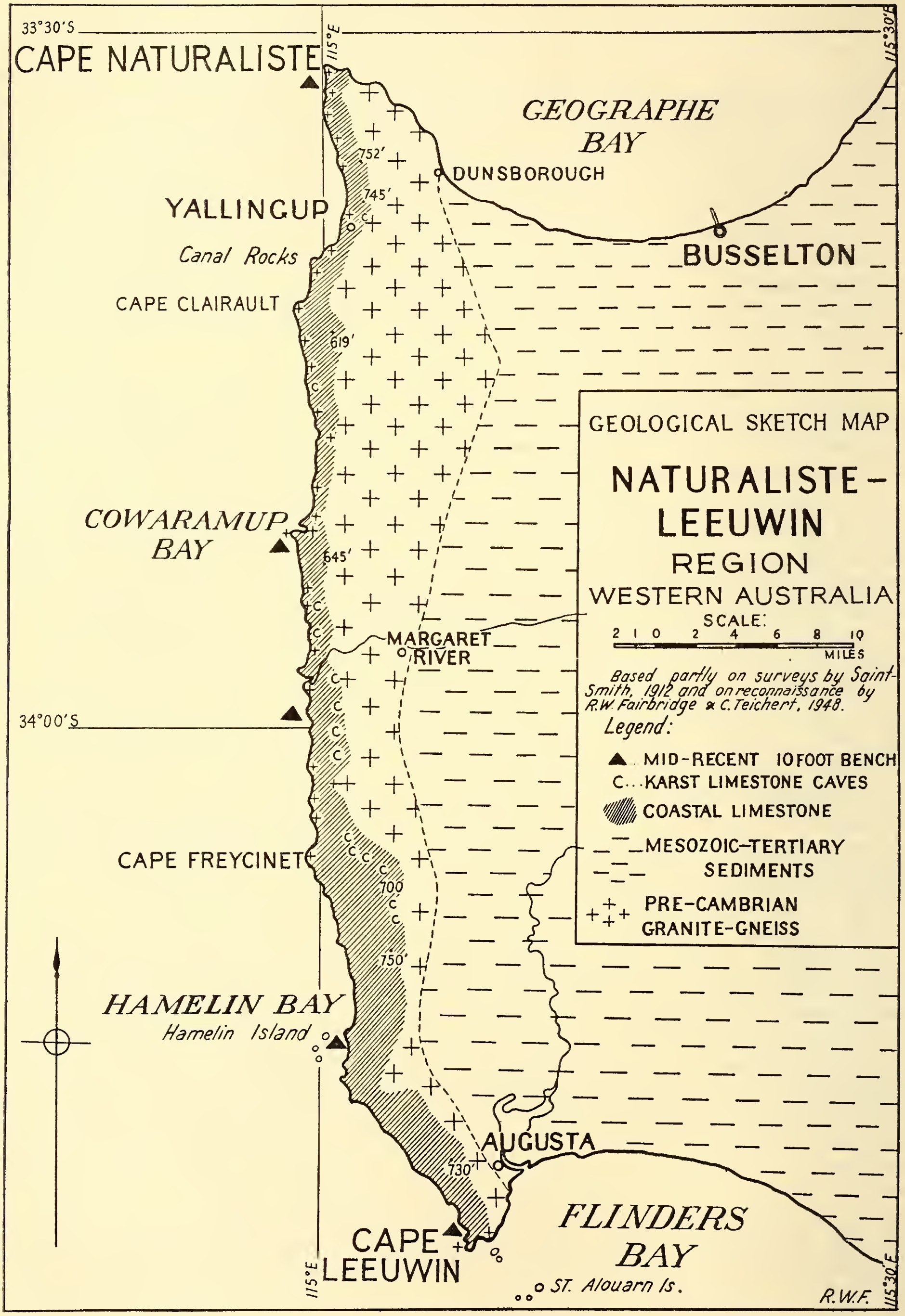
Identical formations are found on Bermuda (Sayles, 1931) on the Bahamas, Barbados, Madeira, Cape Verde Islands, at Alexandria, and on the coasts of Palestine, of Morocco, of Ecuador, of South Africa, on the south coast of Arabia and on the western shores of India, in Hawaii, and elsewhere.

In Australia the Coastal Limestones are found intermittently along 4,000 miles of coastline and are of great value to those interested particularly in the last 50,000 years of our history. In South Australia they are found on Eyre Peninsula, Yorke Peninsula, Kangaroo Island, and in south-eastern South Australia (Tindale, 1947 ; Hossfeld, 1950 ; Sprigg, 1952). Their characteristics are similar to those of Western Australia. Fossil soils developing on them are mostly of the terra rossa type, but rendzinas occur intermixed with them on Eyre Peninsula (Crocker, 1946). In Victoria both æolianites and fossil soils are known from Portland Bay to Barwon Heads (Hills, 1939 ; Coulson, 1940 ; Gill, 1943 ; Keble, 1946). Johnston's (1888) " Helicidæ Sandstones " of the Bass Strait Islands are the same.

This paper will be devoted largely to a description of certain features of the Western Australian Coastal Limestones where they overlie a ridge of pre-Cambrian granitic gneiss, extending in a north-south direction for 60 miles between Cape Naturaliste (33° 32′ S., 115° 00′ E.) and Cape Leeuwin (34° 23′ S., 114° 38′ E.) and rising to 750 feet in places (Fig. 1).

The presence of Coastal Limestone here was reported as early as 1849 by J. W. Gregory, Senr., who described the lower part as a " grey marble " with marine shells and with 2-3 foot blocks of gneiss cemented to the basement in a coarse conglomerate. He also mentioned " the remains of an ancient sea-beach near Cape Naturaliste " and its water-worn boulders, a statement which was later misquoted as " 15 miles south (*sic*) of Cape Leeuwin " by F. T. Gregory (1861) and others. The general relationships were seen again by H. Y. L. Brown (1872), who observed the garnet-gneisses of the pre-Cambrian basement. E. T. Hardman (1884) expressed the opinion that the overlying limestones were Cretaceous or Eocene in age and noted the presence of caves therein, which would be likely spots for digging for extinct marsupial remains. As predicted, they were later found in great quantities (see Glauert, 1910). An Eocene age was also attributed to the " coast limestone " by H. P. Woodward (1894), and in another report he mentions sending the marine fossils from the lower part to England for description.

The first general account of the geology of this area came from E. S. Simpson (1902), who recognized the mainly æolian character of the Coastal Limestone and its interesting karst features. Further notes on the area appeared in survey




Text-fig. 1.—Geological Sketch-map of Naturaliste-Leeuwin Region, W.A.

bulletins by Saint-Smith (1912) and Woodward (1915), but since then it appears to have been neglected, apart from a short paper on granitization of the Leeuwin gneiss by Carroll (1940).

The Coastal Limestone tends to dominate the landscape with karst features, caves and underground streams. Instead of it being barren, however, there are rich soils derived from the old rocks, which, coupled with the heavy rainfall, support a very flourishing vegetation, except immediately on the coast. On the shoreline the Coastal Limestone is etched by spray into bizarre shapes and in the intertidal zone the evidence of marine solution of limestone is demonstrated by the deep, etched undercuts and broad horizontal reef platforms. As indicated elsewhere (Fairbridge, 1948*a*, 1950) the effect on limestones of this corrosive activity in sea-water and spray near the shore is to produce perfectly truncated horizontal reefs at low-tide level.

On a visit to this area in January, 1948, we paid attention mainly to two aspects of the Coastal Limestone, both connected with climate and eustatic processes. These less usual features were soil horizons with a fauna of land snails and a thin marine member with shell beds and massive conglomerates. Both of these are better developed here than anywhere else we have seen on the Western Australian coast, but some other occurrences will be briefly described for comparison.

## II. Soil Horizons.

### (*a*) *Hamelin Bay and Island.*

Fossil soils in the Coastal Limestone may be seen at many points between Cape Naturaliste (Plate VII, fig. 3) and Cape Leeuwin, as well as elsewhere along the Western Australian coast, but the finest development is at Hamelin Bay (Plate VII, figs. 1, 2) and on Hamelin Island, about one mile offshore (Text-fig. 2). The calcareous æolianite between the soil bands here is normal, except that vertical pipes are rather rare.

The average soil horizon is about 1–3 feet in thickness, but in hollows it was found up to 8 feet. Features of the soil are its lack of stratification, its soft, " earthy " feel (where not travertinized) and fineness of grain, all in contrast to the æolianite. A typical section of one of these soils shows from top to bottom :

(iv) Travertine " cap-rock ", smooth and hard on top, soft below ; interfingered by fossil root structures, also preserved in travertine $\frac{1}{2}$–1 foot

(iii) Soft, brown humic layer ; often full of land snails (*Bothriembryon* spp.) and slightly calcified insect cocoons (probably of the weevil *Leptops duponti*, see Lea, 1925) .. .. .. .. .. 1–3 feet

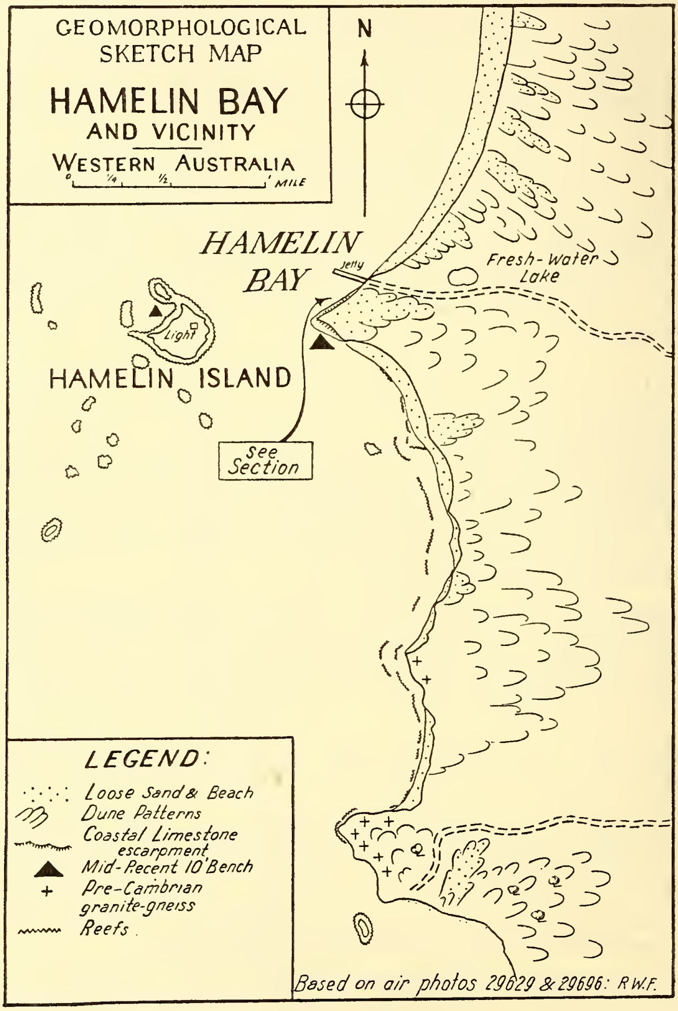
(ii) White, leached layer ; also penetrated by root structures ; in places this contains knobby concretions of travertine.. .. 1–4 feet

(i) Basal travertine ; in places merely a thin plaster on the irregular underlying surface, but sometimes cementing a layer of breccia or conglomerate (pebbles from an older travertine cap) .. $\frac{1}{4}$–1 foot

These divisions are not constant. In places the travertinized cap-rock is missing ; in others the whole band is travertinized from top to bottom. Thus in places the soil horizon stands out ruggedly, while in others it is so weathered away as to look like a narrow cleft cut in the cliff wall.

On the mainland cliff, four soil zones (Text-fig. 3) are marked on the attached diagram (A, B, C and D), while on Hamelin Island no less than six were noted (A to F), rising to about 65 feet above sea level. There are local differences in each soil (varying travertinization, varying humic content), but they do not seem to be constant. For that reason it would not seem desirable to apply stratigraphic names to each horizon (as, for example, in Bermuda).

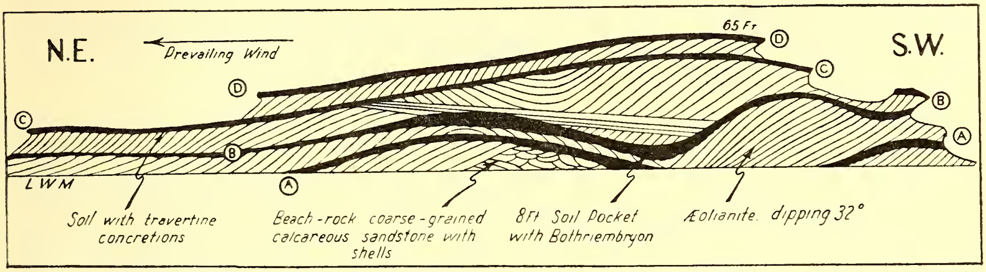
The soils are rich in carbonates (Table I). The calcium carbonate and magnesium carbonate content is generally only slightly lower than that of fresh æolianite (in one case even slightly higher) and the insolubles are more concentrated in the two lower soils. There is a varying percentage of organic matter




Text-fig. 2.—Geomorphological Sketch-map of Hamelin Bay and vicinity.

which is absent from the parent rock. The test for phosphate was negative in every case. On the whole these soils seem to be of the rendzina type. Their special interest lies in the fact that they represent fossil rendzinas in which the development of a mature soil profile has been arrested. An important point is the absence of thick travertine crusts, pipes and other karst features, indicating that the periods of soil formation were not of long duration and that the dune developments were in rapid sequence.

All soil horizons contain abundant specimens of the land snail *Bothriembryon.* This genus is at present restricted to the south-west of Australia, where it occurs from Eucla to Shark Bay. It has developed into a large number of local races or subspecies, which were given specific rank by Iredale in his revision of the land molluscs of Western Australia (Iredale, 1939).




Text-fig. 3.—Pleistocene æolianites and fossil soil horizons at Hamelin Bay, W.A. Length of section about 300 yards.

Recent shells collected on Hamelin Island and Hamelin Bay seem to belong to *Bothriembryon trilineatus* Kobelt, which Iredale regards as a synonym of *Bothriembryon kingii* Gray (Iredale, 1939, Plate 2, fig. 27). He records this species from the King George's Sound area. The same form also occurs in Soil Horizon D, but not in the earlier horizons. The material at our disposal is insufficient for a thorough study of the affinities of the species from the various horizons. This is, moreover, made difficult by the fact that Iredale is silent on the subject of variation of the individual " species ", for each of which he figures

TABLE I.

*Analyses of Soils and Parent Rock in Coastal Limestone of Hamelin Bay.*

| | 1<br>% | 2<br>% | 3<br>% | 4<br>% | 5<br>% |
|---|---|---|---|---|---|
| Calcium carbonate .. .. | 87·90 | 78·98 | 91·57 | 88·51 | 89·94 |
| Magnesium carbonate .. .. | 5·75 | 4·33 | 4·87 | 4·77 | 7·68 |
| Insoluble in acid .. .. .. | 2·95 | 9·99 | 0·49 | 0·51 | 0·46 |
| Organic matter as humus .. | 1·45 | 2·08 | 1·73 | 2·29 | — |

1. Soil Horizon A, Hamelin Bay.
2. Soil Horizon B, Hamelin Bay.
3. Soil Horizon C, Hamelin Bay.
4. Soil Horizon D, Hamelin Bay.
5. Fresh æolianite, Hamelin Bay.

one representative only. However, specimens from Soil Horizons A and B resemble in general the specimen figured as *Bothriembryon perditus* by Iredale (1939, Plate 2, fig. 32) and specimens from Soil Horizon C are most similar to *Bothriembryon leeuwinensis* Smith (Iredale, Plate 2, fig. 17). Both these " species" are now restricted to the extreme south-west of Western Australia. The occurrence of different forms in different soil horizons does not, therefore, seem to indicate climatic fluctuations. The meaning of these changes in the composition of the snail fauna cannot be evaluated until systematic collecting of large series of both recent and fossil shells from many localities has been made.

(*b*) *Other Fossil Soil Localities.*

Fossil soil horizons of the rendzina type are well exposed along the coast, especially near the Margaret River mouth. Farther north at Cowaramup Bay a soil horizon has formed on beach conglomerate and marine shell beds. It contains *Bothriembryon trilineatus* as in Soil D of Hamelin Bay. At Cape Naturaliste, owing to recent disturbance to the vegetation, the old dune covering is partly stripped off by wind erosion, exposing a large area of the fossil soil, in which the travertinized roots are standing up. The local people refer to it as " The Petrified Forest ".

Some 100–150 miles to the north, at Penguin Island and Point Peron (Fairbridge, 1950) and at Rottnest Island (Teichert, 1950), there are further developments of fossil soil, but there are generally not more than two bands, and these are rather thin, though a pocket at Point Peron is 8 feet thick. These more northerly soils generally have the appearance of terra rossa, though locally they are dark brown and phosphatized. Deep solution pipes, descending beneath sea level, are more important in this area, and the walls of these pipes are characteristically banded with travertine and terra rossa. The egg-shaped fossil cocoons of *Leptops* are also common here.

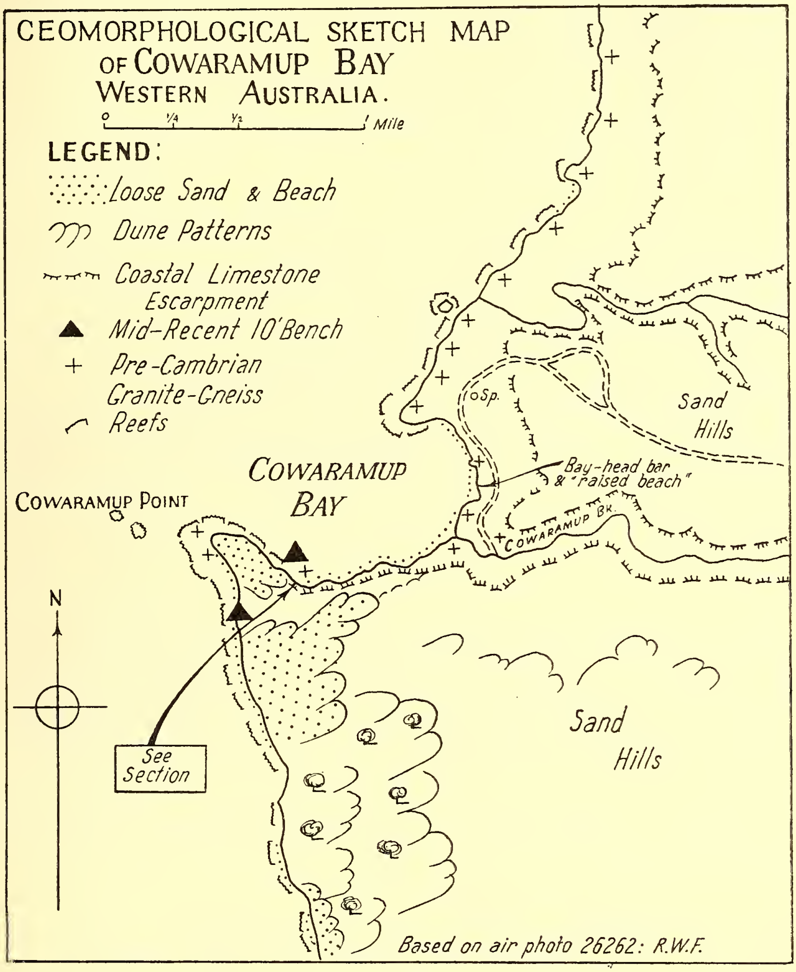
Still farther north, in the Wallaby Group of Houtman's Abrolhos Island (Teichert, 1947*b*) there are only a few thin bands of travertinized " root horizons " in the Coastal Limestone.

It appears therefore that the number and thickness of the soils decrease as we go north. At the same time there is a change from rendzinas to travertine and terra rossa, indicating, as might indeed be expected, climatic zoning and decreasing humidity from south to north. It should be remembered that rendzinas form at present in central and western Europe, whereas terra rossa is the product of weathering in Mediterranean climates. It is the rendzina which is forming to-day on the limestones of the south-west, while the terra rossa soils are restricted to the coast about 500 miles to the north. Evidence from the soils confirms our impression that at times during the Pleistocene almost the whole of south-west Australia suffered from hot and arid conditions, but that it was frequently relieved by wetter conditions in the south-west. This line of reasoning may also perhaps help explain the extraordinary concentration of marsupial life in this area at that time, for nowhere else in Western Australia has such a rich and varied fossil marsupial fauna been found (e.g. Margaret River Caves, see Glauert, 1910).

## III. Marine Bands.

As indicated above, the Coastal Limestone is essentially an æolian, continental deposit. It is accordingly difficult to date except on geomorphological evidence. The development in it of sporadic marine bands and littoral conglomerates is thus of particular interest, and for this reason Cowaramup Bay is selected as a type locality.

(*a*) *Cowaramup Bay* (33° 51′ S., 114° 59′ E.). This is a rocky horseshoe-shaped anchorage about 1,000 yards across (Text-fig. 4). The basement rocks outcrop in rugged cliffs on the north side and on the floor of the bay. The hills inland and at Cowaramup Point (on the south side) consist of Coastal Limestone, but close to sea level around the south side of the bay there is a basal conglomerate of granite-gneiss boulders cemented into a thin deposit of hard cream-coloured marine limestone with pockets of shells, and overlain by thin layers of beach rock and less consolidated shell-beds, followed by a fossil soil and eventually æolianites. The section is indicated in Text-fig. 5. The boulders in the conglomerate are mostly 2–4 feet across; they are well rounded and thus differ markedly from the angular blocks of the same gneissic rocks being thrown up on the shore to-day. In places on the present beach the two are mixed, the former



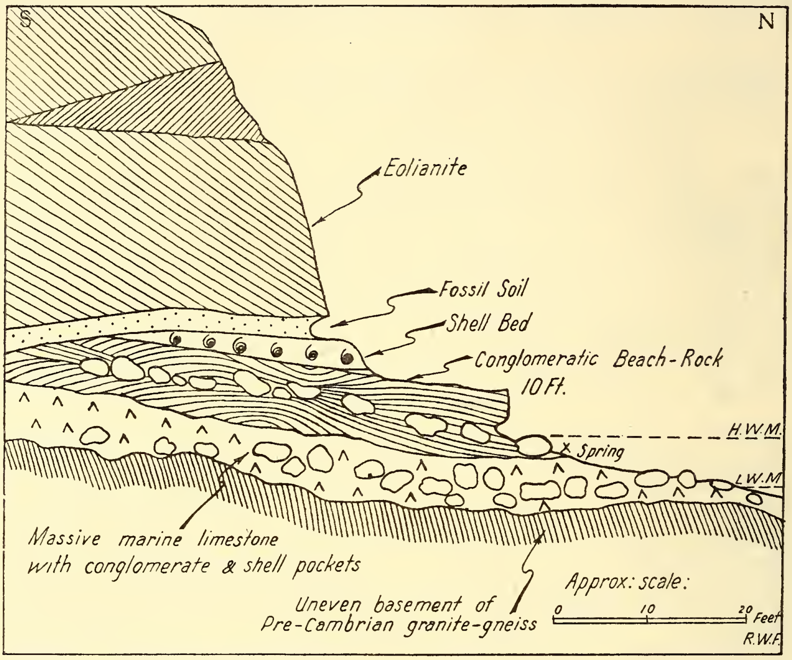

Text-fig. 4.—Geomorphological Sketch-map of Cowaramup Bay.

being reworked. In the overlying beach-rock there are also some boulders but they are more rounded and smaller (1–2 feet). Springs of fresh water occur at the base of this beach-rock.

The bed of soft, unconsolidated calcareous sand which follows is apparently an old storm beach and is full of *Patella*, *Nerita*, *Turbo*, *Marginopora*, sharks' teeth, etc. It is proposed to call the whole of this marine sequence, conglomerate, limestone, beach-rock and shell beds, after its dominant feature, the "Cowaramup Conglomerate" as part of the "Coastal Limestone" Group (Plate VIII, figs. 1–4).

During its formation the sea level must have risen at least 10 to 12 feet above its present level.

The age of these various deposits is not apparent from the contained fossils, all of which seem to be of living species, although not necessarily from the local station.*




Text-fig. 5.—Section of Coastal Limestone on south side of Cowaramup Bay, showing Cowaramup Conglomerate resting on basement of pre-Cambrian granite-gneiss, and containing rounded blocks of the latter up to 4 feet long. The lower part of the conglomerate has a matrix of massive marine limestone, with fossil shells in pockets, and the upper part passes into a conglomeratic beach-rock (calcareous sandstone). There is next a shell-bed (a Pleistocene " raised beach "), followed by a fossil soil band and steeply bedded æolianite.

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* The fauna from the shell bed, overlying the Cowaramup Conglomerate, has been kindly identified by Miss E. Dixon, as follows :

Phylum .. Protozoa.
*Marginipora vertebralis.*

Phylum .. Arthropoda.
Family Xanthidæ, *Actœa* sp. (1 only claw).
Family Grapsidæ (1 only claw) : Cirripedia : *Tetracleta.*

Phylum .. Mollusca.
Amphineura.
*Ischnochiton.*
Pelecypoda.
*Brachyodontes erosus, Divalucina occidua.*
Gastropoda.
*Marinauris roei, Ianthina violacea, Euplica bidentata, Josepha tasmanica, Stomatella imbricata, Cocozeliana granosa, Campanila lœvœ, Propesium* sp., *Melarhaphe unifasciata, Nerita lineata, Melanerita melanotragus, Cantharidus lehmanni, Mimeclanclulus ventricosa, Vicimitra rhodia, Tallopia callifera, Patelloida alticostata, Siphonaria baconi, Cellana limbata, Sabia conica, Antisabia erma.*

It is interesting to note that this assemblage is a typical reef group (dominated by the " periwinkle " *Melarhaphe unifasciata* and numerous limpets) commonly found associated with contemporary intertidal reef facies near Perth, some 150 miles to the north. The foraminifer *Marginopora* is also a standard warm-water reef form.

Physiographic features around Cowaramup Bay shed some light on the age problem. The gneiss hills around the bay appear to show a rough terracing, at about 25, 40 and 100–120 feet (illustrated by Clarke *et al.*, 1944, p. 174), but this does not extend to the Coastal Limestone hills, so if they are true coastal terraces, they must be older than the last period of dune-building. If they are taken to be Pleistocene eustatic terraces (see discussion in Section V), the age of the Cowaramup Conglomerate must be very late Pleistocene.

The head of the bay is cut off by a bay-head bar, a " raised " beach now rising to 13 feet above datum, preserving a coastal flat within at about 9 feet above datum, the inner edge of which is marked by subdued " fossil " cliffs and truncated spurs. On the south side of the bay there are several indications of a 10-foot bench eroded in the Coastal Limestone. This is clearly the mid-Recent (Flandrian) shore-platform. In places it is overlain by a plaster of Recent shelly beach-rock.

It may be seen that the coincidence in heights between this mid-Recent 10-foot sea level and the Pleistocene sea level of about the same elevation, when the shell beds and older beach-rock were formed, is a pregnant source of confusion, unless great care is taken. Below the 10-foot level the lithology is so varied with conglomerates, massive limestone and granite-gneiss *in situ* that it is impossible to trace out the 5- and 2-foot benches often found elsewhere, though small patches of lower beach-rock plasters were found.

On the south side of Cowaramup Point there is a particularly fine contemporary limestone bench about 200 feet wide, studded with gneissic boulders. The limestone is reduced by marine solution to low-tide level, while the resistant conglomerate boulders stand up from it like giant cannon-balls. There is a somewhat similar " plum pudding " bench like this in Hawaii (Wentworth and Hoffmeister, 1940, p. 57).

(*b*) *Other Occurrences of Marine Members.*

We also found traces of the Cowaramup Conglomerate at several other points in the Naturaliste-Leeuwin region. At Cape Naturaliste there is a conglomerate with lenticular shell beds 10–23 feet above datum, unconformable on the gneiss, and capped by fossil soil and æolianite. A mid-Recent 10-foot bench cuts into it and there is also a 5–6 foot beach-rock plaster.

The granitic gneiss conglomeratic phase is seen at Yallingup and the shelly limestone is undercut in cliffs and forms the floor of the present shore platform. Ordinary æolianite overlies it at 10–12 feet above datum. At Canal Rocks, a 25-foot erosion terrace (shore-platform) in the pre-Cambrian is overlapped by the conglomerate, again with shell beds and followed by æolianite.

About ½ mile north of Cape Leeuwin the shelly conglomerate may be traced over an uneven gneiss from 3 to 25 feet above datum, but in places passes into an evenly bedded grey sandy limestone (marine " calcarenite "), a rather unusual rock type. There is the usual 10-foot bench and a 5-foot beach-rock occurs. At Hamelin Bay a beach-rock facies, underlying soil A in the æolianites, extends from datum to 15 feet above, thus indicating a sea rising to 10 feet (assuming a tidal range of 5 feet) prior to the dune formation here.

Outside our area, along the south coast the basal conglomerate has been noted at several points: at Malamup near Cape d'Entrecasteaux (by Montgomery, 1904), at Knapp Head (R.W.F.), with the shell beds underlying the æolianite at Point Hillier (R.W.F.), and so on. Along the west coast on the Swan River near Perth, the Peppermint Grove and Minim Cove shell beds (3–24 feet above datum), characterized by *Anadara trapezia*, and underlying the æolianite, have long been known (Somerville, 1920), and they have recently been found at intermediate points: Mandurah and Myalup (R.W.F.).

Somewhat farther inland the *Anadara* beds are reported in the Guildford Clay, which is clearly an estuarine facies. At Cottesloe and Fremantle there is a lower, beach-rock and sandstone reef facies with coral boulders, rising from 5 to 15 feet above datum. On Rottnest Island at Salmon Bay an analogous position (up to 8–10 feet) is occupied by a coral reef (Teichert, 1950), and north of Perth, at Sorrento, a *Lithothamnion* reef was recently found at the same horizon. Similar coral reefs and lagoon limestones (up to 18 feet above datum) occur in the Abrolhos Islands (Teichert, 1947*b* ; Fairbridge, 1948*a*). From the evidence of bores in the western parts of the Coastal Plain and on Rottnest, these marine intercalations may be quite thin, and æolianites appear to extend down to at least 230 feet below sea level.

While it is impossible to go into more detail here, it appears from a general correlation of the Western Australian Quaternary (Fairbridge, in press) that these Pleistocene marine shoreline deposits may be divided into two categories : those that rise up to about 25 feet, and a slightly younger set that do not rise more than 10–15 feet above datum. These separate different generations of æolianite. The Peppermint Grove beds and Cottesloe beach-rock carry conglomerates of earlier æolianites and travertines.

## IV. Interpretation of the Æolianites and Their Soils.

Interpretation of the dune rocks of Australia can probably benefit from comparison with well known dune systems of Western Europe. The analogies are closest with those of two outstanding belts :

(1) The great dune area of the Gascony district in France, about 150 miles long and 2–5 miles wide, and

(2) the great dune systems along the south coasts of the North Sea and the Baltic Sea, which, with interruptions, are over 2,000 miles long and are similar in width.

These dune belts are very similar to the dune limestone belt of Western Australia in dimensions, but differ in material, the European dunes being mainly of quartz sand.

In the Gascony district two generations of ancient dunes are present. Both are of Pleistocene age and are now fixed by vegetation.

The origin of the North German dune belt on the other hand probably only dates back to about 3500 to 4000 B.C. The development of the latter dune system is best known and has been well described by Keilhack (1917 ; see also review in English by Johnson, 1919). The coastline then (part of the Littorina time) differed but little from that of to-day and the sandy beaches which are now generally less than 100 yards wide, were probably not much wider when the dune formation began.

The main body of the dunes was probably formed within a few hundred years. They then became vegetated and soil formation began. The old podsols show a thickness of up to 3 or 4 feet. In favourable areas dunes continued to be built up in successive belts right up to the present time. One such area is the gap between the islands of Usedom and Wollin, at the mouth of the Oder, where 150 dune ridges have been formed. Keilhack (1912) concluded that 35 years are sufficient for the building up of one dune ridge about 20 feet high. As evidence of the speed of dune formation, there is the record of the rapid migration of sand on the Kurische Nehrung after the deforestation of the 18th century, when, within 50 years, enormous wandering dunes had been formed, piling up to heights of 200 feet, burying many villages.

Pertinent to the Australian development are the following significant points in the formation of these North German dunes :

(1) The restricted width of the beaches in Littorina times, which would have required a ready supply of sand by waves and longshore currents.

(2) A climate which was temporarily unfavourable to fixation by plant growth.

(3) The rapid accumulation of sand, the main dune belt being formed within a few centuries.

The main development of the æolianite belt in Western and southern Australia is in close proximity to the present shoreline and on islands that rise from the continental shelf. The dunes were probably built up in successive belts from a depth of about 200 feet below sea level to several hundred feet above, though a number of marine intercalations occur up to 25 feet above present sea level.

Following Sayles and others, one of us (Teichert, 1947*b*) has previously held that the calcareous dunes of Western Australia were formed when " sea level stood lower than now and large parts of the Western Australian shelf were exposed to wind erosion ". Although similar suggestions have been made for the South Australian æolianites by Tate (1879) and by Crocker (1946) we now believe that such statements need modification.

First of all, it would seem that dunes may be built either during emergence *or* submergence ; in the former case they would tend to be left behind with every temporary pause in the sea's retreat ; in the latter case they would tend to be driven forward to the maximum limit of the sea's advance.

It follows from this that the Western Australian æolianites may have been formed at any time when sea level stood anywhere between +25 feet and —230 feet relative to its present height, and that the distribution of these rocks is satisfactorily explained by assuming that they were formed along a shoreline that was not very different in character from that of the present. It would not be necessary to imagine a wide desert of sand during the low Glacial sea levels, but merely a normal width of beach under conditions of advance or retreat. The climatic conditions need not have been particularly arid, since even to-day, if the normal vegetation on the very youthful soft dunes of Western Australia is disturbed or destroyed, a new dune is rapidly initiated.

From observations in Hamelin Bay and elsewhere it is clear that the main æolianite ridges were built up in stages, quiescent periods being indicated by formation of soil horizons. The next question to be answered is how long are the time intervals which these soil horizons represent.

Sayles (1931) was the first to consider the problem of soil horizons in dune limestones. In Bermuda he observed six generations of æolianites separated by five fossil soils, and he named them as stratigraphical units. His conclusions, which have since been widely quoted, were that each æolianite corresponded to a glacial stage of the Pleistocene, when the sea levels were low and a broad insular shelf was exposed to wind erosion. The fossil soils formed during interglacial stages when sea level rose and dune formation temporarily ceased.

Sayles' ideas were strongly influenced by Verrill (1902–05), who published analyses of the limestones which showed that " impurities " in them were often " not more than 0·5 per cent." From this he concluded that 100–200 feet of dune limestone were required to form 1–2 feet of soil. This figure may be seriously challenged because the soil horizons are obviously not merely residuals from solution.

Furthermore, it is generally accepted that sea level rose well above its present stand several times during the Pleistocene, but of such multiple high sea levels there is no sign in Bermuda. It is, therefore, almost certain that the æolianites of this island and their soils represent a very much shorter span of time than envisaged by Sayles—probably only a short period of the late Pleistocene.

Few facts seem to be known which would allow one to form an accurate estimate of the rate of soil formation under various conditions. As is well known, depth of weathering has been used to calculate the length of Pleistocene interglacial periods, e.g. by Kay (1931), whose figures were, somewhat uncritically, used by Sayles for Bermuda. He proceeded on the assumption that post-glacial soils in the U.S.A. were as a rule 6 inches thick and from this concluded that 1 foot of Bermuda soil might have accumulated in 50,000 years. There is little doubt that such figures are much too high. Thick mature brown-earth and podsol profiles of north-western Europe are not more than 10,000–15,000 years old, and maturity may be reached fairly quickly.

Under entirely different conditions in Alaska, Judson (1946) found three generations of dunes, each with a soil (typical podsol) 2–5 feet thick, overlying weathered till; it would seem that the formation of the oldest dunes could hardly have begun before the latest Pleistocene, or even post-Pleistocene.

From the analyses of the Western Australian fossil soils (see Table I), it is apparent that the profile has been arrested at an early stage by renewed dune-building.

Any explanation of the origin of the æolianites of W.A. must take into account their repeated generations within narrow belts. Obviously the formation of any one dune ridge required a rather specialized combination of conditions which could not be expected to recur within a narrow zone several times during a period of several hundred thousand years. The superposition of half a dozen dune generations, as seen for example at Hamelin Island, suggests, on the contrary, that all of them were formed within a comparatively short time. Thus we are forced to the conclusion that, given the right combination of physiographical, geological and climatic conditions, the formation of the calcareous dunes, their fixation, accompanied by soil development, followed by the destruction of their vegetation and renewed growth of sand, a cycle repeated again and again, and finally the gradual consolidation into dune limestone, were processes that followed each other in fairly rapid succession.

## V. Correlation with England and North Africa.

Since it has been generally conceded that there has been no appreciable warping of southern England since the close of the Pleistocene, and south-Western Australia also seems to be a pretty stable sector of an ancient pre-Cambrian shield, a tentative correlation may be attempted between the two for the late Pleistocene-early Recent history, based on absolute eustatic levels and palæoclimatic oscillations. It is also fairly generally agreed that the "25 foot" or "pre-Glacial Raised Beach" and fluvial *Muscliff Terrace* of southern England may be correlated, with Zeuner (1945), on absolute elevation and other evidence, with the Mediterranean Late Monastir eustatic sea level (7·5 m.). Precise correlation of the latter, however, is still conflicting. Zeuner puts it as most probably pre-Würm I (his Last Interglacial), but Cooke (1930) puts the 25 foot terrace as mid-Wisconsin (thus post-Würm I–probably pre-Würm II). The same course is now followed by Gigout (1951), as will appear in the comparison with North Africa.

Precise data are scarce on the younger terraces and raised benches in southern Britain, the bulk of the evidence probably being destroyed owing to the large tidal ranges. Green (1946, p. 92) defined a fluvial *Christchurch Terrace*, which may have been formed when the sea level stood about 15–17 feet O.D. (personal communication). This, he says (1946, p. 94), " must be very recent geologically ", seeming to correspond with Daly's " six-metre bench ", but this is not very helpful, since Daly confused both late Pleistocene and early Recent levels (Fairbridge, 1948*b*). In a later paper Green (1949) compared the Christchurch terrace with the Middle Sebilian of Egypt, which, according to Ball (1939), corresponds to a 10-foot sea level that antedated the last big eustatic drop at the end of the Pleistocene (and formed the " Lower Buried Channel " of Britain).

A still younger and very recent terrace was reported at Southampton, Christchurch and Totnes (Green, 1949, p. 117), at 10–12 feet O.D., and this may correspond to the Tilbury Stage of King and Oakley (1936). In a personal communication (to R.W.F.) he correlated this " beach " with the Recent

TABLE II.

*Late Quaternary Correlation in the South of England.*

| Absolute Chronology (1). | Culture. | Terrace. | Beach. | Eustatic Sea Level. | Substage Correlation. |
|---|---|---|---|---|---|
| 115,000 | Mousterian. | ———First Buried Channel——— | | Low | Würm I. |
| 85,000 | Early Aurignacian. | Muscliff 41 ft. | " Pre-Glacial 25 ft." | 25–30 ft. | Ouljian= ? Late Monastir |
| 70,000 | Solutrian. | ——Second Buried Channel—— | | Low | Würm II. |
| 45,000 | Magdalenian. | Christchurch 22 ft. | " 10 foot " in part. | 10–15 ft. | (2) |
| 25,000 | Mesolithic. | ——Third Buried Channel—— | | Low. | Würm III. |
| 4,000 years B.P. | Neolithic. | Tilbury (3) 10 ft. | " Post-Glacial ", " 10 foot " in part. | ? 5–10 ft. | Recent (" Atlantic "). |

(1) Zeuner (1945). These figures are given here as a general indication. No unconditional acceptance of the " Absolute Chronology " is implied.

(2) Unnamed; Zeuner's " Interstadial slightly above O.D." (p. 252).

(3) Tilbury Stage of King and Oakley (1936); also described from Southampton by Green (1949).

" Atlantic " stage; he indicated, however, that the " 10-foot " beach is often only the seaward end of a buried 25-foot beach, which is also our experience sometimes in Australia. At Gower, T. N. George (1932) demonstrated that there is a distinct cemented beach-rock (*Heatherslide Beach Conglomerate*) at about 10 feet O.D., which is definitely post-Glacial and plastered on the late-Pleistocene terrace.

On this basis there are in the south of England three sets of river terraces and raised beaches of late- and post-Glacial age, as indicated in Table II. In this connection Zeuner (1952, p. 47) writes: " Altogether, exceptionally favourable circumstances are required for the distinction of the three latest high sea level phases, namely the Late Monastirian, the Würm Interstadial and the post-Glacial (which may in itself be double). These shorelines are less than 8 m. apart from each other, so that detailed evidence for high water mark is required to sort them out on morphological grounds. Their independent existence, however, can no longer be doubted . . . "

In North Africa, along the western shores of Morocco, the events of late Quaternary history correspond more closely to those of the Australian coastline than anywhere else in the world. Here the general picture may be obtained from two fine memoirs by Neuville and Ruhlmann (1941) and by Gigout (1951).

Valuable additional material is contained in papers by Bourcart (1949, etc.) but his interpretations are made under the assumption of tectonic warping, his " continental flexure ", which though a most valuable concept, does not seem to be applicable for the very short duration of the late Quaternary of either Morocco or south-western Australia. Successive generations of æolianites during the Pleistocene are found to correspond to the interglacial arid periods. These dune rocks are separated by marine intercalations, corresponding to the high eustatic sea levels, which initiate the pluvial stages. The maxima of the pluvials correspond to the glacial maxima, when all the climatic belts migrated equatorwards, and the temperate-wet climates interrupted the desert conditions when the æolianites were formed. However, with the glacial culminations the sea levels dropped sharply, separating each major cycle of dunes and high shorelines from the next by the erosional phenomena of a short period when the base level was considerably lowered.

This interpretation of Pleistocene events is quite different from that generally adopted in Australia, where we have been inclined to regard the glacial low sea levels as inducing the aridity which led to extensive dune formation ; and these would be interrupted by the high sea levels corresponding to the pluvial stages.

The evidence derived from this study of the Naturaliste-Leeuwin area seems to correspond precisely with the conclusions reached in Morocco, where, in addition to geological and geomorphological evidence, there are extensive palæontological data and material of human industries, to support a general correlation with the classical Pleistocene divisions of Europe. Gigout (1951) appears to have solved the problem of the 25-foot sea level, placing it in the first Würm Interstadial (Mousteriam), and proposes the name " Ouljian " for it ; this seems much better than Zeuner's problematic " late Monastir ". He also emphasizes the great importance of the Flandrian (Neolithic) 10-foot shoreline on the Moroccan coast and in western Europe.

Turning now to the Australian evidence, it may be assumed that if limestone terraces and " raised beaches " do not display any karst features which descend beneath the present sea level, then these terraces are younger than the last low sea level (Würm III). Those Quaternary formations in Western Australia which *do* show far-reaching karst channels are taken to be Würm III or older. In these pre-Würm III formations we believe we can detect two high sea levels reaching to 5–15 and 25–30 feet, which would logically belong to warm interstadials prior to Würm III and Würm II.

Our correlation may now seem almost complete, but further surveys and palæontological studies in Australia are badly needed. In the south-western province a general correlation has recently been prepared by one of us in connection with a regional stratigraphy (see Fairbridge, in press), but it is still with diffidence that this picture of local stratigraphic history is presented, as appears in Table III.

## Conclusions.

Observations along the Western Australian coasts have shown that the Coastal Limestone is older than the early Recent, or " Flandrian " period, when the sea level was 10 feet higher than it is to-day, because these rocks have been widely benched at that level.

In many places along the coast the æolianites are intercalated with marine deposits of reef or shoreline facies which, on the Abrolhos Islands, reach 18 feet, and near Perth (Peppermint Grove) reach up to 25 feet above sea level. These deposits are correlated with the First Würm Interstadial (Ouljian of Morocco or ? Late Monastirian level in Europe and the Mediterranean).

TABLE III.

*Late Quaternary Correlation in Western Australia.*

| | Absolute Chronology. | South-west and South Coast. | West Coast. | European Correlation (R.W.F.). |
|---|---|---|---|---|
| PLEISTOCENE. | 130,000<br>115,000 | ——<br>—— | First Æolianite (mostly below sea level).<br>Consolidation, travertine and karst. | Riss-Würm Interglacial.<br>Würm I glacial-pluvial maximum. |
| | 85,000 | —— | Peppermint Grove Formation (beach-rock shell beds and calcarenite).<br>Guildford Clay (estuarine facies) with *Anadara trapezia.*<br>Pelsart Reef Limestone. | 25 foot shore (beginning of First Würm Interstadial). |
| | 80,000 | —— | Second Æolianite (slightly lowered sea level). | First Würm Interstadial. |
| | 70,000 | ——(1) | Consolidation, travertine, karst. | Würm II glacial-pluvial maximum. |
| | 45,000 | Cowaramup Conglomerate (also Hamelin Bay beach-rock, etc.). | Cottesloe beach-rock.<br>Salmon Bay reef-rock. | 5–15 foot shore (beginning of Second Würm Interstadial). |
| | 40,000 | Third Æolianite (with Hamelin Bay soils). | Third Æolianite (with soils and snails). | Second Würm Interstadial. |
| | 25,000 | Consolidation, karst, etc. (as in Margaret R. Caves). | Consolidation, travertine, karst. | Würm III glacial-pluvial maximum. |
| POST-GLACIAL OR RECENT. | 4,000–2,300 B.C. | Beach-rock (at Cowaramup Bay).<br>Ten-foot Shore Platform. | " Raised Beach " and Beach-rock (as at Pt. Peron).<br>Ten-foot Shore platform (3). | Flandrian transgression " Atlantic " warm stage 10-foot shore. |
| | 2,300–600 B.C. | Beach-rock (at Cowaramup Bay).<br>Five-foot Shore Platform. | Emerged reef - rock beach-rock (as in Abrolhos Islands).<br>Five-foot shore platform. | Calais Beds.<br>"Subboreal" climate (2). |
| | 600 B.C.–1200 A.D. | ——(2) | Beach-rock (as at Rottnest I.).<br>Two-foot shore platform. | Dunkerque Beds.<br>"Subatlantic" climate (2). |

(1) The Cowaramup Conglomerate rests on Tertiary or pre-Cambrian on the south coast. Older æolianites may lie buried inland or on continental shelf.

(2) On the south coast greater exposure and greater tidal range may explain general lack of lower terraces. Same may be true in western Europe.

(3) Recent platforms and shell beds have not yet received specific names. Well described examples are cited.

At Cottesloe and on Rottnest Island there are slightly lower (5–15 feet) marine intercalations, and these may belong to the Second Würm Interstadial. In the Naturaliste-Leeuwin area, described in this paper, these marine beds form a basal member, the Cowaramup Conglomerate, which lies on the pre-Cambrian basement. Elsewhere, the marine beds rest on older æolianites which occur mostly below sea level.

We conclude that most of the Coastal Limestones of Western Australia, both æolianites and marine members, have been formed during the latest glacial stage, the Würm, because if they were older there would be signs on them of earlier, higher Pleistocene sea levels of which, in fact, there is no trace, except those cut into the pre-Cambrian rocks of the south coast. However, it is quite possible that truncated cores of still older æolianites exist beneath the present ridges.

The general evidence in W.A. is of a cyclic succession of marine bands and dunes separated by erosive intervals, but the bulk of the æolianites now exposed above sea level along the coast were formed during the last (second) interstadial of the Würm and the sea level then cannot have been very much lower than its present stand.

These dunes most probably started to build up as soon as the sea level reached its highest point (and consequently did not destroy them by further advance). The dune-building then continued as the sea level dropped, probably with a sequence of short oscillations, ceasing in the present belt as the shoreline finally receded (probably most rapidly) to its minimum level, which would coincide with the maximum glaciation.

It is an important conclusion of this study that the significant periods of dune formation did not coincide with the glacial maxima, but were in fact initiated with the highest eustatic sea levels during the interstadial warm-arid periods.

The glacial maxima (eustatic lows) are marked by a lowering of the water table, and solution by underground water caused deep sink holes and underground rivers to develop, reaching down to the lowest base-level. These karst features probably required a much longer period to form than the dunes themselves.

The short duration of the last dune building prior to the Recent epoch hardly needs more emphasis. In places on the coast the younger (third) æolianite is over 300 feet thick, and this itself most likely accumulated in short phases, interrupted by non-æolianite periods when soils developed. The fossil soil horizons which thus separate a number of dune generations in the æolianites may indicate minor and short-lived climatic cycles. They change from rendzinas in the south to terra rossa soils at the latitude of Fremantle and grade into mere travertine crusts farther north. We have therefore concluded that it is utterly wrong to correlate each soil with an interglacial stage, as was done by Sayles in Bermuda, and that any empirical formula deducing an absolute duration of time from a certain thickness of soil accumulation is equally fallacious.

An interesting feature of the Cowaramup Conglomerate in the Naturaliste-Leeuwin area is the light it sheds on the *rate of coast erosion* here. This basal conglomerate was being formed under conditions of littoral erosion perhaps 45,000 years ago. It was then cut off by the fall in sea level, covered over by a protective blanket of dune sands at least 60 feet thick, which was then cut through again by marine erosion in Flandrian times. On the south side of Cowaramup Point the width of the contemporary bench cut in these late Würm æolianites is not less than 200 feet; this has taken 4,000 years to form (aided by a progressively lowered sea level), which gives an average rate of about 0·05 foot per year. But the eustatic drops have been short and sharp, so that the actual rate must have been faster. The boulders of the Cowaramup Conglomerate, however, are now being reworked by contemporary erosion, so that we are now back on the shoreline of the Würm II-III Interstadial, and so the net amount of coastal retreat over the last 45,000 years has been nil.

We may close with the hope that these notes may stimulate further interest in the possibilities of coastal geology as a means of unravelling the history of eustatic and climatic events over the last 50,000 years or so.

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## Explanation of Plates.

### Plate VII.

Fig. 1.—Coastal Limestone æolianites at Hamelin Bay, showing Fossil Soil Horizon B (dark band), which just here is 6–18 inches thick. Immediately beneath it (marked by black notebook) is an irregular band of travertine pebbles. The jagged part of the underlying æolianite is due to travertinized root structures. The upper æolianite shows false-bedding at 25–30° N.E. (away from the prevailing wind).

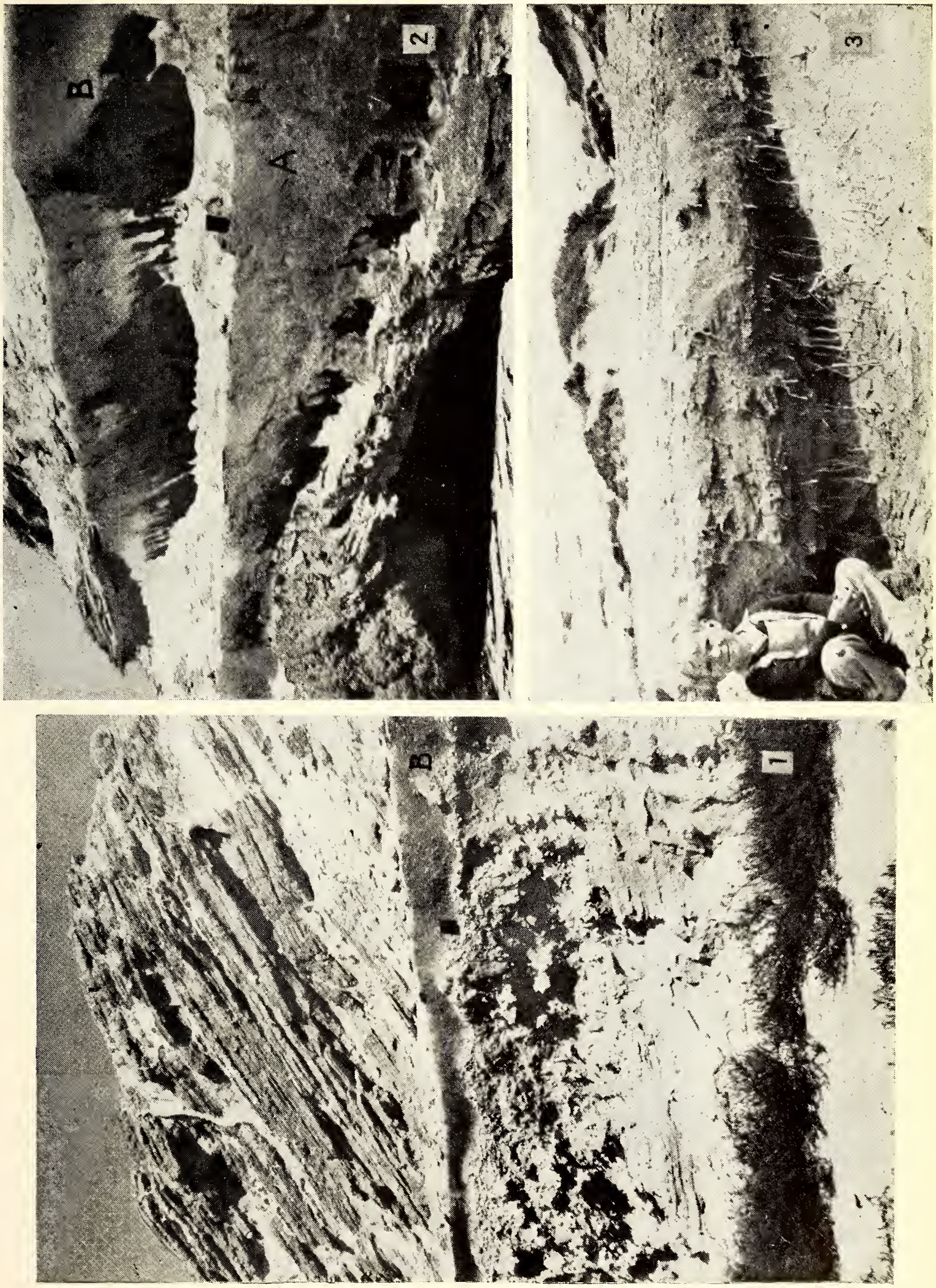
(*Photo.*—R.W.F. 4080.)

Fig. 2.—Two Fossil Soil Horizons (A and B) intercalated in the Coastal Limestone æolianites at Hamelin Bay. The lower band (A) is more heavily indurated with travertine than the upper one and varies from 2–5 feet in thickness here. Only a thin layer of æolianite separates it here from the upper soil (B), which is 3–6 feet thick; note the transition from the dark upper part, rich in organic matter, passing down into a white, leached zone with travertinized roots.

(*Photo.*—R.W.F. 4081.)

Fig. 3.—Fossil Soil Horizon at Cape Naturaliste, 3 feet thick, showing fine travertinized root structures.

(*Photo.*—R.W.F. 4045.)


B
A
2
3
B
1


2


3


4


1
A
B
C
D
E
F

## Plate VIII.

Fig. 1.—Cowaramup Conglomerate, in Cowaramup Bay ; granite-gneiss boulders (A), 4 feet long embedded in creamy white marine limestone (with few shelly fossils), passing upwards into (B) finely current-bedded beach-rock (calcareous sandstone) the top of which is here marked by the mid-Recent 10-foot eustatic bench (C). The beach-rock is overlain by hard and soft shell beds (D), and a 12-inch fossil soil (E), to be capped by the steeply bedded æolianites in the background (F).

(*Photo.*—R.W.F. 4060.)

Fig. 2.—Cowaramup Conglomerate, seen near Cowaramup Point, partly broken up by contemporary erosion. Boulder-bands alternate with white marine limestone. Granite-gneiss basement *in situ* in background.

(*Photo.*—R.W.F. 4064.)

Fig. 3.—Contemporary coastal erosion platform cut in the Cowaramup Conglomerate and its limestone matrix, which dissolves rapidly under inter-tidal marine erosion, leaving the resistant boulders on the reef platform. Looking south from Cowaramup Point.

(*Photo.*—R.W.F. 4065.)

Fig. 4.—Cape Naturaliste. Detail of contact between deeply weathered pre-Cambrian gneiss and schist and the overlying Cowaramup Conglomerate and its matrix of calcareous shell beds.

(*Photo.*—R.W.F. 4046.)

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CONTENTS

# VOLUME LXXXVI

## Part IV

Page

ART. X.—A Contribution to the Geology and Glaciology of the Snowy Mountains. By A. S. Ritchie .. .. .. .. .. .. .. .. .. .. 88

ART. XI.—Graptolite Zones and Associated Stratigraphy at Four-Mile Creek, South-west of Orange, N.S.W. By N. C. Stevens and G. H. Packham .. .. .. 94

ART. XII.—MARTINIOPSIS Waagen from the Salt Range, India. By Ida A. Brown .. 100

ART. XIII.—Contributions to a Study of the Marulan Batholith. Part II. The Granodiorite-Quartz Porphyrite Hybrids. By G. D. Osborne and J. S. Lovering .. 108

ART. XIV.—The Replacement of Crinoid Stems and Gastropods by Cassiterite at Emmaville, New South Wales. By L. J. Lawrence .. .. .. .. .. .. 119

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FOR

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# A CONTRIBUTION TO THE GEOLOGY AND GLACIOLOGY OF THE SNOWY MOUNTAINS.

By A. S. Ritchie.

With one Text-figure.

*Manuscript received, October 14, 1952. Read, November 5, 1952.*

## Introduction.

Considerable evidence of Pleistocene glaciation in the Kosciusko summit area was recorded by David (1908) and David and others (1901). Later, Browne and others (1944, 1946) recorded further evidence both in the summit area and in the country north of it.

Some years ago the writer turned his attention to an area of about twenty square miles, between the two already investigated, in what might be called the Granite Peaks-Rolling Ground region. The eastern boundaries of the region are the Snowy and Munyang Rivers, while the northern and western boundaries are Dicky Cooper's Creek and the precipitous gorge of the Geehi River respectively. In the south it is bounded by the Snowy River, the Guthega River and Three Rocks Creek.

The present contribution is a progress report on investigations made during visits to the region in January, 1945; January, 1948; January, 1949; November, 1950; and March, 1952. The area is not easily accessible and all work was done on foot. The weight of food carried limited each visit to eight or ten days' duration. Stormy weather with snow, even in summer, often restricted field work.

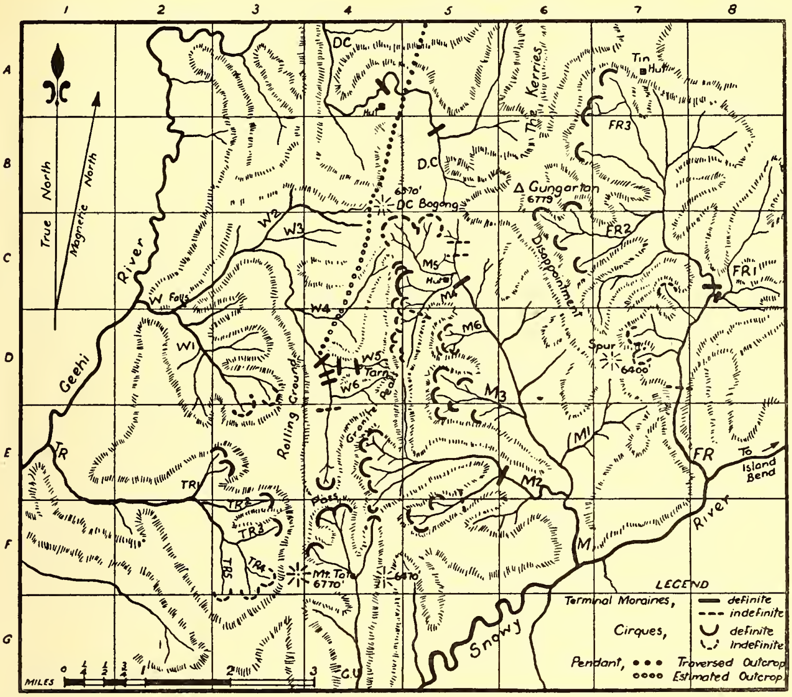
Text-figure 1 is mainly a copy of the map of the Snow Leases and Permissive Occupancies of the Department of Lands. Minor variations have been made in the light of field observations. The field notes were related to the streams since anomalous variations in the magnetic declination have been suspected by the writer. The simple grid system of the map has been introduced to facilitate the location of points in a region where few physiographic features are named. The main streams and their tributaries are lettered for the same reason.

## Physiography.

The Granite Peaks-Rolling Ground area is the northern continuation of the Main Range of the summit area, the Great Divide extending from Consett Stephen Pass (location F4) near Mt. Tate (F3) in the south to the saddle (B5 and C5) between the sources of Munyang River and Dicky Cooper's Creek in the north. The greatest elevation is at Dicky Cooper's Bogong (B4), which stands at 6,570 feet above sea level. The whole area is mostly above 6,000 feet, although the lower valleys of the streams descend to about 4,200 feet on the east and to about 3,000 feet on the west of the divide.

The drainage is effected chiefly by four streams which show remarkable parallelism in a sub-meridional direction. These streams are the Munyang and Guthega Rivers on the east of the divide and Dicky Cooper's Creek and Windy

Creek on the west. The collinearity of (*a*) Windy Creek and Guthega River, (*b*) Dicky Cooper's Creek and Munyang River and the parallelism of all these with each other, with some of their tributaries and with Finn's River is striking. The explanation probably lies in the step-faulting as suggested by Browne and others (1944). Some of the tributaries of these streams are large enough to deserve names. Similarly, numerous peaks in the area should be named.




Text-fig. 1.—Granite Peaks—Rolling Ground Region, Snowy Mountains, N.S.W.

| | |
|---|---|
| D.C.—Dicky Cooper's Creek. | T.R.—Three Rocks Creek. |
| M. —Munyang River. | W. —Windy Creek. |
| F.R.—Finn's River. | G.U.—Guthega River. |

## Erosion.

Most of the area is above the tree-line and is well grassed except for the rocky pinnacles. In sheltered places a thick stunted heather-like growth abounds. Soil erosion seems to be at a minimum and, in normal weather, the streams are very clear and flow through grassy banks. After heavy rain, however, the streams become very muddy and leave no doubt that very active erosion is in progress.

Snow-patch erosion and nivation (Browne and others 1944) were noted throughout the area. The role of snow daisies as a retardant should be recorded. Where the ice thins around the margin of the snow-drifts the snow daisies, as if anticipating their release, make considerable growth while still covered by up to half an inch of ice. During this growth the leaves are sheathed in a gelatinous film. Thus the soil surface is covered to a considerable extent before the snow melts.

West of the divide the stream gradients are very steep and hence very active stream erosion is in progress.

In the upland valleys and swamps the present streams are incised into the floors of the valleys to a depth of from two to twenty feet.

## Evidence of Glaciation.

There is widespread evidence of glaciation throughout the area. This may best be described by considering each main stream system in turn. The observations are merely recorded. Conclusions mostly have been left to the future, when sufficient data are available for the whole Snowy Mountains area.

(1) *Munyang River* (also known as White's River).

This stream has its source on the south-eastern slopes of Dicky Cooper's Bogong (B4) and flows in a south-easterly direction into the Snowy River. The upper valley is glaciated. The most prominent evidence is a terminal moraine just downstream from White's River Hut (C5) at an elevation of 5,500 feet (by aneroid). It is proposed to call this *White's Moraine*. Large faceted boulders here form a pronounced barrier which is slightly breached to permit the stream to cascade down some thirty feet to a rocky valley floor. This was observed independently by Browne and others (1946). Upstream from the moraine the valley is wide and the main stream and its tributaries meander in front of the hut. A spur near the hut appears to have been truncated. Further upstream there is less distinct evidence of two smaller terminal moraines at elevations of 5,670 and 5,760 feet. There is definite evidence of ground moraine right up to the saddle between this stream and Dicky Cooper's Creek, the elevation of the saddle being 5,930 feet. Some of the drift appears to have come down from Disappointment Spur. Only minor tributaries feed the river above the 5,670 feet level. Two large creeks (M4 and M5) join the river in the upper part, one on either side of White's River hut. The stream M5 has faceted boulders near the hut but these may have been left as marginal moraines or kame-terraces by the glacier in the main valley through which this stream (M5) flows. Further upstream in M5, the sources of this stream are found in two indefinite large cirques on the south-eastern slopes of Dicky Cooper's Bogong. The elevation of these cirques is about 6,400 feet and the westerly one has a terminal moraine across it. The stream M4 has faceted boulders and is fed in summer by a number of snow-drifts which are cradled in as many cirques on the eastern slopes of the Granite Peaks (C4 and D4). Some of these cirques, at elevations of from 6,200 to 6,420 feet, are very definite, possessing steep walls in a semi-circle with flat floors sometimes terminated by small moraines now breached by the small streams. The stream M4 rises at the head of a long, wide upland swamp. Remarkably constant changes of height on both the eastern and western sides of the swamp suggest step-faulting with strikes parallel to those already mentioned. An indefinite terminal moraine is located at the lower end of this upland swamp (D5). During the ice age, much ice must have accumulated on the site of the present swamp. The main egress was probably down the valley of M4 but some spillways over the eastern side of the valley into M6 seem possible. Downstream from the top of White's Moraine, a great accumulation of large boulders extends for almost a mile and is probably the lower part of White's Moraine. The elevation of the lowest of these boulders is 5,250 feet. Thus a considerable gradient exists and the stream appears somewhat youthful in character. The valley is much wider than the stream, however, and is clothed in an almost impenetrable scrub. This forms the most difficult country on the eastern side of the divide. Below the moraine the valley opens out and, just below the tributary M3, displays valley-in-valley structure and some degree of maturity due to a more gentle gradient. The altitude here is about 5,000 feet. About a quarter of a mile upstream from M1, the Munyang River becomes quite youthful and pot-holes and cascades are prominent. The sudden change of gradient here suggests more faulting. The lower mile of the Munyang River is entrenched about thirty feet into a broader valley. The stream M1 has not yet been examined.

(2) *The streams between Guthega and Munyang Rivers* have not been examined.

(3) *Guthega River.*

This stream rises with several arms, some of which begin in small cirques on the eastern side of Mt. Tate (F3). Nivation appears to have played some part in cirque formation here. The eastern arms of the Guthega rise in slightly cirquated land a little north-west of the 6,470 feet peak (F4). At first the upper valley is wide and glaciated but it soon assumes a youthful character and flows through a rugged valley until it meets the Snowy River. Dr. W. R. Browne, in a private communication, states that there appear to be truncated spurs on the right bank of the Guthega valley as viewed from Guthega Camp.

(4) *Dicky Cooper's Creek.*

This stream rises in a low col which separates it from the Upper Munyang River. It receives tributaries from Dicky Cooper's Bogong on the west and from the Kerries and Gungartan (B6) on the north and east. A number of small cirques on the north-eastern slopes of Dicky Cooper's Bogong are perched high above the valley of the creek and any relationship between the glaciology of the two is obscure. The valley of Dicky Cooper's Creek is wide and displays considerable scattered ground moraine in its upper part. The present stream is entrenched from about three to seven feet into the wide floor of the valley. The wide valley narrows at a large terminal moraine (B5), which, it is proposed to call *Dicky Cooper's Moraine.* Its elevation is 5,850 feet and it is comparable in size to the upper part of White's Moraine. Below the moraine the valley narrows considerably and turns sharply to the west. The writer did not follow the stream further than the track which leads northwards from Dicky Cooper's Hut. Here another moraine has been reported by Browne and others (1946). This valley appears to have received ice from Gungartan and the Kerries but the bulk of the ice from Dicky Cooper's Bogong appears to have gone down the Munyang Valley.

(5) *Windy Creek.*

Members of this stream system drain to the west all that country from Consett Stephen Pass (E4 and F4) to Dicky Cooper's Bogong and its upper valley is wide and very deep. This valley shows the most pronounced glaciation of any the writer has seen in the Kosciusko area. The glaciation of this valley was recorded independently by Browne and others (1946). In the valley there are four terminal moraines, all breached by the stream which is entrenched from five feet (near the source) to fifteen feet (two miles downstream) into the wide valley floor. Most tributaries spill over into this valley from hanging valleys perched two or three hundred feet above the valley floor. A notable exception is stream W6, in which the glacial erosion seems to have kept pace with that of the main valley. Below the confluence with stream W2 the main valley becomes very youthful and the gradient very steep. Further downstream the Leaning Rock Falls (C2) make passage on foot impossible.

Stream W6 rises on the west of the Granite Peaks (E4 and D4). The gradient at first is relatively slight but soon steepens and a wide glaciated valley enters the main valley. Morainic material in stream W6 is slight and indefinite.

Stream W5 rises in a similar manner to W6 but in its course there are two terminal moraines. The upper one, the less distinct, is breached, but nevertheless dams the stream to form a small tarn which persists throughout the summer. Downstream from this moraine the stream cuts into its own valley to a depth of about five feet and exposes a fine till, which extends downstream for about two hundred yards. About half a mile below the upper moraine is a very large moraine, which appears to have been built up near the end of a hanging valley. A great mass of morainic matter has tumbled into the main valley. A small swamp lies upstream from the moraine.

Streams W3 and W4 drain the south-western slopes of Dicky Cooper's Bogong. Their upper valleys are wide and swampy. These streams have not been closely examined. Downstream they assume a youthful condition before entering Windy Creek. Browne and others (1946) observed the glaciated character of these streams.

(6) *Three Rocks Creek.*

This stream drains the western slopes of Mt. Tate, the southern slopes of Tate West Ridge and the northern slopes of Mann Bluff (G3). The lower parts of the stream plunge steeply into the Geehi River and display active erosion. The upper parts show glaciated valleys, two of which, from Tate West Ridge, are very striking. The west slopes of Mt. Tate and the northern slopes of Mann Bluff are strongly cirquated but no close examination was made.

(7) *Finn's River.*

No thorough examination of this valley was made but strong evidence of glaciation was noted *en route* to and from Island Bend on the Snowy River. The amount of evidence of glaciation here is surprising and the area warrants closer attention. The following were noted :

(*a*) The sources of Finn's River are in large cirques near Tin Hut (A7). This was noted also by Browne and others (1946).

(*b*) The upper four miles of the valley is U-shaped, with slight gradient and, in places, forms upland swamps.

(*c*) One very large terminal moraine occurs at and above the confluence with Farm Creek (FR1). This moraine is larger than any in Cootapatamba Valley (David and others, 1901). Another probable terminal moraine occurs about one mile upstream from the Snowy River. Above this point the stream becomes swampy and is very wide and flat. No close examination of this was made.

(*d*) Tributaries draining Gungartan (C6) and Disappointment Spur (C6) and (D7) rise in cirques and some appear to have terminal moraines.

(*e*) Farm Creek (stream FR1) has a terminal moraine just above its confluence with Finn's River. This moraine is large but is made up of much finer material than any other the writer has seen in the Kosciusko area. Some special circumstances are indicated here. This evidence indicates a valley glacier from the south-west slopes of Toll Bar Ridge. It would not be unreasonable to suspect glacial evidence in upper Toll Bar Creek on the north-west slopes. This locality is well worthy of further investigation.

(8) *Petrological Evidence.*

The only outcrops of metasediments known to the writer in the area lie to the west of the divide. Nevertheless, fragments of quartz-schist are common on the N.E. slopes of Dicky Cooper's Bogong on the eastern side of the divide. Similar specimens were found in upper Munyang River and in White's Moraine. This may be an important clue to the movement of the ice.

## Geology.

A moderately gneissic granite makes up almost the whole area. Brief mention should be made, however, of what appears to be a remarkable roof pendant of metasediments in the gneissic granite. This was first noted about half a mile west of Dicky Cooper's Bogong. The dip was vertical and the strike 181°. The width here was about three hundred yards. The rocks were determined in the field as quartz-schist, phyllite and milky quartz (in wide veins), quartzites and highly cleavable slates. In 1946 Browne and others independently observed this occurrence north of Dicky Cooper's Bogong. Subsequently, the pendant was traced by the writer northwards along its continuous outcrop to the saddle near The Ghost on the track from Dicky Cooper's hut to Mawson's hut. The outcrop was lost on this saddle, the last width noted being twenty-five feet. No search was made further north. From the head of Barber's Creek (W2), the outcrop of the metasediments can be seen stretching to the south from near Dicky Cooper's Bogong. The outcrop was located again in Windy Creek valley just downstream from the confluence with W5. Here the width was about one hundred feet and the nature of the rocks about the same as those further north. No outcrop of the pendant was found on the south-western side of Windy Creek nor in the high country beyond. The abrupt cessation of this rock mass in the creek bed confirms the faulting which has been suggested along these streams. The writer believes this southernmost outcrop is continuous with those already noted. It would appear then that this pendant is at least four miles long.

## Acknowledgements.

The writer wishes to thank Drs. W. R. Browne and G. D. Osborne for advice and constructive criticism of this contribution ; the Kosciusko State Park Trust for access to the 1946 Report ; Mr. T. Vallance for assistance ; Miss P. Grieves for the tracing of the map, and the officers of the Snowy Mountains Hydro-Electric Authority for much assistance and hospitality. Finally, the writer's thanks go to Mr. S. G. Alley and other field companions without whom the journeys could not have been undertaken.

## Summary.

Observations and evidence of Pleistocene glaciation (in an area between the two previously described) are recorded. Numerous terminal moraines and cirques are recorded. A sketch-map is provided to indicate the locations of the evidence. Brief mention is made of a remarkable roof pendant of metasediments in gneissic granite.

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# GRAPTOLITE ZONES AND ASSOCIATED STRATIGRAPHY AT FOUR MILE CREEK, SOUTH-WEST OF ORANGE, N.S.W.

By N. C. Stevens
and G. H. Packham.

With two Text-figures.

*Manuscript received, October 30, 1952. Read, December 3, 1952.*

## Introduction.

In the small area described in this paper, Ordovician, Silurian, Upper Devonian and Tertiary rocks outcrop, The age of the Lower Palæozoic rocks has been determined by the graptolites they contain, which show that strata of Upper Ordovician, and Lower, Middle and probably Upper Silurian age are present. Lower Silurian fossils have been recorded from only two other places in New South Wales (Naylor, 1935; Fletcher, 1950), and at no place have definite Lower, Middle and Upper Silurian strata been found in sequence.

Four Mile Creek Post Office is 14 miles from Orange in a south-westerly direction and four miles west of the old iron and copper mines of Cadia, which were believed to be in Ordovician andesites and tuffs (Jaquet, 1901).

Ordovician graptolites from a locality "four miles from Cadia" (Smith, 1899) have probably been collected near Four Mile Creek, but apart from this reference there is no geological literature concerning the area.

## Stratigraphy

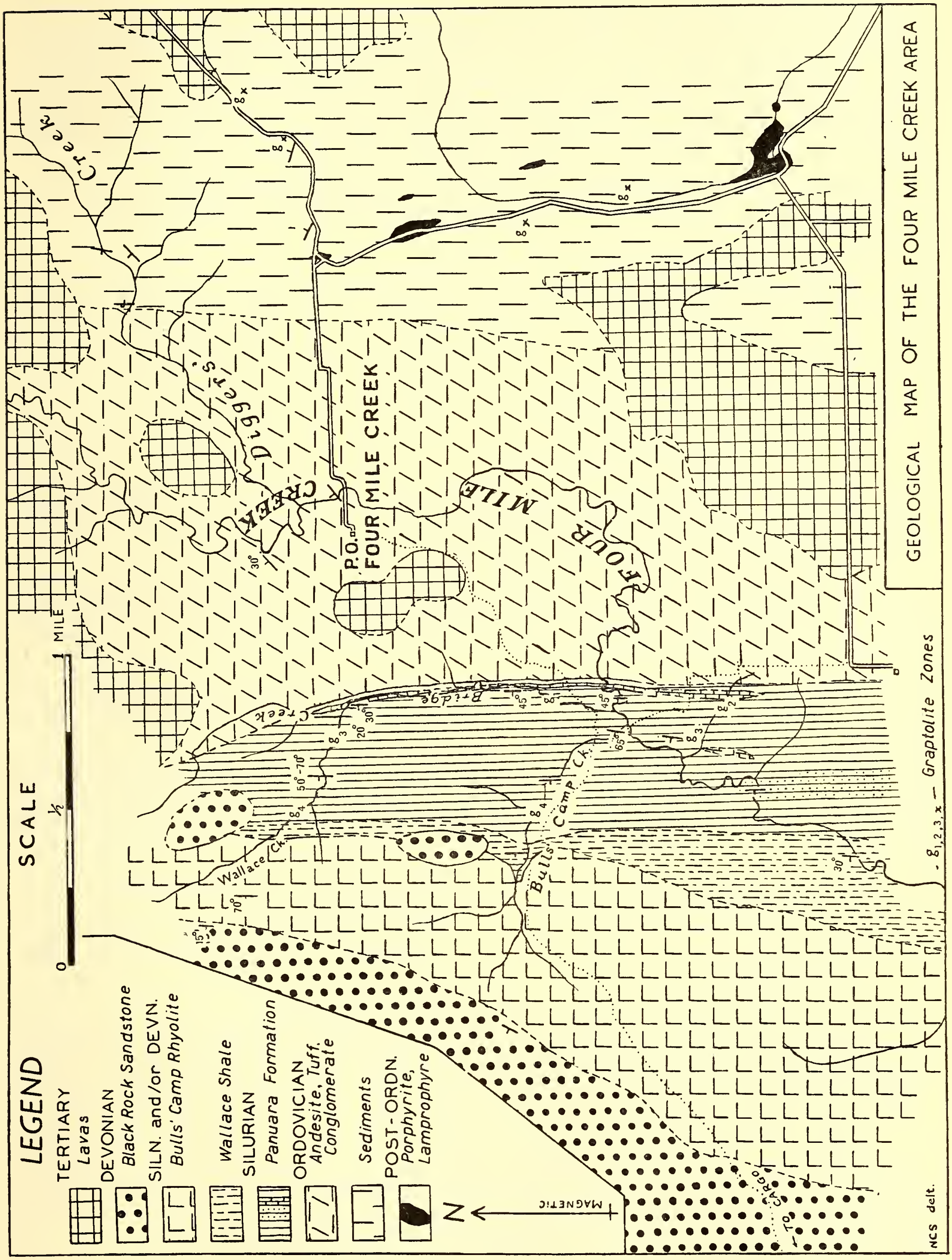
### I. Ordovician.

1. *Malongulli Formation* (?). Fossiliferous Ordovician rocks occur east of Four Mile Creek; they are covered by Tertiary lavas to the north and their southern and eastern extensions have not been ascertained.

For the most part they are calcareous siltstones; dark grey and compact when fresh but light grey and slaty when weathered. They are usually laminated and show some variation in grain size. Some are impure limestones and resemble types occurring in the Malongulli Formation of the Cliefden Caves district to the south (Stevens, 1952); others have dominant intermediate plagioclase with calcite and chlorite, and appear to have been derived from andesitic rocks. Fragments of fine-grained andesites are recognizable in some of the coarser varieties.

Good exposures of strongly folded Ordovician rocks occur between Digger's Creek and the Orange-Angullong Road. Along this road north-east of the turnoff to the Post Office the strata dip gently to the north, but in the creek at their western margin they dip west at steep angles.

Graptolites (mostly *Glyptograptus teretiusculus*) have been found at a number of places along the Orange-Angullong Road ($g_x$, Text-fig. 1). Specimens from Digger's Creek in the collection of the Geological and Mining Museum, Sydney, are probably those recorded by Smith (1899). According to Mrs. Sherrard (personal communication) these, and others in the collection of the Australian Museum, Sydney, from the same district, indicate the zone of *Nemagraptus gracilis*, the lowest zone of the Upper Ordovician.




Text-fig. 1.—Geological Map of the Four-Mile Creek Area, near Orange, N.S.W.

2. *Angullong Tuff* (?). On the west of the Upper Ordovician graptolite-bearing strata is a belt of andesitic rocks about one mile in width. Andesitic lavas and tuffs make up the bulk of the formation, with no discernible order. Breccias and pebbly tuffs grade into conglomerates, and locally, fine and coarse tuffs are intermingled as a result of slumping, giving the impression that one has been invaded by the other. Conglomerates with pebbles of sediments similar to the underlying graptolite-bearing rocks are present near the base of the formation, suggesting a possible disconformity between the Upper Ordovician siltstones and these andesitic rocks.

This formation, overlying the probable equivalent of the Malongulli Formation, may well be correlated with the Angullong Tuff to the south.

**II. Silurian and Devonian.**

The Silurian and Devonian rocks of this area have been divided as follows in descending stratigraphical order :

| | *Approx. Thickness* |
|---|---|
| 4. Black Rock Sandstone .. .. .. | 800 feet |
| 3. Bulls' Camp Rhyolite .. .. .. | 1,200 ,, |
| 2. Wallace Shale .. .. .. .. .. | 300 ,, |
| 1. Panuara Formation .. .. .. .. | 2,000 ,, |

The three lower formations have their typical development on Bulls' Camp Creek and the lower part of the Panuara Formation is best seen on Four Mile Creek, just upstream from the junction with Bulls' Camp Creek.

1. *Panuara Formation.* The lowest member of the Panuara Formation is a conglomerate with a red matrix and pebbles of weathered andesite. It rests on weathered andesite of the underlying formation and some time break between the two is indicated.

Above it are fine grey to green felspar sandstones which consist essentially of material derived from the andesites, and which become more calcareous upwards, grading into limestone.

This lower limestone bed (here called the *Bridge Creek Limestone Member*) has a maximum thickness of about 50 feet and consists of rhythmically bedded limestone and marl, richly fossiliferous. The following forms have been identified (G.H.P.) :

*Halysites orthopteroides* Eth. fil.
*H. cratus* Eth. fil.
*H.* sp. aff. *cratus* Eth. fil.
*Heliolites* sp.
*Desmidopora* sp.
*Mycophyllum liliiformis* (Eth. fil.).
*Cystiphyllum* sp.
?*Lambeophyllum profundum* (Conrad).
*Kloedenia* aff. *concinna* (Jones and Holl.).
*Leperditia* sp.

Shales and siltstones rest on the Bridge Creek Limestone, and less than 50 feet above it the lowest Silurian graptolites *Monograptus gregarius* and *Climacograptus* sp. occur in black shales in Bridge Creek ($g_1$). The zone is that of *M. gregarius*, equivalent to the top of the Lower Llandovery (Lower Silurian).

About 70 feet above the Bridge Creek Limestone, a graptolite assemblage, which includes *Monograptus exiguus*, *M. marri*, *M.* (?) *galaensis* and *Retiolites geinitzianus*, is found in sandstones and interbedded shales 30 chains south of the junction of Bridge and Four Mile Creeks ($g_2$). The zone is that of *M. crispus*, about the middle of the Upper Llandovery (Lower Silurian).

Several hundred feet of shales follow, then 50 feet of green felspathic sandstone, which may be tuffaceous. Directly on top of this bed is another graptolite horizon ($g_3$), which contains *Monograptus priodon*, *Cyrtograptus* aff. *insectus* and a *Monograptus* of the *vomerinus* group. These forms suggest a zone fairly low in the Wenlock (Middle Silurian). In the southern part of the area a lenticular outcrop of massive limestone containing a few corals (*Halysites*, *Favosites*) occurs about this horizon, and it is followed by shales, then fine-grained quartzose sandstone and interbedded shales.

TABLE I.

*Summary of Stratigraphic Relations of Graptolite-bearing Strata.*

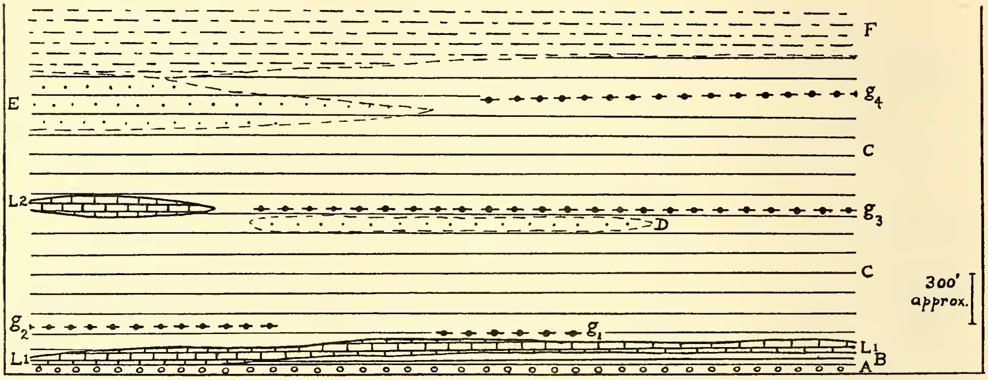
| | | | | |
|---|---|---|---|---|
| SILURIAN | Lower Ludlow. | PANUARA FORMATION | Un-named member (interbedded fine sandstone, siltstone and shale) | *M. dubius*, *M.* cf. *vulgaris*. |
| | Wenlock. | | | *M. priodon*, *M.* sp., *Cyrtograptus* aff. *insectus*. |
| | Llandovery. | | | *M. exiguus*, *M. marri*, *M.* (?) *galæensis*, *Retiolites geinitzianus*. |
| | | | | *M. gregarius*, *Climacograptus* sp. |
| | | | Bridge Creek Limestone Member | *Halysites* etc. (See list in text.) |
| | | | | Break in sedimentation (boundary either near base of Silurian or high in the Ordovician.) |
| UPPER ORDOVICIAN | Ashgillian. | | | |
| | Caradocian. | Andesitic rocks (?=Angullong Tuff.) | | |
| | Llandeilian. | Calcareous siltstone (?=Malongulli Formation.) | | *Glyptograptus teretiusculus*. |

To the north, the rocks overlying the $g_3$ horizon are shales and siltstones which show small-scale current bedding. Overlying strata are shales and sandstones, and a fourth graptolite horizon ($g_4$) occurs in grey shales in Wallace Creek, a tributary of Four Mile Creek. The graptolites present are *Monograptus dubius* and *M.* cf. *vulgaris*, which are either Upper Wenlock or Lower Ludlow types. The same zone is probably represented by very poorly preserved graptolites in an impure black limestone in Bulls' Camp Creek.

The Panuara Formation (which takes its name from Panuara Rivulet, an alternative name for Four Mile Creek) is thinly bedded, and all the strata dip to the west at angles which increase from 30° to 70° in this direction.

The Bridge Creek Limestone is the first in eastern Australia for which a basal Silurian age has been proved. It may in part extend down into the top of the Ordovician. The fauna contains elements known elsewhere in the Silurian of New South Wales (except for *Desmidopora* sp. and ? *Lambeophyllum profondum*), but none of the forms present in the Cliefden Caves Limestone (Stevens, 1952).

Age determinations of coral faunas in N.S.W. by graptolites are confined to high Wenlock and Lower Ludlow assemblages. At Yass (Brown and Sherrard, 1952) and in the Nanima-Bedulluck area (Sherrard, 1952) graptolites of the abovementioned age have been found, but in both cases the *Halysites*-bearing fauna is stratigraphically beneath the graptolites. At Four Mile Creek *Halysites* occurs in rocks from Lower Llandovery to Lower Wenlock. Unfortunately, no limestone occurs higher in the sequence.




Text-fig. 2.—Diagrammatic Columnar Section illustrating Silurian Stratigraphy at Four Mile Creek.
*A*, conglomerate ; *B*, felspar sandstone ; $L_1$, Bridge Creek Limestone ; *C*, shales and sandstones ; *D*, felspathic sandstone bed ; *E*, quartzose sandstone ; $g_1$, $g_2$, $g_3$, $g_4$, graptolite zones ; $L_2$, massive limestone lens. *A-E*, *Panuara Formation* ; *F*, *Wallace Shale*.

2. *Wallace Shale.* This formation, which overlies brown shales of the Panuara Formation with apparent conformity, consists of green and red highly-jointed shales. The base of the formation is marked by the first thick bed of green shale. The bedding is characteristically wider-spaced and less well-defined than in the Panuara Formation. A few minor sandstone beds a foot or so thick are present ; no fossils have been found.

In the southern part of the area dips are relatively gentle but to the north they steepen and some minor folds occur.

3. *Bulls' Camp Rhyolite.* The Bulls' Camp Rhyolite, which overlies the Wallace Shale, consists mainly of rhyolites, which are interbedded with pebbly tuffs, especially near the top of the formation. The tuffs contain pebbles of rhyolite, intermediate to basic igneous rocks and rarely, limestones with poorly-preserved corals.

Structural relations with the underlying rocks are not clear on Bulls' Camp Creek, but both dip gently to the west in the southern part of the area. Angles of dip increase towards the north.

4. *Black Rock Sandstone.* The rocks of this formation, which rest with probable unconformity on the rhyolites and tuffs noted above, are interbedded sandstones and quartzites, somewhat pebbly in places. The western boundary of this formation has been mapped previously (Stevens, 1950), and it has been shown that it underlies conglomerates and shales and forms the eastern limb of a syncline. Further north, Sussmilch (1906) found *Camarotœchia pleurodon* and

*Cyrtospirifer disjunctus* at the base of the sandstone, for which he deduced an Upper Devonian age.

**III. Tertiary.**

The Tertiary lavas of Mt. Canobolas occur chiefly in the higher country to the north, but remnants still exist south and south-west of Four Mile Creek Post Office at altitudes as low as 2,400 feet above sea level. The pre-lava land surface was irregular but sloped in a general south-westerly direction.

The lavas are mainly alkaline trachytes except along the Orange Road N.E. of Four Mile Creek, where basalts cap the ridge.

## Acknowledgements.

We wish to thank Mrs. K. Sherrard for her determination of the Ordovician graptolites and advice on the Silurian graptolites; also officers of the Mines and Forestry Departments, N.S.W., for access to aerial photographs.

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# *MARTINIOPSIS* WAAGEN FROM THE SALT RANGE, INDIA.

By Ida A. Brown, D.Sc.
(Mrs. W. R. Browne.)

With Plate IX and three Text-figures.

*Manuscript received, November 12, 1952. Read, December 3, 1952.*

**Abstract:** Description is given of the external and internal characters of the genotype of the Permian brachiopod *Martiniopsis* Waagen, 1883, based on complete and serially sectioned specimens from the Permian Productus Limestone, Salt Range, India.

A new term, *adminicula* (sing. *-um*), is introduced for supporting plates in the umbonal regions in the Spiriferidæ.

## Introduction.

In 1883 Waagen described a collection of Permian fossils from the Salt Range, India, including a new genus of brachiopod, which he named *Martiniopsis*. He did not describe fully the internal characters, but suggested that some of the smooth spirifers occurring in the Permian of eastern Australia might be placed in his new genus. Etheridge, Junr. (1892) adopted Waagen's suggestion, apparently without having examined any specimens from the Salt Range, and since then the name has been generally accepted for a number of species of Australian spirifers.

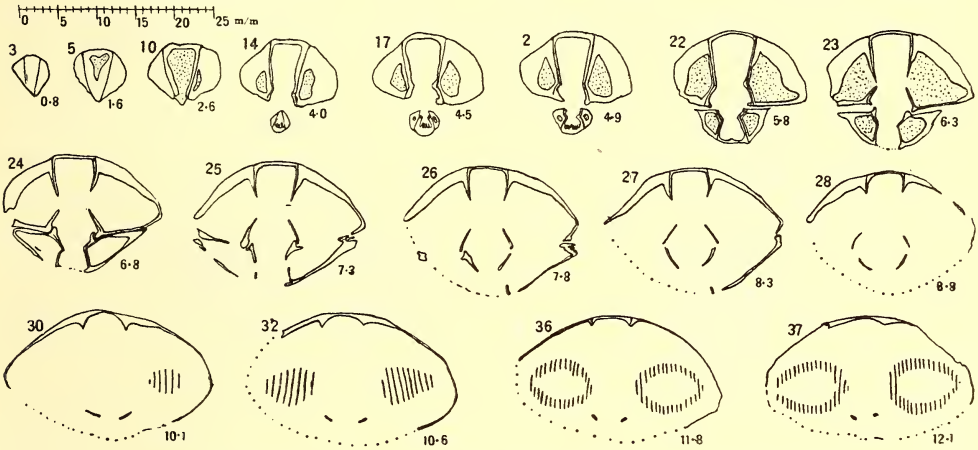
In the course of my revision of the Permian spirifers of south-eastern Australia it therefore became necessary to investigate the characters of *Martiniopsis* Waagen. Waagen had only about 12 specimens from the Salt Range, which he placed in two species: the shells are still rare in more recent collections. By the kind permission of the Director of the Geological Survey of India I was able to examine six specimens of *Martiniopsis* in a collection being investigated in 1938 by the late Dr. F. R. Cowper Reed, Palæontologist to the Geological Survey of India, at Sedgwick Museum, Cambridge, England, and I am indebted to the Director and to Dr. Reed for permission to make serial sections of one of these specimens, which form the basis of the present paper.

I have seen one specimen from Amb, Salt Range, in the British Museum (N.H.), B18596; one complete specimen and six fragments in the Schuchert Collection, Peabody Museum, Yale; and four recently acquired specimens in the Australian Museum, Sydney, all from the Productus Limestone of the Salt Range.

Since Waagen's work was published some 15 additional species of *Martiniopsis* (other than Australian) have been named by Tschernyschew (1902), Grabau (1936), Diener (1911), Huang (1933), Fredericks (1929), Reed (1930) and others, chiefly from the Ural Mountains, Shan States, Tibet and China. They are all small, smooth spirifers, externally similar to those from the Salt Range.

I am indebted to Dr. G. Marshall Kay of Columbia University, New York, for the gift of two specimens of *M. uralica* Tscher. collected by him in 1938 from the *Pseudoschwagerina princeps* zone of the Sakmarian at Tratauchikan, Bashkiria, Urals, U.S.S.R. (Plate IX, figs. 4*a*-4*c*).

The specimen (K31.326) described below was identified in 1938 by Dr. F. R. C. Reed as "*Martiniopsis subpentagonalis* Waagen, Horizon: Lower Productus Limestone (Wynne's Bed No. II), Locality: Right bank of Baral Nala, S.W. of Amb, Salt Range. (Sheet 38P/15)." In his monumental work on the fossils of the Salt Range (1944) Reed gives no description of *Martiniopsis*, but quotes identifications of certain specimens as *Martiniopsis* spp. in the fossil-lists in the second part of the memoir, and a specimen bearing the same number as that he gave to me (K31.326) he identifies (Reed, 1944, p. 403) as *Squamularia* (*Neophricodothyris*) *baralensis* Reed. This is certainly not the correct identification of the specimen given to me, which is undoubtedly a *Martiniopsis*. Waagen named two species of his genus, *Martiniopsis inflata* and *M. subpentagonalis*, based on a dozen specimens, without clearly defining the distinction between




Text-fig. 1.—Camera lucida drawings of serial sections of *Martiniopsis inflata* Waagen. The numbers in the upper left corner of each section refer to numbered cellulose peels in the Australian Museum, Sydney. The figures on the lower right of each section are distances in mm. from the top of the ventral valve.

them. A study of the measurements and proportions of the specimens available suggests that only one, variable, species is involved. It is my opinion that the specimen, K31.326, agrees with that identified by Waagen as *M. inflata*, which was chosen by Hall and Clarke (1894) as the genotype.

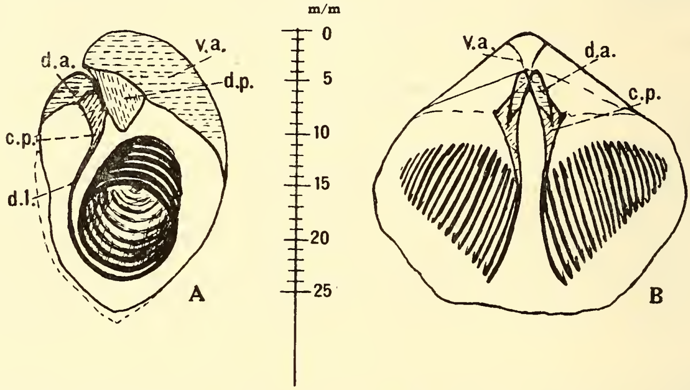
The specimen (K31.326) was photographed (Plate IX, figs. 1*a*-1*d*) and plaster casts were made before mounting it for serial sectioning. It was ground by hand on glass from the umbonal region to the anterior margin. The sections are parallel to one another, separated by distances that were carefully measured by spherometer, so that the position of any point can be fixed by three-dimensional co-ordinates. Consequently the appearance of any desired section may be plotted graphically. Cellulose peels were made at intervals of 0·3mm. (average), but closer at critical points; in all 76 sections in a depth of 24·20 mm. These have been mounted and photographed.

Although the surface of the dorsal valve and the anterior commissure of the specimen were somewhat weathered, the internal structures were perfectly preserved; camera lucida drawings of selected sections are reproduced in Text-fig. 1. The structures revealed by the sections have been plotted in scale drawings of two aspects: Text-fig. 2A, the median vertical view, and Text-fig. 2B, the dorsal view (with the dorsal shell removed).

The terminology used is in general that of Schuchert and Cooper (1932) and Cloud (1942) with the following exceptions :

*Dental plates*, subvertical plates in the ventral valve which bear the hinge teeth on their outer dorsal ends. They occur along the inner margin of the delthyrium, increasing in depth from the tip of the umbo, and converging towards the floor of the valve, although as in the case of all Permian spirifers I have examined, they do not reach the floor of the valve. Equivalent to the " receding dental plates " of Schuchert and Cooper (1932, p. 7) and Miloradovitch (1937) ; to the " carinæ delthyriales (delthyrial ridges) " of Fredericks (1927) ; and to the " dental lamellæ " (*pars*) of Muir Wood (1934) and others.

*Adminicula*, new term (sing. *adminiculum*), a pair of subvertical plates that may occur in the apical region of the ventral and sometimes also the dorsal valves, especially in very rostrate shells, extending from the inner tip of the umbo to the floor of the valve, and appearing to buttress the arch of the valve. The ventral adminicula do not reach the hinge-teeth or the margin of the delythrium,




Text-fig. 2.—Scale drawings based on serial sections of *Martiniopsis inflata* to show internal structures. (A) Median vertical view. (B) Dorsal view, with the dorsal valve removed.

v.a.—ventral adminiculum. d.a.—dorsal adminiculum.
d.p.—dental plate. c.p.—crural plate.
d.l. —descending lamella of spiralium.

but converge slightly and unite with the ventral margins of the dental plates along a suture-line from the tip of the umbo to the antero-ventral ends of the dental plates. They are not co-planar with the dental plates, but are equivalent to the " septa " of the *spondylium duplex* of the pentamerids.

In the spirifers the muscle-scars occur on the floor of the ventral valve between the adminicula, when these are present. The dental plates and the adminicula form a structure resembling the *spondylium discretum* of Schuchert and Cooper (1932, p. 10, Pl. 14, fig. 20). With the deposition of callus in the posterior portion of the delthyrial cavity, the site of muscular attachment moves anteriorly and the muscle track is overlain by callus or secondary shelly material producing a " pseudospondylium " (Schuchert and Cooper, 1932, p. 10).

The ventral adminicula are the " dental plates " of many authors, including Miloradovitsch (1937), the " lamellæ apicales (dental lamellæ) " (*pars*) of Fredericks (1927) and the " apical plates " of other authors.

The existing confusion in the nomenclature appears to have been due to the former lack of recognition of two distinct pairs of plates in the apical region of the ventral valves of certain spiriferidæ.

## Systematic Description.

### Genus **Martiniopsis** Waagen, 1883.

(Plate IX, figs. 1–4.)

Waagen, W., 1883.—Salt-Range Fossils. *Mem. Geol. Surv. India, Palæontologia Indica*, Ser. XIII, Vol. 1, Pt. 4, fasc. 2, p. 524, Plate 41, figs. 7, 8.

Etheridge, R., Junr., 1892.—In Jack and Etheridge: Geology and Palæontology of Queensland and New Guinea, p. 236. Govt. Printer, Brisbane, Qld.

Hall, J., and Clarke, J. M., 1894.—Genera of Palæozoic Brachiopoda. *Pal. of New York*, Vol. 8, Pt. 2, pp. 34, 40.

Genotype (by subsequent designation, Hall and Clarke, 1894): *Martiniopsis inflata* Waagen, 1883.

*Diagnosis.*—Small (usually less than 40 mm. in width) biconvex spiriferids, sub-globular. Width approximately equal to length, but greater than the thickness. Hinge-line short, ventral beak rostrate, tip of umbo incurved, almost touching that of the dorsal valve; cardinal extremities rounded. Shell smooth, no fold or sulcus: anterior commissure rectimarginate or faintly sinuate. Small interareas on both valves, not visible from outside. Shell impunctate.

Relatively large open delthyrium in the ventral valve, bounded internally by divergent dental plates bearing small insignificant teeth on their antero-dorsal edges. The dental plates unite ventrally with well-developed adminicula (see Introduction) to form a " spondylium discretum ". Muscle-scars not known. Shell generally is thin; some secondary thickening may occur in umbonal cavities, but not in the delthyrial cavity.

Notothyrium in dorsal valve is open. There is no cardinal " process "; a small striated cavity inside the beak received the diductors. Divergent hinge-plates bear small inner socket-ridges. Small convergent dorsal adminicula support the hinge-plates, which give rise to the crura, from which the descending lamellæ proceed anteriorly. Near the anterior commissure the lamellæ swing laterally and coil towards the ventral valve to commence the spiralia, which are directed postero-laterally. There are about twenty turns in each spire. No jugum or other jugal structure is developed. Pallial markings unknown.

*Discussion.*—Waagen states (1883, p. 524): " It was not possible for me to expose also the internal characters of the genus, partly on account of the hardness of the sandy limestone in which these fossils are preserved, and partly on account of the scarceness of the specimens." However, he was of the opinion that the shell was punctate; I have been unable to find true punctæ in the available specimens, and suggest that " the perforations arranged in quincunx ", noticed by Waagen in the Indian specimens and by Etheridge in some Queensland spirifers, are in fact fine surface ornamentation, not uncommon in certain spirifers.

*Martiniopsis* differs from all other spirifers except *Squamularia* and *Phricodothyris* by its complete lack of sulcus in the ventral valve and lack of fold in the dorsal valve, with corresponding rectimarginate anterior commissure. H. and G. Termier (1948, 1949) have shown that these characters among the brachiopods are closely related to and dependent on the system of respiration and circulation, and should therefore be of prime importance in the classification of the group.

*Squamularia* Gemmellaro, 1899, is based on an early Permian species from Italy (*Spirifer rotundata* Gemm.). The genus has been discussed in detail by Dunbar and Condra (1932); it is distignuished from *Martiniopsis* by its thicker shell, fine surface ornamentation and its complete lack of internal plates, " dental or septal lamellæ ".

*Phricodothyris* George, 1932 (genotype : *P. lucerna* George, 1932) is distinguished by its surface ornamentation of biramous, barbed spines and the usual absence of internal plates.

Waagen and Etheridge apparently placed greater emphasis on the smooth surface ornamentation of the shell, and made comparisons with *Martinia* McCoy, 1844. The genotype of *Martinia* has been regarded as " *Conchyliolithus Anomites* (*glaber*) Martin, 1809 " (see Plate IX, figs. 5*a* and 5*b*), but following the ruling of the International Commission on Zoological Nomenclature that Martin's species are invalid, Dr. H. Muir Wood (1951) has applied to the Commission for the designation of *Spirifer glaber* J. Sowerby, 1820, as the type-species of the genus *Martinia* McCoy, 1844. This form has a smooth surface ornamentation, but towards the anterior margin develops a marked fold and sulcus, producing a strongly sinuate anterior commissure. Internally it has no dental lamellæ or septa (adminicula).

*Reticularia* McCoy, 1844, may be regarded as a homœomorph of *Martinia* in which the internal plates (dental plates and adminicula) are well developed. Thus both of these genera are quite distinct from *Martiniopsis*.

With regard to the designation of the genotype of *Martiniopsis*, Schuchert and Le Vene (1929) quote Hall and Clarke (1894) as having selected the type. It may be pointed out, however, that previously Etheridge (1892, p. 238) had stated, after discussing the genus *Martiniopsis*, " *Types. Martiniopsis inflata* Waagen (Indian) ; . . . "

### **Martiniopsis inflata** Waagen, 1883.

(Plate IX, Figs. 1*a*-3*c*, Text-figs. 1-3.)

*Martiniopsis inflata* Waagen, 1883. *Mem. Geol. Surv. India, Pal. Indica*, Ser. XIII, Vol. 1, Pt. 4, fasc. 2, p. 524, Pl. 41, figs. 7, 8.

*Martiniopsis subpentagonalis* Waagen, 1883. *Ibid.*, p. 527, Pl. 42, figs. 9-10.

*Holotype.*—Specimen figured by Waagen, 1883, Pl. XLI, figs. 8*a*-8*d*, from the Upper Productus Limestone, Chidru, Salt Range, India.

TABLE 1.

Measurements of Specimens of *Martiniopsis inflata* from Salt Range, India. All lengths are in millimetres.

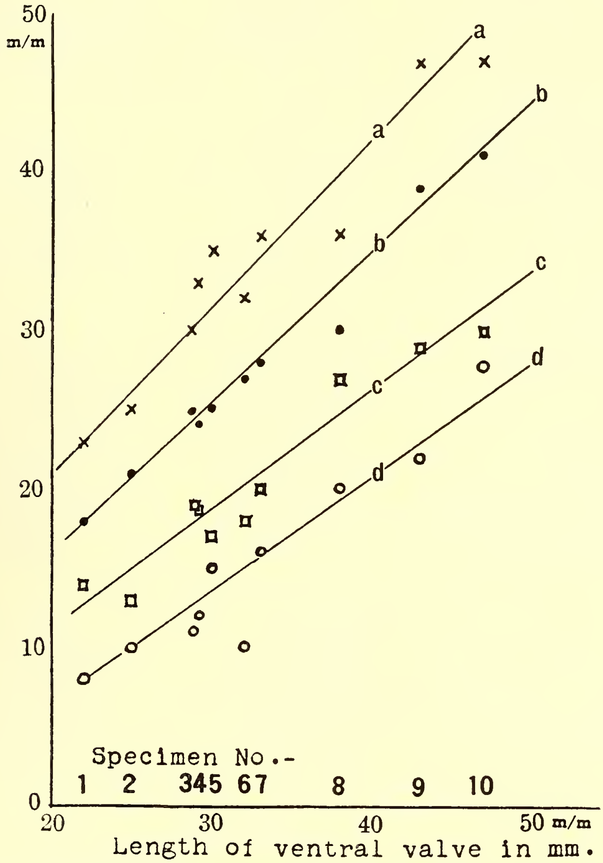
| Specimen Number. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Length of ventral valve .. .. | 22 | 25 | 29 | 29 | 30 | 32 | 33 | 38 | 43 | 47 |
| Width of valves .. | 23 | 25 | 30 | 33 | 35 | 32 | 36 | 36 | 47 | 47 |
| Length of dorsal valve | 18 | 21 | 25 | 24 | 25 | 27 | 28 | 30 | 39 | 41 |
| Thickness of shell | 14 | 13 | 19 | 19 | 17 | 18 | 20 | 27 | 29 | 30 |
| Length of hinge-line | 8 | 10 | 11 | 12 | 15 | 10 | 16 | 20 | 22 | 28 |
| Apical angle of ventral valve .. .. | 103° | 105° | 105° | 110° | 100° | c.82° | 103° | 110° | 112° | 105° |
| Apical angle of dorsal valve .. .. | 130° | 125° | 126° | 130° | 137° | 128° | 130° | 120° | 128° | 122° |

1. Aust. Mus. specimen F39605 ; (G.S. India, K29/242), Loc. Amb.
2. Peabody Museum, Yale, specimen S2948 ; Loc. Amb, 21.
3. Aust. Mus. specimen F39604 ; (G.S. India, K31/126) ; Loc. Buri Khel.
4. Aust. Mus. specimen F44674 ; (G.S. India, K31/326), Loc. Amb.
5. Waagen's measured specimen (p. 528, col. II), Loc. Amb.
6. Waagen's measured specimen (p. 528, col. I), Loc. Amb.
7. Aust. Mus. specimen F39602 ; (G.S. India, K30/805), Loc. Trimu Wàhan).
8. British Mus. (N.H.) specimen 18596 ; Loc. Amb.
9. Waagen's measured specimen (p. 526, col. II) ; Loc. Chidru.
10. Waagen's measured specimen (p. 526, col. I) ; Loc. Chidru.

Numbers 1, 9 and 10 are those previously identified as *M. inflata* and the others as *M. subpentagonalis*.

Characters of the shell as for the genus. Waagen's separation of the few specimens available to him into two species appears to be unnecessary now that additional specimens show regular gradation amounting only to variation of a single species, and I therefore place his second species, *M. subpentagonalis*, in synonymy.

The table above shows the principal dimensions of ten specimens (including the four measured by Waagen) from the Salt Range, India. They are arranged




Text-fig. 3.—Graphical representation of the variation in the measurements of specimens 1 to 10 of *Martiniopsis inflata* listed in accompanying table. The horizontal axis represents the length (in mm.) of the ventral valves, against which are plotted vertically

*aa.* Width of valves (×).
*bb.* Length of dorsal valve (●).
*cc.* Thickness of shell (□).
*dd.* Length of hinge-line (○).

in order of increasing size (length of the ventral valve) and the measurements are shown graphically in Text-fig. 3. In view of the smallness of the specimens and the difficulty of making accurate measurements of weathered specimens there is remarkable approximation to a linear arrangement of corresponding points for specimens of varying size, which surely indicates identity of species.

The umbonal angles are fairly constant, averaging 108 degrees (with one abnormality) for the ventral valve, and 128 degrees for the dorsal valve. This is probably a specific character.

In this species the width of the shell is typically greater than the length. The convexity of the valves is illustrated in Plate IX, figs. 1-3, and is seen to be less marked than in *M. uralica* Tschern. shown in Plate IX, fig. 4. The hinge-line is about half the width of the shell, and the interareas are small. There is no trace of fold or sulcus and the anterior commissure is rectimarginate in the young and mature shells, but there is a tendency for it to become slightly sinuous in the larger, older shells. No covering plates have been observed either on the delthyrium or the notothyrium.

The internal characters have been studied by means of serial sections of specimen 7 in the accompanying table, as described earlier in this paper. Some of the sections are illustrated in Text-fig. 1, and the internal structures are indicated in Text-fig. 2. In the ventral valve well-developed dental plates extend from the margins of the open delthyrium ventrally to meet the large adminicula, which extend half-way down the valve. The junctions of the latter with the ventral valve are visible through the translucent shell and have been called previously the " dental plates ".

In the dorsal valve there is a short low euseptum, probably not of taxonomic significance, and small adminicula support the hinge-plates and crura. The descending lamellæ curve smoothly towards the anterior, without any jugal processes and support the spiralia. These are directed postero-laterally and have 19 turns in the spire. The ribbon is 1·2 mm. in width and 0·04 mm. in thickness ; the length of the spire is about 13 mm. and its diameter about 9 mm.

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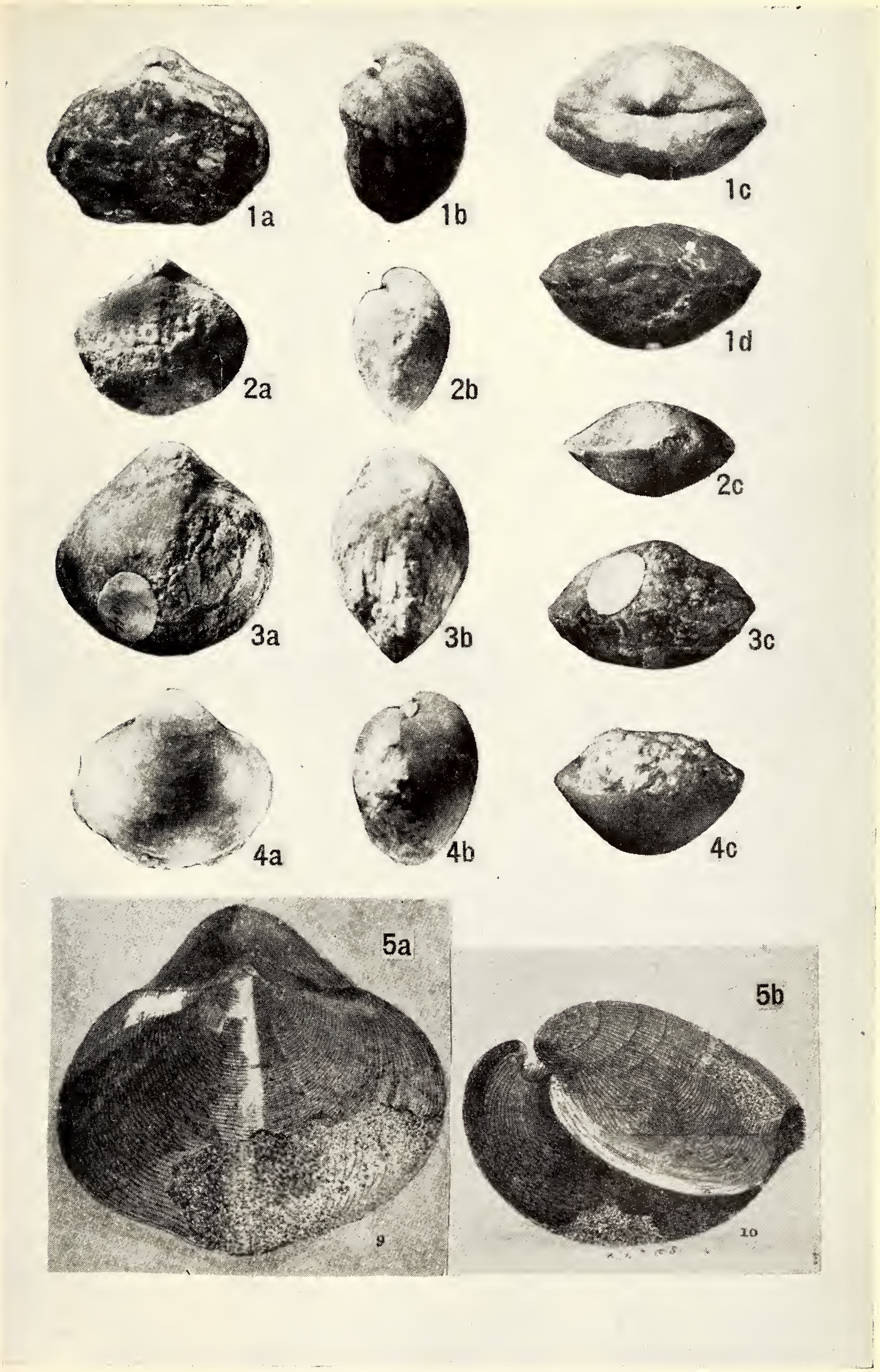
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1b
1c
1d
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2b
2c
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## Explanation of Plate IX.

(All figures are natural size.)

Figs. 1*a*–1*d*.—*Martiniopsis inflata* Waagen. Specimen from which serial sections were made, presented to the author by the Geol. Surv. India, 1938. *Horizon :* Lower Productus Limestone (Permian). *Locality :* Right bank of Baral Nala, S.W. of Amb, Salt Range. India. (Sheet 38P/15.) Geol. Surv. India (K31.326). Plaster cast of this is in Australian Museum (F44674).

1*a*, dorsal view ; 1*b*, side view ; 1*c*, posterior view with ventral valve above ; 1*d*, anterior view with ventral valve below.

Figs. 2*a*–2*c*.—*Martiniopsis inflata* Waagen. ? Young specimen. *Horizon :* Lower Productus Limestone. *Locality :* Just N.W. of Amb, Salt Range, Punjab. Geol. Surv. India, Reg. No. (K29/242). Presented to Australian Museum (F39605).

2*a*, dorsal view ; 2*b*, side view ; 2*c*, anterior view showing rectimarginate anterior commissure.

Figs. 3*a*–3*c*.—*Martiniopsis inflata* Waagen. *Horizon :* Lower Productus beds. *Locality :* About 3½ miles W.N.W. of Buri Khel, Salt Range, Punjab. Geol. Surv. Ind. Reg. No. (K31/126). Presented to Australian Museum (F39604).

3*a*, dorsal view ; 3*b*, side view ; 3*c*, anterior view.

Figs. 4*a*–4*c*.—*Martiniopsis uralica* Tschernyschew. Coll. Dr. G. Marshall Kay. *Horizon : Pseudoschwagerina princeps* Zone, Sakmarian. *Locality :* Trataushikan, Bashkiria, Urals, U.S.S.R. Australian Museum (F45581).

4*a*, ventral view ; 4*b*, side view ; 4*c*, anterior view of ventral valve showing rectimarginate anterior commissure.

Figs. 5*a*–5*b*.—Reproduction of illustration of " *Conchyliolithus Anomites* (*glaber*) Martin, 1809 ", in " Petrificata Derbiensis ", Plate 48, figs. 9 and 10, usually regarded as the type of *Martinia* McCoy, 1844. (See also H. M. Muir Wood, *Annals and Mag. Nat. Hist.*, Ser. 12, Vol. iv, p. 109, Feb., 1951.)

# CONTRIBUTIONS TO A STUDY OF THE MARULAN BATHOLITH.

## Part II. The Granodiorite–Quartz Porphyrite Hybrids.

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With Plates X, XI and one Text-figure.

*Manuscript received, November 18, 1952. Read, December 3, 1952.*

### Introduction.

In Part I of this series of papers (Osborne 1949) it was explained that a number of specialized petrological investigations upon various components of the batholith (particularly regarding hybridism, igneous metasomatism and related phenomena) would be necessary before the magmatic and tectonic history of the complex could be elucidated and recorded. The present paper is the result of intermittent research by the first author over several years, and of recent study by the second, upon the hybrid-zone.

*General Geological Setting.*

The zone of hybrid-rocks (see Text-fig.) stretches from the township of Marulan in a general south-south-east direction to the neighbourhood of South Marulan, and outcrops over an area about four and a half miles long by one mile wide.

The surface of the country in the Marulan-Glenrock district is part of the Southern Tableland of N.S.W., here of gently undulating character, approximately 2,000–2,100 feet above sea-level, and topped by some residual ridges rising to a height of 2,300 feet. The latter are composed of Lower Palæozoic metasediments, mostly quartzites and cherty claystones.

In the region under discussion there is a noticeable ridge surmounted by two low hills, on one of which stands Barber Trig. Station, 2,232 feet above sea-level. The hybrid-zone outcrops almost entirely around the periphery of this ridge, and the topographical details indicate the probability of the under-surface of the Barber Hills chert, slate and quartzite mass being approximately horizontal—an idea suggested long ago by W. G. Woolnough (1909).

Contiguous to the hybrid-zone to the west is the Marulan quartz porphyrite, outcropping in an elongated area running north and south. Further westward this is succeeded by the Marulan " granite " and the Longreach porphyry, which also trend in more or less meridional belts. The relationships of these members of the batholith are complex and not yet unravelled, but it is clear that the Marulan " granite " is not the product of direct magmatic crystallization. Contiguous to the hybrid-zone on the east is the Glenrock granodiorite, exposed on Glenrock Station and neighbouring pastoral properties.

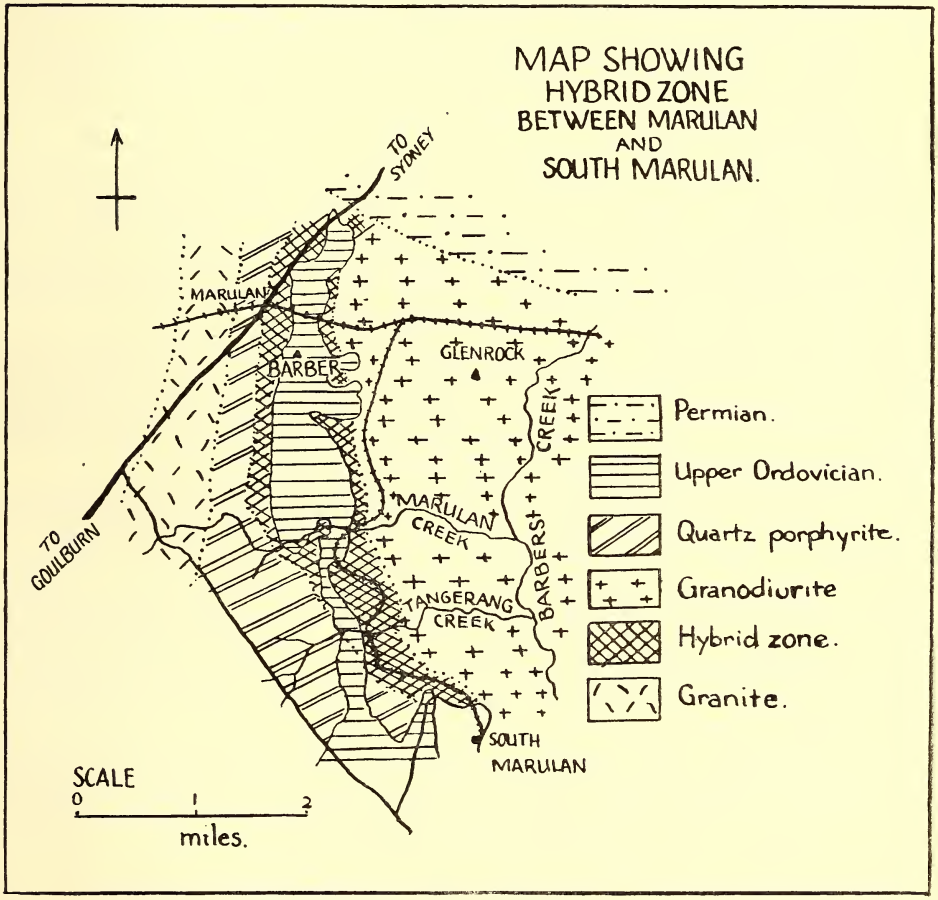
## Field Occurrence of the Hybrids.

With the data available from the abundant outcrops in the paddocks and the excellent exposures in portions of Marulan and Tangerang Creeks, it is possible to delineate three sub-zones of the hybrid-belt. These are respectively:

(*a*) Sub-zone I, westernmost, passing into the quartz porphyrite,

(*b*) Sub-zone II, occupying a median position, and

(*c*) Sub-zone III, easternmost, passing very gradually into the granodiorite.




Field, petrographic and chemical data establish the hybrid character of all the rocks in the region intermediate between the granodiorite and quartz porphyrite. As will be shown below, some rather unusual features are displayed by some of the hybrids, such as partial or selective recrystallization; such conditions have tended to make difficult the determination of the sequence of intrusions responsible for the mixed rocks, but it is our view that the quartz porphyrite was the earlier, and the granodiorite the later intrusion.

The following criteria have been used to establish this relationship:

(*a*) There is quite a number of xenoliths of fine-grained partially recrystallized porphyrite in the granodiorite in the north-western part of the zone.

(*b*) Veins of tourmaline-bearing aplite, practically identical with syngenetic veins in the Glenrock granodiorite, have occasionally been seen cutting both the porphyrite and the westernmost Sub-zone I.

(*c*) All the tourmalinization in the Lower Palæozoic metasediments of the region, especially near where the Southern Portland Cement Company's railway crosses Marulan Creek, is due to the granodiorite, and none is associated genetically with the porphyrite, where the latter is seen to invade sediments.

(*d*) Epidotization has been noted in some of the eastern marginal portions of the porphyrite and in some of the hybrids. The occurrence of epidote is a distinctive feature of the Glenrock granodiorite, being related to deuteric phenomena, but is not characteristic of the quartz porphyrite. It would be feasible to say that these facts support the view that the epidote was introduced from the granodiorite, which was thus later than the porphyrite.

*Hybrids of Sub-zone I.* The rocks constituting this zone are dark and very fine-grained with few phenocrysts of quartz and pale-green plagioclase. Iron pyrites, in small amounts, is widely disseminated. The texture of the rocks varies and occasionally there are abrupt and patchy relationships between types of varying grainsize and phenocrystic abundance. Towards associated phases (either on the west or the east) there is a gradation.

*Hybrids of Sub-zone II.* This is the main sector of the hybrids, and embraces an area with abundant outcrops, where variety of texture and composition can be seen macroscopically. The rocks are all dark in colour, good examples being available for study near the Marulan Rectory, in the cuttings of the S.P.C. Railway, and to the north and south of Tangerang Creek.

It is clear that at South Marulan both normal hybridism and later silicification and veining with felspathic material have operated in the production of these rocks.

The chief varieties to be observed throughout the Sub-zone comprise (*a*) almost lithoidal phases, which are seen under the microscope to be practically biotite-free, and (*b*) finely crystalline rocks, with " schlieren-like " patches, containing much biotite in nests and clots. There are local patches of highly felspathic material (see petrography) and some " drusy " structure in the light-coloured veins.

*Hybrid Sub-zone III.* These rocks are best studied near Marulan Railway Station and to the north-east thereof. They are also found fairly constantly as a belt about 400 yards wide adjacent to the granodiorite. They are phanerocrystalline, medium grained and fairly uniform in texture.

These hybrids resemble the granodiorite when partially weathered. The freshest rocks are of a pinkish-grey colour and display macroscopically the following: plagioclase (slightly epidotized), hornblende, biotite both in flakes and small clots, orthoclase, quartz and occasional scattered pyrites. By increase in grainsize and decrease in the amount of biotite and quartz the rocks pass into the normal granodiorite.

*Gradations and Widths of the Hybrid Sub-zones.* Fortunately there are sufficient exposures to establish the gradational relationships between all three hybrid groups, and respectively with the porphyrite and granodiorite, which were the compositional poles involved in the hybridization processes. From west to east the relations are such that one can confidently assume that Barber Trig. Ridge conceals hybrids mainly of the median zone and to some extent of sub-group III.

The maximum width of hybrid-rock development is about 2,000 yards, to be observed at the latitude of a point half a mile north of Marulan Creek. In general it may be stated that the average widths of the three zones (from which averages there are no great departures by extreme measurements) are: Sub-zone I, 150 yards; Sub-zone II, 600 yards; Sub-zone III, 550 yards.

## Petrography.

*The Granodiorite* (Plate X, fig. 2). This rock is the western phase of the Glenrock mass which has received some attention in earlier papers (Woolnough, 1907; Osborne, 1931, 1949). The Glenrock type of granodiorite is of more than passing petrological interest and the authors are now preparing a paper (Part IV of the present series) in which the petrology of this unit in the batholith will be discussed.

Along the easternmost margin of the hybrids it is difficult to collect granodiorite which is free from some sign of infiltration of quartz, and of other processes related to the hybridism. However, by collecting from about 50 yards away from the last definite hybrid of sub-zone III, one obtains material typical of the granodioritic parent.

The rock is speckled, slightly pinkish in colour and of medium, even grain. Minerals visible are plagioclase (generally palest green, occasionally white), amphibole, biotite, quartz and pyrites. Under the microscope it is seen that some orthoclase (occasionally slightly perthitic), augite and very rarely hypersthene, sphene, apatite, zircon and iron oxide complete the list of primary mineral constituents. The secondary minerals are saussuritic masses, clinozoisite, epidote, prehnite, lawsonite (?), rarely scapolite, chlorite, leucoxene, hæmatite and limonite, and in some cases much kaolin.

The fabric is frequently sub-monzonitic, achieved by the late crystallization of quartz, and sometimes orthoclase, about the idiomorphic plagioclase.

The soda-lime felspar is zoned ($An_{45}$ to $An_{24}$), the most acid zone of this being sheathed by very clear additions of oligoclase, with irregular periphery but sharp interior boundaries against the main crystal. It would appear that the addition of oligoclase was distinctly much later than the progressive growth of the other zones.

Alteration to an irresolvable saussuritic material, and also to chlorite, calcite, kaolin and to much epidote of deuteric origin is characteristic. The rare plates of scapolite occur in cracks through the plagioclase. The potash felspar is poorly cleaved and clouded by weathering. In places it is finely perthitic. Biotite ($\beta=1\cdot639$) is brown and possesses characteristic intracleavage masses of brightly birefringent material, which has caused slight bulging of the host-mica, due to volume increase.

The nature of these intracleavage masses suggests that they are additions along the planes of easy access, and are related to deuteric reactions. The minerals occupying this rôle, and not to be confused with chloritic and muscovitic derivatives from biotite, are clinozoisite, prehnite and lawsonite (?). Another form of alteration is to confused masses of granular sphene plus leucoxene, indicating a not inconsiderable proportion of $TiO_2$ in the mica.

The amphibole comprises light greyish-green hornblende with twinning, and extinction $Z\hat{}c=15°$. There is an approach to idiomorphism, and chloritic decomposition is typical. This mineral is seen sometimes to be developing from pyroxene in the manner of the Reaction Principle. The other amphibole is a very pale grey-green fibrous uralite, which may be the result of hydrothermal influence. The pale variety is close to tremolite in some optical properties, such as R.I.$=1\cdot616$, and $Z\hat{}c=18°$, positive elongation.

The pyroxene is the least constant of the constituents. There are frequent cores of the augitic variety with twinning and poor cleavage, surrounded by hornblende. Occasionally an idiomorphic crystal indicates the primary character of the augite, and its antecedence to the hornblende in the order of crystallization. The possible petrogenetic significance of the pyroxene in the Glenrock granodiorite will be dealt with in a later paper. Hypersthene, partly altered to bastitic material, is not common in the western margin of the granodiorite, and therefore will not be considered in the present study. An analysis of the typical western phase of the Glenrock Granodiorite (just slightly more basic than the rock from much of the pluton) is given below and will be considered in the chemical discussion.

*Quartz Porphyrite* (Plate X, fig. 1).—From Marulan, both north and south, the distinctive Marulan quartz porphyrite may be seen. It is best exposed in Marulan Creek and in the neighbourhood of the old Limekilns west of South Marulan village.

The age and magmatic affinities of this mass in the complicated evolution of the Marulan batholith are not yet known, but we can treat the present discussion objectively and consider the rock as one of the parent types in the hybridism.

There is a fair variety of appearance in hand-specimen, but the average body-colour of the fresh rock is dark-greenish black to greenish grey, the groundmass betraying some recrystallization, and showing phenocrysts of pale green plagioclase, pyroxene and quartz. Some of the rocks are relatively rich in pyrites and there are fine-grained, almost aphanitic varieties, especially at the eastern margin of the mass and against the Lower Palæozoic hornfelses, *e.g.*, near Tangerang Creek.

Microscopically we note phenocrysts of plagioclase (average diameter 2 mm.), $An_{55}$ to $An_{30}$, measured from centre to penultimate zone. The outermost layer is pure albite and represents later sheathing. Alteration is to turbid masses in which chlorite and epidote can be determined. Quartz phenocrysts with maximum diameters of about 3 mm. show embayment of periphery. Orthoclase is sparingly present, but some $K_2O$ must be in the groundmass as indicated by the analysis. The femic minerals are unsatisfactory to deal with. Pale green hornblende with X=greenish grey, Y=leek green, and Z=green, $Y > Z > X$, and $Z \wedge c = 20°$ may occur in aggregates of ill-defined units with a good deal of blotching and development of chlorite. The patchy and inhomogeneous character of the hornblende suggest that it may have suffered some thermal change, but it is not clear whether or not the aggregates have become stable in the magma of the porphyrite groundmass. In places, brownish biotite in flakes and prismatic units appear to be intimately associated with and perhaps to have been derived partly from the hornblende.

The groundmass has corroded the phenocrysts indicating a former liquid condition. It consists of cryptocrystalline material comprising silica and other irresolvable matter. It has in some rocks been partially recrystallized, and this will be discussed below.

An analysis of the quartz-porphyrite is given in Table I.

*Hybrids of Sub-zone I* (Plate X, fig. 3; Plate XI, fig. 3). Many of the rocks are very similar to the porphyrite except that there are fewer phenocrysts and the groundmass shows a greater amount of recrystallization, so that hitherto cryptocrystalline material is now converted to a finely textured quartzose mass with hornfels structure. The rest of the rock is not so altered, but the phenocrystic minerals show some signs of changes having been wrought by fluids derived from the granodiorite after its first main stage of crystallization had finished, and hydrothermal or possibly pneumatolytic conditions obtained.

The soda-lime felspar has been strongly altered with considerable epidotization. Hornblende and pyroxene have been chloritized and thin borders of chlorite have been deposited around the peripheries of quartz and rarely of orthoclase grains. Biotite is scarce and always comes from interaction between hornblende and liquid from the second intrusion.

TABLE I.

| | (1) | (2) | (3) | (4) |
|---|---|---|---|---|
| $SiO_2$ .. .. | 73·54 | 63·95 | 63·86 | 57·66 |
| $Al_2O_3$ .. .. | 10·95 | 15·24 | 15·84 | 17·36 |
| $Fe_2O_3$ .. .. | 1·08 | 1·03 | 0·49 | 0·94 |
| FeO .. .. | 4·39 | 4·87 | 5·31 | 6·54 |
| MgO .. .. | 0·08 | 2·53 | 2·42 | 4·07 |
| CaO .. .. | 1·68 | 5·32 | 5·53 | 7·28 |
| $Na_2O$ .. .. | 2·79 | 2·40 | 1·96 | 1·56 |
| $K_2O$ .. .. | 4·80 | 2·17 | 2·13 | 1·38 |
| $H_2O+$ .. .. | 0·21 | 1·53 | 1·37 | 2·24 |
| $H_2O-$ .. .. | 0·08 | 0·12 | 0·33 | 0·20 |
| $TiO_2$ .. .. | 0·60 | 0·52 | 0·66 | 0·55 |
| MnO .. .. | tr. | 0·09 | 0·04 | 0·04 |
| $P_2O_5$ .. .. | — | 0·09 | 0·08 | 0·14 |
| $CO_2$ .. .. | — | tr. | abs. | abs. |
| | 100·20 | 99·86 | 100·02 | 99·96 |
| Sp. Gr. .. .. | — | 2·771 | 2·773 | 2·82 |

*Norms.*

| | (1) | (2) | (3) | (4) |
|---|---|---|---|---|
| Quartz .. .. | 33·60 | 23·04 | 25·74 | 17·28 |
| Orthoclase .. | 28·36 | 12·79 | 12·23 | 8·34 |
| Albite .. .. | 23·58 | 20·44 | 16·24 | 13·10 |
| Anorthite.. .. | 3·34 | 24·19 | 26·97 | 35·31 |
| Corundum .. | — | — | 0·51 | 0·41 |
| Diopside .. | 4·43 | 1·17 | — | — |
| Hypersthene .. | 3·93 | 14·68 | 14·22 | 20·36 |
| Magnetite .. | 1·62 | 1·39 | 0·70 | 1·39 |
| Ilmenite .. .. | 1·22 | 0·91 | 1·22 | 1·06 |
| Apatite .. .. | — | 0·34 | 0·34 | 0·40 |

(1) Quartz porphyrite, South Marulan. Anal. L. A. Cotton.

(2) Hybrid, Sub-zone I, South Marulan. Anal. W. H. Herdsman.

(3) Hybrid, Sub-zone II, near Tangerang Creek. Anal. W. H. Herdsman.

(4) Granodiorite, South Marulan. Anal. W. H. Herdsman.

In one specimen near the head of Marulan Creek a thin vein of amphibole (more or less uralitic) one half-millimetre in width was found cutting the porphyrite. This had resulted from the segregation of hornblendic molecules during the hybridization, and later deposition of the same in cracks, which developed on shrinkage of the porphyrite, following the increase of volume on the first impact of the granodiorite magma.

*Hybrids of Sub-zone II* (Plate X, fig. 4 ; Plate XI, fig. 1). This is the most important of the series. Microscopically one sees that there is considerable variation in grainsize and in the proportions of the various minerals, but no great differences in general mineralogical constitution. Average grainsize varies from 0·1 mm. to 0·35 mm. In the commonest types the minerals are present in approximately the following proportions: quartz 28%, plagioclase 30%, orthoclase 20%, hornblende 10%, biotite 10%, augite and accessories 2%. In certain types, poor in biotite, there is an increase in hornblende, but the other constituents remain in about the same proportions.

Quartz forms a kind of groundmass through which most of the other constituents are set, giving a sub-monzonitic fabric. In other cases there are sectors of crude-graphic, or coarse-aplitic crystallization of orthoclase and quartz. The plagioclase crystals have many features in common with the phenocrysts of the porphyrite, but there are distinct additional layers of oligoclase attached to the altered, zoned units.

Orthoclase is non-perthitic, and the quartz is invariably recrystallized, so that some large grains show a division into various sectors with sutured or crenulated boundaries. The biotite is often ragged and wisp-like. Its pleochroism is X=brass-coloured, Y=vandyke-brown, Z=dark brown, with Z>Y>X. $\beta$=1·638.

A study of the several phases of biotite-development in these rocks indicates that the evolution has been

hornblende→reddish-brown biotite→brass-coloured biotite,

with evidence of $TiO_2$ being more prominent in the lighter-coloured and less ferriferous varieties.

The hornblende occurs in clots which have aggregate-structure (Plate XI, fig. 2). This is dependent upon sectors or groups of crystals being orientated in preferred directions. Some of the hornblende is uralitic and some is ferriferous. Varying double refraction and lack of uniformity in maximum extinction-angles indicate the lack of equilibrium at the time of final congealing. As hybridism has proceeded the passage of hornblende to biotite has increased, and in some places complete change to mica has been achieved by interaction between hornblende and the liquids available. Harker (1939) has recorded and figured clots of biotite-crystals and flakes possessing the same structure as those shown in Plate XI, fig. 1. He ascribes them to action of porphyry liquid on granite xenolith at Dundalk, Ireland. There has been removal of iron in the production of light-coloured biotite. Intracleavage deposition of epidote and prehnite in the mica indicates that deuteric conditions had developed.

Some of the biotite clots have been penetrated by salic liquid which has crystallized as quartz and albite.

Thus the general heterogeneity, the occurrence of clots in various stages of evolution, and the failure of the pyroxene to pass to lower members of the reaction-series all suggest that the onset of cooling prevented this group of hybrids from reaching finality of development.

*Recrystallization.* Partial recrystallization is common in rocks of Sub-zones I and II. As a result, the siliceous mesostasis of the less altered porphyrites and the dominant quartzose ground of many of the hybrids show a hornfelsic texture. A less common and somewhat puzzling type of recrystallization is seen in the case of certain dark inclusions scattered through some of the Sub-zone II hybrids, both near Marulan East and a little to the north of South Marulan. These patches appear to be remnants of primary granodioritic crystallization. Their petrographic features indicate that when recrystallization of the quartzose portions of the porphyrites and hybrids was effected, local greater elevation of temperature led to the formation of hypersthene. Thus we find the following constituents—plagioclase (a little more acid than in the granodiorite), orthoclase, augite and hypersthene, with a little biotite. The fabric is sub-ophitic to hornfelsic, in which irregular sutured borders mark the hypersthene, and the biotite has sieve-structure.

The biotite has resulted from reaction between pyroxene and the liquid in which these xenoliths were immersed, with or without the intermediate formation of amphibole. Deuteric action has produced clinozoisite, chlorite and calcite from the felspars.

*Hybrids of Sub-zone III.* The rocks in this subzone present greater homogeneity over large areas than anywhere else in the main zone. Texturally they resemble the granodiorite and the main minerals of that type are present, but in addition there has been a distinct accession of quartz, which has ramified through earlier-formed minerals. This late quartz has been recrystallized only in small degree, and not so strongly as in the hybrids of zone II, but the effects of its renewal and penetration have led to cracking of the pyrogenetic quartz, due to volume change under the thermal increase involved.

There is a notable increase in the amount of biotite at the expense of amphibole, and in some places near Marulan Station deposition of considerable sodic plagioclase has occurred, mantling the pyrogenetic individuals of the soda-lime felspar.

No pyroxene is seen in this zone and it is possible that any which existed has been made over into hornblende and/or biotite.

## Chemical Discussion.

In Table I, page 113, are listed analyses of the porphyrite, of two hybrids (Sub-zones II and III), and of the normal granodiorite from the south-west portion of Glenrock Estate. Analysis No. 1 is an old one (recorded by Woolnough, 1909) and represents one of the phases of the quartz-porphyrites met with both to the south-west of South Marulan and on the Limekilns Road about four miles from Marulan. This type always shows some recrystallization and effects of infiltration of silica and alkalic liquid. This rock becomes a source of abundant biotite when hybridized.

As to chemical comparison of the rocks in the table, it is very difficult to adopt any satisfactory basis for quantitative discussion. Number 3 is an advanced hybrid, but it is not clear from the microscopic evidence whether it has received much or little from the invaded rock by chemical reaction. Then again, the quartzo-felspathic mesostasis may reflect some hydrothermal activity which succeeded the main hybridism.

Concerning the relations of No. 2 and No. 3, it must be remembered that the rocks as we see them now are the products of early crystallization of pyrogenetic minerals, which later were affected mechanically by salic infiltration, and to only a small extent by chemical action. Altogether it is felt that a direct comparison of the analyses, even conducted with due attention to the relative densities of the rocks, would not be valid or trustworthy in the present study, because the hybridism was not carried to completion of equilibrium. Nevertheless we can note certain chemical relationships shown by the analytical data and gain some help in this discussion by study of the norms.

The true hybrid is distinctly more acid than the unaltered granodiorite, due to the presence of the acid mesostasis. It is somewhat higher in alkalis, particularly potash, this being reflected in the abundance of biotite. The proportions of CaO and MgO are related to the amount of mechanical incorporation of material crystallized from the granodiorite magma. The larger plagioclase crystals and hornblende-biotite aggregates have come from this source.

Examining the hybrids we note further the intermediate position of rocks with biotite-clots, because No. 1 has practically no MgO and low CaO, while No. 4 has considerable quantities of both, and the hybrid shows amounts for each lying between these extremes. The comparative values for the alkalis again indicate the intermediate position of the hybrids. It is to be stressed that the variations stated in this discussion would not be eliminated if one made allowances for possible inequality of the volumes of rocks, based on relative densities. In other words, the microscopic, field and chemical evidence all indicate that the hybridism was attended by concentration of MgO and CaO in the mixed rocks.

An interesting feature displayed by the chemical data is the close approach to chemical equivalence of rocks No. 2 and No. 3. This bears out the idea that some of the quartz porphyrite, which has been taken in the field to be unhybridized, is on petrological grounds suspect, on account of the origin of the phenocrysts. It appears possible that some of the eastern marginal porphyritic rock may be a hybrid more advanced than much of the reaction-zone, having reached a state of equilibrium. The quartz, orthoclase, biotite and large derived phenocrysts of plagioclase would then be regarded as having reached stability in the magma, the last-mentioned having become armoured by the deposition of thin external zones of albite.

## The Course of the Hybridization.

After the consolidation of the quartz porphyrite (probably as a sill-like pluton amongst the Lower Palæozoic metasediments) the rocks occupying the present Marulan-Glenrock-Ballanya region were invaded by a mass of granodiorite magma. There is no suggestion of granitization around this mass and the prevalence of xenoliths at the margins and about the roof of the intrusion, as well as the petrographic character and textural uniformity, support the view taken here that the Glenrock granodiorite was emplaced in a liquid condition, thus being the result of magmatism and not metasomatism.

This intrusion was chilled quickly against the sedimentary roof and wall-rocks on the north, east and south-east, but against the western wall of quartz porphyrite hybrid reactions took place. Possibly this was due to the fact that the porphyrite was not wholly cool at the time of the invasion of granodiorite, and also because more strongly endothermic reactions would be involved between granodiorite magma and the metasediments than between porphyrite and granodiorite. Further, it seems probable that the present western sector of the district was underlain by an igneous complex, partly solid, partly liquid, and possessed of sufficient heat to bring about a regional rise of the isogeotherms. Thus the western invasion-margin of the granodiorite was kept at an elevated temperature, whereas on the eastern side of the pluton the fall of temperature was relatively rapid.

Hybrids were developed by the interaction of magma and solid porphyrite. Three distinct zones developed, as described above. There is evidence of little more than a limited chemical change, but of considerable mechanical change.

We may trace the hybrid-evolution as follows :

(1) After limited thermal alteration of the quartz porphyrite by the granodiorite magma, its primary crystallization-period set in, during which hybrid relations began to develop. The magma crystallized in pyrogenetic plagioclase, amphibole, biotite, orthoclase, quartz and limited pyroxene. Contemporaneously, material of porphyrite groundmass and smaller phenocrysts was mobilized and resulting salic liquid set free.

(2) Before the orthomagmatic period had ended, some of the salic (potassic) liquid which was available near the porphyrite reacted as follows—

(*a*) chemically with the phenocrysts of the quartz porphyrite,

(*b*) chemically and mechanically with the partially crystallized network of the granodiorite.

As a result of (*a*) reddish-brown ferriferous biotite developed from hornblende and chlorite from pyroxene. As a result of (*b*) various phases of hybrid-margins to the granodiorite developed. These were produced by the salic liquid disintegrating the pyrogenetic components, and setting into operation the reaction series,

pyroxene–amphibole–biotite.

(3) The migration of soda (or albite-oligoclase molecules) from the granodiorite led to deposition of fringes or sheaths of sodic felspar in the hybrids. Sphene dissociated and the CaO and $SiO_2$ remained, while the $TiO_2$ moved towards the hybrid to be fixed in biotite.

(4) Potash from the groundmass and from some phenocrystic material in the porphyrite was fixed in (i) abundant biotite (light coloured) and in (ii) considerable orthoclase of the hybrids. The light biotite was stable in the magmatic environment. The following reaction sequence seems to be a characteristic feature of the hybridism, viz.—

hornblende→reddish biotite→titaniferous biotite.

(5) Continual partial fluidity in the hybrids (with concentration of apatite molecules) was effected by strong deuteric or hydrothermal activity in the granodioritic magma. When the orthomagmatic stages were completed, vigorous solutions wrought notable changes producing saussuritic masses, epidote, sericite, etc., through the granodiorite, the hybrids and the easternmost porphyrite. The effect of these solutions was to intensify the final aqueous activity which permitted the evolution of the micas from the hornblende and the latter (in small measure) from the pyroxene.

(6) Finally, thermal changes caused recrystallization of various components in the batholith (see above).

The cause of the later thermal change is a matter for further investigation. The authors think that the intrusion of the granite and porphyry to the west of the quartz-porphyrite was responsible for a general engulfing of the pre-existing components of the batholith and its hybrids. This problem will be taken up in a later contribution.

It remains to be stated that no comparative studies of other hybrid occurrences are considered here, as we feel that such would be appropriate when more is known of the history of the batholith.

## Acknowledgements.

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## Explanation of Plates.

### Plate X.

Fig. 1.—Quartz porphyrite from one mile S.E. of Marulan. This is adjacent to Hybrid Sub-zone I and is typical of the least modified parent rock. Corroded quartz, orthoclase (near centre), plagioclase (in N.E. corner), and chloritized hornblende (dark patches). The groundmass is cryptocrystalline. Ordinary light. ×17½.

Fig. 2.—Granodiorite from a little to the north of Marulan Creek at private railway crossing. Large altered plagioclase (in S.W.), orthoclase, cleaved hornblende (towards bottom of picture), dark biotite with intra-cleavage clinozoisite, late crystallizing quartz. Ordinary light. ×17½.

Fig. 3.—Hybrid from Sub-zone I. Rock is partially changed by development of large hornblende phenocrysts. Plagioclase is to be seen to the S.W. and the fine groundmass has been partly recrystallized. Ordinary light. ×23½.

Fig. 4.—Advanced Hybrid from Sub-zone II. Acid mesostasis has been recrystallized. Biotite on right and saussuritized plagioclase on the left side of picture. Groundmass completely recrystallized to give hornfels texture. Ordinary light. ×28.

### Plate XI.

Fig. 1.—Hybrid from Sub-zone II at South Marulan. Shows large clot of biotite in a decussate aggregate surrounded by recrystallized groundmass. Rock has been thermally metamorphosed after hybrid-reaction. Ordinary light. ×40.

Fig. 2.—Partially hybridized rock. Shows development of large patch of hornblende, which is changing over to aggregate of small biotite units. Above hornblende to N.W. is sericitized felspar and to right and along base of photograph recrystallized quartz is to be seen. Ordinary light. ×28.

Fig. 3.—Hybrid from Sub-zone I. Large saussuritized plagioclase to the right, quartz in S.W. quadrant and biotite in N.E. corner, with strongly recrystallized groundmass. The dark spots in groundmass are chlorite and the light material is quartz. Ordinary light. ×57.

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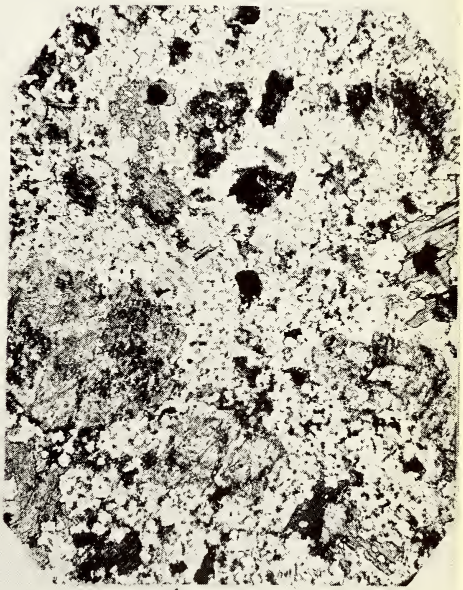

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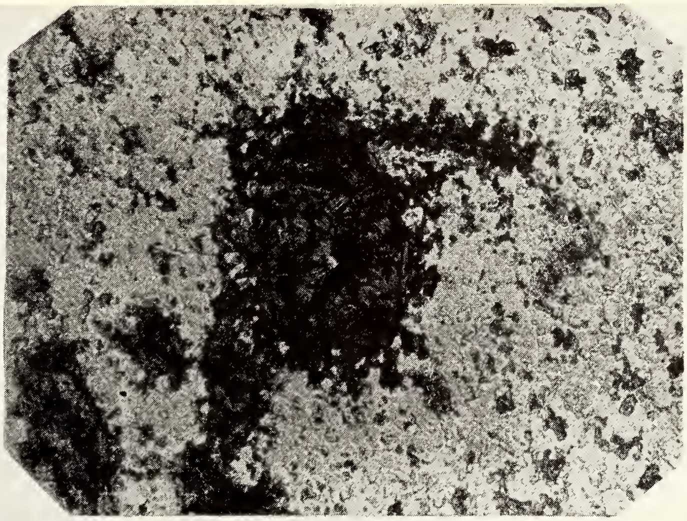

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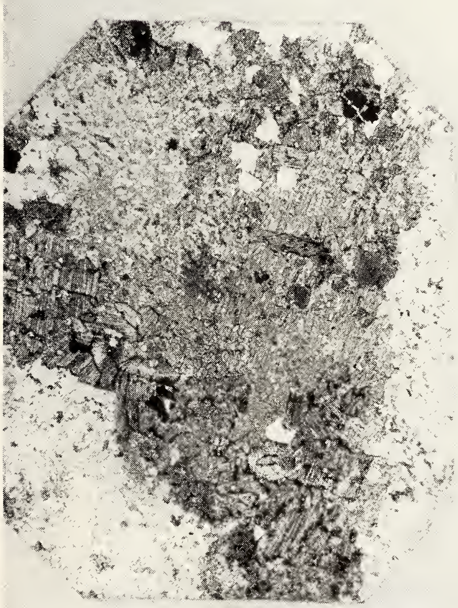

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# THE REPLACEMENT OF CRINOID STEMS AND GASTROPODS BY CASSITERITE AT EMMAVILLE, NEW SOUTH WALES.

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With Plate XII.

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## Introduction.

The country rocks of the Emmaville District or Vegetable Creek tin field consist of Permian claystones, conglomerates and breccias. These are very sparingly fossiliferous. Late Permian intrusives, notably granites and quartz-felspar porphyries, have given rise to veins, irregular stockworks and impregnations of cassiterite-bearing quartz. In a few instances stanniferous veins and stockworks have been developed within the intruded sediments.

Post-Permian erosion has given rise to vast alluvial tin deposits. These have been covered by Tertiary basalts present now as scattered residuals rising up to fifty feet above the otherwise peneplaned surface. Tin recovery thus comprises reef-mining, deep-lead mining (driving into stanniferous alluvium through or beneath the Tertiary lavas) and sluicing the existing streams.

In the various streams and creeks at Emmaville there occur numerous types of alluvial cassiterite: ruby, resin, wood and toad's eye, etc. The most interesting variety, however, is the one termed by the local miners " screw-tin ".* These have been identified as crinoid stems replaced by cassiterite. They have never been found *in situ.* Associated with the " screw-tin " are occasional gastropods, also replaced by cassiterite. Hodge-Smith (1943) originally drew attention to these remarkable fossils.

The mode of replacement is somewhat obscure. The fossils were undoubtedly contained in the Permian sediments originally as calcareous remains. The sediments were intruded and silicified. Judging by the completeness of this silicification one might assume that even the fossil content would have been silicified. However, the only fossils so far collected from this area were found in Recent alluvium and have been entirely replaced by tin dioxide.

It is significant that the so-called wood-tin is also found in the same alluvium. The name is an apt one. The wood-tin is of a pale brown colour ; the fragments are inclined to be somewhat tabular in shape and up to an inch and a half in length and are notably dissimilar to any other type of cassiterite found in the New England. It is not improbable that wood-tin represents fragments of the sedimentary country rock which have been replaced by stanniferous solutions. It may be that these solutions, passing through the bedding and jointing in the sediments, reached a position where metasomatic replacement of both sediment and fossil content ensued. Subsequent mechanical disintegration might have

* So called because of their striking resemblance to worm-screws.

produced fragments of wood-tin and the stanniferous fossils. It should be pointed out, however, that metasomatic replacement of the sediments is not a general feature of the Emmaville mineralization, as far as can be ascertained.

It is interesting to note that throughout this extensive alluvial tin-field fossils so replaced have been found only in two small non-perennial creeks: Steele's Gully and Charcoal Gully, tributaries of Doctor's Gully. They have never been found in the main waterway, the lucrative Vegetable Creek, nor in any of its more prominent tributaries.

The stanniferous crinoid stems were, at one time, fairly plentiful. Many of them undoubtedly found their way into the smelters together with the associated alluvial tinstone. The gastropods were very rare; no more than a dozen or so of these are extant. Further finds are likely, however, since the leases at Doctor's Gully are to be reopened in the near future.

## Description of the Fossils.

(1) *The Crinoid Stems.* These are generally quite circular in cross-section; some are oval. The diameter ranges from 1 cm. to 2 mm. In length they rarely exceed 2·5 cm. The average length, irrespective of diameter, is about 1 cm.

The colour of the specimens ranges from dark steel-grey to reddish-brown, the latter being due to a thin encrustation of iron oxide. All specimens show textural homogeneity under megascopic examination.

In each specimen the constituent ossicles are quite apparent. The ratio of length of ossicle to diameter varies slightly from specimen to specimen. Partial telescoping of adjacent ossicles was noted in a few cases. There were on the average, ten ossicles per centimetre of length.

In those specimens that have not suffered excessive attrition, the central ligament canal is readily discernible. It consists of a small indentation centrally placed within a larger circular depression. This latter depressed area is rimmed concentrically by a circular platform which occupies about half the diameter of each specimen. Radially disposed around this platform are the alternate ridges and furrows which serve as an interlocking device (Plate XII, figs. 1*a*-1*d*).

Longitudinal thin sections show (Plate XII, fig. 2*a*) that the crinoid stems have been completely replaced by cassiterite. The entire stem appears as a homogeneous aggregate of fine-grained cassiterite. In ordinary light the aggregate is of a pale brownish colour, with occasional opaque patches of reddish-brown iron oxide. Running through the centre is a zone of coarser-grained cassiterite. This zone was originally the central ligament canal. In this region of greater pore space the cassiterite has assumed a coarser texture. This also applies to a number of zones set at right angles to the ligament canal. These are undoubtedly due to replacement of zones where adjacent ossicles have been parted slightly. Under crossed nicols the replacing grains, especially the larger ones, show pearly interference colours indicating extremely high birefringence.

In transverse sections (Plate XII, fig. 2*b*) one sees, again, an aggregate of cassiterite grains all closely interlocking and showing patches of iron oxide. In Plate XII, fig. 2*b* the central ligament canal is not apparent; this is due to the fact that the section has been cut through a zone of parting between ossicles. The effect of this can be seen by studying Plate XII, fig. 2*a*.

The identity of the crinoids which yielded these stem fragments has never been established positively. J. E. Carne (1911) reports Mr. W. S. Dun, former Palæontologist to the New South Wales Geological Survey, as suggesting that calcareous crinoid stems from an adjacent region may belong to the genus *Phialocrinus*. No reasons were given for the above suggestion but it is possible that calices of this genus occur in the area referred to by Dun.

(2) *Gastropods.* These are also of a reddish-brown colour due to a coating of iron oxide derived, no doubt, from the decomposition of the Tertiary basalt which formerly covered the alluvium.

It is probable that two different species (or sub-species) are represented. Of the specimens examined some had apical angles of from 65° to 75° (Plate XII, figs. 3*a* and 3*c*). These had a ratio of height to diameter of last whorl of 1 : 1. Others had an apical angle of from 38° to 42° and gave a height-diameter ratio of 3 : 2 (Plate XII, fig. 3*b*). *Ptycomphalina morrisiana* McCoy (Permian) is known from a number of localities adjacent to the Emmaville District. The specimens here described would appear to belong to this genus (Hodge-Smith, 1943). Although most of the cassiterite replacements have suffered abrasion, one or two specimens show what is probably a selenizone (Plate XII, fig. 3*b*). In all cases the whorls, of which there are four, increase rapidly in size. The mouth is large and is situated slightly away from the axis of coiling. A small umbilicus was observed in a couple of specimens. Because of the rarity of the gastropods no thin sections were made.

The following table of specific gravities is of interest:

| *Crinoid Stems.* | *Gastropods.* |
|---|---|
| (*a*) 6·688 | (*a*) 5·785 |
| (*b*) 6·378 | (*b*) 5·281 |
| (*c*) 6·504 | (*c*) 5·511 |
| (*d*) 6·560 | |

Dana gives the specific gravity of cassiterite as ranging from 6·1 to 6·99 (Palache *et al.*, 1944).

It is interesting to note that in all cases the values for the gastropods are lower than those for the crinoid stems. This is probably due to the presence of small quantities of clay or of iron oxide in the body cavities and umbilicus.

Chemical analysis of a crinoid stem gave the result in Column I.

| Column I. | | Column II. | |
|---|---|---|---|
| $SnO_2$ | 63·5 | Calcium phosphate | 80·04 |
| $Al_2O_3$ | 17·7 | Calcium carbonate | 2·24 |
| $SiO_2$ | 12·4 | Calcium fluoride | 0·50 |
| $Fe_2O_3$ | 6·0 | Ferrous disulphide | 1·66 |
| MgO | 0·2 | Ferric oxide | 0·62 |
| CaO | trace | Stannic oxide | 2·60 |
| | | Silica | 0·22 |
| Total | 99·8 | Organic matter and loss | 12·12 |
| | | Total | 100·00 |

It is clear that the analysed specimen had a cassiterite tenor distinctly lower than would be expected from the specimens whose specific gravity measurements are given above. These specimens of greater density and higher cassiterite content were not available for chemical analysis as they constitute type specimens in the collection of the Australian Museum, Sydney.

J. H. Collins (1888) reported on the replacement of deer horns by cassiterite in the stanniferous alluvium of Cornwall and gave an analysis quoted in Column II above. He stated that " The oxides of tin and the iron pyrites have found their way to the interior of the bone and are visible throughout the structure, although somewhat more abundant near the periphery ".

Since the deer horns could not be replaced by direct emanations from the Late Palæozoic tin-bearing intrusives of Cornwall, their replacement must be either the result of penetration by secondary stanniferous solutions or be due to mechanical infilling by finely-divided mineral

The degree of replacement of the deer horns from Cornwall is very small compared with that of the Emmaville specimens.

The author wishes to thank Messrs. R. Millett and K. Nash of the C.S.I.R.O., Sydney, for the photographs accompanying this paper.

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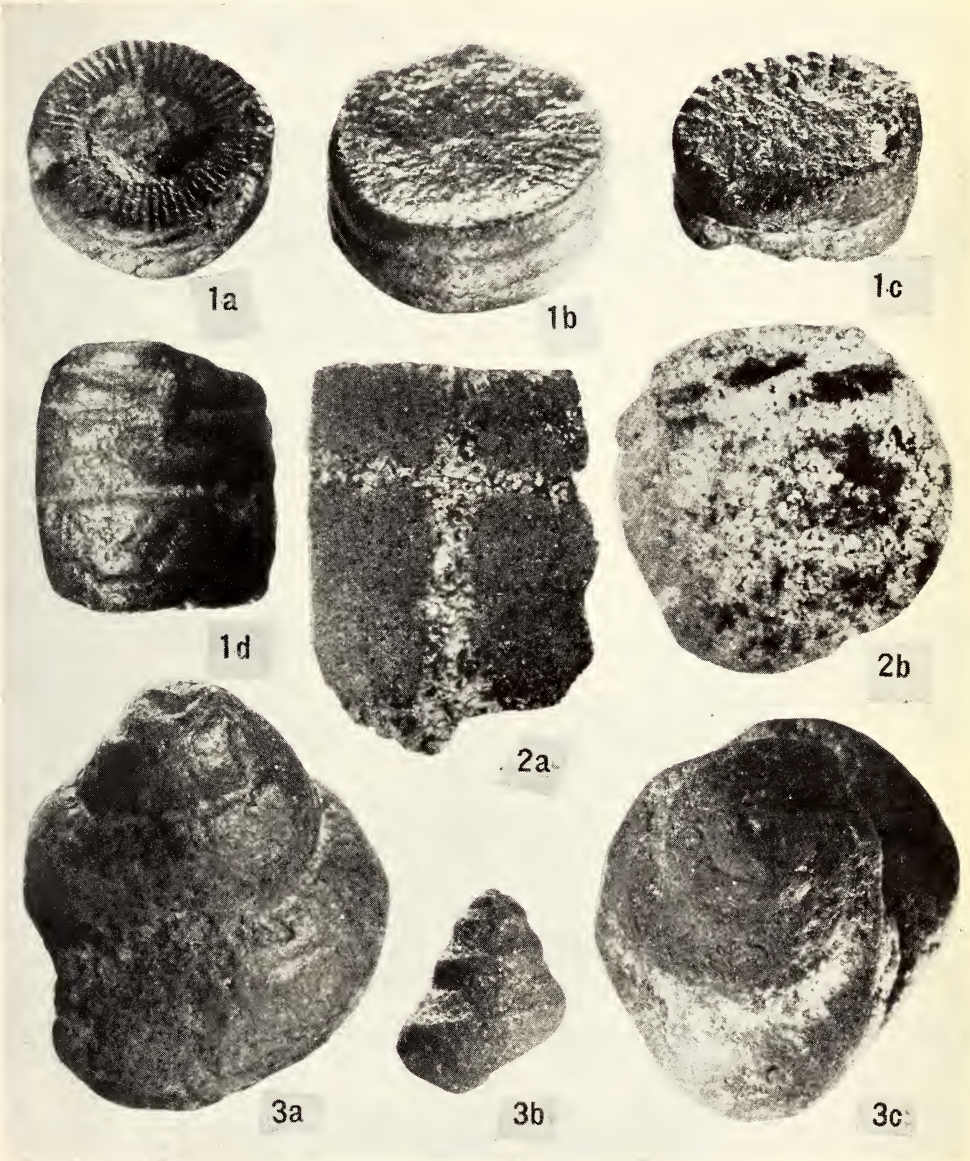
## Explanation of Plate XII.

Figs. 1*a*–1*d*.—Crinoid stem fragments replaced by cassiterite. Loc., Emmaville, N.S.W. (×8.)

Figs. 2*a*–2*b*.—Thin sections of stanniferous crinoid stems. 2*a*, longitudinal section 2*b*, transverse section. Ordinary light. (×10.)

Figs. 3*a*–3*b*.—Gastropods replaced by cassiterite. Loc., Emmaville, N.S.W. (×4.)




Specimens 1*a*, *b*, *c* and *d* are in the Australian Museum ; specimens 3*a*, *b* and *c* are in the possession of Mr. L. Collins, Emmaville.

# INDEX


## A

Page

A Contribution to the Geology and Glaciology of the Snowy Mountains, New South Wales .. .. .. 88
A Geological Account of Heard Island .. 14
Alteration of Rule IX .. .. .. viii
Annual Dinner of the Society .. viii
Annual Report of the Council .. vii
Atherton Tableland, Climate and Maize Yields on the .. .. .. .. 22
Authors, Guide to .. .. .. iv
Awards of the Society .. .. .. vi

## B

Balance Sheet .. .. .. .. x
Bequest, Form of .. .. .. iv
Birrell, Septimus.—Obituary Notice .. xiv
Bolton, J. G.—Award of Edgeworth David Medal for 1951 .. .. vi
Bosworth, R. C. L.—Presidential Address—
  I. The Society's Activities .. 1
  II. Transport Processes in Applied Chemistry .. .. .. 3
Brown, I. A.—
  *Martiniopsis* Waagen from the Salt Range, India .. .. .. 100
  Permian Spirifers from Tasmania .. 55

## C

Cheel, Edwin.—Obituary Notice .. xiv
Clarke Memorial Medal—
  For 1951 .. .. .. .. vi
  For 1952 .. .. .. .. viii
Climate and Maize Yields on the Atherton Tableland .. .. .. 22
Coastal Limestones of Western Australia, Soil Horizons and Marine Bands in the .. .. .. .. .. 68
Commemoration of Great Scientists .. vii
Contributions to the Study of the Marulan Batholith. Part II, The Granodiorite-Quartz Porphyrite Hybrids .. .. .. .. .. 108
Conversazione—Jubilee .. .. .. viii
Crinoid Stems and Gastropods, The Replacement of, by Cassiterite at Emmaville, New South Wales .. 119

## D

David Medal, 1951, Awards of the Edgeworth .. .. .. .. vi
Davies, N. R., and Dwyer, F. P.—Induced Optical Activity of the Tris-1 : 10-Phenanthroline and Tris-2 : 2′-Dipyridyl Copper II Ion .. .. 64

Page

Distinguished Visitors .. .. .. viii
Drane, N. T.—See Simonett, D. S., and Drane, N. T.
Dwyer, F. P.—See Davies, N. R., and Dwyer, F. P.

## E

Edgeworth David Medal for 1951 .. vi
Emmaville, New South Wales, The Replacement of Crinoid Stems and Gastropods by Cassiterite at .. 119
Exhibits .. .. .. .. vii, xiii

## F

Fairbridge, R. W., and Teichert, C.—Soil Horizons and Marine Bands in the Coastal Limestones of Western Australia .. .. .. .. 68

## G

Geology and Glaciology of the Snowy Mountains, A Contribution to the .. 88
Geology, Report of the Section of .. xiii
Government Grant to the Society .. viii
*Grantonia hobartensis* Brown, 1953, *gen. et spec. nov.* .. .. .. .. 61
Graptolite Zones and Associated Stratigraphy at Four-Mile Creek, Southwest of Orange, N.S.W. .. .. 94
Gregg, N. McAlister—Award of the James Cook Medal, 1951 .. .. vi
Guide to Authors .. .. .. iv

## H

Heard Island, A Geological Account of .. 14
Hoggan, H. J.—Obituary Notice .. xiv
Honorary Member .. .. v, viii

## I

India, *Martiniopsis* Waagen from the Salt Range .. .. .. .. 100
Induced Optical Activity of the Tris-1 : 10-Phenanthroline and Tris-2 : 2′-Dipyridyl Copper II Ion .. .. 64

## J

James Cook Medal for 1951 .. .. vi
Johnson, T. Harvey.—Obituary Notice xiv
Judd, W. P.—Obituary Notice .. xiv

L

Page

Lambeth, A. J.—A Geological Account of Heard Island .. .. .. 14
Lawrence, L. J.—The Replacement of Crinoid Stems and Gastropods by Cassiterite at Emmaville, N.S.W. .. 119
Library, Report on Society's .. ix
List of Members .. .. .. .. v
Liversidge Lecture—Electron Diffraction in the Chemistry of the Solid State.. 38
Livingstone, S. E.—Palladium Complexes. Part V. Reactions of Palladium Compounds with 2 : 2′ Dipyridyl .. .. .. .. 32
Lovering, J. F.—See Osborne, G. D., and Lovering, J. F.

M

Maitland, A. Gibb—Obituary Notice .. xv
Maize Yields on the Atherton Tableland, Climate and .. .. .. .. 22
*Martiniopsis* Waagen from the Salt Range, India .. .. .. .. 100
Marulan Batholith. Part II. The Hybrids, Contributions to the Study of the .. .. .. .. .. 108
Members, List of .. .. .. v

N

Notices .. .. .. .. .. iv

O

Obituary .. .. .. .. .. xv
Occultations Observed at Sydney Observatory during 1951 .. .. 20
Officers for 1952-1953 .. .. .. iii
Orange, N.S.W., Graptolite Zones and Associated Stratigraphy at Four-Mile Creek, South-West of .. .. 94
Osborne, G. D., and Lovering, J. F.—Contributions to the Study of the Marulan Batholith. Part II. The Granodiorite-Quartz Porphyrite Hybrids .. .. .. .. .. 108

P

Packham, G. H.—See Stevens, N. C., and Packham, G. H.
Palladium Complexes. Part V. Reactions of Palladium Compounds with 2 : 2′ Dipyridyl .. .. .. 32
Penfold, A. R.—Award of the Society's Medal, 1951 .. .. .. vi
Permian Spirifers from Tasmania .. 55
Popular Science Lectures .. .. viii
Presidential Address .. .. .. 1

R

Page

Rees, A. L. G.—Liversidge Lecture—Electron Diffraction in the Chemistry of the Solid State .. .. .. 38
Report of the Council .. .. .. vii
Ritchie, A. S.—A Contribution to the Geology and Glaciology of the Snowy Mountains .. .. .. .. 88
Robertson, W. H., and Sims, K. P.—Occultations Observed at Sydney Observatory during 1951 .. .. 20
Rule IX, Alteration of .. .. viii

S

Salt Range, India, *Martiniopsis* Waagen from the .. .. .. .. 100
Science House Management Committee, Society's Representatives .. .. viii
Simonett, D. S., and Drane, N. T.—Climate and Maize Yields on the Atherton Tableland .. .. .. 22
Sims, K. P.—See Robertson, W. H., and Sims, K. P.
Snowy Mountains, A Contribution to the Geology and Glaciology of the .. 88
Society's Medal for 1951 .. .. vi
Soil Horizons and Marine Bands in the Coastal Limestones of Western Australia .. .. .. .. 68
Spirifers from Tasmania .. .. 55
Stevens, N. C., and Packham, G. H.—Graptolite Zones and Associated Stratigraphy at Four-Mile Creek, South-West of Orange, New South Wales .. .. .. .. .. 94
Stillwell, F. L.—Award of the Clarke Medal for 1951 .. .. .. vi
Stratigraphy at Four-Mile Creek, South-West of Orange, N.S.W., Graptolite Zones and Associated .. .. 94
Subscription, Alteration of Rule IX .. viii
Sydney Observatory during 1951, Occultations Observed at .. .. 20

T

Tasmania, Permian Spirifers from .. 55
Teichert, C.—See Fairbridge, R. W., and Teichert, C.
The Replacement of Crinoid Stems and Gastropods by Cassiterite at Emmaville, New South Wales .. .. 119
Transport Processes in Applied Chemistry—Presidential Address .. 3
*Trigonotreta stokesii* Koenig, 1825 .. 56

W

Western Australia, Soil Horizons and Marine Bands in the Coastal Limestones of .. .. .. .. 68
Wood, J. G.—Award of the Clarke Memorial Medal for 1952 .. .. viii

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