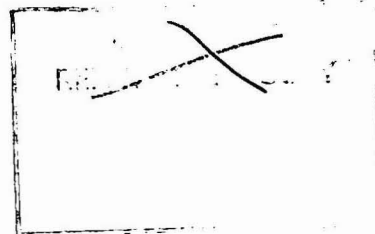


COMMONWEALTH OF AUSTRALIA.

DEPARTMENT OF NATIONAL DEVELOPMENT.
BUREAU OF MINERAL RESOURCES
GEOLOGY AND GEOPHYSICS.

RECORDS.

1957/84



REPORT ON OVERSEAS VISIT

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The work covered during the year was divided into three main sections; they were -

1. The study of X-ray diffraction, both theoretical and practical, at Cambridge University.
2. The use of X-ray fluorescent spectrometry at Massachusetts Institute of Technology, Massachusetts, U.S.A.
3. Some aspects of ore microscopy, at Heidelberg University, Germany.

1. Cambridge University.

The first section commenced at Cambridge in the first week in October 1956, and continued throughout the academic year there until 16th June 1957, with the Easter vacation of six weeks spent at Massachusetts Institute of Technology, U.S.A.

The courses taken as part of the ordinary University curriculum were: crystallography, X-ray crystallography, X-ray practical work, petrogenesis, geochemistry, metamorphism, theoretical ore microscopy, as well as the post-graduate X-ray diffraction course given once every three years.

It was found necessary on my arrival at Cambridge to commence the study of crystallography from first year level, their courses in this subject being far in advance of anything taught at Sydney University for the B.Sc. degree. It included geometrical crystallography and the use of stereographic and gnomonic projections and spherical trigonometry, and provided the necessary basis for the X-ray course which commenced in second term.

The whole first term was occupied with this work. In addition, during this time, theoretical X-ray diffraction was dealt with, so as to give a basis for the practical work, which commenced in second term.

Professor Tilley's lectures on petrogenesis were also taken; these provided an excellent demonstration of the application of principles of thermodynamics to the study of igneous petrology, as well as some interesting concepts of their role in rock-forming processes.

During the Christmas vacation research students were allowed full use of the department's facilities, and the period was used to do some practical work on interpretation of single crystal oscillation and Weissenberg photographs. The work was undertaken at the suggestion of my tutor, Dr. Peter

Gay, as being a valuable preliminary to the second term practical X-ray work.

The main X-ray course commenced in second term, continuing with theoretical X-ray diffraction, as well as starting a series of practical exercises. The theoretical part of the course dealt with types and uses of X-ray tubes, production and uses of characteristic and continuous radiation, powder diffraction methods and the various film arrangements used with them, single crystal stationary and moving film methods, and the calculation of crystal constants using both these methods.

The single crystal methods are a useful supplement to the powder diffraction technique and offer an accurate means of obtaining identification of platy minerals which do not lend themselves readily to the powder method. They are also useful to identify those minerals of the lower symmetry groups which give a complex and sometimes partly diffuse powder pattern. Some of the secondary uranium minerals fall into this group. The method is useful for measuring crystal constants of unknown minerals and can be used to give axis dimensions, specific gravities, unit cell contents, unit cell composition, structural formulae, axial angles and space groups, and has many applications in the accurate identification of minerals incapable of identification by any other means except with great difficulty.

Also given in this series of lectures and practical demonstrations was the theory and application of the geiger counter diffractometer. In X-ray powder cameras the whole of the diffraction pattern is recorded simultaneously on the photographic film. Alternatively it is possible to study the powder pattern by scanning with a geiger counter which is moved either continuously or in steps across the pattern. This has many advantages, particularly for powder work, e.g., in rapid identification, in the examination of a diagnostic line without recording the full pattern, in intensity measurements, etc.

Some interesting geological applications are:-

- (1) Rapid identification - quick identification of unknown materials can be made from charts. A smear mount is prepared and a record made at a relatively fast scanning speed ($1^{\circ}20'/\text{min}$). The material can then be identified in the usual way, either by using the A.S.T.M. index, or by comparison with charts of known materials.
- (2) Examination of diagnostic spacings - often the accurate position of a single line is required, e.g., in the determination of composition within a mineral series. The diffractometer, with its high accuracy, speed, and resolution is probably the most accurate and convenient instrument for this purpose. Some typical applications are -
 - (a) Olivine determination - the shift of the $d_{(130)}$ line gives the composition to $\pm 2\%$ of fayalite.
 - (b) Nephelines - the shift of the $d_{(21\bar{1}0)}$ and $d_{(20\bar{1}2)}$ lines, if the excess SiO_2 is not too high, gives CaO to $\pm 3\%$.
 - (c) Alkali feldspars - $d_{(130)}$ line shift detects monoclinic-tridinic inversion.

These are just some applications for which this method can be used, giving comparable or greater accuracy with much less expenditure of time than that needed for other methods.

The practical work consisted of a series of exercises dealing with -

The construction and use of the reciprocal lattice, as used in single crystal X-ray diffraction.

The construction and use of the Bernal Chart, used for interpretation of single crystal photographs.

Interpretation of oscillation photographs.

The construction of the Weissenberg chart for moving film methods.

Construction of $\rho\phi$ and Θ charts for crystal orientation studies.

Determination of an orientation of a single crystal of diamond using $\rho\phi$ and Θ charts.

Space groups.

Calculations of optimum potentials for various targets and absorption effects.

Filters.

Choices of radiation to avoid fluorescence.

Indexing of powder photographs using the "Q" value method and the accurate determination of the cell dimensions of quartz.

The use of Weissenberg photographs in the study of triclinic crystals.

Geiger counter diffractometer methods.

The complete study of a new mineral.

In the final term at Cambridge, Professor Tilley suggested that I do a complete study of a mineral hitherto not described by X-ray methods. The zinc manganese silicate, hodgkinsonite, from Franklin Furnace, New Jersey, was selected. During the course of this investigation the axial ratios, axial angle, crystal system, space group, structural formula, specific gravity, volume of unit cell, contents of unit cell, and refractive indices were determined. An accurate powder pattern was taken using the geiger diffractometer and the resulting spacings and intensities tabulated for future identification. Previous work done by Palache on this mineral, based on crystal morphology only, was found in many instances to be incorrect. Two refractive indices remain to be determined at Canberra, and the completed paper will be sent to Professor Tilley at his request for publication in the Mineralogical Magazine.

2. Massachusetts Institute of Technology.

An important aspect of the work at Cambridge during the first and second terms was that, having the background of theoretical X-ray diffraction, I was able to devote the whole of my six weeks in America to actual X-ray fluorescent

spectrometry, which I would not have been able to do had I not had the theoretical grounding. The similarity between diffractometry and spectrometry can be readily understood when one considers that in diffractometry, a single known wavelength is used to analyse a diffracting specimen for all d-spacings present, whereas in spectrochemical analysis a single known d-spacing of a diffracting crystal is used to analyse the spectrum of the specimen for all wavelengths present. Thus in diffractometry the specimen is rotated, and the different angles 2θ at which diffracted energy is detected are related to different d-values. In spectrochemical analysis the crystal is rotated and the different angles 2θ at which diffracted energy is detected are related to different wavelengths.

X-ray diffraction patterns reveal differences in the character, dimensions, and orientations of crystals. Hence diffraction analysis identifies compounds by their specific crystal structure and lattice spacings, and distinguishes between different crystalline modifications of compounds (e.g., rutile and anatase). It permits quantitative analyses of mixtures of crystal substances, distinguishes between mixtures and solid solutions, and gives information on the orientation of crystallites in a sample. That is, diffraction studies are used in materials in the crystalline state.

The characteristic X-ray spectra, however, are emitted by an atom regardless of the crystal structure or chemical composition of the sample and are independent of the physical condition of the sample. Therefore X-ray spectrographic analysis supplements the diffraction analysis in giving information on the elemental composition of the sample.

The period of the Easter vacation at Cambridge University, from March 15th until April 27th, was spent in the U.S.A. at the Massachusetts Institute of Technology, Cambridge, Mass., where a study was made of X-ray fluorescence analytical methods, and to a lesser extent the physical-chemical approach to rock-forming geological processes.

The work on X-ray analysis can be divided into two sections, theoretical and practical, and was carried out exclusively in the Department of Metallurgy, the Geology Department having no equipment for this type of work. The theoretical aspect was carried out through the study of literature recommended by Professor R. Ogilvie of the X-ray metallurgy section. It included the study of various methods by which satisfactory analyses may be carried out, and, what is more important from the mineralogical standpoint, the study of matrix effects on the accuracy of the analysis.

In order to justify the time spent on using the fluorescence equipment, I was given a project to carry out which was part of a Massachusetts Institute of Technology contract with a private company in Massachusetts. This project aimed at finding out whether the X-ray method was suitable for the ratio analysis of columbium and chromium in oxidised alloys used in the manufacture of guided missile casings, with a view to ultimately determining the behaviour of the alloy under service conditions. It hinged upon finding the most suitable method for the preparation of the oxidised material for analysis, as well as the preparation of standards which would give good reproducibility, coupled with speed of analysis and hence refinement of accuracy in the result.

This result was finally achieved, showing the method to be entirely satisfactory, and several sets of analyses of oxidised material were carried out giving highly reproducible results. The project gave valuable practice in the operation of the fluorescent spectrometer as well as various methods of specimen preparation.

During any time when the instrument was not being used by members of the department, samples of rare earth minerals such as euxenite, polycrase, samarskite, monazite, etc. were prepared and analysed. These minerals are extremely difficult to analyse by wet chemical means, and take a great deal of time. It was found that a successful complete qualitative analysis could be done on the most complex of these (euxenite, polycrase) in a matter of ninety minutes to two hours. As an example, in euxenite twelve elements were detected; they were Cb, Y, U, Fe, Ta, Th, Zr, Gd, Dy, In, Mn, Pb, all of which could also have been quantitatively determined. Of the elements detected, Y, Th, Zr, Gd, Dy, In, are all extremely difficult to detect and determine by wet chemical methods. Specimens of sulphide minerals were examined by this method, and similar successful results obtained.

Any other time available at M.I.T. was used for the study of literature on fluorescence analysis, with the emphasis on specimen preparation, selection of standards for quantitative analysis, and disturbing effects on the spectral lines. No time was available for practical work in these matters, however, so further work will have to be carried out in the Canberra laboratory.

In brief, the procedure for quantitative analysis is similar to that for optical spectrography, which requires the preparation of a number of reference standards, i.e., specimens of known composition in different concentration regions. These standards are used to prepare working calibration curves of X-ray fluorescent intensity as a function of the concentration of each constituent.

It may be of interest here to compare the X-ray fluorescence method with the standard optical method of spectral analysis. In general it may be said that the X-ray method cannot compete with the optical one in the analysis for trace elements; the optical method will in some cases go down to concentrations of one part in 10^6 . On the other hand, the optical method is less sensitive to differences in the concentration of a major constituent, which are most easily measured by the X-ray method. Another general aspect is the range of elements for which the methods are useful. The optical method is generally used for about 65 or 70 elements scattered all over the periodic system; it is not generally applicable to the electronegative elements such as the halogens, sulphur, etc., which have spectra in the far ultraviolet. This X-ray method is useful for all elements above atomic number about 13, but cannot at present be applied to the lower end of the periodic table, although improvement in instrumentation should, in the near future, overcome this to a certain extent. An outstanding advantage of the X-ray method is that the sample is not destroyed in the course of analysis, and another is its ability to cope with all types of specimens. It can be applied to crystalline as well as amorphous materials, and the specimen can be in the liquid or solid state, in powder, or glass, or metal form, with constituents dispersed or dissolved. This compares more than favourably with the optical method on which the state of the specimen imposes certain limitations.

Finally, it is interesting to compare the ways of handling overlapping spectra. The only way of dealing with this problem in the optical case is by the use of high dispersion, and, owing to the complicated character of most optical spectra, this may necessitate the use of grating spectrographs of very great length. The X-ray spectra, being much simpler, cause much less overlapping, and moreover there are several methods other than increased dispersion for separating adjacent lines. The following quotation gives some idea of the possibilities of the method -

"X-ray fluorescence has proved to be a reliable method for the analysis of Cb and Ta, in ore minerals, and for following the increase in concentrations during mineral dressing processes. It takes a competent chemist five to fifteen days to make a chemical analysis for these elements, while ten to fifty samples can be analysed with comparable accuracy in a day by the X-ray method".

The programme of work in fluorescence analysis in the immediate future after setting up the instrument in Canberra will be -

- (a) Testing as many as possible of the methods of specimen preparation described in the literature, and evaluating their worth for application to the problems encountered in mineralogical determinations;
- (b) Selecting suitable internal standards for the combinations of elements likely to be met with in our analyses;
- (c) Combining (a) and (b) to form a rapid and accurate quantitative and qualitative analytical scheme suitable for use in a geological laboratory.

The carrying out of the programme in X-ray fluorescence analysis left very little time for the study of the physical chemistry part of the programme. However, Professor MacDonald kindly gave me a complete set of his lecture notes on the subject, as well as giving freely of his time for discussions, which, coupled with a cursory reading of the notes, proved to be of great benefit. Professor MacDonald suggested that I ask to be placed on the mailing list of Dr. J. Boyd, of the Geophysical Laboratory, Washington, whose section is studying the phase chemistry of the sulphide systems, on which, to date, very little experimental work has been carried out. This was done, and some useful material for the study of ore mineralogical problems should be forthcoming.

Of particular interest to the Bureau was the offer by Professor Hurley of the Geology Department of Massachusetts Institute of Technology to carry out age determinations on Australian rocks. The method used has the advantage that it is quicker than most existing methods, and, as he has been perfecting the method since the early 1930's, he also claims greater accuracy.

Several visits were made to the Mineralogical Department at Harvard University, and the acquaintance made of Professor Frondel. He has offered to exchange minerals with the Bureau, and also to give any information he may have on the X-ray diffraction patterns of the uranium minerals, on which he has done a great deal of work. This latter offer will be of great benefit for the accurate determination of the secondary uranium minerals in particular.

Part of the programme in the U.S.A. was to visit the Bell Telephone Laboratories - Hartford Connecticut, to study their application of X-ray fluorescence analysis. However, the information I received in Australia that this company has a laboratory at Hartford is incorrect. As my time was fully occupied at Massachusetts Institute of Technology, and as it was possible there to obtain very full information in the use of the method of X-ray fluorescent analyses, the omission of this part of the programme was of no importance.

3. Heidelberg University.

On June 16th the final period of the year's programme commenced - the study of ore mineralogy at Heidelberg University. The work here was concerned mainly with going through Professor Ramdohr's extensive mineral collection and examining in particular those minerals which have not been observed in the specimens examined to date in the Canberra laboratory.

About 150 different minerals were studied, and notes taken on characteristics which would help in their future identification. Of particular interest was the examination of specimens from the gold-uranium deposits of the Witwatersrand and Dominion Reef, South Africa. Professor Ramdohr made available a copy of the results of his work on the genesis of the uranium in the Witwatersrand, and much valuable information on this type of deposit was obtained by concurrent examination of the specimens and reading of his report. His evidence in support of a "placer" origin for these deposits is particularly convincing and extremely informative.

At Heidelberg I was fortunate enough to have some discussions with geologists from the Italian and Swedish Atomic Energy Commissions. Specimens obtained from the uranium deposit in the Preit area of North Italy were polished and examined and found to **closely resemble** material from Rum Jungle, both in rock type and mode of occurrence of the pitchblende. The Swedish geologists stated that the deposit at Alnö, Sweden, is identical with this Italian occurrence. These observations were of particular importance in helping to strengthen a theory of mine on the genesis of the uranium in the Rum Jungle deposit.

Many informative discussions were held with Professor Ramdohr, particularly on physico-chemical aspects of ore deposition. He has generously supplied me with a collection of rare minerals and ore specimens which will be invaluable in the compilation of X-ray data, and for other determinative procedures. Professor Ramdohr has also offered to make available to the Bureau any specimens of such minerals as he has available if at any time we require them for our work. This would be a very valuable source for obtaining specimens from some of the German and European ore deposits.

I left Heidelberg on the first stage of the return journey to Australia on September 3rd, 1957.