

CENTENARY PRESIDENTIAL ADDRESS, 1976

Progress in mineralogy

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SUMMARY. The Mineralogical Society celebrated its 50th Anniversary in 1926; this address attempts to summarize the substantial developments in the subject over the past 50 years and looks ahead to the future. Up to 1926, only the techniques of goniometry, optical investigation of non-opaques, and classical chemical analysis had been fully exploited. X-ray crystallography, though already 14 years old, had made little impact but was to advance with great rapidity to achieve, for example, the modern conception of silicate structure by 1934. The insight into the atomic structure of minerals provided by this technique has been central to the advancement of the subject. The powder camera and more recently the counting diffractometer have become the chief determinative tools, though microscopy is still important. Diffractometry with a tied computer has greatly speeded up structural work. Advances in electron microscopy may soon make it possible to produce direct images of atomic structure. Meanwhile wet-chemical procedures have largely given place to spectroscopy (optical emission, X-ray, and atomic absorption), to the electron microprobe and to various still more advanced techniques, including the investigation of stable and unstable isotopic composition by mass spectrometry. Independently, the optical identification of opaque minerals has been brought to an advanced state. All these developments have opened the way for progress in the understanding of the paragenesis and genesis of minerals, subjects to which experimentation at high temperatures and pressure now contribute materially; and for practical applications in many fields, including ore deposits, beneficiation, ceramics, refractories, cement, sinters, and fuels.

JUBILEE celebrations held in 1926 included an address by the President, Professor William Whitehead Watts. It was, he said, only the fifth such address given to the Mineralogical Society during its first half-century. In it, he included an interesting outline of the Society's history, and summarized its principal activities under the headings of: petrology, crystal-optics; other physical properties and characters; descriptive and topographic mineralogy; meteorites; chemical mineralogy; growth etc. of minerals; economic mineralogy; crystallography. It is not our Society's custom to devote either time or publication space to addresses of this sort, and I think I am right in saying that the present one is only the sixth in a century, justified only by the special nature of the occasion. Dr. Campbell Smith has dealt fully with the history of the Society up to this year of grace (1976); I shall attempt a review of the main lines of progress during the half-century now ending, referring particularly to contributions from members of our Society.

The year 1926 could well be regarded as the end of an era and the beginning of an epoch in mineralogy. The era that was ending was concerned with the description of minerals, their morphology, symmetry, twinning laws, optics, chemistry, and paragenesis. The goniometer, the transmitting microscope, and the paraphernalia of wet chemistry were the chief instruments. The epoch that was beginning was to witness the establishment, for practically all minerals, of their atomic structures. In 1938 Charles Palache could still write 'No property of a mineral is so characteristic as its crystal form'; but how many mineralogists of today could honestly subscribe to this dictum? Palache himself was quick to qualify it by referring to the new tools of research opened up by X-ray analysis. Nevertheless in 1926 morphology still seemed to offer the possibility of a complete determinative method. Federov (1920) had made his over-complicated proposals and Barker (1930) was laying the foundations for the Index which R. C. Spiller and Mary Porter were eventually to complete (Porter and Spiller, 1956).

Determination of non-opaque minerals by measuring their optical properties under the microscope was reaching its zenith; E. S. Larsen, Jr. (1921) had published his tables with hundreds of new determinations on analysed minerals; Hartshorne and Stuart (1934) and Winchell (1933) were soon to follow, but papers from some great practitioners of the art, like C. E. Tilley, still lay ahead as also did R. C. Emmons's double variation method (1931). Descriptive petrography, with the impetus of Rosenbusch, Teall, and Harker behind it, had begun to do justice to the microscopical aesthetics of the igneous rocks and combined with chemical analysis was to achieve genetic status in the hands of Harker, H. H. Thomas, Arthur Holmes, and H. H. Read. Much remained to be done in the metamorphic area and sediments were simply not taken seriously as objects of mineralogical research; clays, in particular, were still out of reach. The study of opaque minerals using metallographic methods had begun, but had far to go.

Crystal structure. By 1926 X-ray crystallography was already 14 years old, but although it had been applied to the structures of natural oxides, sulphides, and sulphates, its impact on mineralogy generally had been minimal. Apart from a review by W. L. Bragg (1922) the first four papers in the *Mineralogical Magazine* making use of X-ray data were published in 1925, and only one of these (Buckley and Vernon, 1925) was a full modern structure determination. Tomkiewf (1925) was pessimistic about the application of X-ray intensities to complex minerals. Even in 1927, the implications had not convinced some chemists that halite was not molecular (Bragg, 1975, 148) or some mineralogists that silicates could no longer be interpreted in molecular terms.

The first eight years of our period witnessed an almost unbelievably rapid advance in the understanding of silicate structures, mostly as a result of the work of a handful of physicists who were building on the earlier foundation provided by Bohr, Planck, and Einstein who had discovered the theoretical basis for the electronic architecture of atoms in propounding the quantum theory. W. H. and W. L. Bragg, following the investigations of von Laue, had developed the theory of X-ray diffraction and invented the X-ray spectrometer. From this early period Jackson, Mauguin, Pauling, W. H. Taylor, Warren, West, and Wyckoff also deserve mention, but if any paper is to be regarded, in retrospect, as the breakthrough, it is probably that on diopside (Warren and Bragg, 1928). As a result, Bragg was able to devote half of his *Atomic Structure of Minerals* (written 1934, published 1937) to the silicates. The principles of ortho-, soro-, ring-, chain-, sheet-, and framework-silicates were all established, and one or more detailed structures typical of a species in each group had been determined. Among these determinations the chain silicates were represented by both pyroxenes and amphiboles, the sheet silicates by micas, talc, chlorite, and kaolin, the frameworks by orthoclase, albite, and analcime. Bragg (1937) could write 'the mineralogical classification, in laying more stress on physical properties than on chemical composition, has been absolutely sound' although 'in some cases X-ray examination has revealed relationships which were hitherto unsuspected or has disproved relationships which had been held to exist'. Most important of all was perhaps the realization of the dual (octahedral and tetrahedral) role of aluminium, which simplified silicate formulae and clarified the nature of isomorphism. Of all the work done in this period, almost everything has stood the test of time except the structure of chrysotile. It is interesting to recall that the axial ratios as ascertained from goniometry on high-quality crystals, in many, perhaps most instances proved to be identical with, or a simple multitude of, the unique unit cell offered by X-ray determination (Donnay and Harker, 1937; Palache, 1938; Donnay, 1946; Seager, 1959). The achievements of the X-ray crystallographers have been central to almost all developments in mineralogy during our half century.

However, after the successes of the early period, subsequent mineral structure work has

proved less exciting. Among the silicates, the only new principles uncovered have been associated with N. V. Belov's school and concerned with the larger cations (Na, Ca, Mn), which impose different requirements on the SiO_4 tetrahedra to those associated with smaller ions. There has also been a steady trickle of determinations of unusual rare silicates (such as ænigmatite, zussmanite, and joesmithite), which serve to illustrate nature's versatility. Since about 1960, multiple refinements of the same structures at different points along solid solution series, at different temperatures, and following different thermal histories have gone a long way towards establishing the basis of ordering of Si and Al over tetrahedral sites, and of Mg, Fe, Al, Ti over octahedral sites within given mineral structures, and to reveal factors controlling bond lengths and angles. This phase of the subject is still very active.

Improvements in the theory of electron diffraction used in constructing electron microscopes have led to the production of direct images of some silicate structures with a resolution intermediate between unit-cell and atomic dimensions. This development may point to future progress. As a result some structural features have become visible, like the familiar rings in beryl (Buseck and Iijima, 1974), local atomic arrangements on twin planes in pyroxenes (Buseck and Iijima, 1975), and in amphiboles on thin lamellae of triple-chain structures as well as on twin planes (Hutchinson, Irusteta, and Whittaker, 1975).

Two recent adjuncts to structural studies are nuclear magnetic resonance (Bloch and others, 1946; Purcell and others, 1946) and electron-spin resonance (Zavoisky, 1945). The former permits the observation of the splitting of the resonance line of a nucleus in a magnetic field. Nuclear species in crystallographically distinct sites have distinct resonances for each site. An ordered crystal has only one electrostatic field gradient for each site whereas a disordered crystal has a range of gradients and the resonances are diffuse. This has proved to be a valuable tool, for example in the investigation of the feldspars. It has also been used to study lunar 'soils'. Electron-spin resonances of atoms with uncoupled electron spins, such as Fe^{3+} , Mn^{2+} , Ti^{3+} , and Pb^{2+} gives information about their environment and identifies electron-hole centres. It is very sensitive, permitting detection of only a few parts per million of these elements, and indicating where replacement by these atoms has occurred, for example as in the case of Fe^{3+} replacing Al^{2+} in microcline.

Mineral and rock chemistry

The structural studies of 1926–34 inevitably threw new light on crystal chemistry; to quote V. M. Goldschmidt (1927), 'the crystal structure of a substance is determined by the relative amounts and sizes, and the degree of polarisation of its structural units . . . atoms, ions, or groups of atoms'. The chemical possibilities now had to be seen as circumscribed by the structure. Isomorphism became more intelligible once it was realized that replacement is controlled by atomic radii rather than by chemical similarity. Molecules no longer had any meaning. Further, as F. A. Bannister (1931) first pointed out, as Hey (1939–1954) later emphasized, one consequence of the determination of the actual size of the structural unit of crystals was that if chemical composition and density are known, 'counting the numbers of atoms per unit cell' becomes possible, instead of the old hit-and-run search for integral atomic ratios to establish a chemical formula. A crystallographer (Palache, 1938) noted with some relief that Bragg did not find it necessary to suggest a new classification that cut across the old chemical boundaries; he also noted that defect structures like that due to the deficiency of iron in pyrrhotine are more common than might have been expected.

Analytical methods. Development since 1947 has followed that of the electronics industry; improvements in photon detection and in amplifiers have led to physical instrumentation, which with the aid of microprocessors or dedicated minicomputers is capable of the accurate

determination of major, minor, and trace amounts of elements within seconds or minutes instead of days or weeks. Despite these advances, a gravimetric determination by a competent analyst, together with a check on the purity of the separated components, and, where appropriate, of the stoichiometry of the weighing forms, is still the yardstick to test an instrument. Most instruments require meticulous standardization if they are to produce accurate results.

The findings of H. W. Fairbairn (1951) of poor precision and accuracy in the world-wide test on two silicate rocks stimulated research on silicate analysis and led to a proliferation of geochemical standards (S. Abbey, 1975). Various schemes for the rapid analysis of silicates, such as that of L. Shapiro and W. W. Brannock (1956), were published, but the colorimetric and volumetric methods employed, notwithstanding the development of many new reagents, were soon superseded by spectroscopic methods. Spectrochemical methods of analysis were, of course, well known in 1926 but it was difficult to correlate the observed intensity of emitted radiation from the arc or spark spectrum with concentration. W. Gerlach's (1925) work using internal standards to a large extent overcame this difficulty. V. M. Goldschmidt's geochemical studies, referred to below, did much to stimulate spectrographic work, and the 1950s saw a revival of interest. Visible and ultraviolet spectrography and spectrophotometry were now in their heyday but were soon to decline in popularity when commercial X-ray vacuum fluorescence spectrometers came into production. This instrument had been introduced by H. Friedman and L. S. Birks (1948); it proved to be capable of providing accurate determinations of many elements over a wide range of concentrations, once mathematical procedures for making matrix corrections had been worked out. These require the use of computers. Full XRF equipment is therefore mainly found in laboratories dealing with large numbers of mineral or rock samples.

Following H. Lundegårdh's pioneering work (1928), flame spectroscopy had been applied to a few elements, but the atomic absorption instrument, devised by A. Walsh (1955), has brought about a widespread application of this method. New excitation sources, such as inductively coupled plasma (S. Greenfield and others, 1964) seem to offer the possibility of a multichannel instrument for simultaneous determination of many elements; whereas the other possible method using atomic fluorescence spectrophotometry at present appears to offer many difficulties.

Nuclear gamma resonance, discovered by R. L. Mössbauer in 1957, became a routine research tool after 1965 when it was realized that it offers a new and sensitive method for determining the oxidation state of iron, a determination unobtainable by X-ray instruments, and sometimes unreliable when carried out by wet chemistry. Space does not permit a full account here, but essentially what is done is to bombard the sample with gamma rays of varying intensity and to measure the electrostatic interaction between the metal ion and its surroundings.

Microanalysis. The need for accurate analysis of very small samples has for long been apparent in mineralogical research. Density, flotation, magnetic, and electrostatic separation procedures, while they have been considerably improved, may either be very onerous when a large sample of high purity of a mineral phase is required, or may be incapable of providing it. Refinement of classical chemical methods, using ultrasensitive balances, went some way to meet the situation. The minimum amount of material required for a top-grade analysis had been fixed at about 1 g by the sensitivity of the analytical balance (assessed by Berzelius in 1841 at 0.1 mg) for about 80 years when the Kuhlmann balance, weighing to 0.01 mg, or even, with stringent precautions, to 0.001 mg permitted the development of microchemical methods (Emich, 1926). Dr. Hey tells me that accurate work with the original Kuhlmann balance at the 1 microgram level is difficult and tedious, but semi-micro determinations, using 100 mg samples, give excellent results on rocks and minerals (for example, Guthrie and Miller, 1933).

On homogeneous mineral samples, 10 mg is sufficient, and when all the constituents can be determined colorimetrically, a mineral sample can be as little as 1 mg (Hey, 1973).

The electron microprobe analyser. Microanalysis has been revolutionized during the past two decades by the invention of this instrument. Moseley's fundamental discovery of 1913 that the frequency of emitted X-radiation is a function of the atomic number of the element being bombarded was first tested as an analytical tool in the 1930s, but the least area capable of analysis proved to be about 1 mm². By combining this method with electron optics, Castaing and Guinier (1950) produced the 'microsonde electronique'. Castaing realized that the limit of resolution was 1 μg, however small the beam diameter, because of penetration and electron scattering. This has not, however, proved to be a serious disadvantage. The first commercial instrument, the Cameca, appeared in 1956. This used a stationary focused beam, but in the same year Coslett and Duncumb at the Cavendish Laboratory, Cambridge, designed and built the first scanning electron microprobe, permitting a scanned image to be obtained showing the distribution of a particular element in the crystal under investigation, a very significant contribution. Further progress was made in the 1960s when diffracting crystals with large interplanar spacings came into use, enabling long-wave-length X-rays from light elements such as oxygen, fluorine, and carbon to be measured. The most commonly used detector with microanalyser crystal spectrometer systems is the gas flow proportional counter, but in 1968 Fitzgerald, Keil, and Heinrich described the use of a solid-state detector of the Si(Li) type. The primary advantage is the ability to collect and process X-rays simultaneously from all elements with atomic numbers above fluorine. Almost instantaneous quantitative analysis can also be obtained, using a dedicated computer for the necessary corrections. The ideal microprobe would combine the advantages of both crystal spectrometers (for resolution) and Si(Li) detectors (for speed). A great deal of work has been done on the essential matrix corrections, which are now reasonably well understood and in full use.

The microprobe technique nevertheless suffers from one serious disadvantage: it cannot give any indication of the oxidation state of elements such as iron and manganese. For many purposes, this information is important. Some auxiliary method is therefore necessary. Mössbauer technique (p. 10) can give useful results in favourable cases, for example where Fe²⁺ is approximately equal to Fe³⁺ and there are not too many distinct sites, but several mg of material are required. Fast neutron activation for oxygen is promising but the accuracy is not yet adequate and in many cases there is still no substitute for wet chemical methods. Ferrous oxide determinations on as little as 10 mg were made as early as 1940 (Hey, 1941; Hey and others, 1969) and further developments on two distinct methods permit determinations to be made on as little as 3 mg (A. J. Easton, private communication; Hey, 1974). However, although accurate results for Fe²⁺:Fe³⁺ can now be obtained on very small quantities of material, they cannot be obtained at a speed to compete with the microprobe analyser, and a problem for future research remains.

The electron microprobe has made accessible the observation of an amazing range of composition in micron-size and larger particles and it has revealed for the first time very fine-grained intergrowths, for example those due to exsolution in silicates. For these reasons it has become a major tool of petrological research, but its impact on pure mineralogy has also been significant. Up to 1969, Springer records that fifty new minerals had been described for which the electron microprobe furnished the analysis; some forty-three more had been added up to 1975 according to Reed. The fact that the technique is non-destructive has made it especially valuable in the analysis of meteorites and of lunar samples where each one may be unique and limited in quantity.

Trace-element analysis. Very large numbers of trace- and minor-element analyses of rocks

and minerals carried out by V. M. Goldschmidt and his associates during the 1930s were largely accomplished by means of optical emission spectroscopy. In 1944 E. B. Sandell published the first edition of his work on colorimetric determination of the metals, which has influenced terrestrial geochemistry and also the chemical investigation of meteorites. These and other methods, together with the major element data collected by F. W. Clarke (1924) and V. I. Vernadsky (1924), form much of the basis for our understanding of fundamental geochemistry as presented by Goldschmidt (1954), Rankama and Sahama (1950), and subsequent authors, including A. P. Vinogradov (1962). The massive revision of Clarke's *Data of Geochemistry* undertaken by the United States Geological Survey has brought together contributions by a very large number of authors, with new data from many parts of the world.

Among other methods capable of giving accurate data on small concentrations, two further developments in the past decade must be mentioned. Neutron activation analysis, using solid-state detectors, can often be applied to minerals and rocks without the need for other chemical treatment. The method provides a routine procedure for the rare earth elements down to concentrations of 10^{-3} $\mu\text{g/g}$; it has been used in studies of the platinoids, with determinations of Ir down to 10^{-2} $\mu\text{g/g}$; and using a fast (14 MeV) neutron generator, it makes activation analysis for oxygen and silicon possible.

The ion-probe technique has opened up new possibilities in selected-area analysis of minerals. The pioneer work of Castaing and Slodzian (1962) in France led the way to instruments, similar in concept to the electron probe, but giving images of ions, in the U.S.A. and U.K. A focused beam of primary ions impinges on the specimen, producing secondary ions, which are detected in a mass spectrometer. This gives increased sensitivity over the electron probe to concentrations down to 1 p.p.m. for a number of elements; it brings the light elements Be, Li, and B within range and it makes possible measurements of isotopic abundances in selected areas of a polished specimen (for example, Hinthorpe and Anderson, 1974). Considerable progress has been made in modelling the process of secondary ion production so that measured intensities can be interpreted in terms of concentration; but much remains to be done before the results are comparable in accuracy with those provided by the electron microprobe.

Radioactive methods. The rapid increase in nuclear science during this half-century has given rise to many new techniques of interest to mineralogists. The detection and measurement of radioactivity is achieved by means of Geiger-Muller, scintillation, and semi-conductor detectors. Multi-channel analysis systems applied to α , β , and γ spectrometers allow discrimination between naturally occurring radioelements. Autoradiography, though an old technique, has been improved by the use of new emulsions (Bowie, 1967). Following pioneer work at Harwell in 1958-9 a charged-particle track analysis technique was devised at the General Electric Laboratories, New York (Fleischer, Price, and Walker, 1975); here neutron-induced fission of uranium gives rise to trails of structural damage in polycarbonate plastic or natural mica detectors, from which quantitative estimates to 10^{-3} p.p.m. or below can be obtained. This technique may be applicable to thorium also. The whole field of track registration is still open to exploration, though notable results have already been obtained (for example, Kleeman and Lovering, 1967). Fission track dating is referred to later.

Isotopic mineralogy. Although some of the first work on the use of unstable isotopes for dating minerals was stimulated by Arthur Holmes, following his early work on U/Pb and Th/Pb ratios with Rayleigh, there was no capacity for geochronological work in this country until units in L. R. Wager's department at Oxford and at the Department of Geodesy and Geophysics at Cambridge were established with D.S.I.R. backing in the 1950s. Groups dealing with general geochronology have subsequently been set up at the Institute of Geological Sciences, London, at Leeds University, and at the Scottish Reactor Centre, East Kilbride.

The ratios $^{40}\text{K}/^{40}\text{Ar}$, $^{87}\text{Rb}/^{87}\text{Sr}$, $^{238}\text{U}/^{205}\text{Pb}$, $^{235}\text{U}/^{207}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, $^{40}\text{Ar}/^{39}\text{Ar}$ can be used between them to cover geological time from 4600 million years to 100 000. The ^{14}C method covers the period from present back to about 50 000 years. Advances during the past two decades in mass spectrometry and in trace-element determination make possible a precision of about 2 to 3% in favourable cases. Many common rock-forming minerals, formerly regarded as unsuitable, can now be dated. Crystallization dates can be assigned to minerals in igneous and metamorphic rocks, in recrystallized sediments, and to authigenic minerals in sediments. The timing of the mineral response to orogenic uplift can be derived, but orogenic belts may exhibit discordant cooling dates over a range of tens or even a few hundreds of millions of years. Geological interpretation of the discordant age-patterns has been one of the major advances in the past fifteen years. Where very slow cooling of deep-seated minerals has occurred, discordant dates may be obtained because of the differing times and temperatures at which particular minerals become closed systems. The introduction of Rb/Sr whole rock dating is another major advance since it makes it possible to 'see through' intense katazone metamorphism to the date of original formation of the rock. This is because, although radiogenic ^{87}Sr is lost by minerals like biotite and potash feldspar, adjacent plagioclase acts as a sink and traps it.

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ and lead isotope ratios have been shown (for example by Faure and Hurley, 1963) to yield direct information on the source regions of igneous magmas, whether from the upper mantle, from subducted oceanic lithosphere, or the base of the continental crust. The nature and degree of interaction between mantle-derived magmas and continental crust can also be investigated. This is a highly active field from which further progress may be expected in the future; see, for example, Moorbath (1975) on the evolution of Precambrian crust.

Determinations of the ratios between stable isotopes of certain elements in minerals began to become significant after the theory of isotopic fractionation was formulated by Urey (1947) and Bigeleisen (1949). The equilibrium constant in isotopic-exchange reaction (for example, of oxygen in carbonates) was shown to be temperature-dependent, so that the first outcome was a geological thermometer. At about the same time, A. O. C. Nier and his associates produced the mass spectrometry necessary to measure the small differences in stable isotope ratios involved. Palaeotemperature scales for carbonates were produced by McCrea, Epstein, and others, and Urey, all in 1950. Urey's work will be remembered particularly for his belemnite from the Isle of Skye, which experienced seasonal temperature changes of 6°C , lived for $3\frac{1}{2}$ years, and died in the Spring (Urey and others, 1951).

Oxygen geothermometry has been widely applied but a number of problems have arisen in interpreting results. The biggest growth-areas for stable isotope studies, using D/H, $^{12}\text{C}/^{13}\text{C}$, $^{16}\text{O}/^{18}\text{O}$, $^{28}\text{Si}/^{30}\text{Si}$, and $^{32}\text{S}/^{34}\text{S}$ have been in investigations of fluids—juvenile(?), modified connate, sea water, and rain water—involved in the genesis of minerals in rocks and ore deposits. The whole spectrum of water/rock interaction has been among the major areas of recent progress.

Mineral identification. Crystal morphology, colour, hardness, streak all form part of the mineralogist's stock-in-trade for first identification of crystals; optical properties, already well established for the non-opaque minerals, have now been systematized for the opaque minerals and are discussed below. The use of X-ray powder diffraction dates from Hull (1919) but it was first systematized by Hanawalt and Rinn (1936), whose work led to the A.S.T.M. Powder Data File (now J.C.P.D.S. Powder Diffraction File). This has become a routine tool in mineralogy, essential to clay mineralogy, vital to experimental mineralogy for the identification of phases. The counting diffractometer has improved performance over photographic recording, except where material is scarce, for powder photographs can be obtained from as little as 0.1 mg of mineral.

Clay minerals. The exceedingly small particle-size precluded investigation by normal mineralogical methods until the 1930s when L. Pauling elucidated the structure of the mica-type minerals as a layer lattice, and it was realized that the clays were crystalline species based on similar atomic arrangements, and not largely colloidal and amorphous, as was previously believed. In many cases there proved, however, to be a variable spacing in the direction of the *c*-axis, accounted for by internal adsorption of removable water and of exchangeable cations. By 1940 it had become possible to identify the members of the kaolin group, the montmorillonites and the clay micas (under the family name illite) and to recognize in the attapulgite (palygorskite)–sepiolite group linked chain structures establishing connections with the amphiboles and the zeolites. The electron microscope now began to afford the means of studying the morphology of clay particles, and by the 1960s the beam scanning technique had greatly improved the resolution. Recent improvements such as the ultramicrotome and the ion-beam thinning equipment now make it possible to undertake single-crystal work on clay particles *in situ*, and have led to the recognition of the mixed-layer character of many common clays. Differential thermal methods and, more recently, infrared analysis have also contributed usefully, especially to the study of less well crystallized clays and of mixtures.

In 1947 the inauguration of a Group within the Society devoted to clay research provided a needed common forum for the exchange of information and ideas between clay workers in different disciplines. Through its scientific programme, inter-Society gatherings and technical visits, by overseas contacts and by the publication of monographs and of the journal *Clay Minerals*, the Group has contributed in no small measure to progress in study of the complex inter-relations of structures and properties of clays. Its continuing vigour is demonstrated in the recent alteration of the status of the journal, which now becomes the quarterly organ of the Western European Clay Groups.

Opaque minerals. The determination of the opaque minerals under the microscope was systematized long after that of the transparent minerals; indeed some petrographers still continue to use the meaningless term 'ores' for these minerals in thin section and make no attempt to identify them. The qualitative approach to the opaques was refined as far as it could be by M. N. Short (1931, 1940), the basis of his system being etch, hardness, and microchemical tests carried out under the reflecting microscope. Reflectance, now accepted as the primary measurement, had to await the appearance of a good light source. The first collection of reflectance measurements was by Schneiderhohn and Ramdohr (1931) but these authors did not themselves use the values obtained in their book. In 1946 a punched-card system was devised by Fairbanks¹ that included reflectance data; Volinsky about the same time produced one in the U.S.S.R. Uytendogaardt in 1951 gave reflectance data but made polishing hardness his primary criterion. The quantitative period came only with the publication of Bowie and Taylor (1958), which used white light reflectance and microhardness as bases for the determination of 103 opaque minerals.² This break with the past has affected all new work subsequently published. The establishment of the Committee on Applied Mineralogy in 1963, which later became the Group, did much to foster the development of techniques in opaque mineral determination and was a motivating factor in the founding of the Commission on Ore Microscopy in 1964. This led to world-wide standardization and an increased flow of high-quality quantitative data. Significant contributions include Uytendogaardt and Burke (1971), Galopin and Henry

¹ This was used by him as a basis for naming after me (but without my agreement) an opaque mineral I had recorded from New Mexico (Dunham, 1935) but which I had left un-named for lack of adequate material. Dr. Spencer (1949) insisted that it be re-named microdunhamite, since it rested only on microscopical characters.

² These authors were unaware of a publication by Siebel (1943) in a German metallurgical journal, in which the use of microhardness was advocated; the publication remained unknown to mineralogists for a quarter of a century.

(1972), and Vyalasov (1973), the last-mentioned giving spectral reflectances of 224 opaque minerals. The Commission's own tables of spectral reflectances published in provisional form in 1970 are now available as a card index (1976). Also, the original suite of minerals of Bowie and Taylor have been remeasured at the four primary wavelengths of 470, 546, 589, and 650 nm (Bowie, Simpson, and Atkin, 1975). For future work it may be regarded as essential to separate clearly qualitative from quantitative data, to exploit fully the spectral reflectances, and to assign a quantitative meaning to mineral colour.

Experimental mineralogy

By 1926 the Geophysical Laboratory of the Carnegie Institution of Washington had already made considerable progress in investigating synthetic systems relevant to the genesis of rock-forming minerals. Experimentation required, of course, high temperatures, but work at high pressures was not yet within reach. The publication by N. L. Bowen of his *Evolution of the Igneous Rocks* (1928) was a milestone in these studies. In his chapter on crystallization in silicate systems, he was able to cite and illustrate results from seven binary systems (one with water) and five ternary systems. This work had a most important influence on petrological thought about magmatic differentiation during the next two decades especially in regard to the reaction principle (Bowen, 1922) and to fractional crystallization. In its turn, it was influenced by the observations of classical petrologists, like Alfred Harker in Skye (1904), H. H. Thomas and E. B. Bailey in Mull (1924). After World War II, the improvement in materials as a result of wartime development allowed experimentation under water pressure to begin, the first significant paper being that of Bowen and Tuttle (1949); nine years later came the paper on granite systems by the same authors. At about this time, experimental work on hydrothermal syntheses was begun by W. S. MacKenzie in W. A. Deer's department at Manchester; this subsequently received support from the Department of Scientific and Industrial Research, eventually evolving into an experimental petrology unit, which has grown under the Natural Environment Research Council. Special interests here have included the genesis of alkaline rocks and petrogeny's residual system; the partition of elements between mineral phases and melts, thermodynamic properties of silicates melting under pressure, and of multicomponent phases, among others. C. E. Tilley and R. N. Thompson carried out melting and crystallization experiments on natural basalts, and W. S. Fyfe during his years with the unit brought special interests in metamorphism and geochemistry.

A second experimental unit was set up at F. H. Stewart's instance at the Grant Institute of Geology, Edinburgh, in 1965 with N.E.R.C. financing and aid from industry and the university. Led by M. J. O'Hara, this began work with 1 bar equipment but quickly moved on to high-pressure fields, particularly those relevant to the upper mantle such as the partial melting of peridotites and related rocks. Work has also been carried on in the section $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-MgO-SiO}_2$ and other areas, too numerous to detail here. A report upon the two experimental laboratories was issued by N.E.R.C. in 1969. Although these are the largest groups in this country, experimental mineralogy is also carried on at a number of other universities; and it must be recalled that some industrial laboratories, notably those of the British Ceramic Research Association, have undertaken long-continued and extensive synthetic studies.

The paragraphs above represent, perhaps, a parochial point of view, for experimental studies of artificial systems, with or without obvious application to geological problems, continue on a world-wide scale. The latest summary (Levine, Robbins, and McMurdie, 1969) shows that altogether nearly 2000 systems have now been investigated. The appearance of the electron-microprobe analyser during the last decade has resulted in a flood of pressure/temperature information. At the same time it has to be recognized that few if any of the investigated systems

approach the complexity of even the simplest natural melt, so that a great area of work remains. It would not be appropriate to close this section without a further reference to the leadership provided by the Geophysical Laboratory throughout the half-century. Most of the leading men in the newer laboratories gained their first experience in Washington, or return there as collaborators.

Nor must it be forgotten that the art of synthesizing good crystals has made much progress. Examples include large quartz crystals for telecommunication purposes, fluorite for optical work, corundum (ruby), even the diamond.

For most earth scientists the main interest of experimental mineralogy lies in those areas where it can throw light on the natural minerals and their origins. Experimental work on partition of trace elements has already been mentioned; in natural rocks, partition of incompatible elements such as the rare earths may yield important evidence on the origin of magma types (Gast, 1968) and on the partial melting of the upper mantle (O'Nions and Pankhurst, 1974), to quote only two possible uses. In the course of experimental work, much-needed thermodynamic data is being obtained on many mineral reactions. The whole question of reaction rates is a field of mineralogical research that is expanding rapidly. It requires determinations of rate of diffusion of chemical species in minerals and magmas, quantitative rates of growth of minerals and times of solidification of magmas. Great advances could come from experimental investigation of solid state (*sic*) reactions such as those evidenced by prograde and retrograde metamorphism, and by metasomatic processes that also appear to have occurred in solid rocks. The post-depositional reactions that have affected the minerals of igneous rocks are equally of interest (for example, Henderson, 1975).

The introduction of water into experimental systems liberated them from the limitations of atmospheric pressure, but it is also yielding considerable evidence on the role of water in mineral genesis. Of potential equal importance is the effect of changes in oxygen fugacity. The first paper with experimental data was that of Osborn (1959), who discussed the implications for the basalts. The importance of this factor is nowhere shown more completely than in the lunar rocks, mentioned later.

Already at the beginning of the last decade, anvil-type experiments had been devised that enabled pressures up to 50 or 55 kb to be exerted on small quantities of material. During the past year, a remarkable development of this technique at the U.S. Bureau of Standards using diamond of gem quality for the anvil is claimed to bring 500 kb within reach of experimentation (A. L. Ma, 1975). This is the pressure expected at roughly 1000 km depth. Moreover, work at the Geophysical Laboratory and at the University of Rochester has applied laser-beam heating so that the sample can be heated to 2000 °C without affecting the anvil (Bell and Mao, 1975). Conditions in the lower mantle may thus be simulated with this apparatus. Already the B1-B2 change of state in NaCl at 300 kb has been observed and the whole development must be regarded as a very significant growing point for the future of mineralogy.

Genesis of minerals and rocks

Igneous and metamorphic minerals. So far I have dealt mainly with the technical innovations of the past fifty years, and particularly those of the years since World War II. They have been formidable and expensive; it is true to say that the applied physicist has revolutionized mineralogy and in doing so has opened up great new vistas in earth science. I now propose to refer to some of the principal results, of more than local importance, that have been obtained, but space and time dictate that these must be chosen very selectively. R. A. Howie (1967) has already reviewed a number of mineralogical topics that need not be repeated here.

As our half-century opened, the classic petrological studies of the Hebridean volcanoes by

the field mappers and petrographers of the Geological Survey of Great Britain were drawing to a close; starting with Skye (Harker, 1904), continuing with Mull (Bailey and Thomas, 1924), Arran (Gunn, completed by Tyrrell, 1928), Richey and Thomas's work on Ardnamurchan completed the cycle (1930). The combination of microscopical petrography with high-quality analysis had led to many interesting conclusions, not least to proposals for contrasting magma-types, with distinct differentiation trends.

A new chapter in petrology opened with the study by L. R. Wager and W. A. Deer of the layered basic intrusion at Skaergaard, East Greenland (1939), for here detailed mineralogy based on optical measurements became of first importance in establishing the cryptic variation (Wagner's term) from layer to layer, throughout the intrusion. It was now possible to study the detailed course of fractional crystallization of basaltic magma and to deduce the changing composition of the liquids. The original magma composition was known from the chilled margin of the intrusion. A strong trend towards iron-enrichment was established. The Skaergaard material was exhaustively investigated in subsequent years; for example the distribution of trace elements during fractionation (Wager and Mitchell, 1951), the iron-titanium oxides (Vincent and Phillips, 1954), the sulphides (Wager, Vincent, and Smales, 1957) all yielded interesting results. The Skaergaard studies stimulated interest in layered intrusions in many parts of the world and Wager's last work (Wager and Brown, 1967) gives a wide conspectus.

In the war years, in departments denuded of students, H. H. Read, Arthur Holmes, and Doris Reynolds pondered about the role of metasomatism in the origin of rocks such as the granites, not being satisfied that all or even most examples were products of fractional crystallization of basic magmas. Read's eight addresses (five were presidential addresses, but none unfortunately to this Society) brought together in 1957, give a remarkable survey of the world literature and showed that transformist ideas go far back in the history of petrology. The granite controversy, intentionally started by Read's earlier addresses, involved petrologists and mineralogists from many parts of the world, some impressed by the transitions from schist to gneiss to granite in the field; others by arguments from experimentation with silicate systems, though here there was (and is) no adequate data on quasi-solid-state reactions. The xenoliths in granites provide some of the most striking evidence (Reynolds, 1946). Fronts of alkali- or magnesia-enrichment were postulated, and 'basic behinds'. In the end, many agreed with Read's dictum that there are 'granites and granites', accepting an apparently unavoidable multiple hypothesis. What did perhaps emerge was a more general acceptance of partial melting of the crust, and a new interest in the subtle changes produced by metasomatism at all levels.

C. E. Tilley meanwhile, scornful of the granitizers, continued to produce beautiful work based on microscopical studies, high-quality analyses, and experimental systems, particularly directed to limestone syntaxis and the origin of alkali rocks (1952, 1954). The availability to him of borehole material from the Haliburton-Bancroft area, Quebec, led his interest to nepheline syenite gneisses and to his postulation of nephelinization (1958), a metasomatic process.

Without any disrespect to the people involved, we may I think regard those post-war years as the romantic period of petrology. They were followed, as the newer and more rigorous techniques came in, by a more severely practical approach. In this the Cambridge department, with its excellent workshops, gave a strong lead. Knowledge of the rock-forming minerals has greatly increased; to take only one example, the feldspars were the subject of an advanced study institute in Oslo in 1962, the 606-page publication from which involved 49 leading mineralogists as authors (Christie, 1962).

Studies of granites, alkali rocks, even of the feldspars, taken in conjunction with volcanic and mineralizing processes, have all given increased importance to the roles of fluids and volatiles.

In recent years a quantitative approach to this problem has begun to emerge, based upon direct observations of eruptions and their associated gases and sublimates, upon the evidence from fluid inclusions in minerals and upon experimental work using controlled vapour phases, as well as the detailed evidence of petrography and mineral chemistry. It now appears that small mass-ratios of vapour:solid profoundly affect rock melting and the chemistry of the melts. Some of the major differences between, for example, basalts, andesites, and nephelinites may be a function of vapour composition during magma genesis, and variations within the groups may, as already noted, reflect change in activity of oxygen. At appropriate temperatures, influx of volatiles into volatile-deficient rocks may produce melting without change of temperature or pressure, a mechanism that could be significant in regions of mantle degassing.

Turning to the less extreme changes comprehended by metamorphism, inability to experiment at high pressures limited the impact of experimental work here until the 1950s, although some contact-metamorphic studies had been interpreted in terms of subsolidus data (Tilley, 1924) and successfully tied in with Eskola's facies concept (1921, 1939). The dominant influence, however, was that of Harker (1932) in emphasizing interpretation of textures and progressive metamorphism, and Bowen (1940) in showing how decarbonation and dehydration sequences could be analysed. The somewhat standardized metamorphic sequences proposed by these authors came under attack in the decade after the war, leading to Myashiro's enunciation of the facies concept tied to geological environment (1973).

Partition of elements between coexisting metamorphic minerals, providing they were formed under near equilibrium conditions, may form an important aspect of facies investigations. For example the ratio $Mg/(Mg+Fe+Mn)$ in coexisting biotite and garnet shows a linear relationship for a given grade, the partition coefficient linking the two values being a function of temperature and pressure (Atherton, 1968). Partition data may in many cases be regarded as having verified the basic assumption of equilibrium but there are instances, for example when zoned porphyroblasts are found, when partitioning in terms of interface equilibrium has to be considered.

Extrapolation from experimental systems and thermodynamic data to ascertain temperatures and pressures under which natural minerals in igneous and metamorphic rocks formed is a research area of growing importance. Torgeson and Sahama (1948) measured heats of formation of forsterite, enstatite, and wollastonite; the compilations of Kelley (1960) and Robie and Waldbaum (1968) show how rapidly new data came forward up to 1968. Meanwhile the simple systems $MgO-SiO_2-H_2O$ (Bowen and Tuttle, 1950) and $MgO-Al_2O_3-SiO_2-H_2O$ (Yoder, 1952) enabled some important metamorphic reactions to be calibrated, while the systems diopside-enstatite (Davis and Boyd, 1966) and enstatite-pyroxene (Boyd and England, 1963) are of special interest for geothermometry and geobarometry. The last-mentioned system has recently been used to define a 'fossil geotherm' for the source-region of inclusions of lherzolite in kimberlite penetrating the African Shield (Boyd, 1973). The most widely used geothermometer so far, however, has been the coexisting iron-titanium oxides (Buddington, Fahey, and Vlisidis, 1955), used in connection with oxygen data for barometry.

Finally among petrological topics, some reference must be made to the contribution of mineralogists to the international Upper Mantle Project. The sole direct means of ascertaining the nature of the rocks composing the upper mantle lies in the inclusions brought up by kimberlite pipes. These strongly suggest that the upper mantle is not homogeneous. Three broad groups of rocks occur: in order of decreasing abundance, peridotites and pyroxenite, eclogites, and granulites, but there are many variations within these groups. The first group includes chromite-harzburgite and garnet-lherzolite (only the second of these could produce basalt in quantity by partial melting). The wide variation of enstatite in solid solution in the

clinopyroxenes of the lherzolites suggests equilibration over a wide temperature range. This is also true of the eclogites, as determined by partitioning of Mg/Fe between garnets and pyroxenes. The diamond-bearing eclogites, formed at more than 150 km depth, carry garnets with small amounts of Na₂O and pyroxenes with small amounts of K₂O; interesting features when the storage of alkalis in the mantle is considered. The granulites—less common than the other groups, but widespread nevertheless—appear to lie mineralogically on the pressure gradient between eclogite and gabbro, and may therefore form a zone within the lowest part of the crust or the highest part of the mantle. They contain plagioclase in addition to ferromagnesian and may also have scapolite and potash feldspar. The ultrabasics, in addition to magnesian olivine, orthopyroxene, and chromite, contain clinopyroxene, pyrope, phlogopite, with minor sulphides, diamond, graphite, moissanite, and rutile, kyanite, and corundum in some eclogites. At present, Dr. J. B. Dawson tells me, there is an apparent gap in the stratigraphy of the upper mantle, with no rocks corresponding to temperature and pressure expected between 35 and 100 km depth; this zone may, however, be represented by dunitic rocks unsuitable for geothermometry. Lherzolites, with some eclogites, predominate below 100 km, but there is little doubt that the mantle is not homogeneous (Hutchison & others, 1970, 1975). The earlier work, for example by P. Wagner, A. F. Williams, and A. Holmes was on South African material, but the discoveries of kimberlites in Siberia have added considerably to recent research (for example, V. S. Sobolev, 1959). As already noted (p. 16), experimentation may soon be able to simulate conditions deeper than the deepest source of kimberlites. On the degassing of the mantle, the carbonatites and associated alkali volcanics have been held by some investigators to provide significant evidence. These rocks are of great mineralogical interest; names associated with work on them include Harry von Eckermann, Frank Dixey, K. A. Davies, Tom Deans, M. S. Garson, B. C. King, W. Pulfrey, and S. J. Shand (Campbell Smith, 1956).

Pegmatite and ore minerals. Returning now to the continental crust, the residual system in granitic rocks is now much better known as a result of experimental work, and simple pegmatites correspond well with expected compositions. Field studies have failed, however, to reveal a direct linkage between pegmatites and mineral veins in all but a few rare cases, and it can be argued that the volatiles that became concentrated to produce the late suite of beautiful minerals in complex pegmatites had little to do with metal concentration in general.

Study of the origin of ores has benefited not only from the fast-developing metalliferous mining industry, but also from the improved techniques in the laboratory; as a result of both, there has been a revolutionary change in thinking. Fifty years ago the accepted orthodoxy was the juvenile-hydrothermal hypothesis, which relates all ore concentration, save that due to secondary processes, to igneous activity and postulates concentration of the metals in the residua, mainly of granites. Only a few voices, like Crook (1933) were raised against it. Where the parent igneous rocks were not visible at surface, or within range of mining, they were believed to lie concealed in depth. A test of this became possible in the northern part of the English Pennines, where the lead-zinc-fluorite-baryte-witherite deposits had been shown to be systematically zoned in a lateral sense (Dunham, 1934), corresponding with the outer zones in south-west England (Dines, 1956). A gravity survey (Bott and Masson Smith, 1957) had given *a priori* evidence of granite concealed beneath the inner zones, and a borehole proved its presence; but it was found to pre-date the Carboniferous host-rocks of the mineral field, and could not therefore be its direct source (Dunham and others, 1965). Three main lines of advance in explaining ore deposits not obviously grouped around igneous sources have come from fluid inclusion studies, and from isotopic studies of water and of sulphur. The fluid inclusions (Ermakov, 1965; Roedder, 1967) provide palaeotemperatures and evidence that the mineralizing solutions were brines, with up to six times the salinity of sea water. The D/H

and $^{16}\text{O}/^{18}\text{O}$ measurements have failed to prove the existence of juvenile water in fluid inclusions or associated with ore deposits (D. E. White, 1974), though some contribution from magmatic water often cannot be ruled out. The sulphur isotopes in many cases point to a biogenic or sea-water source rather than to primary sulphur (M. L. Jensen, 1967). The mineralizing fluids may have started as rain or sea water and acquired their high salt concentrations by membrane filtration, base-exchange reactions, or solution of evaporates. The solubility of metals in chloride- or sulphide-complexed form makes the chemistry of the mineralizing process easier to understand (Helgeson, 1964). Ore mineralization may be independent of igneous activity if the heavy brines sink to great depths in the crust and are then driven back under tectonic pressures; in this case the source of the metals is the trace quantities in the rocks through which the solutions passed. Igneous activity may contribute only heat; or granites may perhaps incorporate groundwater from sediments they invade or from which they are formed by anatexis and so produce hydrothermal end-products.

The techniques of mineralogical investigation already mentioned have had a great impact on the study of polycomponent ores with associated complex alteration. This is particularly the case with the 'porphyry' copper deposits (Lowell and Guilbert, 1970) where the recognition of zoned alteration with potash feldspar passes upward and outward through several stages to an outer fringe of argillic products. The problem of the stratiform and concordant base-metal deposits has been widely discussed. Some of them can now be identified as submarine spring deposits, associated with volcanic activity, for example the 'kuroko' ores of Japan (Tatsumi, 1970) and this may well be how many of the massive sulphide lenses in Palaeozoic and pre-Cambrian rocks originated before metamorphism. The concept is far less satisfactory when biogenic limestones are the host rocks. In mineralized shales like the Kupferschiefer, addition of mineralizing brines to sea water, as appears to be happening in the bottom of the Red Sea, may have been the explanation. The mineralogy of uranium deposits, poorly known until the 1940s, has probably made the most progress, yielding almost 200 species of radioactive minerals.

Thermodynamic methods are now beginning to make an impact on the chemistry of ore formation (Holland, 1965) and on the study of ore textures (Stanton, 1964), but notwithstanding the experimental studies of sulphide systems (for example, Kullerud, 1964) the experimental approach to the deposition of complex mineral assemblages from hot brines has hardly yet begun. It should offer a fertile field for the future.

Mineral genesis in sediments and evaporites. The aqueous phase likewise receives considerable emphasis in recent work on sedimentary mineral assemblages. W. C. Krumbein and R. M. Garrels (1952) have played a fundamental role in the application of redox and hydrogen ion data. The development of quantitative models for sedimentary processes are beginning to be possible in the light of chemical kinetics. Equilibrium and steady-state models for the oceans are also being attempted in which the composition of ocean water is regulated by mineral equilibria and the rate of addition of elements by rivers is balanced by authigenic mineral formation.

Among the deposits formed from the evaporation of sea water, the physical chemistry was long ago worked out by van t'Hoff; but modern work has shown how numerous are the mineralogical transformations that take place during their evolution (Stewart, 1949, 1951; Armstrong, Dunham, and others, 1951). The recognition of the significant part played by deposition under sabhka conditions (Shearman, 1966) also throws new light on evaporite genesis.

Cosmic Mineralogy

Meteorites. The mineralogy and metallurgy of meteorites has been a recurring theme in the *Mineralogical Magazine*, thanks among others to the distinguished work of the officers of the

British Museum (Natural History). Among the most interesting are L. J. Spencer's descriptions of the material from the meteorite craters of Henbury (Australia) and Wabar (Arabia) (1933), including not only iron but silica glass formed under conditions such as to suggest strongly that the silica had boiled and exploded, implying a temperature of the order of 3500 °C.

Among recent falls, that of a type III-V carbonaceous chondrite at Allende, Mexico, deserves mention. Over 1000 kg was recovered, the rock proving to be a stony meteorite in which inclusions of melilite, perovskite, anorthite, Ti-rich pyroxene, and spinel, and grains of forsterite and enstatite occur with chondrules in a low-temperature matrix of iron-rich olivine. The mineralogy of the inclusions corresponds with that predicted for the earliest high-temperature condensates of a gas of solar composition, indicating that this meteorite might be from some of the oldest material in the solar system. Among the meteors, observations of various kinds of spectra has shown that some produce emission lines from Ca, Al, Mg, and Si, but not for Fe and Na; these might therefore be similar to the refractory material in the Allende fall. Further, the oxygen in anhydrous high-temperature minerals of the Allende meteorite and some others is peculiar is being strongly depleted in the heavy stable isotopes ^{17}O and ^{18}O , probably resulting from very early admixture of almost pure ^{16}O . This component, according to Clayton, Grossman, and Mayeda (1973) may in fact pre-date the solar system.

The existence of impact craters on the earth means that a special class of facies of terrestrial metamorphism needs to be recognized, an impact facies. Evidence of shock metamorphism in the meteorite itself can also be recognized (Baldanza and Levi-Donati, 1971).

Lunar mineralogy. Since the first manned landing on the moon on 25 July 1969, almost 386 kg of lunar rock fragments have been returned to earth. The mineralogy of the moon is essentially that of a huge igneous complex subjected to bombardment by meteorites. There are no sediments or equivalent metamorphics, and hydrous alteration is absent. As a result of the moon's simple history, only about 60 minerals have been recognized (compared with about 2200 on earth). Several groups are common to earth and the major division of the lunar crust into primitive highlands and mare basins corresponds in simplest terms to a division into plagioclase-rich cumulate rocks and plagioclase-pyroxene basalts. The plagioclases are calcic (often with An greater than 90) while the pyroxenes span the common diopside-hedenbergite-enstatite-ferrosilite quadrilateral but include metastable phases such as the new mineral pyroxferroite. Silica also occurs metastably as cristobalite or tridymite, sometimes with Mg-olivine. A low oxidation state is indicated by the absence of ferric iron from any mineral and the presence of nickel-iron and troilite; low-valency state cations enter into crystal structures. In the basaltic mesostasis area, minerals include tranquillityite (new), (zirconolite = zirkelite) and whitlockite, all carrying rare-earth elements. Most basalts carry a new iron-titanium-rich oxide, armalcolite. The whole lunar mineral assemblage, including impact and base surge breccia areas, has been documented by Judith W. Frondel (1975). The minerals hold the key to much of the moon's history; it was frozen at least 3000 Myr ago, and its feldspathic crust was formed over 400 Myr ago. Many interesting comparisons with the earth are possible.

Applied mineralogy

Although the crystalline phases found in man-made materials such as refractories, slags, ceramics, cement, and sinters are not, according to the strict definition, minerals, the same techniques of investigation are applied to them and the distinction between natural and artificial is here regarded as merely academic.

Refractories and slags. Here the uses depend more on physical properties in the refractories and chemistry in the slags than on mineralogy. The literature of slags is relatively sparse, the next notable contributions after J. H. L. Vogt's early work being by Agrell (1945) on basic

steel-making slags and Nurse and Midgeley (1953) on blast-furnace slags. A number of species are found such as the wüstites and ferrites that are rare or absent in natural rocks. The refractories have been much more extensively studied, especially for their physical properties at high temperature (for example, Insley and Frechette, 1955; Chesters, 1963).

Ceramics. Whereas the mineralogical techniques available in the 1920s were of little value to the ceramist, who has very fine-grained materials to deal with, modern equipment has changed the outlook. X-ray diffraction enables the mineral phases to be identified, and by its use the thermal expansion in various crystallographic directions can be studied. The amounts of phases, for example of silica, can be estimated. Phase transitions, lattice defects, and particularly the investigation of glass ceramics has been made possible by electron diffraction, and the scanning electron microscope is beginning to find useful applications. Reflected light techniques have been found to be well suited to the study of the mineralogy and microtextures of refractories.

Cement. Portland cement, which remains the predominant construction material, consists in the anhydrous state of four phases, all solid solutions, based on $3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$; to these a proportion of gypsum is added to control the set. The chemistry of clinker formation in terms of high-temperature phase equilibria is reasonably well understood but much remains to be done in assessing the roles of impurity atoms, which are always present. The crystal structure of the phases has been worked out, mainly in the late J. D. Bernal's laboratory. Fast hydration of the phases leads eventually to five hydrated solid phases including a hydrogarnet, a calcium sulphoaluminoferrite, and a calcium sulpho-hydroxyaluminate hydrate. However, the heart of the concrete is a colloidal gel, on which much research is proceeding. Other research aspects of present interest include the effect of adding glass fibres to the cement and the failure of certain quick-setting high-alumina products.

Sinters, coal, and coke. Since 1945 a major effort in applied research has been the sintering and pre-treatment of iron-ore pellets to improve furnace efficiency. This has involved highly detailed study of the ores and artificial products. In this country, the British Iron and Steel Research Association, and Professor W. Davies and his associates have been prominent. Mineralogical techniques, especially reflected-light microscopy, have also contributed to the understanding of coal petrology and coke structure.

The Society and the future

Learned societies exist to promote the discipline they represent by encouraging communication between their members. This may take the form of holding meetings, publishing journals or abstracts, and perhaps, in the future, it may involve the use of other methods of data storage and processing. The quality of any society depends upon its membership, its officers, and those who serve it. In the last respect, the Mineralogical Society has been particularly fortunate in its century of existence, which has included Dr. L. J. Spencer's outstanding performance as Editor of the *Mineralogical Magazine* for the 55 years from 1901 to 1956, a period during which he made it, single-handed, one of the best journals of its kind. It must not be forgotten that we have also been very fortunate to have Dr. Max H. Hey for twenty years as Principal Editor of the Magazine, carrying it on, and introducing the new format. *Mineralogical Abstracts*, founded by Dr. Spencer as part of the Magazine, has grown and prospered under the care of Dr. Phemister, Dr. Henry, and Professor Howie, and is now the part property of the Mineralogical Society of America. We have also been fortunate in the Society's trustees, and it is difficult to believe that it can come to much harm while it can attract men as responsible as Sir Henry Miers, F. N. Ashcroft, C. E. Tilley, W. Campbell Smith, J. H. Taylor, Sir Frank Claringbull, and B. R. Young.

During the century, 154 new mineral species (not all valid) have been described in the pages of the Magazine, or about 7% of the known species. With the very sensitive equipment now available, the metastable condition has become accessible for investigation and we may expect an increasing amount of mineralogical work to be devoted to it, as J. D. C. McConnell (1971) has described. Perhaps it is permissible to wonder whether a new revolution in the subject, such as began the era discussed in this address, is approaching. Certainly there are many exciting lines of earth science in which mineralogy is central: the lower mantle, the upper mantle; crustal differentiation and mineralization; pre-cosmic dust and the materials collected from planets, to name only a few.

Specific topics which have emerged in the course of this address have included: the production of direct images of atomic structure; the identification of replacement sites by E.S.R.; the development of multi-channel atomic-absorption equipment; improvement of Mössbauer or fast neutron activation for oxidation-state determination as a counterpart to microprobe analysis (or better still, some method of determining oxidation state on the microprobe); partition of trace elements in magmatic, metamorphic, and mineralizing processes; implications of the distribution of ^{87}Sr and other isotopes, and further development of stable isotope studies, especially of oxygen; water/rock relationships at all levels; experimental mineralogy applied to the mantle, the cosmos, and the practical problems of everyday life.

It may well be that in addition to the three successful Groups already organized within the Society (Clay Minerals; Applied Mineralogy; Geochemistry) others may need to be added, but I express the hope that not too much fragmentation will take place into narrow specialisms; we have too much to gain from one another.

On the international front, in addition to our close link with the American Mineralogical Society, we organize joint meetings with our European colleagues, particularly in France and West Germany, and maintain wider contacts through the International Mineralogical Association. Perhaps the future may see a strengthening of the ties between the old societies, like ours, in Europe, but I doubt if any of them are yet anxious to lose their identities in a pan-European Mineralogical Society. At the present stage in history, cordial relations but not total merger seems to me to represent the order of the day.

Acknowledgements. In preparing this review, I have been fortunate to have advice and, in some cases, written notes from the following members of the Society, experts in their own fields: S. O. Agrell, M. P. Atherton, D. K. Bailey, J. A. Bain, I. R. Basham, R. D. Beckinsale, S. H. U. Bowie, B. C. M. Butler, G. M. Brown, G. A. Chinner, C. D. Curtis, J. B. Dawson, A. C. Dunham, H. Elderfield, C. J. Elliott, D. C. Goldring, C. Halls, P. Henderson, N. F. M. Henry, R. A. Howie, R. Hutchison, J. V. P. Long, A. J. Majumder, W. S. MacKenzie, S. Moorbath, A. H. Rankine, J. A. T. Smellie, R. F. Symes, D. Taylor, E. J. W. Whittaker, and B. J. Wood. I am most grateful to them all but must add that any mistake of fact or emphasis is to be ascribed to me, not to them. I also wish to thank the Principal Editor and the General Secretary of the Society for their invaluable aid.

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