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MINERALS, MINERALOGY AND MINERALOGISTS: PAST, PRESENT AND FUTURE*

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ABSTRACT

Minerals are the basic materials of the Earth, and virtually everything one does in the Earth Sciences involves minerals in one way or another. Minerals furnish a good part of the wealth that is the basis of our society, not just as commercial products but as the soils that support our agriculture and the aquifers that hold our water supplies. Minerals have played a key role in the development of humanity. One of our first scientific acts was to distinguish between different rocks and minerals, and use them as tools according to their properties. With the widespread development of mining and trade, it became important for people to recognize minerals, and writings on mineral recognition and properties were common in many societies: China, Greece, Rome, Persia, Arabia, Italy, Germany.

Extensive chemical work on minerals began in the late 18th century, resulting in the development by Berzelius of the "anionic" classification of minerals. The development of crystal-structure analysis had a major effect on Mineralogy; the work of W.L. Bragg gave an atomistic basis for our knowledge of mineral chemistry and properties, and the work of V.M. Goldschmidt gave a theoretical basis for the behavior of elements in geochemical processes. The last 30 years has seen a flood of new techniques into Mineralogy: electron-microprobe analysis and crystal-structure refinement were followed by numerous spectroscopic techniques, many new microprobe methods for both elemental and isotopic analysis, and both scanning and transmission electron microscopy. The immense amount of data stimulated the development of Theoretical Mineralogy. Atom ("ionic") and electron ("covalent") models are now capable of accurately calculating stereochemical details and a wide array of physical and dynamic properties. The first steps to understand the thermodynamic basis of element ordering, element exchange and mineral reactions have now led to geothermobarometers capable of determining equilibration conditions to $\pm 25^\circ\text{C}$ and ± 1 kbar. Recent initiatives in surface mineralogy have been encouraged by the importance of surface properties of minerals in environmental problems.

Mineralogy permeates every facet of Earth Sciences, and reaches out to many contiguous areas in Physics, Chemistry and Materials Science. Unfortunately, this great diversity has adversely affected the general view of Mineralogy within the Earth Sciences: many Earth Scientists are not conversant with the breadth and intellectual vitality of current work in Mineralogy. With pressure on University budgets, both from decreasing Government support and from the development of important new areas (e.g., Environmental Sciences), there is a danger that Mineralogy will be discarded as a specific core discipline of Earth Science research and teaching. If Mineralogy is taught haphazardly as parts of the other subdisciplines in Earth Sciences, students will not develop a feel for the diversity of minerals and their behavior in the wide variety of terrestrial environments. The end result will be a generation of Earth Scientists who lack fundamental understanding of the materials with which they work, and who will be incapable of adapting to new areas of expansion within and peripheral to Earth Sciences. It is up to Mineralogists to prevent this from happening.

Keyword: Mineralogy.

* Presidential address delivered at Wolfville, Nova Scotia on May 26th, 1992.

SOMMAIRE

Les minéraux constituent les matériaux de base de la terre; d'une façon ou d'une autre, les activités de tout géoscientifique gravitent autour des minéraux. Ce sont les minéraux qui fournissent une partie importante de la richesse qu'est le fondement de notre société, non seulement sous la guise de produits commerciaux, mais aussi comme constituants des sols qui supportent notre agriculture et des couches aquifères qui contiennent les ressources d'eau souterraine. Les minéraux ont joué un rôle-clé dans le développement de l'humanité. Un des premiers gestes scientifiques a été la discrimination parmi les différentes roches et minéraux, afin de mieux choisir les matériaux propices à la fabrication d'outils. Avec le développement de l'industrie minière et des échanges commerciales, il s'est avéré important de reconnaître les minéraux. Aussi, les écrits sur les caractéristiques et les propriétés des minéraux ont-ils été courants dans plusieurs sociétés, en Chine, en Grèce, en Perse, en Arabie, en Italie et en Allemagne, à titre d'exemples.

L'étude de la chimie des minéraux a débuté vers la fin du dix-huitième siècle; de telles études ont mené au développement de la classification "anionique" des minéraux par Berzelius. La possibilité de déterminer la structure cristalline des minéraux a eu un effet majeur sur la Minéralogie. Les travaux de W.L. Bragg ont donné une base atomiste à nos connaissances de la composition chimique et des propriétés des minéraux. Les travaux de V.M. Goldschmidt ont fourni la base théorique du comportement des éléments dans les processus géochimiques. La dernière trentaine d'années a vu une flopée de techniques nouvelles en Minéralogie: la possibilité d'effectuer des analyses à la microsonde électronique de minéraux et d'en affiner la structure cristalline a été suivie par de nombreuses techniques spectroscopiques, avec plusieurs méthodes nouvelles d'analyses par microsonde pour déterminer soit la teneur des éléments ou les rapports isotopiques, et la microscopie électronique à balayage et par transmission. La quantité immense de données nouvelles a stimulé le développement de la Minéralogie théorique. Des modèles atomiques ("ioniques") et électroniques ("covalents") sont maintenant capables de calculer les détails stéréochimiques et un éventail imposant de propriétés physiques et dynamiques. Les premières ébauches d'une compréhension de la base thermodynamique de la mise en ordre des éléments, de leur échange, et des réactions parmi ces minéraux ont permis de formuler des géothermobaromètres capables de déterminer les conditions d'équilibre à 25°C et à 1 kilobar près. Des initiatives récentes dans l'étude des surfaces ont été entreprises à cause de la grande importance des propriétés des surfaces dans les problèmes de l'environnement.

La Minéralogie influence profondément chaque aspect des sciences de la terre, et elle établit des liens avec les domaines contigus en physique, chimie, et science des matériaux. Malheureusement, cette grande diversité a exercé un effet négatif dans l'opinion qu'ont plusieurs à propos du rôle de la Minéralogie dans les sciences de la terre. Plusieurs géoscientifiques ne sont pas bien renseignés à propos de l'envergure et de la vitalité intellectuelle des travaux courants en Minéralogie. Avec les compressions budgétaires dans nos universités, à cause d'une diminution dans les octrois gouvernementaux et du développement de domaines nouveaux, comme par exemple les sciences de l'environnement, je perçois un danger que la Minéralogie sera rayée de la liste des disciplines essentielles dans l'enseignement et la recherche en sciences de la terre. Si on enseigne la minéralogie de façon aléatoire comme partie d'autres sous-disciplines dans les sciences de la terre, comment les étudiants pourront-ils apprendre à propos de la diversité des minéraux et leur comportement dans une variété de milieux terrestres? Il en résulterait, éventuellement, une génération de géoscientifiques qui ne possèdent pas une maîtrise des matériaux qu'ils étudient, et qui sont incapables de s'adapter aux nouvelles disciplines au sein des sciences de la terre et dans les domaines pluridisciplinaires connexes. Il incombe aux minéralogistes de faire les démarches nécessaires pour contrer cette évolution néfaste.

(Traduit par la Rédaction)

Mots-clé: Minéralogie.

INTRODUCTION

Many years ago, I was an undergraduate in Geology at the Royal School of Mines in London. I remember that minerals and their recognition were emphasized from the start of the undergraduate program, and this continued through to the end. The message was simple: *if you can't recognize minerals, you won't find mines!* Mineralogy was emphasized as one of the core disciplines of Geology, what today is more fashionable to call Geological Sciences. It has always been surprising to me that Mineralogy receives much less attention in the Earth Sciences curricula of North America, as *minerals are the basic materials of the Earth* (and planets), and furnish a good proportion of the wealth that supports our society.

THE CENTRAL ROLE OF MINERALOGY
IN THE EARTH SCIENCES

The central role of Mineralogy in the Earth Sciences is illustrated schematically in Figure 1. There are many more branches of the Earth Sciences that could be included (*e.g.*, geochemistry, paleontology, geochronology), and toward the end of this article, I will mention the role of Mineralogy in some of the less traditional areas of the Earth Sciences (*e.g.*, Environmental Sciences, Atmospheric Sciences). However, the subset of topics in Figure 1 is sufficient to make the point that virtually everything one does in the Earth Sciences involves minerals in one way or another.

In Petrology, be it igneous, sedimentary or metamor-

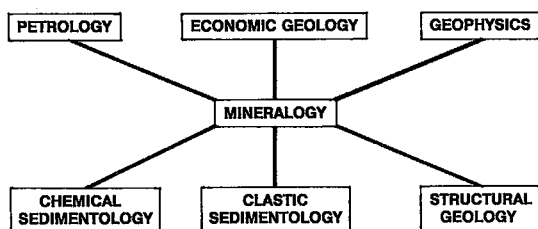


FIG. 1. The central role of Mineralogy in the Earth Sciences.

phic, one looks at the minerals in the rocks. The petrologist determines the major- and trace-element compositions of the minerals, either directly by electron-, ion- and PIXE-microprobe analysis, or indirectly by petrographic methods, cathodoluminescence or epifluorescence microscopy; chemical zoning is characterized, and both stable- and radiogenic-isotopic characteristics are measured. Physical parameters such as grain shape, roughness and fractal dimensions of grain boundaries are measured. Nearly all of these characteristics are properties of minerals, and the intrinsic structure of the minerals constrains their variation just as the petrogenetic conditions promote their variation. Without understanding the relative roles of these two factors in influencing mineral composition, we constrain ourselves to imperfect models of petrogenetic processes. Likewise, the role of fluids within rocks hinges on the details of the surface structure and chemistry of minerals (possibly moderated by biofilm activity in many environments), and if we are ever to develop mechanistic models of fluid-rock interactions, a knowledge of the surface structure and properties of minerals is essential. Note that we have discussed Petrology as a single topic rather than dividing it up into its traditional subdivisions. Historically, there was often a tendency for a mineralogist to be associated with one specific area of Petrology, to the ultimate detriment of Mineralogy as a separate discipline. Mineralogists are interested in minerals and their behavior, and this interest thus pervades *all areas of Earth Sciences*. There is nothing to stop a mineralogist being simultaneously interested in the properties of $(\text{Mg,Fe})\text{SiO}_3$ perovskite, the dolomite problem, and the staurolite problem; such a catholic range of interests would be considered bizarre in a petrologist, but such a wide range of interests on the part of a mineralogist can lead to important cross-fertilization between subdisciplines.

In Economic (or ore deposits) Geology, one looks at both ore and gangue minerals with the methods and scientific motivation of the petrologist. Additional factors come into play in terms of resource evaluation and

exploitation, but again Mineralogy has its part to play in designing optimum processes of ore beneficiation and extraction. In Geophysics, one is concerned with the physical properties of minerals. The elastic properties of minerals are of interest to the seismologist, and the magnetic properties of minerals are of interest to the paleomagneticians; this parallelism of interests is apparent in the current cooperative effort of geophysicists and mineral physicists on studies of the Earth's mantle and core. In Physical Sedimentology, the behavior of minerals is governed to a large extent by their physical properties. In Chemical Sedimentology, the dissolution and crystallization of soluble minerals are of primary interest; details of chemical composition, zoning, crystal morphology and habit, paragenetic sequence and relative stability fall directly within the realms of Sedimentology and Mineralogy. In many aspects of Structural Geology, one is concerned with the physical (and chemical) properties of minerals; such contrasting characteristics as brittle deformation and creep can vary radically from one mineral to another, and can be very anisotropic within single minerals. The relationship between structure and properties, and the way in which these changes with pressure and temperature, fall both within Structural Geology and Mineralogy.

Thus Mineralogy is a core discipline within Earth Sciences; the more one knows about minerals, the better Earth Scientist one will be, no matter what one's individual specialization.

MINERALS IN PREHISTORIC TIMES

It is no accident that we date the prehistory of humanity by the materials with which our predecessors made their tools. Tools are one of the more enduring creations of prehistoric humanity, and they document

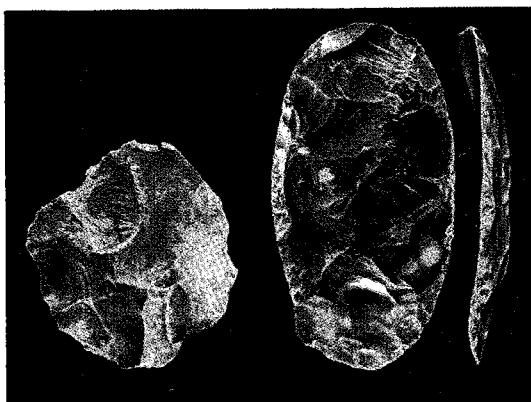


FIG. 2. Stone-age artifacts of flint and obsidian.

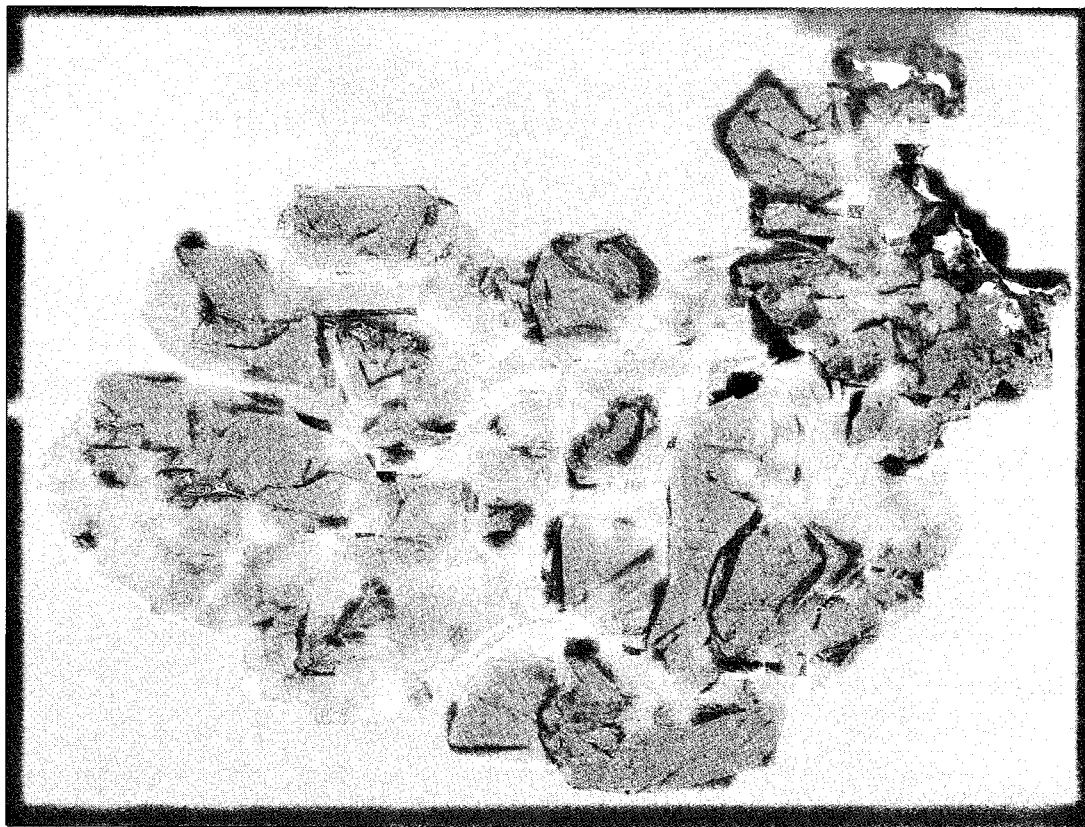


FIG. 3a. Naturally occurring native copper.

increasing technological sophistication. One of our first scientific acts was to distinguish between different rocks and minerals, and use them as tools according to their properties.

"Stone" and the Stone Age

Our early ancestors were vegetarians. With the advent of Cromagnon Man and Woman, our ancestors became omnivorous (with the addition of meat to their diet). The use of tools was an essential adjunct to this change, and spear points, knives and scrapers were developed. The suitability of certain materials for these purposes was realized very rapidly, and obsidian and flint became widely used (Fig. 2). As humanity began to work natural materials, further advances became inevitable. One can picture a skin-clad troglodite on the chalk downs of England (perhaps an ancestor of Roger Mitchell) picking up a heavy pyrite nodule to break a flint into smaller more workable pieces; fire was widely started by striking pyrite with flint. Naturally occurring poisons such as arsenic were known and used. Toward the end

of the Neolithic period, approximately 40 different rocks and minerals were in common use.

Metals and the Bronze Age

The first metals to be used were the naturally occurring native metals (Fig. 3). These were greatly sought after by Stone Age humanity, but for their curiosity and ornamental value rather than for tool-making. The natural metals are all too soft for tools, but could be cold-worked into ornaments and jewelry. Iron, in particular, was greatly prized for its rarity, as it was only known from meteorites – the "Heavenly Metal" of the Sumerians.

Around this time, someone discovered that heating metals greatly promotes the ease with which they can be worked. It is probable that this discovery soon gave rise to the technique of smelting, whereby a mixture of copper ores gave native copper on heating. This is almost certainly the origin of the discovery of bronze; heavy metallic or semimetallic minerals were heated to extract the "copper", but in fact gave bronze. Early bronze was

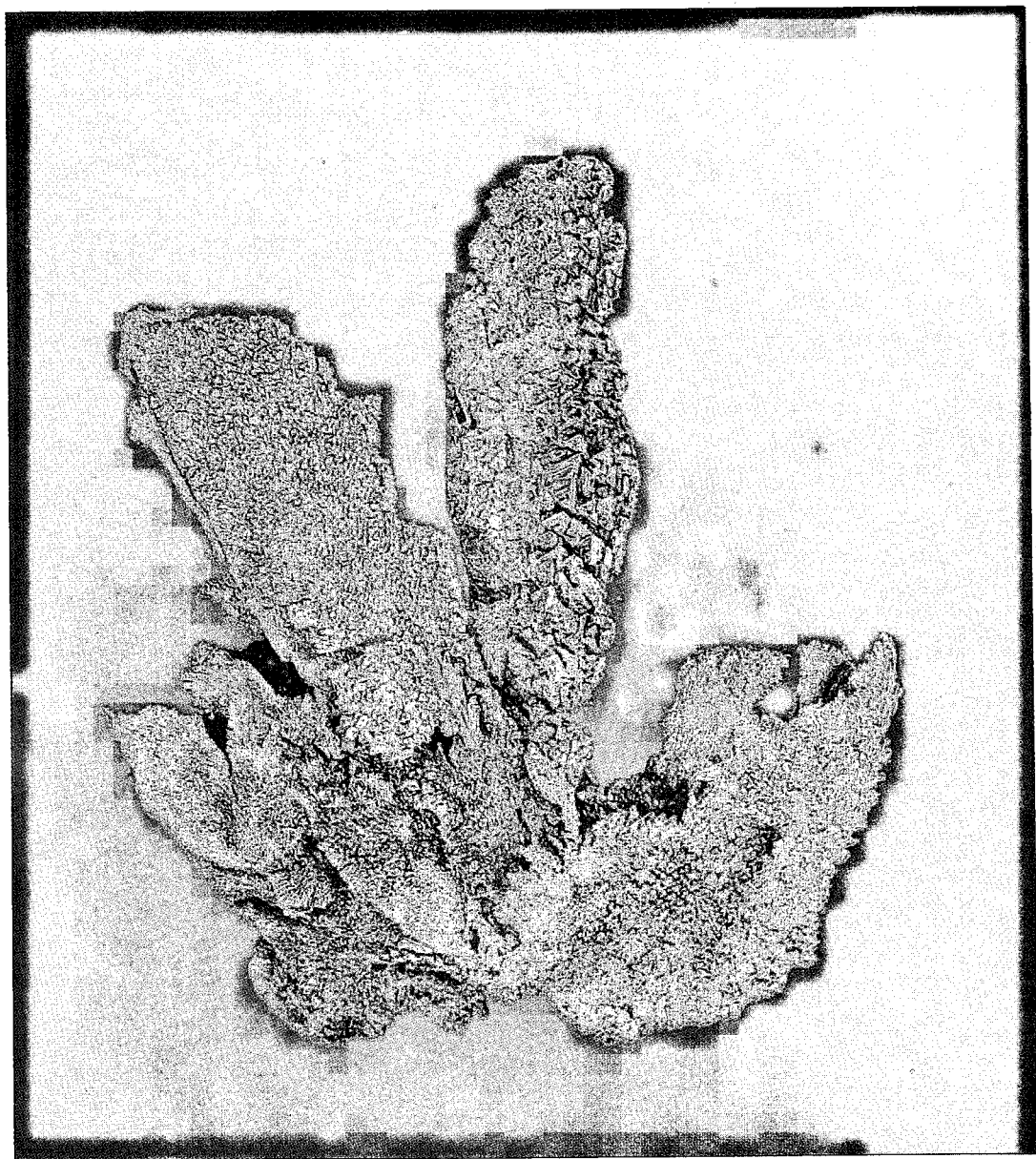


FIG. 3b. Naturally occurring native gold.

a mixture of copper and arsenic, derived from domeykite or algodonite. However, it was soon found that a mixture of cassiterite and copper ore yielded better bronze, and this was the basis of the bronze-age technology that developed throughout Europe and Asia.

The Iron Age

About 1400 B.C. saw the start of the Iron Age. This heralded a major change in human society, as iron ores are very common, and iron forms very hard and durable

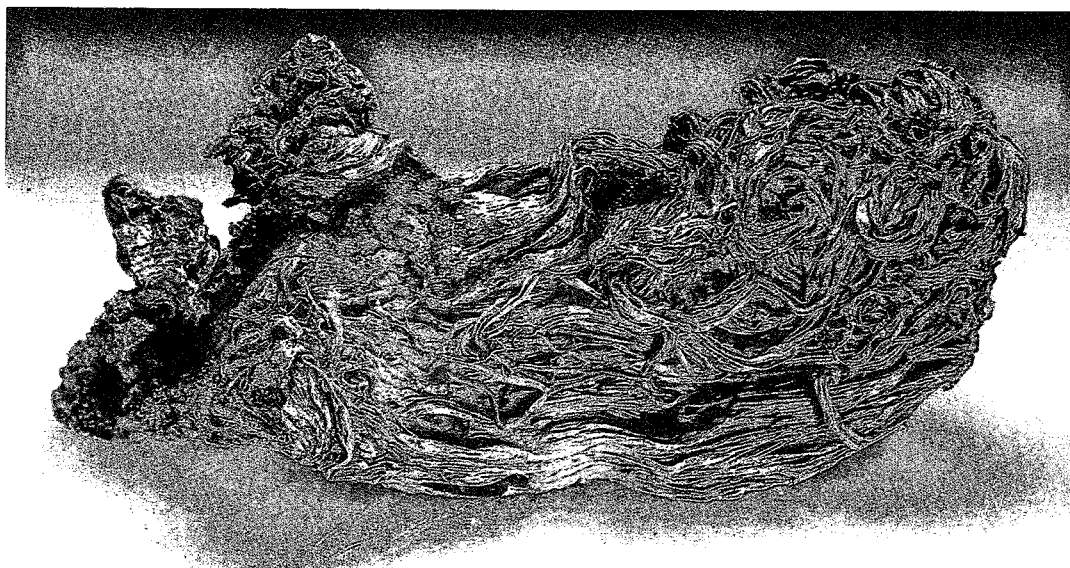


FIG. 3c. Naturally occurring native silver.

tools. In addition, the technology of smelting and working iron is much more complex than that required for the various alloys of copper, and different ores of iron must be treated in different ways. As a consequence of this, it became important that a large number of people be able to recognize the different types of iron ore, and it is perhaps not a coincidence that the earliest writings on minerals date from the early Iron Age.

Nonmetallic minerals

Throughout the Stone, Bronze and Iron Ages, humanity also began to use an increasing number of minerals unrelated to the manufacture of tools. Fascination with Art seems an intrinsic property of the human psyche, a statement that seems as true for our ancestors as it does for us today. Cave art is our earliest record of humanity's

TABLE 1. EARLY WRITINGS ON MINERALS

~1100 B.C.	India	<i>Vedas</i>
~700 B.C.	China	Compilations of minerals
~300 B.C.	India	Descriptions of minerals
384-322 B.C.	Greece	Aristotle - <i>Meteorologica</i>
370-287 B.C.	Greece	Theophrastus - <i>On Stones</i>
23-79 A.D.	Rome	Pliny - <i>Historia Naturalis</i>
8th century	Persia	Jabir ibn Hayyan
9th century	Arabia	Al Khindi
980-1037 A.D.	Persia	Avicenna ibn Sina
1540 A.D.	Italy	Biringuccio - <i>Pirotecnica</i>
1556 A.D.	Germany	Agricola - <i>De Re Metallica</i>

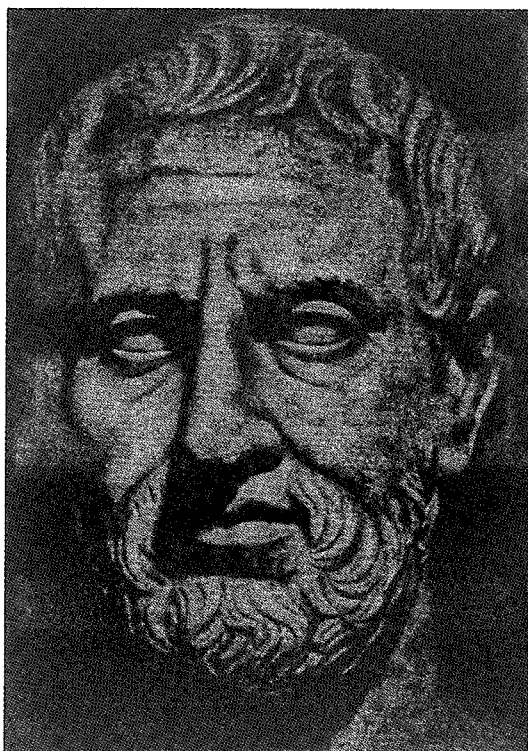


FIG. 4. Theophrastus (370-287 B.C.), author of "History of Stones".

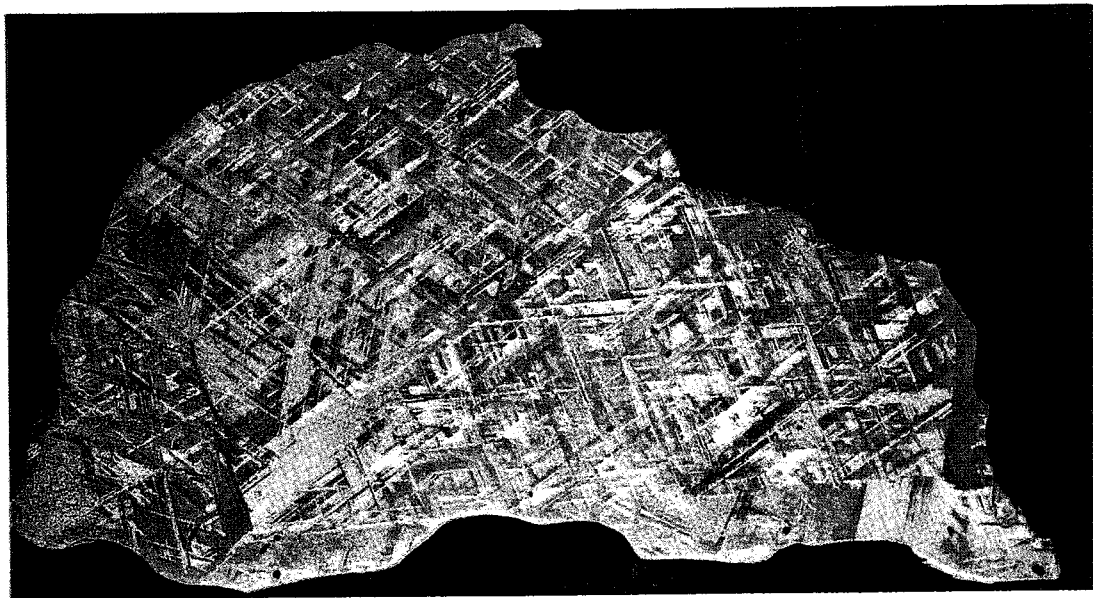


FIG. 3d. Naturally occurring native iron.

artistic spirit. Its first expression is as rough scratchings on cave walls, possibly of religious or superstitious origin. However, this soon changed, and colored pigments became common: manganese oxides for black, hematite for red, malachite for green.

It also seems a characteristic feature of human beings to adorn themselves and their "caves" with beautiful objects. Ornaments of amethyst, turquoise, jade, malachite, garnet, gold and silver were widespread, and trade in precious stones was extensive. In addition, the firing of clay to make pottery was an important advance in human society, and the drive to produce aesthetic objects led to the development of glazing and the manufacture of glass.

Thus the early development of humanity is intrinsically associated with the recognition and use of minerals. As the Iron Age began, there was extensive trade in a wide variety of minerals, and the ability to recognize minerals and be familiar with their properties and uses became of importance to an increasingly large number of people.

EARLY WRITINGS ON MINERALS

The requirement that more and more people be conversant with minerals and their properties led to the first writings on minerals (Table 1). The earliest known literature is the Indian *Vedas* that date from about 1100 B.C. There are Chinese compilations of minerals dating

from the seventh century B.C., and further Indian manuscripts from the third century B.C. The first European work dates from this time: Aristotle (384–322 B.C.) wrote briefly on minerals in his *Meteorologica*. However, the first scientific work on (as distinct from a simple listing of) minerals is due to Theophrastus (370–287 B.C.). Theophrastus (Fig. 4) was a pupil of Aristotle, and succeeded him as the head of the Lyceum in Athens; he wrote the first mineralogy text, the "History of Stones", thought to be his lecture notes. Theophrastus classified minerals according to strict Aristotelian principles, basing his work firmly on the physical properties of minerals, and eschewing any magical or fabled medicinal overtones that were so characteristic of many later compilations.

Pliny (Gaius Plinius Secundius, the Elder, 23–79 A.D.), the celebrated Roman encyclopedist, produced a 37-volume work: *Historia Naturalis* (there may have been more volumes "in the pipeline", but volcanologists will recognize the date of Pliny's death – he was killed at Pompeii by the eruption of Vesuvius). Five of Pliny's volumes deal with minerals, gemstones and their treatment. It is perhaps a reflection on human nature that Pliny goes into detail on the many gemstone-enhancement techniques current at that time: oiling, dyeing, the use of backing foils, and the manufacture of composite stones. He writes: "...there are descriptions as to how to give the colour of *smaragdus* (emerald) to *crystallus* (rock crystal) and how to initiate other transparent

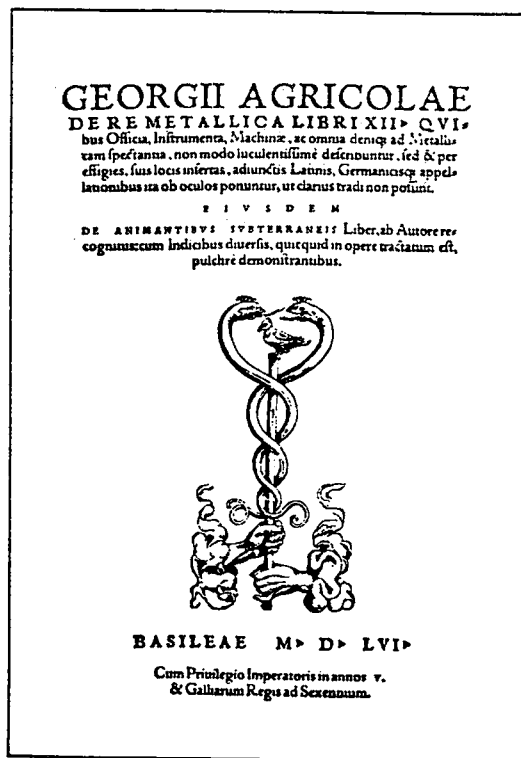


FIG. 5. Illustrations from *De Re Metallica* by Georgius Agricola; left: frontispiece; right: mining in the fifteenth century.

gems... To tell the truth [he *must* be a scientist], there is no fraud or deceit in the world which yields greater gain and profit than that of counterfeiting gems”.

Detailed recipes for gemstone enhancement are given in the *Papyrus Graecus Holmiensis*, transcribed about 400 A.D. in Egypt: “For the preparation of emerald: mix together in a small jar 1/2 drachma of copper green (verdigris), 1/2 drachma of Armenian blue (chryso-colla), 1/2 cup of the urine of an uncorrupted youth, and 2/3 the fluid of a steer’s gall. Put into this the stones, about 24 pieces weighing about 1/2 obolus each. Put the lid on the jar, seal the lid all around with clay, and heat for six hours over a gentle fire made of olive-wood.... You will find that they have become emeralds.”

In 97 A.D., the Chinese ambassador to Antioch, the capital of Roman Syria, included in his report back to China the following: “The articles made of rare and precious stones produced in this country are sham curiosities, and mostly not genuine”. Things apparently became so bad that in ~300 A.D., the Emperor Diocletian ordered all books describing the fabrication of artificial gemstones to be burned. For those further interested in this fascinating topic, the book by Nassau (1983) is recommended.

Many subsequent writings commonly failed to differentiate between fact and fantasy, and the onset of the “Dark Ages” in Europe saw a much-reduced demand for

minerals. The next work to take a more scientific approach is that of the eight-century Persian scientist Jabir Ibn Hayyan. He summarized his philosophy as follows: “The first essential is that thou shouldst do experiments; philosophers delight in the excellence of their experimental methods”, and followed this up by classifying minerals according to their external appearance and physical properties. Such schemes were further developed by the Arab philosopher Al Kindi and the Persian alchemists Ar Razi and Avicenna. Throughout the Pre-Renaissance period, the number of known minerals increased rapidly, and the phenomenological approach taken by the more rigorous of the philosophers was essential to the development of Mineralogy as a useful science.

THE RENAISSANCE AND BEYOND

The Renaissance was accompanied by a great expansion in economic activity throughout Europe. In particular, extensive mining and smelting works arose in Germany at the beginning of the sixteenth century. It was here that George Bauer latinized his name to Georgius Agricola, and published his celebrated work *De Re Metallica*. This work comprehensively documents in detail all aspects of minerals and mining, and describes the metallurgical techniques in use at that time (Fig. 5).

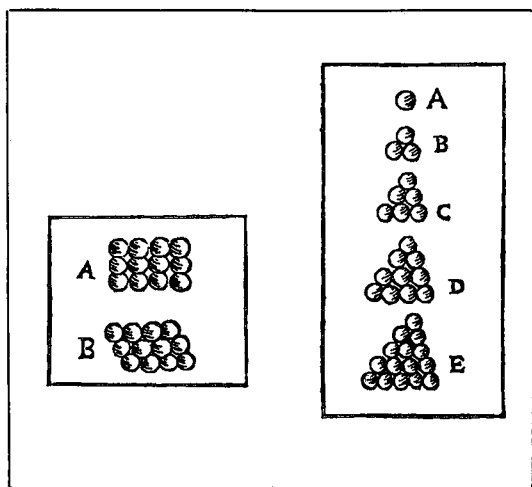


FIG. 6. The formation of snow crystals *via* close-packing of "snow atoms"; after Keppler in 1611.

Agricola formally defined the mineral properties that we are familiar with today: color, transparency, luster, hardness, cleavage and flexibility. He used this as the basis for a classification of minerals based on physical properties. In addition, from his own observations he proposed that the formation of vein minerals is a result of circulating underground fluids. Approximately contemporaneous with Agricola was Vannoccio Biringuccio of Siena, Italy. In his work on metallurgy, *Pirotecnia*, which appeared in 1540, he developed a physical classification of minerals, similar in scope to that of Agricola.

The physics of minerals

Lucretius (99–55 B.C.) had first proposed that matter (he explicitly included minerals) consisted of atoms of the "elements" earth, air, fire and water. However, this was essentially an axiomatic proposition. The first inductive work on the internal constitution of minerals is attributed to Johannes Keppler. In 1611, he gave the first description of the hexagonal symmetry of snowflakes, proposed that they are composed of a planar close-packed arrangement of spherical "atoms" of ice (Fig. 6), and recognized the unique nature of both cubic and hexagonal close-packed arrangements of spheres. In 1669, Nicolaus Steno (the Dane, Niels Stensen) showed that the interfacial angles of quartz crystals are constant, irrespective of crystal habit; he also proposed that crystals grow by the adhesion of particles from an external fluid, and concluded that crystal growth is

TABLE 2. IMPORTANT EARLY ADVANCES IN THE PHYSICS OF MINERALS

Lucretius	99–55 B.C.	Atomic hypothesis
J. Keppler	1611 A.D.	Symmetry of snowflakes close-packing of 'atoms'
N. Steno	1669 A.D.	Steno's hypothesis, constancy of interfacial angles in quartz
A. Werner	1750–1817 A.D.	Last great physical classification of minerals
L. Romé de l'Isle	1736–1790 A.D.	Law of constancy of interfacial angles
R.-J. Haüy	1743–1822 A.D.	Ideas on 'unit cell' and translational symmetry
C. Weiss	1815 A.D.	Crystallographic axes, symmetry axes
F. Mohs	1825 A.D.	Mohs hardness scale
J. Hessel	1830 A.D.	Derivation of the 32 crystal classes
A. Bravais	1848 A.D.	Derivation of the 14 space lattices
E.S. Federov		
A. Schoenflies	1880–1890 A.D.	Derivation of the 230 space groups; close packing, proposed crystal structure of halite
W. Barlow		

directional in nature, crystal habit depending on relative rates of growth in different directions.

Steno's hypothesis was a very important advance, as it established Crystallography as a quantitative science, and external form became of great importance in the ensuing classifications and descriptions of minerals. These reached their zenith in the work of Abraham Werner (1750–1817), professor of Mineralogy* at Freiburg, Germany, who developed a comprehensive scheme of classification for ~300 minerals, that was important for the standardization of mineral descriptions and mineral nomenclature. As an aside, Werner was the first to introduce the custom of naming minerals after specific people (Mitchell 1979): prehnite (after Col. Hendrik von Prehn), torbernite (after Torben D. Bergman, a prominent Swedish mineralogist and analyst) and witherite (after William Withering). Although this created considerable controversy at the time (and has done so ever since), it has proven too popular a custom for its opponents. Although Werner's classification was very important at the time, the development of chemical mineralogy had already begun, signalling the end of physical properties as the basis for mineral classification.

Developments in Crystallography proceeded apace (Table 2). Following the development of the goniometer by Carangeot in 1780, Jean Baptiste Louis Romé de l'Isle (1736–1790) confirmed Steno's hypothesis, establishing the law of constancy of interfacial angles. However, the major advance of this period was made by René-Just Haüy (1743–1822). In his *Traité de cristallographie*, published in 1784, Haüy proposed that crystals consist of identical integral molecules stacked together, and showed how different modifications of the same stacking could give rise to different crystal forms

*It is worth noting that Mineralogy was the first of the Geological Sciences to be sufficiently well established and useful to be taught at University.

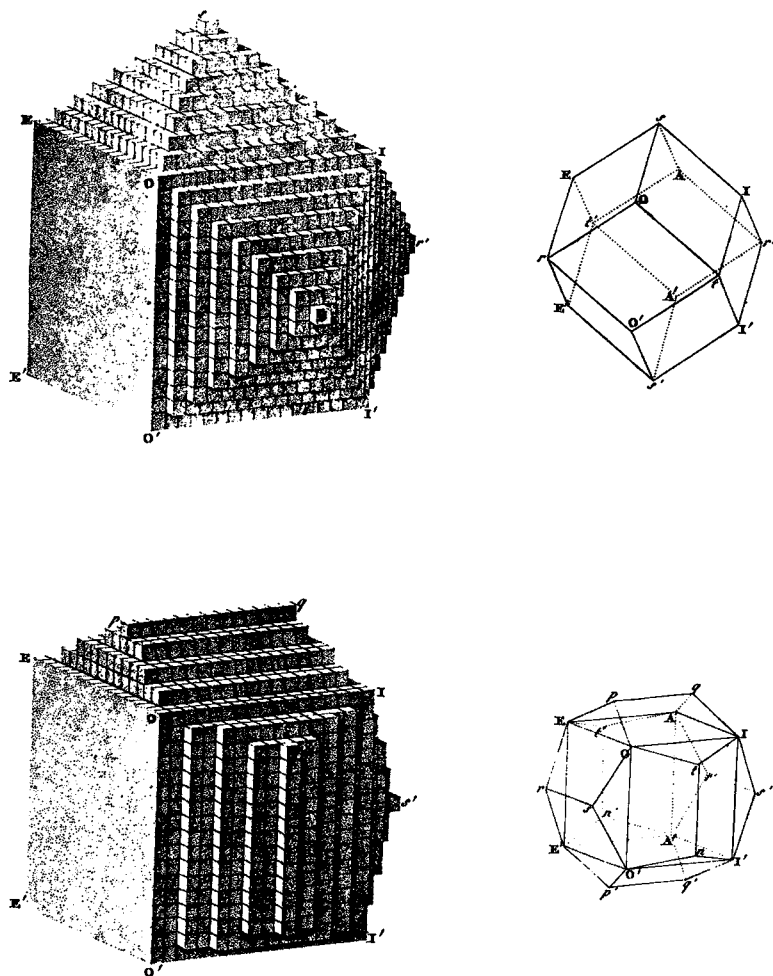


FIG. 7. Different crystal forms derived from the stacking of identical "blocks"; after René-Just Haüy, 1743–1822.

of the same material (Fig. 7). The similarity of his ideas to those of the unit cell and the space lattice is very striking. In 1815, Christian Weiss followed this up by developing the idea of crystallographic axes and their relationship to symmetry axes; he recognized the cubic, tetragonal, orthorhombic, hexagonal and trigonal systems. In 1825, Friedrich Mohs, inventor of the Mohs hardness scale, discovered the monoclinic and triclinic crystal systems, and in 1830, Johann Hessel derived the 32 crystal classes. Auguste Bravais derived the 14 space lattices in 1848, and the classical age of crystallography came to a close with the derivation of the 230 space groups by E.S. Fedorov, Artur Schoenflies and William Barlow. Barlow also took the first steps toward a more fundamental understanding of minerals by proposing the

crystal-structure arrangement of halite; however, this was largely ignored by the science of the day, and vindication of his views had to await the technology of the twentieth century.

The chemistry of minerals

Abraham Werner's great classification of minerals was the last gasp of physical properties as a basis for mineral classification. The work of the more systematic alchemists (Fig. 8) eventually began to bear fruit with the gradual development of chemical mineralogy. In 1758, Kronstedt developed a classification of minerals that was a hybrid of chemical and physical criteria, and the chemical study of minerals began to accelerate,

THE SYSTEM OF MINERALOGY

of James Dwight Dana and Edward Salisbury Dana
Yale University 1837–1892

SEVENTH EDITION
Entirely Rewritten and Greatly Enlarged

By
CHARLES PALACHE
the late HARRY BERMAN
and CLIFFORD FRONDEL
Harvard University

FIG. 8. Frontispiece of the seventh edition of *The System of Mineralogy* of James Doyle and Edward Salisbury Dana (Palache et al. 1944).

particularly with the systematic studies and writings of such scientists as Torbern Bergman (1735–1784). Many famous classical chemical mineralogists* carried out analytical studies of the minerals known at that time. Numerous new minerals and twenty-five new chemical elements were discovered between 1790 and 1830, a period of amazing growth in scientific knowledge. A key factor here was the discovery of the laws of stoichiometry by the English chemist John Dalton (1766–1844). With the development of Dalton's atomic theory, the importance of the chemical constitution of minerals was soon realized, and all serious schemes of mineral classification subsequently had their basis in mineral chemistry.

In this period, one figure stands out above the others: Jon Jacob Berzelius (1779–1848). This famous Swedish mineralogist–chemist developed a mineral classification based on the electronegative elements, giving such classes of minerals as oxides, halides, phosphates, sulfates and silicates, essentially the scheme that we still use today. At this time, François Beudant and William H. Wollaston (who said that naming minerals after people is not a good idea!) discovered the concept of solid solution in minerals, and Eilhardt Mitscherlich (1794–1863) proposed the idea of polymorphism. The sudden success in bringing order to a rapidly increasing number of minerals, to say nothing of discovering many

new elements, established the chemical basis of Mineralogy and the pre-eminence of Berzelius and his idea.

The year 1837 is a landmark in the history of Mineralogy. It marks the date of publication of the first edition of *A System of Mineralogy* by James Dwight Dana (1813–1895). The fourth edition of this work appeared in 1854, and in this edition, Dana introduced the “modern” chemical classification scheme of Berzelius, and systematically applied it to all known minerals. Dana's *System* remains the only all-encompassing mineral classification, and is still in use today (Fig. 8).

I should perhaps say something about the emphasis on mineral classification that pervades the above account of the history of Mineralogy. Many scientists feel that matters of classification are trivial, and belong to the realm of “stamp collecting” rather than “real science”; all this shows is that these people are so narrowly focused that they lack the need to organize their knowledge. *A scientific classification is a distillation of our knowledge concerning the nature of the objects under consideration.* The more fundamental our knowledge, the “deeper” and more effective the classification; perhaps the best example of this is the periodic table of the elements. However, it still needs to be emphasized that the “discovery” of atoms and the development of the periodic table were accomplishments of the “stamp collectors” and the classifiers, and not the result of “more fundamental” discoveries at a later date. We can take the state of mineral classification as a long-term indicator of our fundamental knowledge of Mineralogy: first, the development of a physical classification, then the development of a chemical classification and, in this century, the beginnings of a structural classification of minerals.

THE TWENTIETH CENTURY

The twentieth century has seen a revolution in the basic structure of Science. In 1895, J.J. Thompson (Cavendish Professor of Physics) remarked that Physics

TABLE 3. EARLY CHEMICAL MINERALOGISTS AND THEIR OFFSPRING

Kronstedt	1722–1765	Cronstedtite
Bergman	1735–1784	Torbernite
Berzelius	1779–1848	Berzeliite
Vauquelin	1763–1820	Vauquelinite
Gadolín	1760–1852	Gadolinite
Tennant	1761–1817	Tennantite
Wollaston	1766–1826	Wollastonite
Stromeyer	1778–1835	Stromeyerite
Arfvedson	1792–1841	Arfvedsonite
Rose	1795–1864	Roselite

*Most of the well-known chemical mineralogists have their mineral (Table 3), whereas of the physical mineralogists and crystallographers, only one, René-Just Haüy (hauyne), is so commemorated.

The Structure of Some Crystals as Indicated by their Diffraction of X-rays.

By W. L. BRAGG, B.A.

(Communicated by Prof. W. H. Bragg, F.R.S. Received June 21,—Read June 26, 1913.)

[PLATE 10.]

A new method of investigating the structure of a crystal has been afforded by the work of Laue* and his collaborators on the diffraction of X-rays by crystals. The phenomena which they were the first to investigate, and which have since been observed by many others, lend themselves readily to the explanation proposed by Laue, who supposed that electromagnetic waves of very short wave-lengths were diffracted by a set of small obstacles arranged on a regular point system in space. In analysing the interference pattern obtained with a zincblende crystal, Laue, in his original memoir, came to the conclusion that the primary radiation possessed a spectrum consisting of narrow bands, in fact, that it was composed of a series of six or seven approximately homogeneous wave trains.

FIG. 9. The beginning of W.L. Bragg's historic paper on the structure of crystals; after Bragg (1913).



ATOMIC STRUCTURE OF MINERALS

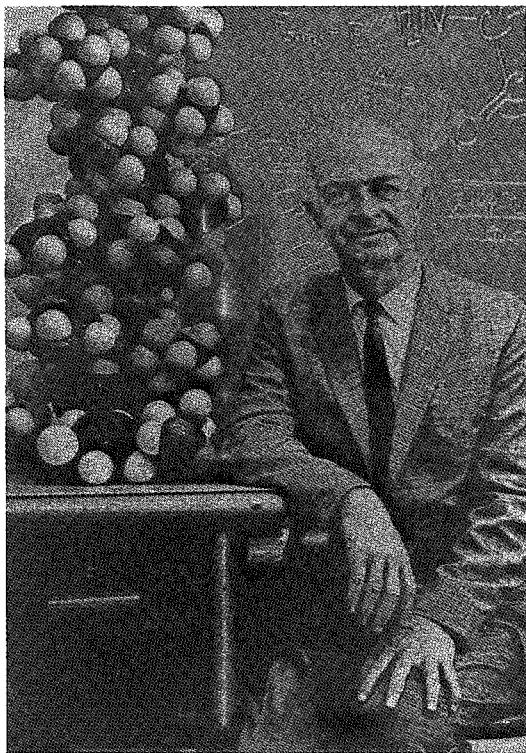
BY

W. L. BRAGG

*Langworthy Professor of Physics in
The Victoria University of Manchester*



FIG. 10. left: W.L. Bragg; right: frontispiece of *The Atomic Structure of Minerals* (Bragg 1937).



THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS

BY LINUS PAULING

RECEIVED SEPTEMBER 5, 1928

PUBLISHED APRIL 5, 1929

1. **The Relative Stability of Alternative Structures of Ionic Crystals.**—The elucidation of the factors determining the relative stability of alternative crystalline structures of a substance would be of the greatest significance in the development of the theory of the solid state. Why, for example, do some of the alkali halides crystallize with the sodium chloride structure and some with the cesium chloride structure? Why does titanium dioxide under different conditions assume the different structures of rutile, brookite and anatase? Why does aluminum fluosilicate, $\text{Al}_2\text{SiO}_5\text{F}_2$, crystallize with the structure of topaz and not with some other structure? These questions are answered formally by the statement that in each case the structure with the minimum free energy is stable. This answer, however, is not satisfying; what is desired in our atomistic and quantum theoretical era is the explanation of this minimum free energy in terms of atoms or ions and their properties.

FIG. 11. left: Linus Pauling; right: the beginning of Linus Pauling's classic paper on "Pauling's rules" (Pauling 1929).

was nearly a "finished" science; two small matters remained to be solved, and Science would become the straightforward application of physical laws. One never ceases to be amazed at such a lack of appreciation for the complexity of Nature; the search for "universal laws" often seems to blind people to the possibility that their "universal" laws may only be applicable (or perhaps "relevant") within a specific domain of conditions. Anyway, the "two small matters" referred to above gave rise to quantum theory and relativity, and revolutionized our practice and understanding of Science, including Mineralogy.

Mineralogy and crystallography

In 1912, under the direction of Max von Laue, Walter Friedrich and Paul Knipping discovered the diffraction of X rays by crystals. This discovery was immediately seized upon by the young William L. Bragg and his father, W.H. Bragg, who gave a simple interpretation of this type of experiment, Bragg's Law, and derived the crystal structure of halite. Although twenty years earlier, William Barlow had proposed that halite was composed of spherical atoms of Na and Cl arranged in a close-packed manner, he had been ignored by the chemists, who considered that NaCl should consist of molecules

of NaCl arranged in some fashion; W.L. Bragg (Fig. 9) showed that Barlow was right and that the conventional view was wrong. The elegance of Bragg's conception is amazing. Normally, an experiment involves *one* unknown and one or more known quantities or facts; in this particular case, there were *two* unknowns: (i) whether X rays have a wave-like behavior; (ii) whether crystals are periodic. Bragg's interpretation showed *both* of these to be true *and*, as a bonus, produced the first experimentally determined atomic arrangement of a crystal.

W.L. Bragg went on to solve other simple mineral structures very rapidly. This work proceeded through the 1920s, dominated by Bragg and his coworkers, names to fire the imagination today: B.E. Warren, who solved the structures of diopside, tremolite and vesuvianite, a truly heroic achievement; J. West, who solved the structures of beryl, muscovite and biotite; W.H. Taylor, who solved the structure of feldspar, a Christmas present for an unsuspecting world. By 1935, the structures of most of the common rock-forming minerals were known (Fig. 10), and W.L. Bragg produced a structural classification for the silicate minerals, based on the polymerization of (alumino-) silicate tetrahedra. This *tour-de-force* of structural mineralogy gave an atomistic rationale for the macroscopic physical properties of minerals, and allowed a more complete interpretation of

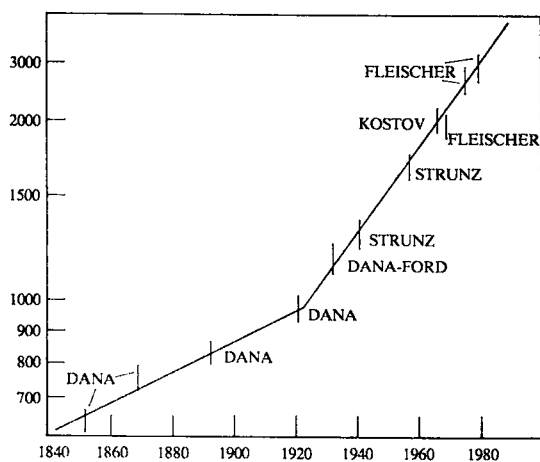


FIG. 12. The increase in the discovery of new mineral species over the past one hundred and fifty years; after Skinner & Skinner (1980).

their chemistry, particularly where complex solid-solutions are involved.

Linus Pauling capitalized on Bragg's work, and produced his famous rules (Fig. 11) that form one of the cornerstones of modern crystal-chemistry. These contributed significantly to the solution and interpretation of some of the more complex silicate structures; when Warren solved the crystal structure of tremolite (Warren 1929), he used Pauling's third rule to show that tremolite contains essential hydroxyl, and that the $(OH)^-$ anion occupies the O(3) site. Pauling's rules have come under criticism at different times as being based on an unrealistic (*i.e.*, the ionic) model of the chemical bond. Of course, this is nonsense. The rules are a set of (*inductive*) generalizations based on the observed stereochemistry of a large number of crystal structures, and on this basis, are valid *observations*; indeed, Burdett & McClarnan (1984) have argued for a molecular-orbital basis of Pauling's rules. In any event, the rules have proven too useful to be discarded, and they [or their generalizations by Brown & Shannon (1973) and Brown (1981)] remain in extensive use today.

The development of powder diffraction occurred in 1917, and was an extremely important event for Mineralogy. It meant that minerals could be identified rapidly and reliably, without the great amount of work associated with chemical analysis. This initiated a new era in the discovery of mineral species (Fig. 12). The rate of discovery increased radically at this point, and it is notable that this rate has been sustained in subsequent decades, primarily by the introduction of new and rapid techniques of characterization, of which electron-microprobe analysis has been the most important.

Mineralogy, geochemistry and petrology

Between 1790 and 1924, an enormous number of minerals and rocks were chemically analyzed. Geochemistry tended to be synonymous with the chemical analysis of Earth materials, and a large amount of data was gathered on the composition of the Earth. However, there was very little adequate interpretative work, except for that of Van't Hoff on the gypsum-anhydrite transition. The detailed chemistry of many of the important rock-forming minerals was not understood, and although the general principle of solid solution had been known for a long time, the true complexity of the solid-solution relationships in many mineral groups resisted efforts to understand them.

The key figure in the resolution of this situation was Victor M. Goldschmidt (Fig. 13). He started out as a petrologist, working on metamorphic rocks in Norway during the period 1911–1922. However, he became disenchanted with the current state of understanding of the chemistry of minerals and the relationships between the compositions of coexisting minerals in rocks. In 1922, he set up a group at Oslo to work on the crystal structures of minerals and inorganic materials. As a result of this work, Goldschmidt (1937) established his general laws governing the distribution of elements in minerals, explaining their behavior in terms of the

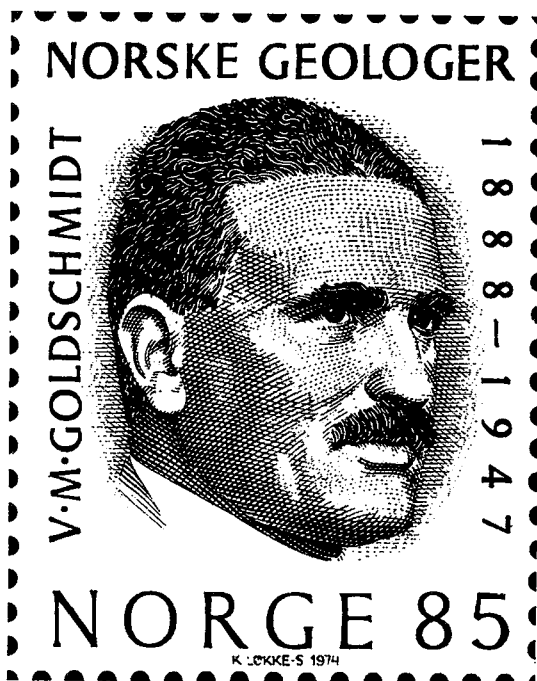


FIG. 13. Victor M. Goldschmidt, geochemist extraordinaire.

MINERALOGY OF THREE SULPHATE DEPOSITS OF NORTHERN CHILE*

MARK C. BANDY, *Harvard University, Cambridge, Mass.*

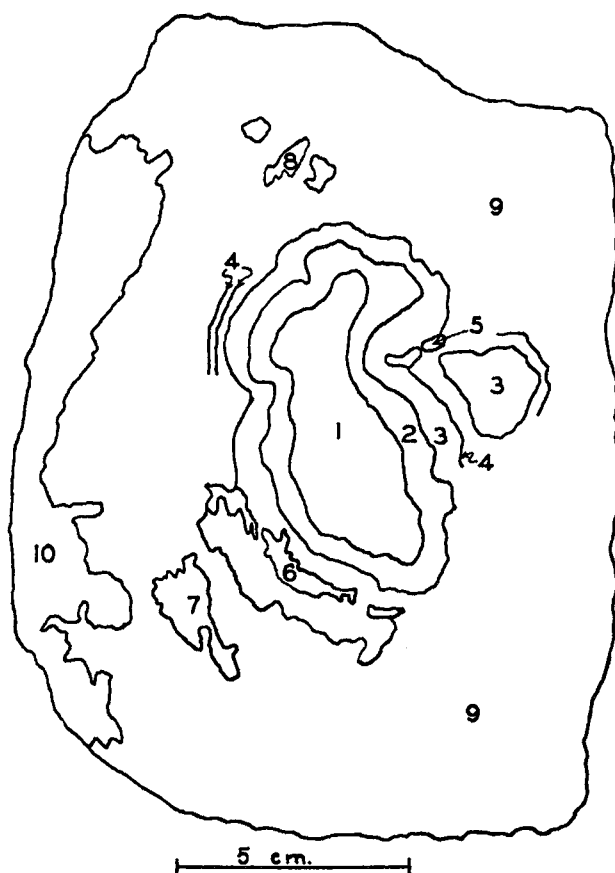


FIG. 3. Sketch of a specimen of zoned sulphates from Quetana, showing distribution of the minerals present.

- | | |
|----------------------------|-------------------------------|
| 1. Pyrite and szomolnokite | 6. Alums |
| 2. Pyrite and halotrichite | 7. Pisanite, var. salvadorite |
| 3. Copiapite | 8. Botryogen, var. quetenite |
| 4. Jarosite | 9. Copiapite and botryogen |
| 5. Parabutlerite | 10. Altered country rock |

FIG. 14. Paragenesis of sulfate minerals from the Quetana deposit in northern Chile; after Bandy (1938).

atomic structure of the minerals and the crystal-chemical behavior of their constituent elements. This work was summarized in his seminal book *Geochemistry*

(Goldschmidt 1954), possibly the most important text in the Earth Sciences this century.

Contemporaneous with the development of Geo-

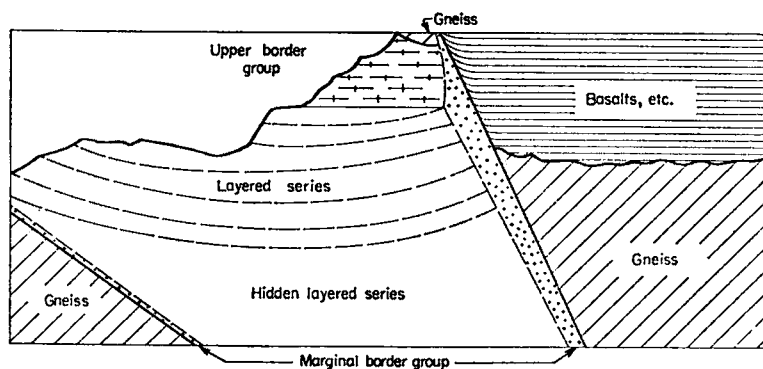


FIG. 15. The Skaergaard intrusion in eastern Greenland; from Wager & Brown (1968).

chemistry was an explosion of work on the synthesis and stability of minerals and mineral assemblages. During the nineteenth century, the advent of the petrographic microscope, when combined with extensive field studies, had led to the development of two schools of thought on the origin of "crystalline" rocks: the "magmatists" and the "transformationists". Pioneering experimental work had been done by Sir James Hall (1761–1832), but the extensive investigations necessary to examine the phase chemistry of granites and basalts were not feasible prior to the development of the platinum thermocouple in 1886. At the turn of the century, the magmatic theories of Rosenbuch were well established, and formed an excellent background for experimental phase petrology to begin. The key figure here was Norman L. Bowen, who joined the newly established (1906) Geophysical Laboratory of the Carnegie Institute of Washington in 1910, and published his seminal work on the plagioclase feldspars three years later (Bowen 1913). This was an important step toward the more complex systems that would give rise to his ideas of fractional crystallization (Bowen 1915, 1928) and the eventual examination of petrologically applicable (*i.e.*, wet) systems. The importance of this new area was that it allowed real temperatures and pressures to be assigned to the breakdown, melting and crystallization of both minerals and rocks, as well as the experimental characterization of such important physicochemical processes as peritectic reaction and crystal resorption in magmas.

While these great developments were occurring in the laboratory, work of fundamental importance was continuing in the field. In particular, detailed field mapping, coupled with textural and chemical studies, revolutionized ideas on mineral paragenesis and on ways that mineralogical studies could be applied to the characterization of petrological processes on a much more detailed scale than had hitherto been realized. I will briefly describe two examples, one relatively unknown

(but of extremely high quality), and the other of considerable fame.

In the late 1930s, W.C. Bandy mapped and carried out detailed mineralogical investigations of the copper deposits of northern Chile, and published a classic study (Bandy 1938) on the paragenesis of the (oxidized) sulfate minerals associated with these deposits (Fig. 14). This work is a masterpiece of careful field work and meticulous observations on both the large scale and the small scale; Bandy recorded both broad trends and local variations in paragenetic sequence. It has significantly influenced contemporary work on what features control the stability and sequence of crystallization of minerals.

Perhaps the best known and most influential work is that of Wager and coworkers (summarized in Wager & Brown 1968) on the Skaergaard intrusion (Fig. 15) in southern Greenland. This work gave us an appreciation for the change in compositions of solid solutions of minerals as a function of conditions of crystallization, and emphasized that there is an enormous amount of information on the petrological history of rocks contained in the detailed compositional variations of their rock-forming minerals. Today there is a synergistic interaction between field work and experimental (phase-) mineralogy and petrology that augments both areas, such that we are now using *specific* field mapping to test hypotheses developed from experimental work, as well as using experimental work to test ideas developed in the field.

"MODERN TIMES": MINERALOGY AND EXPERIMENTAL METHODS

At the beginning of the 1960s, a technological revolution began in Mineralogy with the development of the electron microprobe, and the last thirty years have seen an almost continuous introduction of new instrumental techniques into Mineralogy. Work on mineral

structure and chemistry has been greatly enhanced by the application of many spectroscopic techniques to Mineralogy, beginning in the late 1960s. These techniques are of considerable importance, not the least because they can give short-range structural information, and can be used on noncrystalline materials (glasses, melts, *etc.*). Below, I outline (very briefly) the uses of each technique, together with a short description of its physical basis in the case of those techniques that are of less general familiarity. What is apparent from this discussion is that our capabilities for the characterization of minerals are now far greater than what could have been imagined thirty years ago.

Electron-microprobe analysis

The first instrument was designed and built by J.D. Castaing in the late 1950s, and within a few years, commercial models were on the market. The electron microprobe revolutionized both Mineralogy and Petrology, as the analysis of minerals became rapid and fairly straightforward. Our knowledge of mineral chemistry improved greatly as chemical compositions of minerals were no longer adversely affected by exsolution and inclusions. In addition, such microfeatures as zoning, exsolution and inclusions became chemically accessible, and we began to view Petrology in a more process-oriented way as the temporal and spatial resolution of our knowledge increased. As the technology of the instrument has improved, detection limits have fallen,

such that we can now examine minor elements in minerals. The chemical range for analysis also has expanded; now we can reliably analyze for boron, and even beryllium seems feasible in the near future.

Crystal-structure refinement

With the advent of the electron microprobe, there was an explosion in the amount of compositional data available on common rock-forming and accessory minerals. The resultant thrust to better understand the general chemistry of silicate minerals, and apply thermodynamic models to the intercrystalline distribution of elements, required a much better knowledge of mineral structure and crystal chemistry. This need, coupled with the commercial development of automated four-circle single-crystal (X-ray) diffractometers, combined to produce a rapid expansion of work in mineralogical crystallography. The basic crystal-chemical framework of olivines (Brown 1978), pyroxenes and amphiboles (Clark *et al.* 1969, Papike *et al.* 1969), micas (Bailey 1984) and feldspars (Smith 1974a,b) was put into place during this time. At the same time, work greatly expanded in the determination of unknown mineral structures (Moore 1965, 1970), for the first time providing the opportunity to examine the factors important in determining the absolute stability of a structural arrangement.

Most rock-forming silicates form at high temperatures and pressures (*i.e.*, not at 25°C and 1 bar), and the next step in understanding their behavior was to charac-

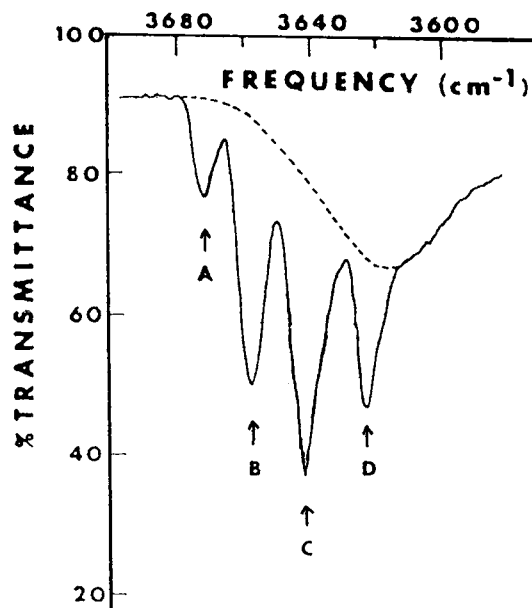
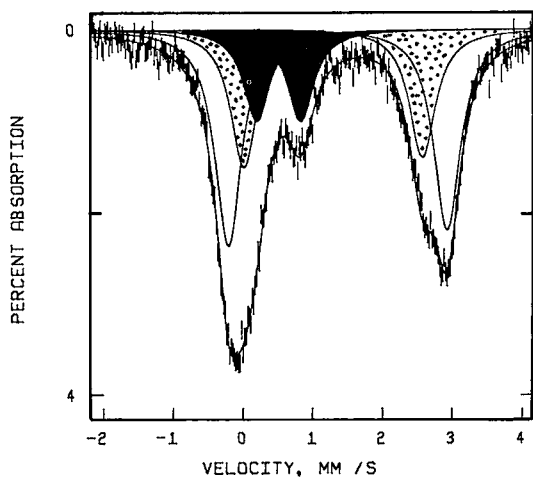


FIG. 16. The spectral expression of Mg-Fe disorder in amphibole: left: Mössbauer spectrum showing contributions from Fe^{3+} at $M(2)$ (black doublet) and Fe^{2+} at $M(1)$ (unshaded doublet) and $M(3)$ (spotted doublet), after Bancroft *et al.* (1967); right: infrared spectrum in the principal OH-stretching region, showing bands (A-D) due to local Mg_3 , Mg_2Fe , MgFe_2 and Fe_3 arrangements, after Burns & Strens (1966).

terize structural change as a function of temperature and pressure. Structure refinement at high temperature (Cameron *et al.* 1973) and high pressure (Hazen 1976) showed previous speculations on structural behavior to be fairly accurate. Macroscopic thermal expansion and compression proceed primarily by bond-bending where possible. Microscopic thermal expansion and compression at the coordination polyhedron level is inversely related to cation-anion bond-strength; strongly bonded units, such as (SiO_4) groups, show low thermal expansion and compressibility, whereas more weakly bonded units, such as (NaO_6) groups, show high thermal expansion and compressibility. To a first approximation, temperature and pressure can be considered as having inverse effects on a crystal structure (Hazen & Prewitt 1977). To date, most work in this area has focused on the measurement of physical properties. However, there is considerable potential in examining the variation in vibrational characteristics of structures as a function of temperature and pressure, as this should afford considerable insight into mechanisms of structural breakdown or transition, mechanisms of chemical reactions in the solid state, and the nature of diffusional pathways in minerals.

A major conceptual advance in the crystal-chemical study of minerals was made by Rossi *et al.* (1983) and Ungaretti *et al.* (1983). They realized that the *large-scale* structure refinement of rock-forming minerals could give greatly increased insight into the crystal-chemical behavior of chemically complex minerals (garnets, olivines, pyroxenes, amphiboles). Of particular significance was the derivation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios in pyroxenes and amphiboles, and the recognition of the importance of unusual constituents (*e.g.*, Li, Zn) and patterns of order in specific petrological environments. The combination of large-scale structure refinement and electron- (and ion-) microprobe work promises to be a powerful tool for a more complete characterization of petrological and tectonic processes (*e.g.*, Ague & Brandon 1992).

Mössbauer spectroscopy

Perhaps the technique with the most immediate impact in the late 1960s was Mössbauer spectroscopy. This involves the resonant absorption and emission of gamma rays by specific atomic nuclei; of most mineralogical interest are ^{57}Fe , ^{119}Sn , ^{121}Sb , ^{153}Eu and ^{197}Au . Iron is by far the most important species, and Fe in different valence states and at different sites in a structure can be recognized and (in many cases) quantitatively analyzed (Fig. 16a). This allows $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios to be more easily measured, and also allows (partial) site populations to be derived (Bancroft *et al.* 1967) in many rock-forming minerals. As time went on, Mössbauer spectroscopy was applied to problems beyond the resolution of the technique, and its reputation suffered accordingly (rather unfairly, as this was the fault of the experimenter rather than the method). However, it now

seems to have recovered from this, and ^{57}Fe work now addresses such diverse topics as next-nearest-neighbor effects (Bancroft *et al.* 1983), intervalence charge-transfer (Amthauer *et al.* 1980), magnetic properties of minerals (Ghose *et al.* 1987), and surface oxidation states (*via* conversion-electron Mössbauer spectroscopy), as well as its more traditional areas of valence state and site populations.

Vibrational spectroscopy

A vibrational mode in a crystal will absorb electromagnetic radiation if the frequencies of the vibration and the radiation are coincident, and if the excited vibration

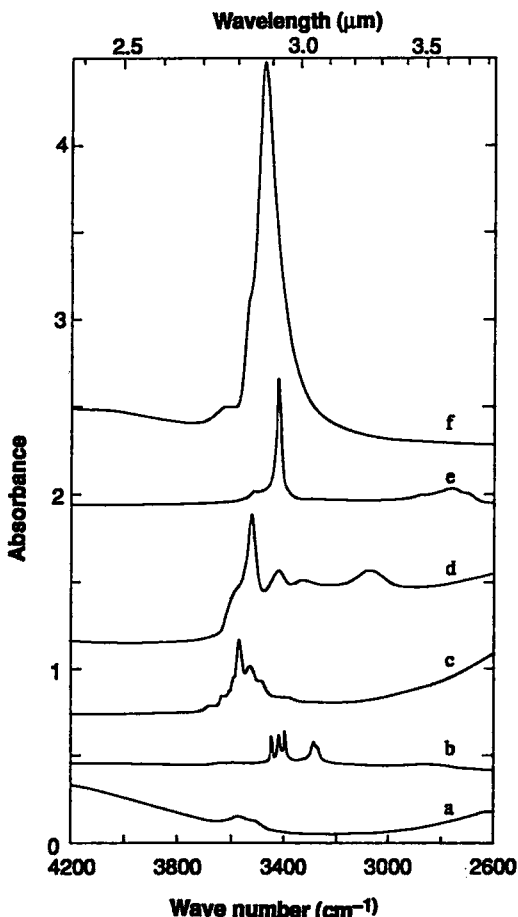


FIG. 17. Polarized single-crystal infrared spectra in the principal OH-stretching region of nominally anhydrous mantle minerals: (a) garnet, (b) kyanite, (c) olivine, (d) enstatite, (e) zircon, (f) omphacite; after Bell & Rossman (1992).

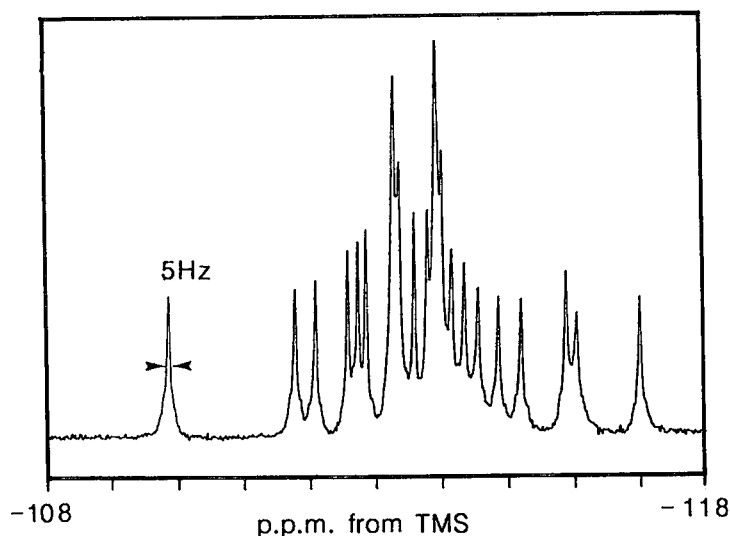


FIG. 18. Ultrahigh-resolution MAS NMR spectrum of highly siliceous ZSM-5 (zeolite), showing 21 of the 24 crystallographically distinct Si sites resolved; after Fyfe *et al.* (1987).

results in a change in the dipole moment of the crystal; this gives rise to InfraRed (IR) absorption spectroscopy. The Raman effect occurs where electromagnetic radiation is (elastically or inelastically) scattered by a crystal, with an ensuing vibrational transition in which energy is absorbed or imparted to the scattered radiation; this gives rise to Raman spectroscopy (McMillan & Hofmeister 1988). Much early work dealt with the degree of order in simple oxides (White 1967). However, IR spectroscopy in the principal OH-stretching region made a significant impact on the characterization of order in amphiboles (Fig. 16b, Burns & Strens 1966) and micas (Vedder 1964) after the initial discovery of this approach by Bassett (1960). Later work showed significant problems in the basic theory underlying this particular application, but it is now being used increasingly to characterize the environment of hydrogen in minerals, both hydrous and nominally anhydrous. The latter use is of considerable geological significance, as nominally anhydrous minerals are a significant reservoir for mantle hydrogen (Bell & Rossman 1992) (Fig. 17), and the presence of hydrogen greatly affects diffusion rates in minerals (Goldsmith 1987). Both IR and Raman spectroscopies are also being used to (partially) characterize the vibrational energy density of states in minerals for thermodynamic calculations (Kieffer 1979).

Both IR and Raman spectroscopies are also effective with noncrystalline materials, and have been important techniques for the structural characterization of glasses. Of particular interest here has been the use of principal

stretching frequencies of silicate groups for the characterization of connectivity in silicate glasses (McMillan 1984), and the use of IR spectroscopy to characterize the role of hydrogen (as OH, H₂O or both) in aluminosilicate glasses and melts (Stolper 1982).

Nuclear Magnetic Resonance (NMR) spectroscopy

NMR involves the resonant absorption and emission of (radio-frequency) electromagnetic radiation by an atomic nucleus via the interaction of its magnetic multipole moment with an applied magnetic field. Transition energies are sensitive to the local electric-field gradient around the nucleus, and hence NMR is a useful technique for the characterization of degree of order in (diamagnetic) minerals. The complexity of the spectra is greatly reduced if the sample is spun at the "magic" angle θ , where θ is given by the equation $3\cos^2\theta - 1 = 0$ (i.e., $\theta = 54.7^\circ$), giving rise to the technique known as Magic-Angle Spinning (MAS). MAS NMR has revolutionized the application of NMR to Mineralogy. Prior to its development in ~1980, there was very little NMR work done on minerals. With the application of MAS NMR to silicates (Lippmaa *et al.* 1980), there was an explosion of work, first on spin $-1/2$ nuclei (of which ^{29}Si is the most important) and then on quadrupolar nuclei such as ^{27}Al , ^{23}Na and ^{17}O . The strength of the method is that it can be used on diamagnetic minerals (and in powdered form) and noncrystalline materials (glasses, melts, gels); its weakness is that the absorption

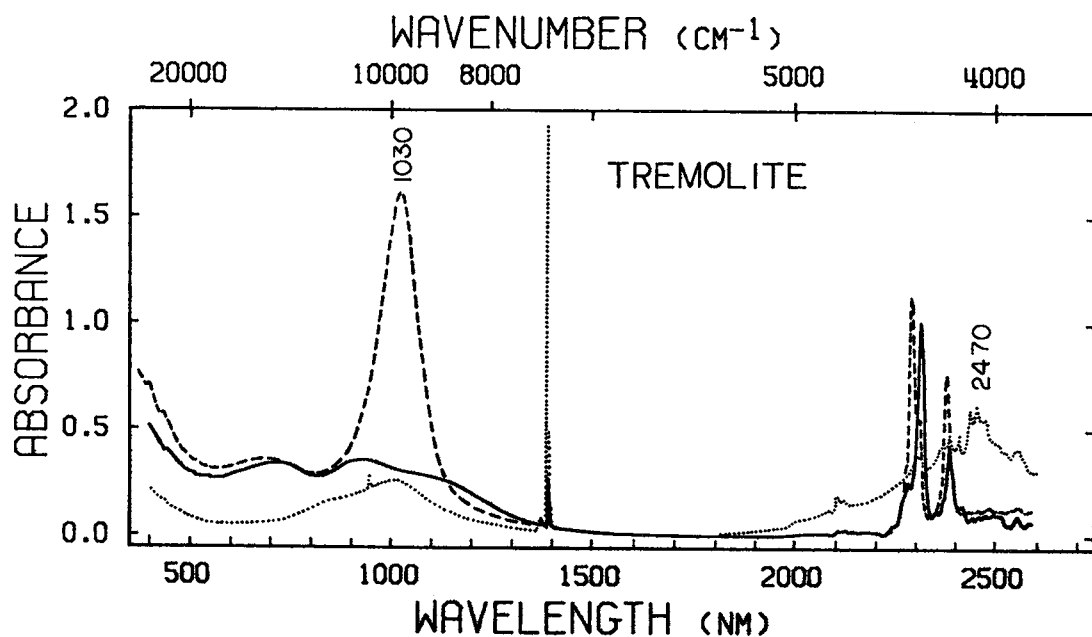


FIG. 19. Polarized electronic absorption spectrum of tremolite; after Goldman & Rossman (1977).

signals are quenched by the presence of significant (≥ 1 wt%) paramagnetic components. Nevertheless, it has been a very important technique in the derivation of Al–Si distributions and local structure in aluminosilicate minerals: feldspars, Kirkpatrick *et al.* (1987); feldspathoids and zeolites, Figure 18 and Fyfe *et al.* (1987), and glasses: Kirkpatrick *et al.* (1986).

Many dynamic processes of interest in Mineralogy and Geochemistry (*e.g.*, diffusion of species in melts and zeolitic minerals) occur on a time-scale that is accessible to NMR spectroscopy (Stebbins 1988). Combined with the possibility of characterizing this behavior at “interesting” conditions (*e.g.*, at high temperatures for the examination of motions associated with melting and magmatic flow; Liu *et al.* 1987), this type of application will be of great geological interest in the future. In addition, new developments in better characterization of quadrupolar nuclei hold promise for much more diverse applications to Earth materials.

Electronic absorption spectroscopy

When light passes through a crystal, it may be absorbed by electronic transitions from the ground state to an excited state of the system. Such transitions commonly involve (1) *d*-orbital transitions in first-row transition elements (*e.g.*, Fe^{2+} , Fe^{3+} , Mn^{2+} , Mn^{3+} , V^{3+} , *etc.*); (2) Inter-Valence Charge Transfer (IVCT),

whereby an electron is transferred from an orbital on one transition metal to an orbital on a locally adjacent transition metal; (3) cation-anion charge transfer, whereby charge transfer occurs between a filled anion-orbital and a partially occupied cation-orbital; (4) transitions between the valence band and the conduction band (*e.g.*, of a semiconducting mineral); (5) transitions between the valence band and any impurity level within the band gap, or between an impurity level and the conduction band. There have been many attempts to use electronic absorption spectroscopy for site-occupancy studies, but with some notable exceptions (*e.g.*, Fig. 19), this has not been very successful. However, it has been very important to our understanding of coloration mechanisms in minerals (Burns 1970, Nassau 1983, Rossman 1988). This is a very difficult area of study; our knowledge is still only qualitative, and in general, very incomplete, as in most common rock-forming minerals, several different mechanisms can contribute to the actual color seen by the human eye. However, recent improvements in instrumentation may increase our understanding in this area.

Electron Spin Resonance (ESR) spectroscopy

ESR involves the resonant absorption and emission of (microwave) electromagnetic radiation by the electrons of a paramagnetic ion. Transition energies are

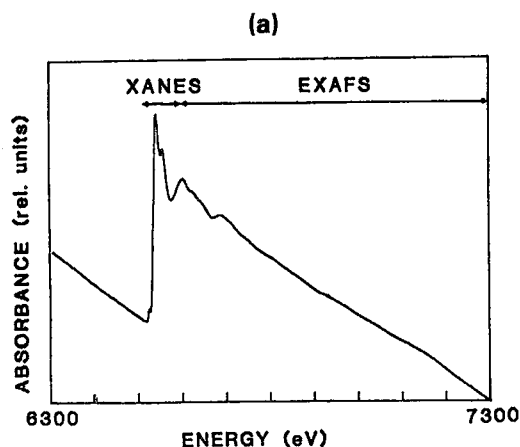
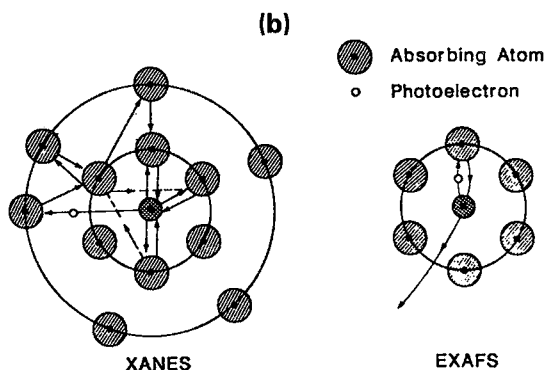


TABLE 4. REE COORDINATION IN F-FREE AND F-BEARING PERALKALINE AND SODIUM-TRISILICATE GLASSES*

F-free glasses		
Complex	coordination	<REE-L> (Å)
La-O	7 O _x	2.42
Yb-O	6 O _x	2.20
Gd-O	7 O _x	2.42
"	6-7 O _x	<2.36>
F-bearing glasses		
Complex	coordination	<REE-L> (Å)
Gd-F	8 F	2.30
Yb-F	8 F	2.23
La-O, F	4 F, 4 O _x	<2.36>

* data from Ponander & Brown (1989a,b)

FIG. 20. (a) K-edge X-ray absorption spectrum of Mn in MnO₂; (b) scattering mechanisms giving rise to the various parts of the spectrum in (a).

sensitive to the surrounding crystal-field; hence the spectra give information on the characteristics of the local environment, and site occupancies can be derived (Calas 1988). ESR is applicable only to paramagnetic species, primarily ions with an odd number of electrons (e.g., Mn²⁺, Fe³⁺), and color centers (unpaired electrons or holes at "lattice" defects). In addition, the paramagnetic species must be very dilute, or else their magnetic moments will interact and result in a broad structureless resonance. Thus ESR is a trace-element technique, and has given us most of the information we have on trace-element ordering in minerals and its possible sensitivity to temperature (e.g., Ghose & Schindler 1969). However, ESR has seen relatively little use in Mineralogy compared with the other spectroscopic methods. Perhaps the increasing interest in trace-element behavior in minerals (promoted by the availability of microbeam analytical techniques for trace elements) will encourage increased use of this technique.

X-ray Absorption Spectroscopy (XAS)

When X rays are absorbed by an element, there is a gradual change in the amount of absorption with energy, interrupted by a dramatic increase in absorption at a specific energy that is characteristic of the absorbing element. This feature is known as an absorption edge (Fig. 20a), and is caused by the excitation of an electron from a deep core level to an empty bound state or a continuum state. When the photoelectron is ejected from the absorbing ion, it may interact with the local environment (Fig. 20b) via (1) strong multiple scattering that produces a modulation close to the absorption edge in the XANES (X-ray Absorption Near-Edge Structure) region of the spectrum, and (2) a weak single-scattering process that produces weaker oscillations at higher energies in the EXAFS (Extended X-ray Absorption Fine-Structure) region of the spectrum. One can derive interatomic distances and coordination numbers of both major and minor elements in both crystalline and noncrystalline materials (Brown *et al.* 1988). Only a small amount of work has been done thus far, partly because of the short time that the technique has been in use, and partly because of the limited availability of the equipment (it needs a synchrotron as an X-ray source; although some normal X-ray sources have been used for such work, they are impractical for most mineralogical and geological uses). Ponander & Brown (1989a,b) examined the behavior of La, Gd and Yb in silicate and aluminosilicate glasses, and derived coordination numbers and *local* mean bond-lengths around the rare-earth species (Table 4), the first information of this sort to be derived. They also showed that in halogen-bearing glasses, there is preferential complexing (Table 4), and here too derived mean bond-lengths to specific ligand types. This sort of work is going to make a major difference to our understanding of noncrystalline materials and the behavior of trace elements in minerals and melts.

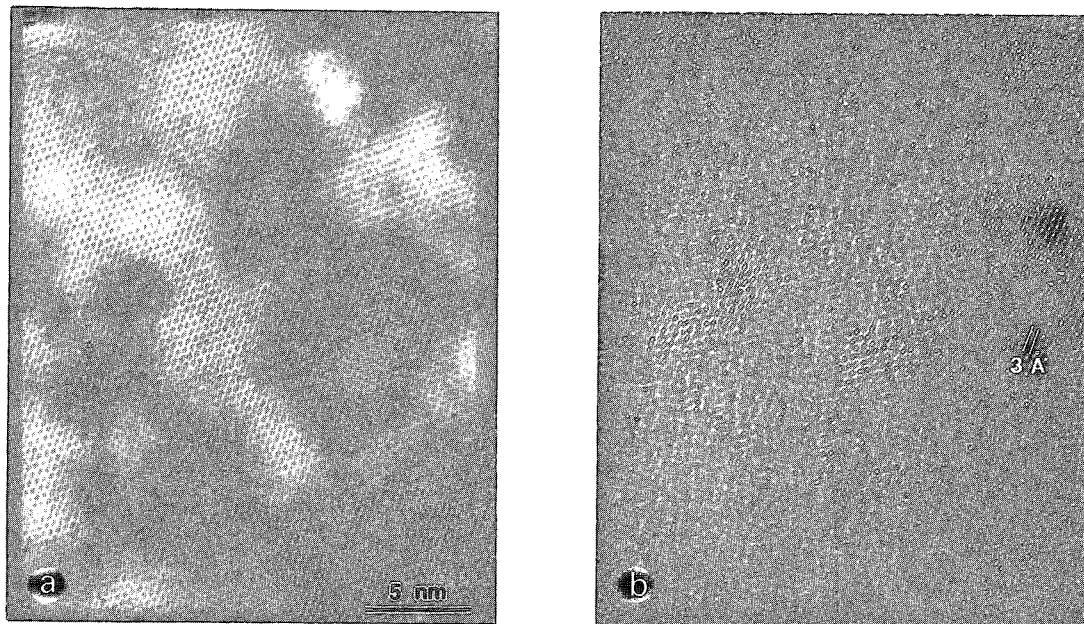


FIG. 21. HRTEM micrograph of olivine partially amorphized by 1.5 MeV Kr^+ ion irradiation; a: amorphous domains the size of displacement cascades in a crystalline matrix (after a dose of 2.55×10^{12} ions/cm²); b: isolated crystalline domains in an amorphous matrix (after 1.7×10^{13} ions/cm²); after Wang & Ewing (1992).

Transmission Electron Microscopy (TEM)

The electron microscope was developed in the 1930s, but was not used widely for mineralogical work until the 1970s. At this time, it began to assume importance in the study of microstructures, as it extended our powers of observation way below the resolution of the optical microscope. Fine exsolution-induced textures revealed the presence of low-temperature solvi in many important rock-forming minerals, and the development of AEM (Analytical Electron Microscopy) played an important role in quantifying the chemical characteristics of such structures. Antiphase domains and twin domains were identified in many minerals that show high-temperature or high-pressure phase transitions. In particular, antiphase domains show wide variation in size and texture within a specific mineral type, and contain significant information on thermal history. Thus Carpenter (1981) showed that domain size in omphacite correlates strongly with peak metamorphic temperature, the minerals originally growing with metastable short-range order and then developing long-range order *via* formation of antiphase domains subsequent to initial crystallization. TEM work on this scale should be of increasing importance in the future, particularly in the interpreta-

tion of physical properties of minerals (*e.g.*, magnetism) that play important roles in other areas of the Earth Sciences.

A major step forward in the further application of electron microscopy to Mineralogy was taken by Buseck & Iijima (1974), who showed that structure images of minerals can be obtained at the unit-cell level; such images can now be obtained with a resolution of ~ 1 Å. This gives us a picture of the "real" structure (unlike X-ray and neutron diffraction, which "image" the long-range average structure), and has contributed greatly to our understanding of atomic-scale processes in minerals. In particular, it has shown the presence of extended defects in chain and sheet silicates (Veblen 1981), and has played an important role in understanding low-temperature alteration reactions in clay minerals (Peacor 1992). High-resolution TEM also has played an important role in work on radiation damage in minerals, a topic that has been of significant economic and political interest because of its importance to the problem of nuclear-waste disposal. It has been possible to trace the development of structural damage with increasing dose of radiation (Fig. 21), confirming the model of Ewing (1975) for the final amorphous structure. HRTEM studies have still scarcely touched the large number of

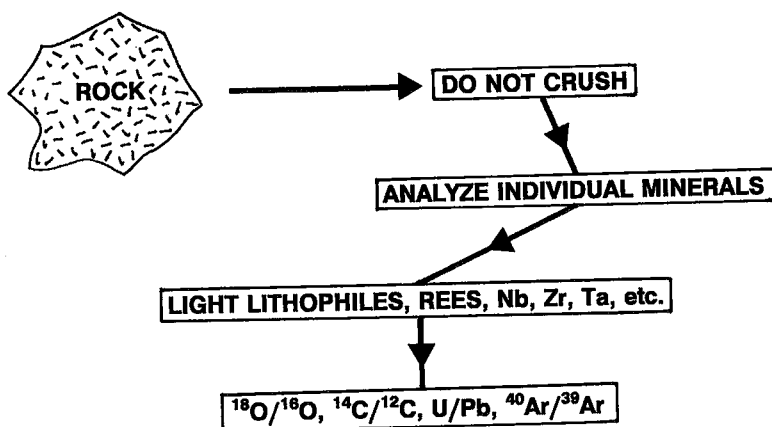


FIG. 22. How to treat a rock.

mineral reactions awaiting study, and a much larger number of these instruments are needed within the Earth Science community.

MICROBEAM TECHNIQUES

In the past, Mineralogy has focused on four main characteristics of minerals: structure, crystal chemistry, major-element chemistry, and physical properties. However, things are changing. Many people are now doing Mineralogy, people who don't consider themselves mineralogists: geochemists, petrologists, sedimentologists, atmospheric scientists, even geochronologists. These people have realized that if you grind up a rock for analysis of any sort, you lose an enormous amount of information (Fig. 22). It is far better to analyze the individual minerals for what you want: light lithophile elements, rare-earth elements (REE), high-field-strength elements (HFSE), oxygen isotopes, carbon isotopes, U/Pb, $^{40}\text{Ar}/^{39}\text{Ar}$, etc. In fact, why analyze the bulk minerals? Again, we are undoubtedly losing information by doing that; we need microprobe methods for this type of work, and we have been getting them in the last ten years.

Secondary-Ion Mass Spectrometry (SIMS)

SIMS uses a focused ion beam to remove ions from the sample and analyze their mass and charge with a mass spectrometer; this was the first microbeam technique to allow the analysis of samples for trace elements and isotopes (Shimizu *et al.* 1978, Lovering 1975). There was some initial trouble in dealing with complexed ions, but improvements in technique and instru-

mental resolution have now resolved many of these problems. The ability to analyze trace samples for REE, HFSE and F is now contributing significantly to studies of mantle processes (Salters & Shimizu 1988). In addition, SIMS is sensitive to parts of the periodic table inaccessible (or only recently accessible) to the electron microprobe, and is important as a microprobe technique for both trace and major light-lithophile elements: H (Hervig & Williams 1988) and Li, Be and B (Ottolini *et al.* 1993). It should not be forgotten that SIMS is an isotopic technique; it has proven very powerful for high (spatial) resolution microprobe dating (Compston *et al.* 1982) of zoned minerals (with different temporal generations of growth) using radiogenic isotopes, and as a microprobe for stable isotopes.

SIMS is also a surface technique, and so by continual analysis of a surface, the *depth profile* of distribution of specific elements can be derived. This has made SIMS an important tool in studies of mineral dissolution and weathering (Muir *et al.* 1990).

Synchrotron X-ray Fluorescence (SXRF)

The fluorescent emission of characteristic X-rays by a mineral or rock has long been used for whole-rock analysis. The recent availability of high-intensity X-ray sources via synchrotron radiation (*cf.* XAS) has allowed the development of a synchrotron X-ray fluorescence (SXRF) microprobe. This has the advantage of very low background signals, and hence is an ideal trace-element technique. Although it must still be regarded as being in the development stage, SXRF shows promise as a trace-element microprobe method (Lu *et al.* 1989) for the future.

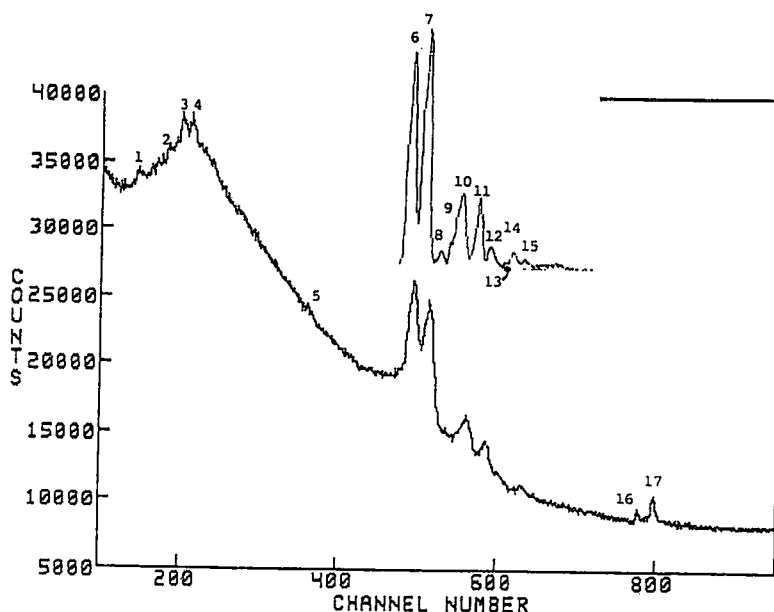


FIG. 23. K X-ray line PIXE spectrum of a sample of apatite from Durango, Mexico, showing the resolution of the various REE K lines; 1 AsK α , 2 RbK α , 3 SrK α , 4 YK α , 5 InK α , 6 LaK α , 7 CeK α , 8 PrK α , 9 NdK α , 10 LaK β , 11 CeK β , 12 SmK α , 13 NdK β , 14 GdK α , 15 TbK α , 16 YbK α_1 and 17 YbK α_2 ; after Durocher *et al.* (1988).

Proton-induced emission methods

The basic principles of this group of techniques are the same as those of the electron microprobe, except that the exciting particles are protons rather than electrons. As the mass of the proton is much greater than the mass of an electron, the bremsstrahlung (the primary contribution to the background radiation) is much lower in proton-induced X-ray emission; hence these techniques are more suitable for trace-element analysis. *Proton-Induced X-ray Emission* (PIXE) is the most common technique, and has been particularly important in the analysis of trace precious metals in sulfide minerals (Cabri *et al.* 1989). In addition, the availability of high-energy (~40 MeV) sources also allows access to K X-ray lines of all elements of the periodic table, making the interpretation of REE spectra much more straightforward (Fig. 23). *Proton-Induced Gamma-Ray Emission* (PIGE) uses the intensities of gamma rays emitted from nuclear transitions in the sample, and *Proton-Activation Analysis* (Halden & Hawthorne 1993) is the proton (and microprobe) analogue of INAA (neutron-activation analysis); these two techniques have not been widely used as yet. Proton-induced methods are not as sensitive as SIMS (but are non-destructive) or SXRF (but they are more developed and more widespread). In addition,

scanning techniques have now been developed, and trace-element mapping is now feasible (Teesdale *et al.* 1993).

Laser-ablation techniques

The availability of lasers has greatly expanded the versatility of many mass-spectrometer techniques, and there is much important development work currently in progress on microprobe and milliprobe sampling techniques (Fig. 24). In some areas, such as $^{40}\text{Ar}/^{39}\text{Ar}$ dating (York *et al.* 1981), techniques are fairly mature, and their application to problems in the Earth Sciences is increasing; others are more in the development stage [*e.g.*, laser ICP-MS (Jackson *et al.* 1993), laser sampling for stable isotopes (Sharp 1990, Powell & Kyser 1991)]. There seems to be no insurmountable obstacles to the future use of these techniques as standard methods for mineral analysis, particularly as they should become more flexible with the future use of excimer lasers.

"MODERN TIMES": THEORETICAL MINERALOGY

The last thirty years have seen the gradual development of theoretical Mineralogy from the isolated work of a very few individuals to a full-fledged major thrust



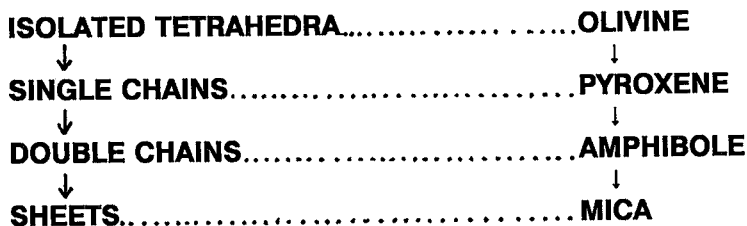
FIG. 24. The wanton destruction of minerals by Hawley medallists involved in laser sampling for mass-spectrometry techniques (from Jackson *et al.* 1993); the sampling diameter has gradually been decreasing, and is currently about 10 μm . Scale bar: 141 μm .

of research by the scientific community. Theoretical Mineralogy is now a recognized area of work, rather than something the field person did when it was snowing, or the experimentalist did when their equipment was broken. The principal effort has involved attempts to understand the structure, crystal-chemistry and properties of minerals at the atomistic level, and further to understand the *dynamic* role that minerals play in geological processes.

Crystal-structure arrangements

The most fundamental work is involved with attempts to order and understand the plethora of complex structural arrangements that occur in minerals. The first step was taken by W.L. Bragg in his well-known classification of the silicate minerals, in which he set up a hierarchy according to the mode of polymerization of the (alumino-)silicate part of the structure. The fundamental nature of this scheme may be seen by comparing it with Bowen's discontinuous reaction series in igneous rocks (Fig. 25); there is a progressive condensation of the tetrahedra with progressive crystallization, indicating the relations between temperature, structural connectivity and stability, with additional implications as to the connectivity of tetrahedra in magmas at different temperatures, pressures and compositions.

There was little further advance until the work of P.B. Moore, who recognized the fundamental nature of this problem. He attacked the structural complexity of the phosphate minerals, hitherto an ugly jungle of ignorance, and showed how order could be brought to the bewildering variety of structural arrangements (Moore



PROGRESSIVE TETRAHEDRAL CONDENSATION WITH PROGRESSIVE CRYSTALLIZATION

FIG. 25. The correspondence between Bragg's classification of the silicate minerals (left) and Bowen's discontinuous reaction series (right).

a

PRIMARY	AMBYGONITE-MONTEBRASITE	Additions, subtractions	TRIPHYLITE - LITHIOPHILITE		Additions, subtractions
METASOMATIC	fremontite	$-Li^+$ $+OH^-$ $+Na^+$ $+Al^{3+}$ $+Ca^{2+}$	NO OXIDATION triploidite-wolfcite natrophilite griphite, scorzalite whitlockite	OXIDATION ferrisicklerite-sicklerite heterosite-purpurite alluaudites	$-Li^+$ $+Na^+, Ca^{2+}$ $+OH^-, H_2O$ $+Ca^{2+}$
EARLY	apatite	$+OH^-, H_2O$	phosphoferrite-reddingite ludlamite hureaulite phosphophyllite scholzite fairfieldite messelite eosphorite childrenite bjarebyite goyazite roscherite moraesite switzerite vivianite	favorite kryzhanovskite rockbridgeite frondelite dufrenite laubmannite (?) azovskite (?) clinostrengite strengite bermanite laueite pseudolaueite stewartite strunzite xanthoxenite coccenite mitridatite leucophosphate avelinoite faheyite	
HYDROTHERMAL	lacroixite marinite wardite brazilianite bertossaite apatite palermito augelite lithiophosphate crandallite montgomeryite	$+Na^+$ $+Zn^{2+}$ $+Ca^{2+}$ $+Al^{3+}$ $+Ba^{2+}, Sr^{2+}$ $+Be^{2+}$			
LATE			residue: carbonate-apatite crandallite	residue: carbonate-apatite crandallite $Fe^{3+}, Mn^{2+}, 3+$ hydroxides	$+Ca^{2+}$ $+K^+$ $+Na^+$ $+Be^{2+}$

FIG. 26a. Paragenetic hierarchies in pegmatitic phosphates; after Moore (1973).

1965, 1970). Furthermore, he followed this up with a detailed paragenetic synthesis (Moore 1973), and showed that, as in the case for the rock-forming silicates, the sequences of crystallization in phosphate paragenesis are related to the underlying structural arrangements (Figs. 26a, b) and to the effects of oxidation and hydrolysis; truly outstanding work!!

Crystal chemistry

The work of W.L. Bragg and Linus Pauling served as a general basis for crystal chemistry up until the late 1960s. However, the rapid expansion in the amount and accuracy of crystallographic data on minerals (and other inorganic materials) caused by the introduction of the automated four-circle diffractometer needed a more quantitative basis. This came first with the empirical "ionic" radii of Shannon & Prewitt (1969) and Shannon (1976). I always get a slightly uneasy feeling here when I use the word "ionic", as it seems to be charged with such emotional significance for so many people, whereas the radii in question have (like many of

Pauling's rules) nothing to do with the models of bonding at all. The radii are essentially the grand mean bond-lengths in crystals, factored into two parts (the "radius" of the atoms at each end of the bond) such that their sums reproduce those grand mean bond-lengths; as such, they are model-independent [except for the choice of a "starting radius" (usually for O^{2-})]. They have played an immensely important role in our understanding of mineral (and general inorganic) chemistry, particularly in complex structures (e.g., amphiboles, micas), where the combination of crystal-structure refinement and crystal chemistry has been very powerful.

Various developments of Pauling's second rule (Pauling 1929) have also been of great importance in understanding structural stability. Again, this work seems to have been driven by the availability of large amounts of crystal-structure data at the end of the 1960s. The scheme of Brown & Shannon (1973) is now widely used in structural inorganic chemistry and mineralogical crystallography. It has played an important role in our understanding of both short-range and long-range order

b

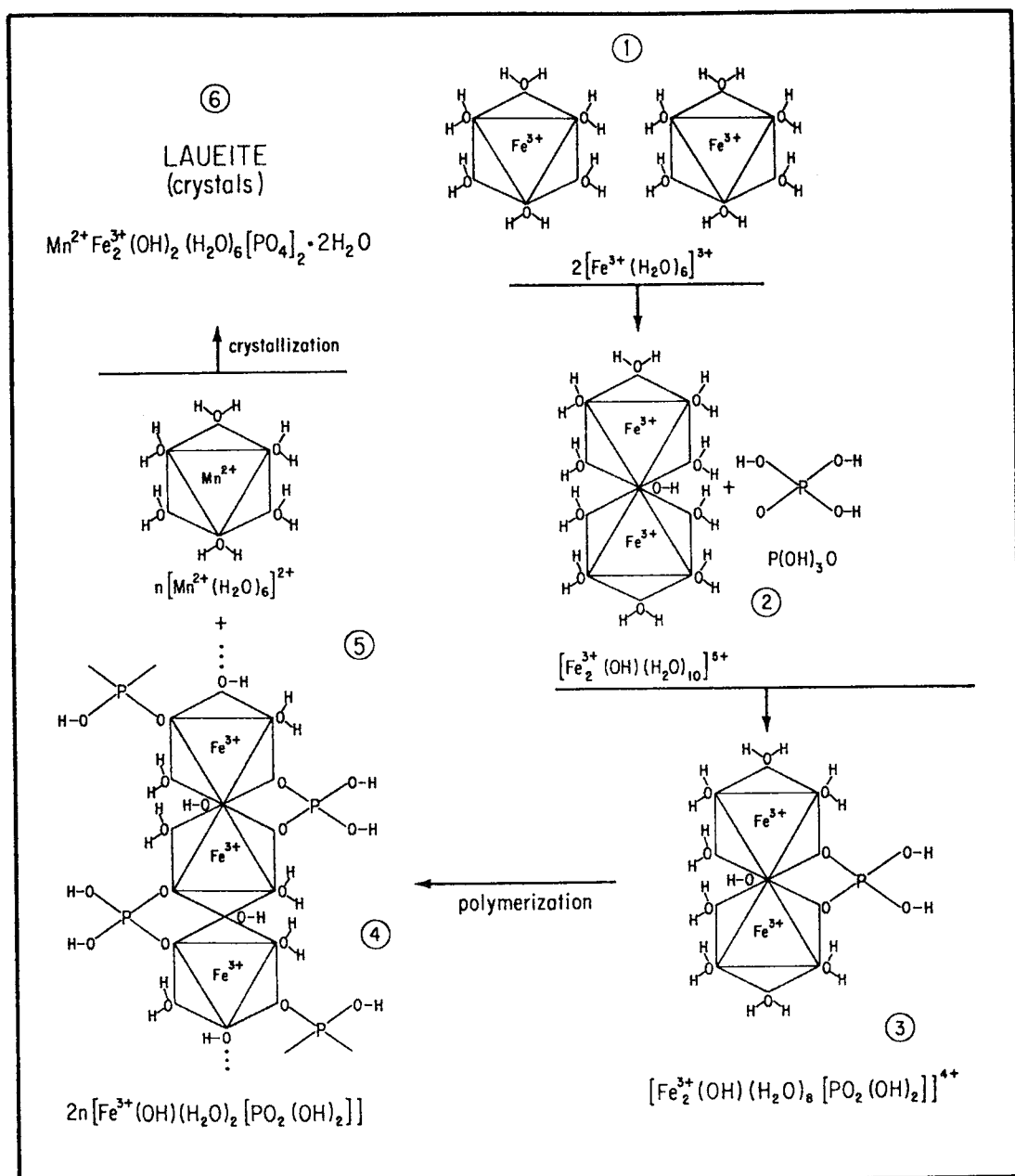


FIG. 26b. Progressive structural condensation in pegmatitic fluids; after Moore (1973).

in crystals, and in combination with the systematization possible using ionic radii, has contributed greatly to our understanding of the more complex of the silicate minerals.

Thermodynamics

In the 1950s, the recognition that there were compositional relationships between coexisting mineral solid-

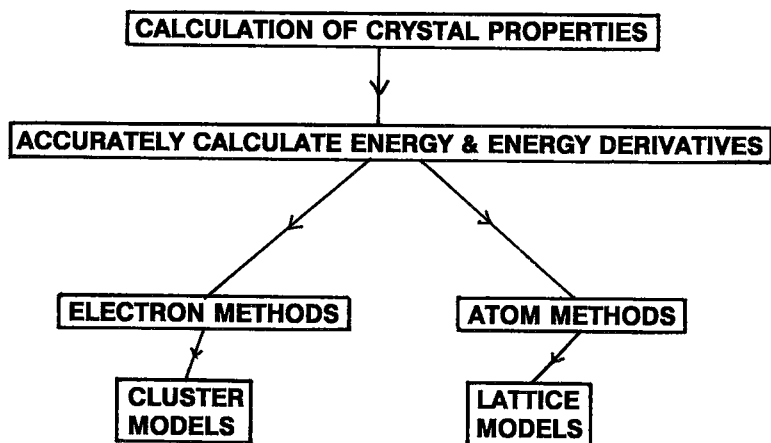


FIG. 27. Some theoretical approaches to the calculation of the structure and properties of minerals.

solutions, and that these relationships seemed sensitive to external conditions, led to the introduction of thermodynamic modeling on a large scale. Classic work by Mueller (1961) and Kretz (1963) on ferromagnesian silicates in metamorphic rocks was followed by much work on common minerals from a wide variety of environments. The general thrust, of course, was to eventually derive geothermometers and geobarometers by which the temperature of "crystallization" of the rock could be measured. It was soon recognized that several barriers lay in the way of this goal. Internal (intracrystalline) ordering also contributed to the exchange process; with increased knowledge of long-range order in common rock-forming minerals, this was (in principle) overcome. However, it was gradually realized that kinetics could play a significant role in controlling the final chemistry of minerals with regard to intercrystalline and intracrystalline order, and that the kinetic aspects of these two processes will also be different.

At some stages in the development of this topic, it has seemed that the difficulties were insurmountable. Nevertheless, the last twenty years have seen the development of numerous geothermobarometers, whereby the conditions of *equilibration* of a rock (or a subsystem within a rock) can be calculated with accuracies commonly approaching $\pm 25^\circ\text{C}$ and 1 kbar.

Structure and properties of minerals

This heading subsumes a variety of topics that generally are given other titles, and overlap strongly with other fields (e.g., thermodynamics). However, they are grouped here as they are usually what can be designated as "model-dependent" approaches. Thus, rather than look at a large number of data and develop *inductive* "rules" (such as Pauling's rules, ionic radii, etc.), these

methods propose a specific model (usually of the chemical bond) and usually proceed in a *deductive* fashion to calculate properties of interest. Of course, not all work adheres to this scheme, and indeed it should not. Many of the calculations are of a complexity to obscure the underlying physics and chemistry, and many investigators have chosen to use a more inductive approach, whereby they rationalize observed stereochemical correlations with qualitative ideas developed from a theoretical model; this has the advantage of conveying a physical-chemical "feel" for the behavior of complex structures.

We may summarize the goals of much of this work in the following way: given an approximate atomic arrangement, we wish to (1) optimize the atomic arrangement to give accurate atomic positions, and (2) calculate the (static and dynamic) properties of the structure. We can recognize two principal approaches to this problem. I thought about the best way to name these without causing religious dispute, and decided that this was best done according to the smallest unit treated: *atoms* or *electrons* (Fig. 27).

The first "atom" model for crystal structures was developed in the 1920s, primarily by Max Born with input from Madelung (1918), and involved a simple two-body interatomic potential (Born & Landé 1918). Most subsequent models have involved some form of two-body potential. Those who don't like the "ionic" tradition of this model prefer a Morse-type potential, whereas the Modified Electron Gas (MEG) model has been introduced for the nonempirical determination of repulsive parameters. Whichever method you choose, deviations from the Cauchy relationship show that a central two-body potential is not sufficient, and all approaches now include additional noncentral potentials of some form. Detailed developments along these lines

are summarized by Burnham (1990). These models have improved out of all recognition in the last twenty years. They are now capable of predicting structural details, phonon-dispersion relations, elastic properties, thermodynamic data and (most impressively) isotope fractionation factors in such anisodesmic structures as calcite (Dove *et al.* 1992) and diopside (Patel *et al.* 1991).

"Electron" methods were introduced into Mineralogy by the pioneering work of G.V. Gibbs (Gibbs *et al.* 1972). This initially involved the use of qualitative molecular-orbital arguments to rationalize observed relations between bond lengths and bond angles in tetrahedral oxy-anions (particularly SiO_4^{4-}) in mineral structures. The success of this approach led to quantitative semi-empirical molecular-orbital calculations on small fragments of silicate structures, the fragment being embedded in a field of some sort. Calculations of gradually increasing sophistication (see the treatment by Tossell & Vaughan 1992) have greatly increased our understanding of stereochemical variations and absorption spectroscopy in minerals. More recently, greatly increased computation power has allowed the generalization of even *ab initio* methods to periodic structures. This can be done either by formulating the molecular orbitals as Bloch functions (Pisani 1987) or by using Local Density Approximation (LDA) methods such as the Linear Augmented Plane Wave (LAPW) method. These have been quite successful in calculating elastic constants, equations of state and the electronic structure of reasonably complicated oxide minerals (Dovesi *et al.* 1987, Cohen 1991). Among other things, such calculations are important in constraining models of the Earth's core and mantle.

Second-order phase transitions are an important factor in the behavior of many minerals, particularly those that show convergent ordering of cations (feldspars, omphacitic pyroxenes, staurolite, *etc.*). A unified approach to such behavior is provided by Landau theory (Salje 1991), in which there is an interaction between crystal structure and thermodynamics *via* symmetry theory (Hatch *et al.* 1987). If $\rho_0(r)$ is the density function of the high-symmetry phase, and $\rho(r)$, the density function of the low-symmetry phase (the space group of which is an isotropy subgroup of the space group of the high-symmetry phase), the difference between these two density functions can be written as $\Delta\rho(r, T, P, \dots) = Q(T, P, \dots)\Delta\rho(r)$, where $\Delta\rho(r)$ is the difference between $\rho(r)$ and $\rho_0(r)$ extrapolated to the same conditions as $\rho(r)$, and Q is designated as the *order parameter*. The form of the function $\Delta\rho(r)$ is dictated by the change in symmetry at the transition (it must transform as the active irreducible representation associated with the symmetry change), and the amplitude of these changes are described by Q , the order parameter [which must also have the same symmetry properties as $\Delta\rho(r)$]. Although as defined here, Q is a thermodynamic quantity, a change in crystallographic parameters (*e.g.*, site occupancies,

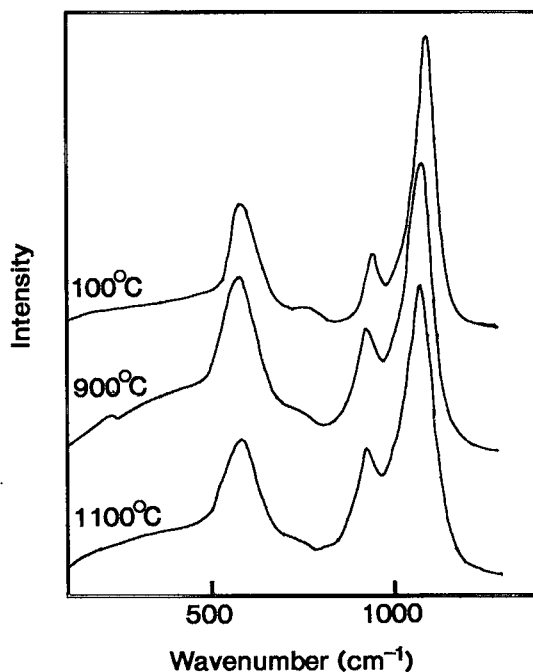


FIG. 28. Temperature-reduced Raman spectra of glass (100°C) and melt (900 and 1100°C) of bulk composition $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 0.027\text{NaAl}_2\text{O}_4$; the liquidus temperature is 850°C. Note the similarity of the spectra of the glass and the melts; after Seifert *et al.* (1981).

positional changes, spontaneous strain) of the correct symmetry can reflect the behavior of Q . This approach has begun to play an important role in understanding the thermodynamic behavior of such important minerals as feldspars, omphacitic pyroxenes, cordierite, *etc.* In addition, it has led to considerable insight into the behavior of incommensurate structures. Commensurate transitions are associated with symmetry points in k -space, where the ordered state is based on a single subgroup-irreducible representation. However, at arbitrary points in k -space, interaction between two different schemes of order can give rise to a structure resonance that results in incommensurate behavior (McConnell 1978).

GLASSES AND MELTS

An adequate understanding of the physical and chemical features of igneous processes is contingent upon an adequate knowledge of the melt phase (magma). We wish to relate the behavior of such melts to their composition and structure in the range of physical conditions in which they occur. However, the physical conditions of many of these processes are particularly

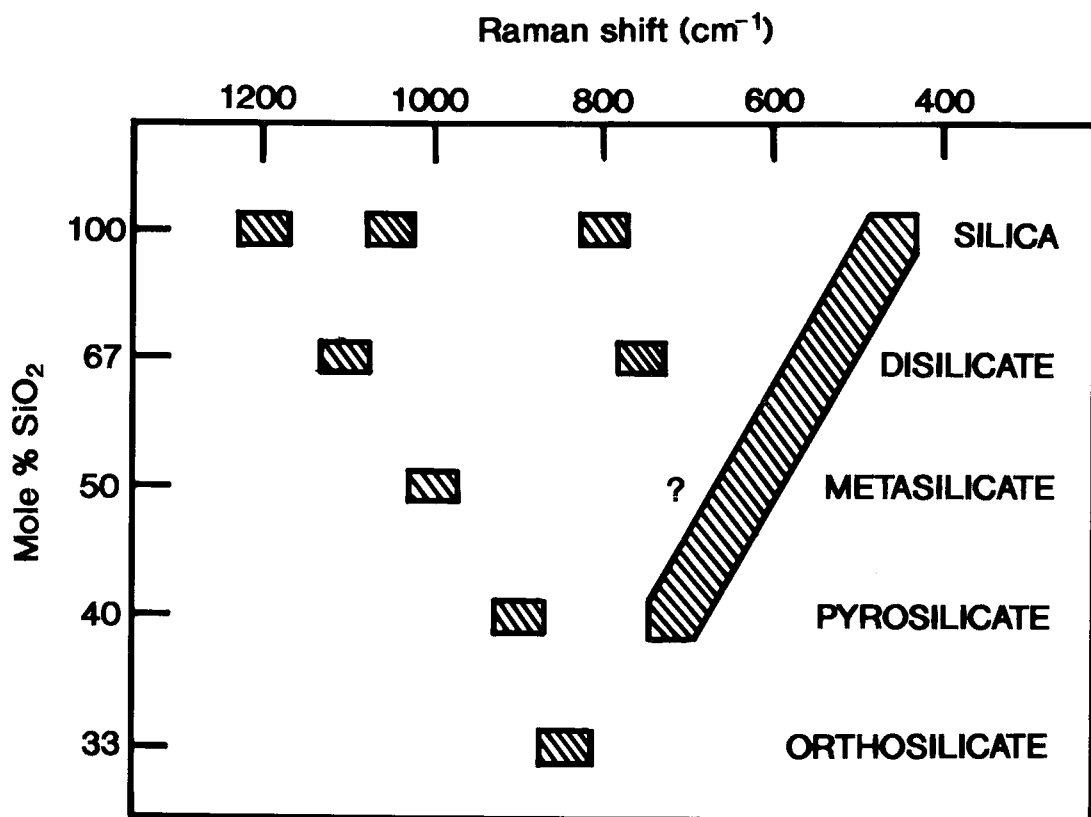


FIG. 29. Frequency variation of the major Raman bands as a function of silica content and long-range connectivity in alkaline and alkaline-earth silicate glasses; after McMillan (1984).

difficult to reproduce in the laboratory, and most work has focused on glasses as melt analogues, as spectroscopic data on silicate glasses and melts are similar (Fig. 28). The study of silicate glasses was initiated by Zachariasen (1932) and Warren (1934), who developed the idea of silica glass as a continuous random network.

Work on geologically relevant glasses did not really develop into a major thrust until about 10 years ago, when spectroscopic techniques (particularly infrared and Raman, NMR, Mössbauer and X-ray absorption spectroscopies) began to be applied to glass structure. Raman spectroscopy has been of particular importance in deriving information on local connectivity in silicate (Fig. 29, McMillan 1984) and aluminosilicate glasses. MAS NMR has been of particular importance in resolving problems of Al coordination, and in detecting unusual coordination numbers for Si that presumably represent transient species quenched from the melt. Of particular effectiveness in deriving coordination numbers for larger and lower-valence cations (*e.g.*, Ca, Na,

REE) is XAS; from a structural viewpoint, such information is of particular importance, as knowledge of the coordination numbers of all species in a glass provide significant constraints on the intermediate-range structure. H₂O is an important constituent of many silicate magmas; infrared spectroscopy has played a significant role in characterizing its solubility and speciation in analogous quenched glasses (Stolper 1989).

Whether a species is a network former, a network modifier or an interstitial constituent strongly affects the physical properties (*e.g.*, viscosity) of a magma. The character of the coordinating anions (*e.g.*, O²⁻, OH⁻, Cl⁻, F⁻, H₂O) gives information on complexing and transport of different elements in the melt. These details of coordination also strongly affect our interpretation of element fractionation between the melt and crystallizing minerals. Until recently, we have had to ignore the structural aspects of silicate liquids (and glasses) because of their intractability. However, this situation is now changing, and the advances of the past few years bode well for the future.



FIG. 30. Malcolm Ross, hero of the asbestos "controversy" and first recipient of the Mineralogical Society of America's Distinguished Public Service Medal.

The asbestos problem

Asbestiform minerals, particularly chrysotile and fibrous amphiboles, have desirable physical properties for many industrial uses, and have been used widely as insulating material, binders and fillers. In addition, many mining and ore-beneficiation processes produce asbestiform minerals as a waste product; this asbestos is usually very finely divided, and is easily transported by wind and water. It has long been recognized that there is a connection between exposure to asbestos and susceptibility to cancer, and for this reason, asbestos has been designated as a known carcinogen. This whole problem is very complex, not the least because political issues have played a major role in its development. Nevertheless, Mineralogy and mineralogists have played a crucial role in this area, and have behaved with an objectivity and integrity (Fig. 30) that some of the other participants would have done well to emulate.

Adequate mineralogical characterization has played an important role in defining the source of the asbestos (for both scientific and legal purposes). Even more, for a long time, mineralogists fought a very difficult battle in trying to investigate the effects of asbestos mineralogy on carcinogenicity in the teeth of opposition from other sectors of the "asbestos community" who seemed more interested in propagating an assumed viewpoint than in learning the truth. However, it is now accepted that the mineralogical characteristics (particularly amphibole *versus* chrysotile) of asbestos are strongly related to carcinogenicity, allowing a much more realistic estimate of hazard due to exposure. Problems of asbestos use continue to arise, and mineralogists will hopefully continue to work on them.

Reactive Acid Tailings (RATS)

ENVIRONMENTAL MINERALOGY

We may divide "environments" into two types: (1) Pristine environments (untouched by Human hand); (2) Perturbed environments (*e.g.*, regions adjacent to tailings piles, smelting plants, coal-fired electricity-generating plants, Kurt Kyser's isotope lab, *etc.*)

All of these environments may display chemical or physical features that are inimical to local inhabitants or undesirable from a global viewpoint, and it is in the general interest of society as a whole that we ameliorate any adverse effects (toxicity, carcinogenicity, physical hazard). Minerals are involved in virtually *all* of these situations, and both the characterization of undesirable processes and the development of solutions to many of these problems will generally fall squarely within the domains of Mineralogy and Geochemistry, with major overlap into Soil Sciences and Geohydrology. We will briefly consider a (very) few examples that emphasize the importance of Mineralogy and Geochemistry in this context.

A feature of many mine sites is the tailings pile, ostensibly an accumulation of "inert" rock. In sulfide mines, these tailings piles often contain considerable residual sulfide minerals (pyrite and pyrrhotite are particularly common). These sulfide minerals are extremely reactive in the oxidizing environment of the surface; they rapidly weather to produce iron sulfate minerals. These sulfates are generally very soluble; they dissolve in vadose groundwaters and find their way into local (and not so local) drainage systems that become extremely acid and overly iron-rich. The result is pollution of local supplies of water, coupled with very adverse effects on local aquatic life. In the last few years, there has been a significant effort to try to understand the mineralogy and geochemistry of these tailings piles, together with the details of their mechanisms of alteration. It is only by understanding the static and dynamic characteristics of these piles that we will be able to ameliorate their deleterious affect on the local environment.

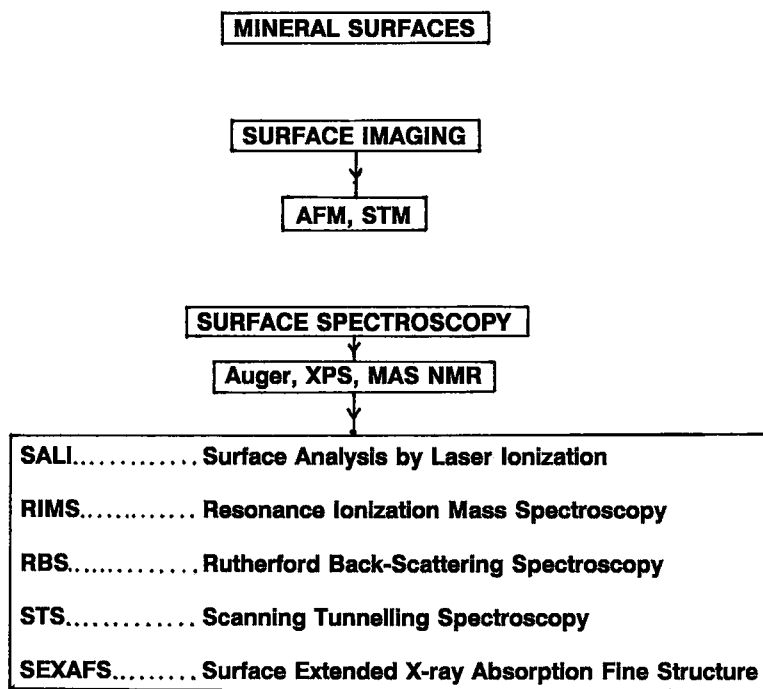


FIG. 31. Surface-sensitive techniques that have been important for the surface characterization of minerals over the last ten years.

MINERAL SURFACES

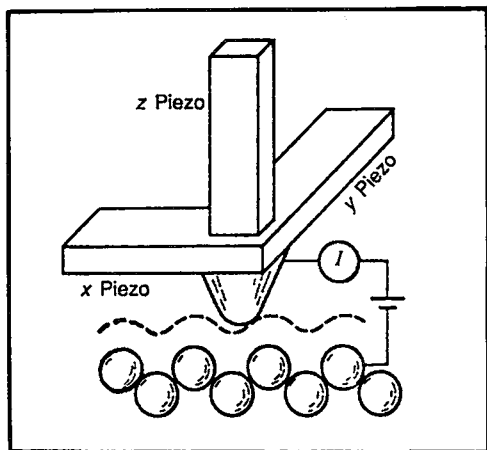
When minerals participate in chemical reactions or processes such as adsorption or dissolution, the "action" often occurs at the mineral surface, the interface between the solid mineral and the medium of interaction, usually (but not always) a fluid of some sort. Although this idea is fairly obvious, it is only the last ten years that have seen an intensive thrust in the study of minerals surfaces. This is primarily because the instrumental techniques whereby we can study mineral surfaces at the atomic or near-atomic level have only been recently available.

Over the past ten years, Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS) (Hochella 1988), various other surface spectroscopies (Fig. 31), and Low-Energy Electron Diffraction (LEEDS) have been used for characterizing surfaces at the atomic level. In particular, AES and XPS have been important in characterizing oxidation reactions at sulfide surfaces, and weathering reactions of silicate minerals, particularly feldspars. However, a major breakthrough came with the development of Scanning Tunnelling Microscopy (STM) and Atomic Force Microscopy (AFM). STM works on electrical conductors, such as native metals and platinum-group minerals, and semiconductors such as sulfides. As shown in Figure 32a, an

atomically sharp conducting voltage-biased tip is brought close to the surface of a mineral. With a positive bias of the tip, electrons tunnel from occupied states (surface electronic-energy states) at the surface of the mineral to the tip; with a negative bias of the tip, electrons tunnel from the tip to unoccupied states in the valence band of the mineral surface. The image of the spatial variations in current gives images of the surface at atomic or near-atomic resolution (Hochella *et al.* 1989); single adsorbed atoms can be imaged, and there is the potential for identifying the chemical species of the atom. AFM produces similar-scale images for insulators. Essentially, it senses the Born-type repulsion between the atoms of the tip and the surface (Fig. 32b), and produces an atomic or near-atomic scale "topographic" map of the surface (Fig. 33) *via* the displacement of the tip. These last two techniques have given us the capability to examine such processes as crystallization, dissolution, adsorption and alteration at the atomic level, and *in situ*, as unlike the electron spectroscopies, STM and AFM can be used in air or water.

This increase in knowledge of the atomic structure of surfaces has also led to extensive modeling of geochemical processes at or near mineral surfaces. This has generally involved following the path of a proposed atomic-scale mechanism and optimizing the structures

(a) STM
↓
SCANNING TUNNELLING MICROSCOPY



(b) AFM
↓
ATOMIC FORCE MICROSCOPY

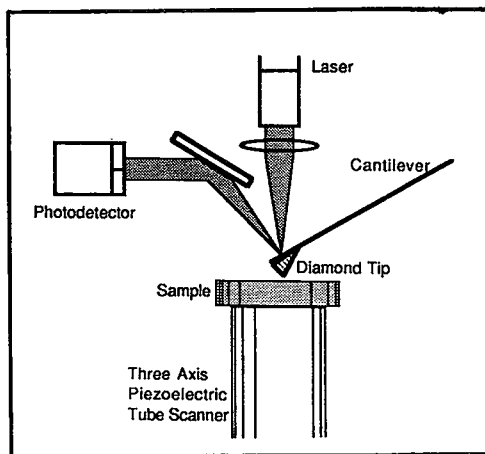


FIG. 32. Surface microscopies. a) Scanning tunnelling microscopy, in which an atomically sharp conducting voltage-biased tip interacts with the surface of conducting and semiconducting minerals to produce atomic (or near-atomic) resolution images of the surface. b) Atomic force microscopy, in which a sharp tip senses differences in the “Born” repulsion between the atoms of the tip and the surface, producing an atomic scale “topographic map” of the mineral surface.

at the various stages *via ab initio* molecular-orbital calculations (e.g., Lasaga & Gibbs 1990). The structure of the intermediate activated complex will have an important influence on the rate of reaction and such key features as isotopic exchange. Not a lot of work has been done as yet in this area, and applications to mineral stability in the natural environment will also have to take into account the common presence of bio-organisms and organic acids (which will presumably modify the hydrogen-bond structure of any activated complex). There is great potential for much interesting work in this area.

THE NEAR FUTURE

What can we expect during the next few years, and what things should we be pursuing? Although the most spectacular advances are usually unexpected in Science, many important directions can be identified (Table 5) by extrapolation of current trends.

Microbeam techniques

As discussed above, there has been a proliferation of microbeam techniques for analysis over the past 10 years. In order for most of these to realize their full

potential, significant improvements in both accuracy and precision are still necessary, as virtually none of them (apart from electron-microprobe analysis) yet approach bulk techniques in this regard. Nevertheless, there is an immense amount of work to do at the current levels of performance, as our knowledge of trace-element and isotopic zoning is minuscule when compared with information available on major-element zoning.

Experimental developments: In the last 25 years, mineral analysis has relied too exclusively on the electron microprobe. As a result, Mineralogy and Petrology have virtually ignored $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios and the light lithophile elements. The ion microprobe should rectify the situation for light lithophile elements, leaving $\text{Fe}^{3+}/\text{Fe}^{2+}$ as a significant problem. Often $\text{Fe}^{3+}/\text{Fe}^{2+}$ can be measured crystallographically on single crystals, but we need smaller-scale information than this, and there is great priority on the development of a microprobe method for $\text{Fe}^{3+}/\text{Fe}^{2+}$. Mössbauer spectroscopy is used on bulk samples, but gamma rays have too short a wavelength to focus either by lenses or mirrors. In principle, the gamma-ray beam could be collimated to form a “mil-liprobe”, but our current gamma-ray sources are too weak to produce an effective microbeam *via* collimation. *Here is a challenging problem for someone!*

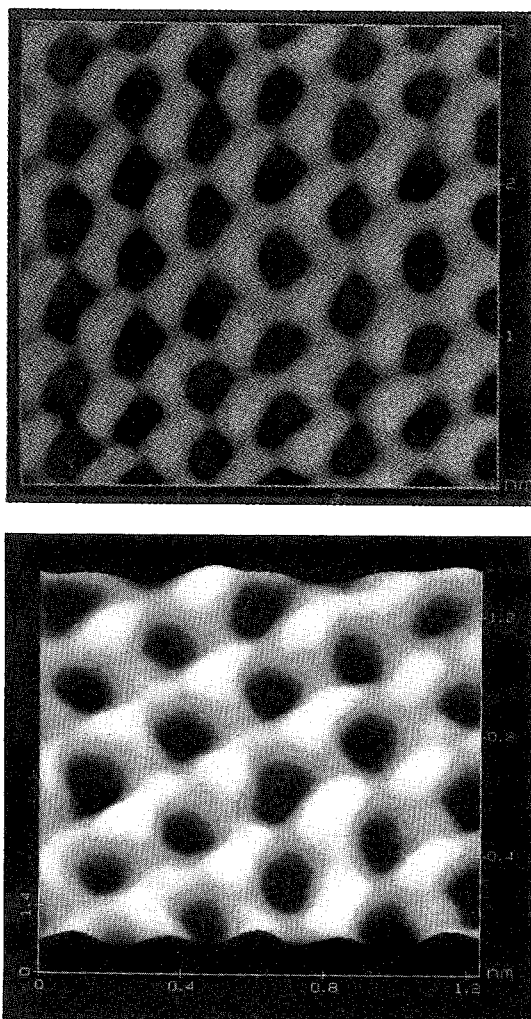


FIG. 33. Atomic resolution images of the {001} surface in lizardite. Top: the silicate sheet, showing the hexagonal rings of (SiO_4) tetrahedra. Bottom: the hydroxyl groups of the octahedral sheet, with the underlying Mg atoms visible; from Wicks *et al.* (1992).

Most of the isotopic microprobes are destructive at the micrometer level. Thus we cannot make repeated analytical measurements on the same point by different techniques (*e.g.*, SIMS and laser-sampled stable-isotope ratios). Usually, this is not a serious problem; however, in cases where there is major heterogeneity on a micrometer scale, this can be a significant drawback. Techniques involving radiation emission *via* nuclear transitions (*e.g.*, PIGE, PAA) do not degrade the sample, and this is one of two reasons why these techniques deserve further development as isotopic microprobes.

Imaging is an extremely important adjunct of electron-microprobe analysis, and Back-Scattered Electron (BSE) images and element maps now play an important role in studies of major-element zoning, mineral intergrowths and alteration. Similar images of other compositional variables (*e.g.*, trace-element contents, isotope ratios) obviously have similar potential, and yet there has been little work in this area. Trace-element mapping by PIXE is now possible (Teesdale *et al.* 1993), but the sensitivity needs to be improved. It is here that the significance of PIGE and PAA becomes apparent, as in principle, maps of isotopic variability could be produced with these techniques. Also of considerable interest is the production of $\text{Fe}^{3+}/\text{Fe}^{2+}$ maps *via* "scanning" Mössbauer spectroscopy. *All of these imaging techniques await development in the next few years.*

Applications: As noted above, the light lithophile elements have been virtually ignored in rock-forming minerals for most of the last 30 years. However, careful work has documented the importance of these elements in minerals, in some cases tracing enigmatic behavior to the undetected presence of these constituents (Dutrow *et al.* 1986, Groat *et al.* 1992). It is obvious that the analysis of samples for H, Li, Be, B (and possibly C) *must* become a normal part of the microprobe analysis of minerals, and that the next few years must see an increase in the number of ion microprobes in the Earth Sciences community.

TABLE 5. IMPORTANT DIRECTIONS FOR FUTURE WORK

MICROBEAM METHODS	
Development of method for $\text{Fe}^{3+}/\text{Fe}^{2+}$	
Further development of PIGE and PAA	
Imaging	- $\text{Fe}^{3+}/\text{Fe}^{2+}$ by SMS (Scanning Mössbauer Spectroscopy)
	- isotopic variations by scanning PIGE
Applications	- EMP <i>must</i> be augmented by IMP and SREF
ATOMIC ORDERING	
Site occupancies of trace elements	- XAS, ESR, luminescence spectroscopy
Zoning in minerals	- major and trace-element zoning
	- oscillatory zoning, feedback effects
	- effects of diffusion in the solid state
SURFACES	
Surface structure in air and water	- at atomic and nano-scales
Adsorption of 'foreign' constituents	- XAS, NMR, STS
Biological interactions	- effects of bacteria, biofilms
GLASSES AND MELTS	
Structure	- characterization of intermediate-range order
	- coordination of minor and trace constituents
Dynamic effects and their relation to physical properties	
PROCESS MINERALOGY	
Detailed application of mineralogical techniques to ore-beneficiation processes	
	- minimization of loss to tailings
	- removal of polluting components prior to pyrometallurgical processing

The same reasoning applies to $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios. Hundreds of thousands of analyses of Fe^{2+} - and Fe^{3+} -bearing minerals have been produced by electron-microprobe analysis over the last 30 years; much of this data is of no lasting value. To test ideas on mineral behavior, one must go back to *complete* analyses done by bulk techniques in the 1950s and early 1960s. Fortunately, some workers are now taking the effort to analyze $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios by "minibulk" methods, and reasonable-quality data are being produced again. However, combination of electron-microprobe analysis with derivation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios by crystal-structure refinement is the best way to go (at least at the moment), and single-crystal diffractometers *should* become as common as electron microprobes for such work.

Ordering, zoning and diffusion

For major elements, the degree of intracrystalline and intercrystalline order can be characterized very accurately by crystallographic, spectroscopic and microbeam analytical techniques. The current experimental need is to develop similar capabilities for trace elements and isotopes.

Experimental methods: Microbeam analytical methods for trace-element and isotopic analysis are currently under development, and should improve in both accuracy, precision and availability in the near future. The primary problem is associated with the characterization of intracrystalline order of trace elements (and possible isotopes). Current techniques available are ESR, various luminescence spectroscopies, and XAS. Both ESR and luminescence spectroscopy are capable of significant improvement, and have the added advantage that the equipment is not prohibitively expensive; however, they can only be used to look at "white" minerals (*i.e.*, minerals poor in paramagnetic species). What has been lacking in the past is a vigorous coherent program of systematic application to well-characterized minerals. Undoubtedly, such an approach would stimulate the improvements in spectral interpretation that are necessary for these techniques to become of significant use. It should also be stressed that this development may possibly be more difficult than for major elements, as trace elements may occupy conventional sites in a mineral structure, or they may be associated with defects. Nevertheless, it is extremely important to understand the structural mechanism of their incorporation, as this will have major implications concerning their thermodynamic behavior.

Theoretical developments: Models of simple equilibrium intracrystalline and intercrystalline order are well developed for several minerals or mineral pairs, and have led to the development of numerous geothermometers and geobarometers. However, in some cases, minerals can show extremely fine-scale complex zoning,

involving both major elements *and* trace elements; in addition, the patterns of zoning of major and trace elements in the same crystal are not necessarily the same. Obviously, these minerals hold a great deal more information on the crystallization process than do homogeneous or monotonically zoned crystals. Do they represent rapidly changing (oscillating) conditions, or do they represent nonlinear dynamic systems involving coupled crystallization and diffusion? There is much scope for work along these lines.

Although conditions of crystallization and equilibration are of interest, many investigators are now becoming interested in rates of cooling (sometimes denoted by the ugly term "geospeedometry"), as these have important tectonic implications. Of particular interest here is compositional zoning in minerals. The zoning profile measured by electron- or ion-microprobe analysis is a convolution of the original zoning profile (produced by crystallization), and the results of subsequent atomic diffusion prior to the "cut-off" temperature for diffusion in that mineral. Work on distinguishing the effects of crystallization and diffusion is now underway (Ganguly 1991), and should prove powerful in deriving cooling rates. The strength of this approach is that it can be applied to several minerals in a rock, *all of which should show the same cooling rate*. There is scope for much work here in the next few years.

Mineral surfaces

Although it seems fairly obvious that mineral surfaces are an area of current *and* future expansion, it seems worthwhile to make a few comments on aspects of particular importance. Although there is much basic science to be done, the important applications are evident right now! Adsorption of toxic chemical species (both natural and industrial) on common surficial minerals is of great importance to many aspects of Environmental Sciences, and must form a significant area of expansion in the future. In many surficial and shallow crustal environments, biological interaction is of great importance, and yet, except for specific well-known examples, has tended to be neglected by the mineralogical community. We are familiar with the effects and importance of *Thiobacillus ferrooxidans* and *T. thiooxidans* in the oxidation and breakdown of sulfide minerals (although what atomic-scale surface mechanisms are involved?). However, what of the almost ubiquitous biofilms and cryptoendolithic organisms? What roles do these play in mineral alteration in near-surface environments? There is great potential for symbiosis between Surface Mineralogy and Microbiology, with significant implications for the Environmental Sciences.

Glasses and melts

Most work to date has focused on the short-range structure of glasses, primarily on the first and second

coordination environments. It is obviously important that this work continue with an expanding range of glass compositions, and both XAS and two-dimensional shift correlated (COSY) MAS NMR spectroscopy should play increasingly important roles in such work. However, there is a pressing need to characterize the intermediate-range structure of glasses. This is quite difficult, as some techniques are not sensitive at this scale, and others have low resolution because of the structural disorder inherent on this scale in glasses. It is possible that differential isotopic neutron scattering (Gaskell *et al.* 1991) may be the key to this problem, but this is not yet clear, as the experiments seem quite difficult to do with sufficient precision.

Of particular interest is the local behavior of trace elements in magmas, as this will significantly affect the partition of trace elements between melt and minerals. XAS seems highly suited to this work, and should hopefully provide much important information on this topic in the next few years.

Process mineralogy

The design of ore beneficiation processes has generally been done on the basis of bulk chemistry, and little attention is generally paid to detailed mineralogy and the behavior of specific minerals through the total beneficiation process. There are three principal reasons for what could be termed as "mineral-based" optimization of a beneficiation process: (1) reduction of commodity loss to the tailings, (2) optimization of energy expenditure, and (3) enhanced removal of undesirable components *prior* to pyrometallurgical treatment. The results of (1) and (2) are of direct benefit to the mill, and (hopefully) give increased return; process (3) results in reduced emission-related problems from the smelter, in accord with both current social mores and Federal regulations. It is not clear why Process Mineralogy is not more widespread and important in this regard at the present time. What is clear, however, is that increasingly severe Federal regulations on industrial emissions are going to greatly encourage such work in the future.

SOME DIFFICULT THINGS TO DO

In case anyone thinks that we have solved all of the difficult problems in Mineralogy, here are some significant problems for a rainy Sunday afternoon.

Structural prediction

Given an approximate atomic arrangement, we can calculate the accurate atomic arrangement and many static and dynamic physical properties. However, we cannot predict the approximate atomic arrangement from the chemical formula. We cannot predict *a priori* the structural arrangements in such simple minerals as halite or periclase, let alone the silicates or the sulfates.

When we treat crystals from any theoretical viewpoint, we deal with them by externally imposing translational symmetry. We cannot *a priori* derive the atomic arrangement of a crystal from any theoretical approach, and any predictions that we may make are based purely on analogy with other structures of the same or similar stoichiometry. So here is a problem really worth solving.

Crystallization and morphology

Figure 34 shows a page from Goldschmidt's Atlas of Crystal Forms (Goldschmidt 1913). Many people view this as a compendium of irrelevant information. They are wrong; Goldschmidt's Atlas is a compendium of information that we are not theoretically advanced enough to understand and interpret. The development of an adequate mechanistic model for crystallization has to include the rationalization and prediction of crystal morphology, as illustrated in Figure 34. One feels that there is a wealth of information on conditions of crystallization contained in the morphology of crystals, if only we could interpret it.

Isotopic order in crystals

Extensive crystallographic and spectroscopic work has shown that both major and minor elements commonly are strongly ordered over nonequivalent sites in a structure. Furthermore, this order contains much information on the history of the crystal, and affects intercrystalline order. Presumably isotopes show similar ordering, and it affects isotope fractionation. However, no one has yet demonstrated the presence of isotopic ordering in a mineral structure, a problem for the experimentalists among us.

THE FRAGMENTATION OF MINERALOGY

There is an enormous amount of work going on in the general area of Mineralogy. However, much of it occurs in such disparate fields that many of us are not aware of the full range of the subject; perhaps even more serious, our peers in contiguous areas (Petrology, Geochemistry, *etc.*) are often completely ignorant of much of modern Mineralogy, and are under the impression that little is going on at all. Here, I will briefly consider a couple of examples.

Zeolites

Natural zeolites are framework aluminosilicates that occur in a variety of igneous, sedimentary and metamorphic environments. They have long been of interest to mineralogists, firstly because of their interesting physical properties, and more recently because of their complex crystal structures. Zeolites have internal atomic- and molecule-scale channels through their structures. This allows them to act as *molecular sieves*, which

Apatit

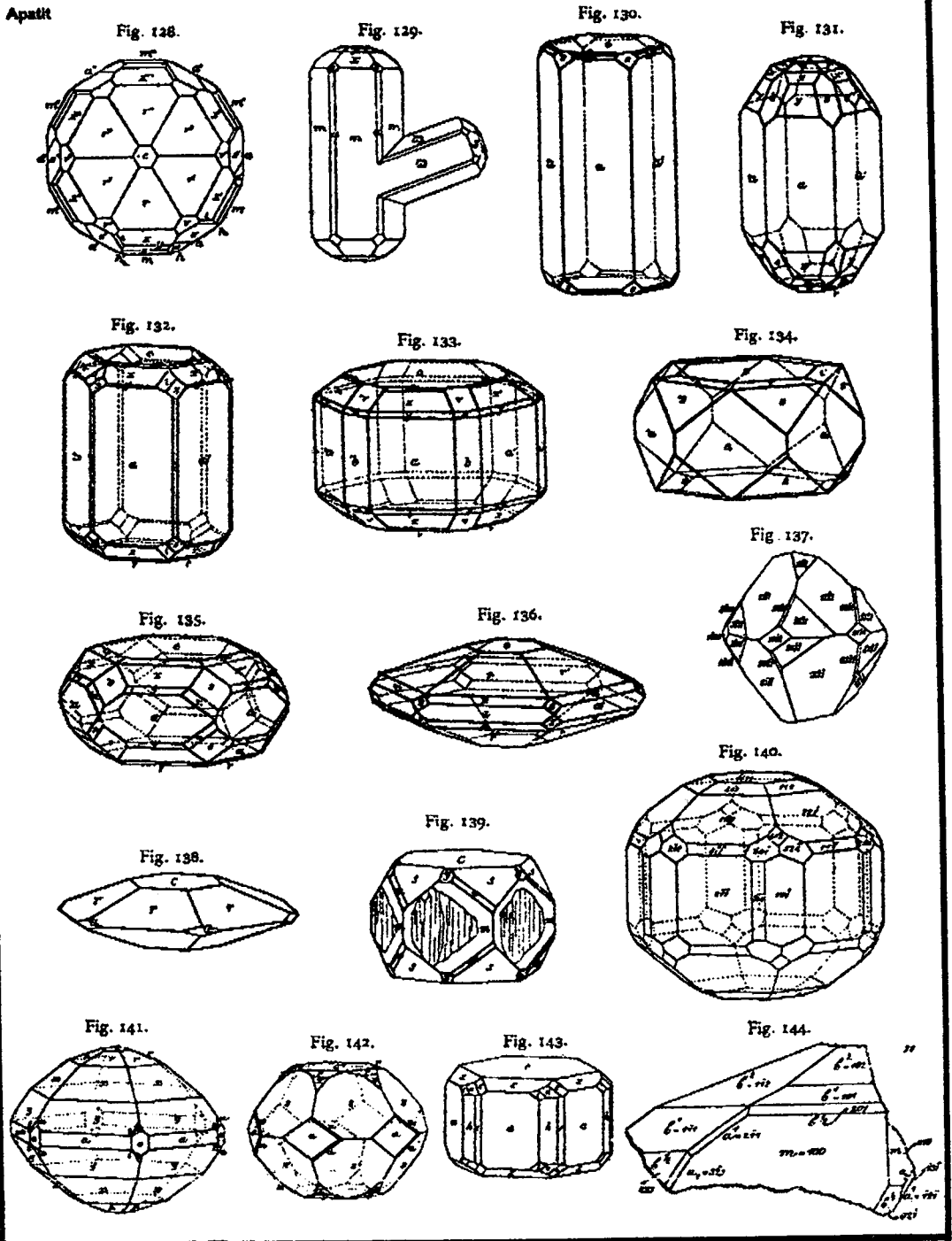


FIG. 34. A page from Goldschmidt's Atlas of Crystal Forms (after Goldschmidt 1913).

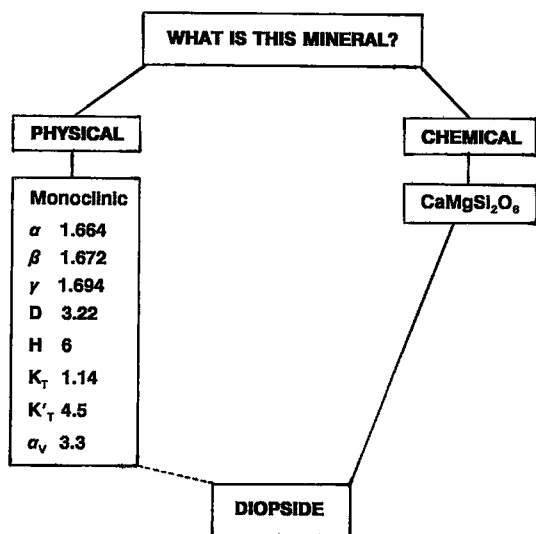


FIG. 35. What is this mineral? Physical and chemical descriptions of the pyroxene diopside.

permit the passage of some molecules and the entrapment of others within their structure. This internal atomic-scale structure also gives them interesting and useful catalytic properties. Consequently, the synthesis and characterization of new zeolitic compounds have become of great interest to some sectors of the chemical industry. This work initially owed much to the general work on natural zeolites done by mineralogists. Indeed, individual mineralogists still play prominent roles in the field of zeolites, and many investigators in the field of zeolites in the industrial sector have been recruited from graduate Mineralogy and Crystallography programs. Nevertheless, most important zeolite work is now published in the chemistry literature rather than in the mineralogical literature, or in specialized journals such as *Zeolites*, a journal that is "invisible" to most Earth Scientists. Thus although much work by mineralogists, and of interest to mineralogists, is done in this field, most Earth Scientists are totally unaware of this aspect of mineralogical work.

Clay Mineralogy

Clay minerals are of great importance to many areas of the Earth Sciences. They are a major constituent of many types of sedimentary rock. They are of crucial importance in controlling porosity and permeability of aquifers and petroleum reservoirs, they are important in many areas of geological engineering, and they are important industrial materials. Nevertheless, most Earth Science students get but a cursory introduction to the

clay minerals in their undergraduate education, and there is an undercurrent of feeling that clays are not "proper" minerals. The result has been that the science of clays and clay mineralogy has withdrawn from the rest of Mineralogy, and now has separate societies, separate journals and separate meetings. They have very strong ties with Soil Sciences, another area with a strong interest in (but not strong ties with) Mineralogy. Again, the result is that all this work in mineralogy is not seen as Mineralogy, but as "something else", to the general detriment of Mineralogy as a whole.

Mineral physics

The current initiative in Mineral Physics has led to a rebirth of interest in the physical properties and *dynamic behavior* of minerals. In addition, the association with Geophysics has been very profitable, in the same way as the interaction between Mineralogy and Petrology. However, I feel this thrust has tended to exclude the *chemical* aspects of minerals, and this is a major error. As indicated in Figure 35, chemistry does play a fairly important role in understanding minerals; the importance of chemistry is also apparent from the rapid development of Mineralogy *via* chemical analysis of minerals in the late eighteenth and nineteenth centuries. It does seem to be an innate characteristic of Physics (or perhaps physicists) to ignore all other branches of Science. This has tended to produce a reaction whereby many people concerned with *dynamic aspects* of mineral chemistry (mineral alteration, transport phenomena, surface properties and adsorption, *etc.*) have aligned themselves with Geochemistry, or even with Chemistry, forming subsections within the major Chemical societies.

This strong polarization into Physics *or* Chemistry (not Physics *and* Chemistry) acts greatly to the detriment of Mineralogy. First, the work done is commonly not visible to the bulk of the Earth Science community. Second, both fields (the *Physics* and the *Chemistry* of minerals) must suffer by not being closely associated with each other, (*i.e.*, by having different societies, different journals of choice, and different scientific meetings).

Why has this fragmentation occurred?

This is not a difficult question to answer; however, some aspects of it may be a little sensitive, as they hinge on what are people's perceptions of "good science". First, a characteristic of very rapid growth (this is illustrated both by plants and by crystals) is multiple branching. To quote a phrase used above, minerals are the fundamental materials of the Earth, and all Earth Scientists need to know about them. The development of a wide variety of analytical methods, and the application of theoretical models and techniques of simulation, have rapidly accelerated in the last 20 years, and have

given rise to all of these "new areas" of mineralogical science. However, the formal Mineralogical community, that is, the major mineralogical associations and societies, have been far too conservative in their treatment of these areas. Rather than recognize that Mineralogy is going through a period of rapid expansion and diversification, we have (by and large) retained our traditional view of the science; we have been unwilling to recognize these new areas, and have been unwilling to expand our area of operations (larger journals, subsections of our societies). Even worse, some have attempted to put limits on what is Mineralogy. Even generic geologists like myself have had articles returned by an editor of a Mineralogical journal with the comment that this would more appropriately be submitted to a Physics journal. Is it any wonder that younger scientists who are leading new areas of expansion in Mineralogy are turning to the Physics and Chemistry societies, organizations that are generally more dynamic, flexible and forward-looking than ourselves? When asked "What is Mineralogy?", I heard a prominent mineralogist (Gerry Gibbs) answer "Mineralogy is what mineralogists do." When acting as reviewers, associate editors, editors and society officials, we would all do well to remember these words of wisdom.

Another important factor in this fragmentation of Mineralogy hinges on the relative scientific importance and perceived level of difficulty associated with various aspects of Mineralogy by practitioners without a wide base of experience. Some people involved in the physics of minerals, chemical modeling, and petrological aspects of minerals, look down on the description of new minerals as a trivial activity. This attitude stems from lack of experience. The characterization of a new mineral *can be* extremely difficult from an experimental viewpoint, and often a very high level of experimental expertise is required, as one is frequently working with minimal amounts (sometimes one grain) of material, and the mineral may be (to use a traditional word) "grungy". The second important point is that without description and characterization of new minerals over time, we would know nothing about minerals at all! Does anyone really wish to publicly endorse the view that now (in 1993) we know enough minerals, and do not need to characterize any more? The reverse effect is also present. Some people involved in the characterization of new minerals have looked askance at the development of Theoretical Mineralogy, with the view that this "non-sense" has little or no connection to reality, and little or no direct application to "real" minerals. A little more tolerance and appreciation of the work done by all sectors of the community working on minerals would go a long way toward pulling all of these branches back into a coherent discipline.

The teaching of Mineralogy

Is this fragmentation of Mineralogy an important

issue? From the scientific viewpoint, one might argue that it is a healthy sign of growth, and that the lack of communication between the subfields is something that will change with time. However, it is of great importance from an educational viewpoint.

Earth Science departments (along with all other departments in our Universities) are under increasing financial pressure because of decreasing (effective) support from Provincial (State) and Federal Governments. This condition is exacerbated by the (quite justifiable) expansion of some areas of Earth Science, particularly those heavily involved in Environmental Sciences and issues of Global Change. As a result of these two factors, the traditional areas of Earth Sciences are under significant pressure. This is particularly true of Mineralogy, primarily because the other subdisciplines view it as a static area where no significant progress is occurring. Above, I have tried to make the case that the latter viewpoint is erroneous. However, it is the fault of us mineralogists that this viewpoint is common. We have not demonstrated the intellectual vitality of our subject to the rest of the Earth Sciences; we have allowed it to fragment and find other "homes" in Physics, Chemistry, and the other subdisciplines of the Earth Sciences. It is up to *us* to "rehabilitate" Mineralogy in the eyes of the Earth Science community while it is still an extant discipline.

If Mineralogy ceases to be taught (*by mineralogists*) as a specific subject in undergraduate curricula, it will have a very detrimental effect on the Earth Sciences. New ideas involving minerals will be slower in being developed and accepted by a community with minimal knowledge of Mineralogy. For example, it has recently been shown that atmospheric dust is an important catalyst for photochemical reactions in atmospheric gases at high latitudes. As a mineralogist, one's immediate thought is that the mineralogy of this dust, plus the associated surface properties of the various constituent minerals, must play a crucial role in this process, as this catalysis presumably involves a surface reaction of some sort. However, as far as I'm aware, no work has yet been done on the mineralogical and surface characterization of this dust. (If I'm wrong about this, and work has been done, it merely reinforces my point on the current fragmentation of Mineralogy).

If Mineralogy is taught by a non-mineralogist, it tends to be treated in a cursory manner, with in-depth coverage of minerals in the area of expertise of the instructor, and superficial coverage or total omission of other areas. We have all met graduates from traditional "hard-rock" schools who are well educated in "igneous" and "metamorphic" minerals, but know next-to-nothing about "sedimentary" minerals (clays, halides, sulfates, *etc.*) or "ore" minerals (PGM, sulfosalts, *etc.*), and *vice versa*. If Earth Scientists are to function well as scientists, they must be conversant with *all* groups of minerals, and must be knowledgeable about current analytical methods. It is the mineralogist that has this expertise, and the

mineralogist must teach Mineralogy as a core part of any Earth Science curriculum.

General disclaimers

I have undoubtedly been influenced in my choice and emphasis of topics by my background. However, as my background is that of a geologist, I do not feel that this is necessarily a bad thing. I have emphasized the importance of experimental techniques very strongly, perhaps overly so. However, I am a strong believer in using complementary techniques to characterize minerals, as the whole is almost always greater than the sum of the parts. We will only understand complex minerals and complex processes by making the difficult measurements that few want to make, while *not* neglecting the standard measurements that are often designated as trivial by the experimentalist with the big instrument. The key is to be interested in the *mineral* and not in the technique.

In writing this paper, I have made no attempt at all to "read up" on Mineralogy after the year 1900. What I have dealt with here is what has caught my own attention over the last 25 years, and has been written "off the cuff"; thus I may not have given due emphasis to some fields of Mineralogy in this article. Fortunately, this is not a significant issue here, as Presidential Addresses are not reviewed. In addition, I wanted to give a general impression of one person's views (my own) at one time; hence the current article was written over a period of two weeks, to give a "snapshot" view rather than a "scholarly analysis" of the situation.

Why did I write this?

When I agreed to stand for President of MAC, I had intended my Presidential Address to be on the topology and energetics of crystal structures. However, I was persuaded to the present topic, a whirlwind tour through Mineralogy, by comments I have heard from Earth Scientists depicting Mineralogy as a "sunset" science. These sentiments are due completely to ignorance and lack of scientific insight. This is a tremendously exciting time to be doing Mineralogy, with the explosion of experimental and theoretical techniques, and the fundamental nature of the many complex problems that need to be solved. *Minerals are the basic stuff of the Earth, and their study will always remain at the core of the Earth Sciences.*

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