ROCK-FORMING SILICATES

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Introduction

Rock-forming silicates are the focus of an active and diverse research effort. In the past quarter-century many researchers have examined these complex phases to gain an understanding of unifying principles of crystal chemistry and physics, while other mineralogists and petrologists have looked to natural silicates as a key to deducing the thermal and barometric history of their host rocks.

The framework for the research described in this review is built on two fundamental questions. The first question is posed implicitly by many of the experimentalists who study silicates:

Given the temperature (T), pressure (P), and composition (A) of an environment, what is the equilibrium phase assemblage and what are the structural, physical, and thermo-chemical properties of each phase?

In recent years much effort has been devoted to the study of variations in crystal structure, optical properties, spectra, and thermochemical parameters with T and P, in addition to more routine experimentation under room conditions. Systematic trends in the T-P-X equilibrium behavior of rock-forming silicates are thus emerging.

Other properties of silicates, including intracrystalline cation ordering, intercrystalline element or isotope partitioning, and exsolution, vary with T and P, but do not equilibrate instantaneously. Kinetics of these diffusion-controlled processes are sluggish below the closure temperature, which differs for each phase but is usually a few hundred degrees Celsius in silicates. The T and P history of a rock may thus be "frozen" into its minerals. It follows that a second fundamental question is asked by mineralogists and petrologists:

Given the structure, composition, and other properties of a mineral or coexisting minerals, what can be deduced about the T-P-X history of the host rock?

Two of the most rapidly developing topics for mineralogical research—transmission electron microscopy (TEM) and kinetic experiments—are a direct response to this question.

This review includes a summary of a broad spectrum of research, from theoretical calculations on bonding and lattice energy to laboratory synthesis and stability experiments, to field studies of mineral paragenesis, alteration, and weathering. It is a healthy sign that many mineralogists, recognizing the interdisciplinary nature of silicate research, have contributed to this entire spectrum of studies.

Several topics directly related to rock-forming silicates are not reviewed in this paper. Many important studies on industrial silicates, such as zeolites, clays, and ceramic minerals, have appeared since 1978 but are not listed systematically because of restricted space. Geochemistry based on uranium- or potassium-bearing silicates is not reviewed. Experimental studies on the stability of individual silicates, either alone or with volatiles, are tabulated, but phase equilibria of multicomponent systems including SiO₂ proved too numerous for the
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limited space available. In spite of these subject limitations, more than 360 papers by 200 workers are cited.

Structure and Bonding

Most of the macroscopic properties of silicates are the direct result of interatomic forces. Relationships between bonding and structure in silicates, though quantitatively complex, are central to an understanding of mineral behavior and were featured at the 1980 conference on structure and bonding at Castle Hot Springs, Arizona (O'Keefe and Navrotsky, 1981).

A patient advocate of computational quantum chemistry has been G. V. Gibbs, who has almost single-handedly educated a generation of mineralogists in the use of molecular orbital (MO) modeling. Gibbs (1982) reviewed "Molecules as models for bonding in silicates" as his Mineralogical Society of America presidential address and thus provided an excellent review of computational methods and their application to understanding silicate stereochemistry.

The ionicity of bonding in silicates remains a matter of debate (Pauling, 1980; Stewart et al., 1980), but modified ionic models are still useful in describing aspects of silicate structure (Tossell, 1980; Dollase, 1980; Bish and Giese, 1981).

Systematic studies of silicate topology have revealed close relationships between seemingly unrelated structures (Thompson, in O'Keefe and Navrotsky, 1981) and have led to identification of unsolved complex structures (Smith and Bennett, 1981).

The determination of silicate crystal structures by x-ray and neutron diffraction, primarily with single crystals but also recently with silicate powders (Lager et al., 1981), continues to be a major research effort in mineralogy, in spite of the fact that virtually all major mineral structures are known. Compositional variants and increased precision are the most common reasons for recent studies, which include several new refinements of micas, feldspars, and olivines.

Modulated structures, as observed in plagioclase (Wenk, 1979), mullite (Nakajima and Ribbe, 1981), and yoderite (Higgins et al., 1982), were also the subject of an American Institute of Physics conference (Cowley et al., 1979).

Comparative crystal chemistry, or the study of structural variations with T, P, and X, has expanded the objectives of many crystallographers. Recent work in this field, including the first combined T-P crystal structure determinations, is described in a monograph by Hazen and Finger (1982).

Elastic properties of silicates have been measured by Brillouin scattering (Levien et al., 1979; Shimizu et al., 1982), shock-wave techniques (Arends, 1980), and acoustic methods (Bonczar and Graham, 1982), as well as by static x-ray diffraction of samples in a diamond-anvil pressure cell (Bassett, 1979; Yagi et al., 1979). In addition, synchrotron radiation combined with energy-dispersive detectors may soon result in the real-time measurement of silicate compressibility (Bassett, 1980). Despite a general agreement between the different types of static and dynamic compression measurements, a few compounds (most notably oxides) yield different values of bulk modulus, depending on the method employed (Jeanloz and Sato-Sorensen, 1982). Differences in starting materials, which are often incompletely characterized, may contribute to these discrepancies.

Optical, electrical, and magnetic properties of minerals are primarily a function of electronic structure. Optical and infrared spectroscopy continue to aid in the understanding of transition-element distribution and electronic structure in silicates. Studies of pyroxenes (Rosman, in Prewitt, 1980), olivine polymorphs (Shankland et al., 1979; Jeanloz, 1980), and mixed-valent iron (Fe²⁺ with Fe³⁺) in minerals (Anhauer and Rosman, 1983) were notable contributions. Mössbauer spectroscopy of amphiboles (Goldman, 1979; Thomas, 1982), clinopyroxenes (Dollase and Gustafson, 1982), and mixed-valent silicates (Burns, 1981) have also been used to elucidate the electronic structure of iron-bearing silicates.

The polarizing microscope, though less widely used now than it was two decades ago, has been championed by P. D. Bloss and his coworkers. Optical properties were used by Selkregg and Bloss (1980) and Armbruster and Bloss (1982) to resolve some of the complexities of channel constituents and Al-Si ordering in corderite. Carson et al. (1982), in a complementary study, employed nuclear magnetic resonance to study the same phenomena. Bloss (1981) has also contributed a comprehensive monograph on the use of the spindle stage. A novel technique, optical second-harmonic analysis, has been demonstrated by Bish et al. (1979) to be a useful method for detecting acentricity in minerals that deviate only slightly from being centrosymmetric.

Electrical conductivity data for silicates are necessary to model the earth's interior. Conductivity studies of pyroxenes (Ruehner et al., 1979) and a review by Shankland (1981) are significant contributions. It is possible, however, that trace intergranular impurities such as carbon (Duba and Shankland, 1982) may alter the actual mantle conductivity by more than an order of magnitude from calculated values.

Synthesis, Stability, and Thermochemistry

Silicate phase equilibria have been studied by experimental synthesis for more than 150 years (Yoder, 1980), and research on phase stability continues to be crucial to our understanding of conditions of formation and equilibration of rocks. Virtually all major groups of rock-forming silicates have received ongoing attention, but renewed interest in feldspar phase relations is of special note. Grove et al. (1983) have reexamined data for plagioclase and propose a novel subsolidus T-X diagram that includes two tricritical points and their associated conditional spinodals. This model is successful in matching plagioclase microstructures to known ranges of stability. More than ten studies of feldspar stability in the presence of volatiles have added to the already vast literature.

Phase equilibria of pyroxenes on the
quadrilateral are better understood as a result of the exhaustive studies of melting relationships by Hübner and Turnock (1980) and Turnock and Lindsay (1981). Pyroxene research has been summarized in an excellent volume of the Reviews in Mineralogy series (Prewitt, 1980).

The complexities of amphibole crystal chemistry and phase equilibria, which seem even more bewildering since the discovery of mixed chain-width minerals, are highlighted in a two-volume Reviews in Mineralogy (Veblen, 1981). Additional studies on the stability of anthophyllite (Chernosky and Autio, 1979; Day and Halden, 1979), and hornblende (Spear, 1981) mark what should be an expanded interest in this common and potentially informative group of minerals.

Yet another of the Reviews in Mineralogy series features chapters on each of the major orthosilicate groups, including garnets, olivines, zircons, and aluminosilicates (Ribbe, 1980). Phase transitions in silicates may profoundly affect physical and thermochemical properties, yet one common type of transformation, the reversible transition, cannot be quenched in a synthesis experiment. In situ, T-P investigation, which is essential, is now possible with a heated, single-crystal, diamond-anvil pressure cell for x-ray diffraction (Hazen and Finger, 1981). Hazen and Finger (1979) documented the characteristics of polyhedral tilt transitions, a common type of reversible phase transition, with high-pressure x-ray techniques.

Melting phenomena of silicates have been reviewed by Boettcher et al. (1982). Much work on both experimental and theoretical aspects of silicate melting, including measurement of P-T-X liquidus surfaces, determination of thermodynamic properties of fusion, and identification of structural properties of the melting temperature, remains to be done.

The measurement of thermochemical properties of minerals is one of the most active subjects for silicate research. Thermodynamics of Minerals and Melts (Newton et al., 1981) provides an excellent current overview by many of the leading researchers. The objectives of mineralogical thermodynamicists, including the experimental determination of thermochemical parameters for minerals and their solutions and the calculation of phase equilibria, though far from being fulfilled, are clearly defined by these authors.

One recurrent theme in silicate research is thermodynamic mixing properties and activity-composition relations of silicate solid solutions. Newton and Wood (1980) have observed a systematic nonideal behavior in the volumes of mixing of binary silicates. Thompson and Hovis (1979) performed detailed calculations of the entropy of mixing of zircon and found it to be asymmetric.

Calculations of phase equilibria require precise thermochemical data. A small group of workers, notably those at the University of Chicago, Arizona State University, University of Michigan, and the U.S. National Bureau of Standards, has steadily added to the store of basic calorimetric data. Another group, notably Belegson and coworkers, has made major contributions to the thermochemical data base of silicates from analyses of experimental phase-equilibrium data. Kieffer (1979) has estimated entropies of a number of rock-forming silicates from analyses of lattice vibrations. In a series of pioneering experiments that may greatly increase our understanding of natural rock-fluid equilibria, Frantz et al. (1981) have measured silicate mineral solubility constants as a function of T and P. Improvements in apparatus and the application of Raman spectroscopy to the identification of fluid species will further enhance this research program.

Natural Occurrences

An important aspect of silicate research is the documentation of new occurrences and their unusual chemical or structural properties. Feldspars, pyroxenes, amphiboles, and micas are most commonly chosen for such research. The majority of papers, though cited in the bibliography that follows, are not discussed here. An exception is the intriguing discovery by Smyth (1980) of H2O cation vacancies in a kimberlitic clinopyroxene. Assumptions of pyroxene stoichiometry, therefore, must be reexamined.

Relationships between silicates and their host rocks are featured in the 50th anniversary perspectives of Bowen’s Evolution of the Igneous Rocks (Yoder, 1979). In spite of 50 years of active research, many of Bowen’s original questions still provide a framework for research in igneous petrology.

Weathering and alteration of silicates, which are crucial to soil formation and groundwater composition, have been the subjects of significant new research, owing in large part to the scanning electron microscope. Weathering studies of feldspars, micas, pyroxenes, and amphiboles reflect the interest in mechanisms of silicate alteration and decomposition.

Diffusion-Controlled Properties

The research described above primarily features equilibrium properties, which adjust rapidly to changes in T and P. Fortunately for the geologist, most minerals are not at structural equilibrium in the field. Sluggish atomic diffusion leads to the preservation of characteristics of the high T and P of rock formation. The kinetics of diffusion-controlled processes, including exsolution, cation ordering, and element or isotope partitioning, thus provide the key to deciphering rock history.

Kinetics of diffusion and crystal growth have become a major focus for mineralogists, as demonstrated by the Mineralogical Society of America’s short course and Reviews in Mineralogy volume on Kinetics of Geochemical Processes (Lasaga and Kirkpatrick, 1981). New kinetic studies of diffusion in olivine, feldspars, garnets, and pyroxenes have also appeared within the past four years. Given the importance of diffusion in mineral systems, it is surprising that more effort has not been devoted to the basic calibration of diffusion rates (Yoder, 1982).
Exsolution is an obvious macroscopic consequence of diffusion in silicates, but microstructures, as revealed by TEM, have provided the most complete picture of these complex features. Pyroxene exsolution has received the most attention (Nord, 1982), because the size, morphology, and composition of coexisting lamellae are particularly useful in deducing cooling histories (McGee et al., 1980; McCallister and Nord, 1981; Grove, 1982). Similar variations of exsolution features have been documented in perthites by several authors. Veblen (1983) has observed novel exsolution behavior in the recently discovered sodium biotite wonesite.

Intracrystalline cation ordering, which may be a sensitive indicator of thermal history, has received ongoing attention. Aluminum-silicon ordering in feldspar (Kroll and Ribbe, 1980; Andersen and Naso, 1980) and Mg-Fe ordering in ferromagnesian silicates (Ghose and Ganguly, 1982) continue to dominate this research, because x-ray diffraction studies of ordering are sensitive only to major-element concentrations. Smyth and Taft (1982) have applied channeling enhanced x-ray emission (CHEX), a new technique for determining minor-element site distribution, to silicates. They observed significant ordering of Ni, Mn, and Ca in olivine, even though concentrations of these cations averaged less than 0.2%.

Intracrystalline partitioning of elements provides yet another diffusion-controlled structural property of silicates. Iron-magnesium partitioning between coexisting pairs of minerals is the most widely used phenomenon for geothermometry and geobarometry in petrology (see review by Loomis, this volume). The importance of element-partitioning studies in the deduction of geological history is well illustrated by many papers, such as those in the Proceedings of the Second International Kimberlite Conference (Boyd and Meyer, 1979a,b), in which chemical analyses of nodule minerals are related to nodule provenance.

The partitioning of isotopes, most notably oxygen, between coexisting mineral phases is yet another test of rock history. Clayton (in Newton et al., 1981) has reviewed aspects of isotope thermometry, and Norton and Taylor (1979) and Rumble et al. (1982) have discussed the implications of data on oxygen-isotope fractionation in terms of fluid flow in natural rocks.

The partitioning of elements between minerals and a melt or vapor phase provides information about the structures of both crystals and fluids involved. Of more than a dozen such studies, most involve partitioning of nickel (Mysen, 1979a) or rare-earth elements (Harrison, 1981). Of special interest is the investigation by Gamble and Taylor (1980) of the variation of crystal—liquid partitioning in augite as a function of cooling rate. This study underscores the complexity of deducing the history of a rock from diffusion-controlled phenomena.

Several other nonequilibrium phenomena in silicates, all of which may be used to document aspects of mineral history, have been revealed by transmission electron microscopy. A useful compilation has been edited by Mulvey (1980). Several researchers have illustrated defects (Wenck, 1980; Carter and Kohlstedt, 1981) and antiphase domains (Carpenter, 1981a,b; Wenck and Nakajima, 1980), which are well-known silicate phenomena. The most dramatic evidence for disequilibrium in rock-forming silicates, however, comes from high-resolution microscopy of the biopyriboles. Ordered and disordered chain-widths in silicates (Veblen and Buseck, 1979a), intergrowths (Veblen and Buseck, 1981), alteration (Nakajima and Ribbe, 1981), and an array of beautiful serpentine combination structures (Veblen and Buseck, 1979b) have added a new and exciting dimension to the study of minerals.

Future Research

A well-defined research program now guides the community of silicate mineralogists; the search for answers to the two fundamental questions noted above will continue for many years. Silicate mineral systems are seldom simple, and the nonequilibrium aspects of silicate structure, when better understood, will provide a detailed history of geological environments.

At least one important question, which may some day represent a major research effort, has failed to capture the attention of mineralogists and petrologists:

What is the nature of intermineralic bonding, and what are the structures and properties of mineral surfaces?

Intergranular surfaces may exert a dominant effect on crystal growth, element diffusion, fluid circulation, electrical conductivity, and other transport properties of rocks, yet mineral surfaces and granular interfaces have received little study. As the physics of surfaces are better understood, the mineralogical community will undoubtedly tackle this complex problem.

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Hazen: Rock-Forming Silicate


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