EXPERIMENTAL MINERALOGY AND MINERAL PHYSICS

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Summary

Many geological processes—including natural hazards such as the generation of earthquakes or the eruptive activities of volcanoes—require knowledge of the materials' properties in order to understand principles of mechanisms and parameters that determine them. The determination of microscopic mechanisms—by observing on an atomic scale—is the basis for our understanding of the macroscopic phenomena of the environment, natural hazards, and natural resources. Since the establishment of the crystal-structure models of minerals in the early twentieth century, the interpretation of structure–property relationships ranks among the most important tasks in current mineralogical research, focusing nowadays on experimental investigations simulating the conditions of interest. It is mineral physics that uses these relations of a mineral's property, such as its mechanical, electric, or transport properties.

Optical and electrical properties are intimately tied to a mineral's mechanical behavior, which makes a large number of mineral crystals prominent for its technical and industrial applications because of, for example, its piezoelectric and pyroelectric behavior or its optical activity. On the other hand, it is heat and mass flow as determined through thermal and electric conductivity, in addition to atomic diffusion and elasticity, that is responsible for the flow dynamics within earth's mantle and core.

The vast majority of the earth's interior is not accessible to direct sampling or observation, and most of our understanding is based on remote-sensing techniques such as seismology. To interpret these observation, it is essential to have complementary measurements that determine the properties of minerals at high pressures and high temperatures, which is the basic task of the current research in experimental mineralogy. The ultimate goal is to determine the complete chemical and physical state of constituent matter and finally to discover the constraints for the dynamics of our planet.

1. Experimental Mineralogy

1.1. Indirect Observation through the Experiment

The discovery of planets around other stars do not come because astronomers have observed the planets, although they would certainly love to. The discovery is more likely to be based on observations of the star's motions, which indicate strong nearby gravitational forces, indirectly giving evidence for the existence of planets. So it is with discoveries about earth's core and mantle: the mineralogy of the deep-earth's interior. Because the deepest well ever drilled extends down just 15 km, not even reaching the outer parts of the mantle, researchers have to employ indirect methods to study the earth's interior, which applies even more for our understanding of the interior of other, more inaccessible planets and extraterrestrial bodies.

Using meteorites and seismological evidence as clues, scientists have known, almost since the beginning of the twentieth century, that the earth has a solid, mostly iron, inner core and a molten outer core with a mantle and crust of rocky, silicate material. But for just as long they have been puzzled about how the core and mantle separated.

The primordial planet earth grew out of bits of gas and dust, aggregating over time into a larger, more solid body. Was there then some cataclysmic event billions of years ago that melted much of the planet, prompting the metals and silicates to separate as oil and water do? Or was the separation the result of a more gradual process, a trickling down of the denser molten metals between solid silicate mineral grains to the center of the earth?

One of the most important objectives in the study of geological materials—be they solid minerals, melts, or fluids—is an understanding of the processes that they undergo as a function of their geological history; whether these depend simply on changes in temperature and pressure or involve changes in their chemical environment. The task of studying the behavior of minerals is difficult as it is often quite impossible to carry out experiments on a timescale relevant to those taking place in nature.

Thus it is necessary to deduce the detailed characteristics of processes and mechanisms from the evidence of a mineral's microstructure, which in many cases allows extrapolation of transformation rates and, finally, timescales to be estimated. This article is an attempt to introduce the basic concepts of mineral behavior in a simple way and to give insight into the most important techniques that are available for the experimental simulation and *in situ* measurement of properties in the laboratory.

1.2. Mineral Transformations

From the time a mineral first crystallizes from a melt or an aqueous, hydrothermal solution, it is subject to many changes in both its physical and chemical environment. One of the remarkable features of minerals is the degree to which they respond to such changes by adapting their structures and compositions to the new environment. These adaptations may be subtle changes in bond lengths or major structural transformations involving rearrangements of atomic configurations; breaking and formation of chemical bonds resulting in the formation of new species.

All these processes follow thermodynamics simplest concept, namely to decrease the free energy of the mineral or of the mineral assemblage at the given conditions. The term "transformation" is used in a very general way to include any structural or chemical change that occurs in response to a change in the parameters that determine the environmental conditions.

1.2.1. Polymorphism

The simplest transformation is the change from one structural form to another modification. Many compounds and minerals have different structural modifications, suitable for different pressures and temperatures. This phenomenon of polymorphism is

very common and may be illustrated by considering the various existing forms of silica, SiO_2 (Figure 1).
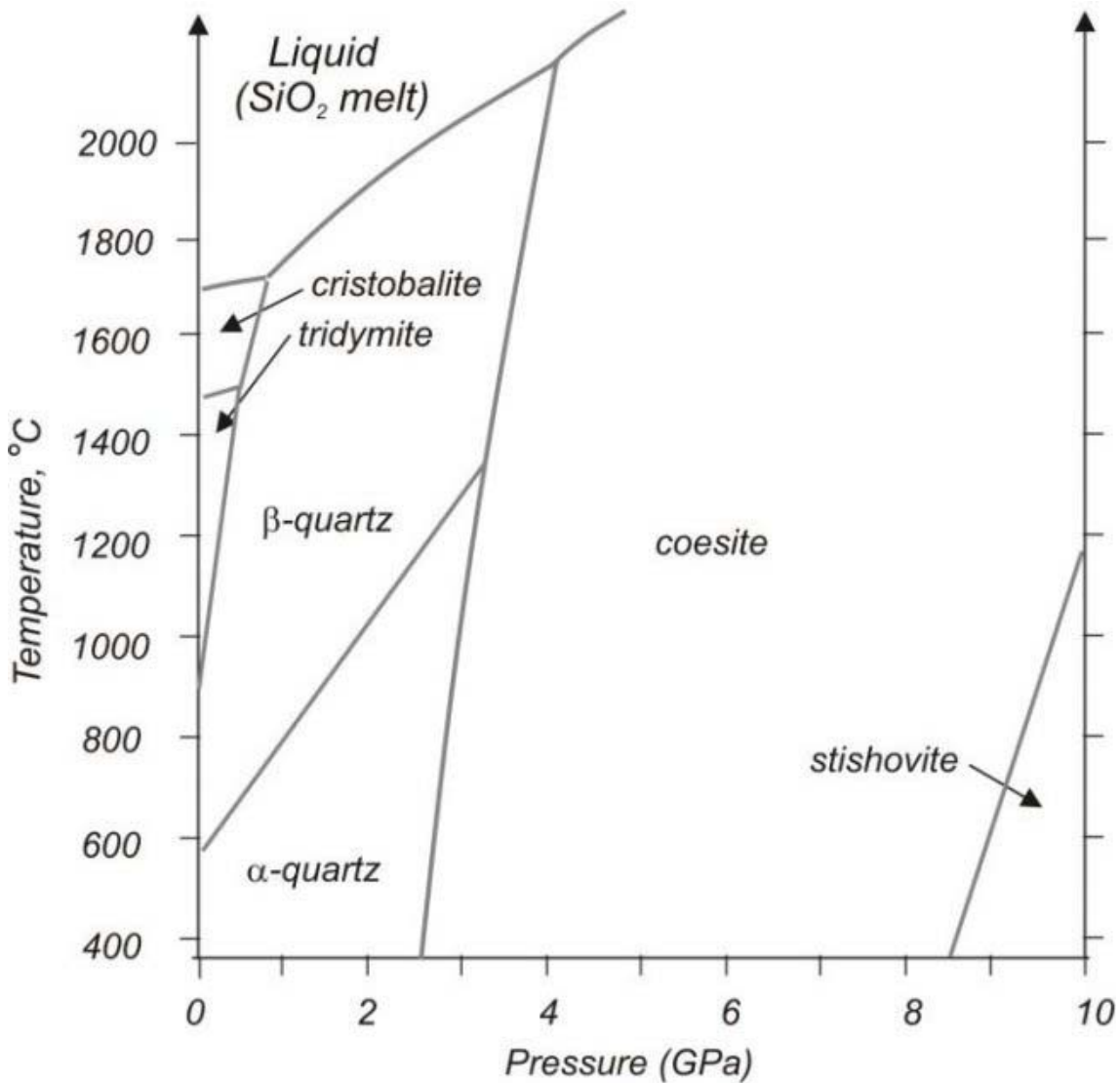

Figure 1. PT-phase diagram of silica polymorphs

Each phase is stable only within a specific range of pressure and temperature, and thus determines the stability fields in the P, T space. Even though there is—from thermodynamic (or energetic) point of view—only one phase (α-quartz) stable at ambient (i.e., room) conditions, polymorphs such as tridymite, cristobalite, coesite, and stishovite are found in rocks exposed at the earth's surface.

Although the energy balance would force a transformation of these polymorphs to α-quartz, the mechanisms of transformation are often too sluggish to be observed or even to take place at all. This problem of kinetics of the transformation process preserves the form metastably outside of its thermodynamic stability field.

One of the most prominent examples is diamond, the high-pressure polymorph of carbon, which in its metastable high-density form provides us with a material of

exceptional physical and chemical properties. Jewelers are in luck, given the kinetical hindrance to diamond transforming back to graphite on pressure release, which actually is the carbon polymorph stable at the earth's surface conditions.

1.2.2. Order–Disorder Transformations

A more subtle transformation within a single compound of a given structure is that of order–disorder. This means that at least two types of atoms, A and B, are distributed in different ways on given sites within a crystal structure (Figure 2a).

If atoms tend to avoid surrounding themselves with unlike atomic neighbors, a state of complete order may be reached, which, from the thermodynamic point of view, is expressed through the entropy part in the free energy.

These tendencies for ordering might be caused through size differences between the different atomic species, size, or geometry differences for the different crystallographic sites on which distribution is possible, or, in the case of metal solids and alloys, different chemical bonding that influences the next-neighbor configurational surrounding it, and its atomic coordination.

Driven by these parameters a chemically complex but homogeneous system can display any degree of order, from completely disordered to ordered for a multiple number of atom types and crystallographic sites.

This often involves complex symmetry changes such as are displayed by superlattice phenomena, polytypism, polysomatic intergrowths, or commensurate and incommensurate lattice modulations.

Considering the tendency to surround themselves with like neighbors with a minimum number of atoms having unlike neighbors, the homogeneous phase will break up into regions of different chemical composition (Figure 2a).

This is again an ordered state, but the system is no longer chemically homogeneous. Such an ordering process is usually termed exsolution and involves migration or diffusion of atoms through the crystal structure.

The fairly complex phase diagram of plagioclase feldspars—a solid-solution series between albite $NaAlSi_3O_8$ and anorthite $Ca_2Al_2Si_2O_8$—displays the complexity induced through order–disorder phenomena with several structure varieties (Figure 2b).

These varieties involve two different incommensurate structures at intermediate composition apart from several monoclinic and triclinic high-temperatures polymorphs.

Ordering and exsolution on cooling is responsible for miscibility gaps, which are known as the "peristerite," "Bøggild," and "Huttenlocher" fields, and describe two-phase fields of coexisting incommensurate, microstructurally intergrown, low-temperature plagioclases.
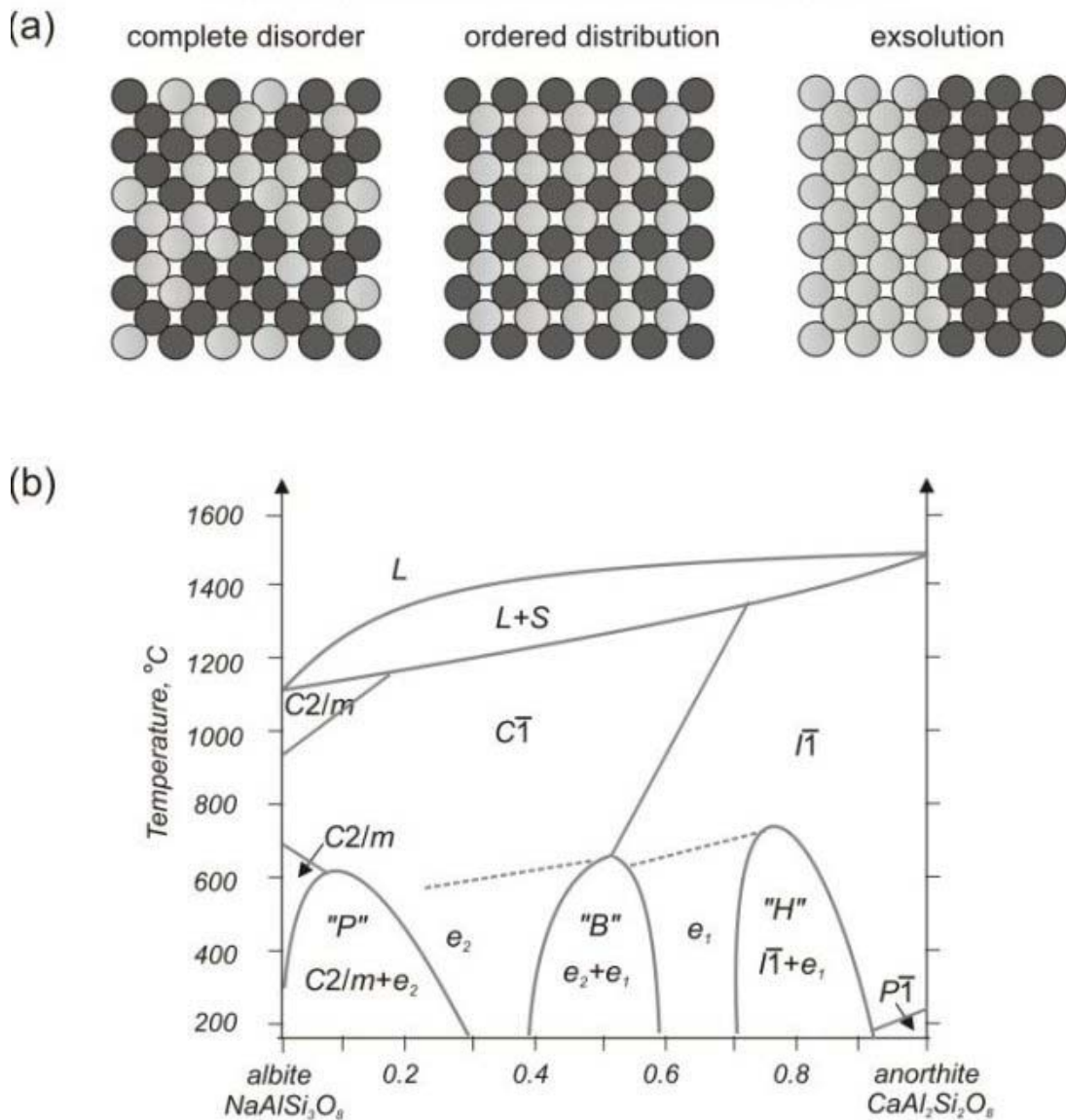
Figure 2. Order–disorder phenomena in minerals
Notes:
(a) Order–disorder states and distribution of A- and B-type atom species in a crystallographic host lattice. Exsolution phenomena due to separation of A and B atoms in two individual crystallographically related domains.
(b) Temperature-composition phase diagram for plagioclase feldspars, the (Na1-xCax)Al1+xSi3-xO8 solid solution between albite and anorthite. C2/m corresponds to a monoclinic structure; C-1, I-1, and P-1 are structure polymorphs of triclinc symmetry; and e1 and e2 refer to two incommensurately modulated structures. Miscibility gaps occur for compositions relevant to the peristerite (P), Bøggild (B), and Huttenlocher (H) fields, which are two-phase stability fields. Liquidus, solidus, and other solid–solid-phase boundaries are shown as full lines; the uncertain phase boundaries to the incommensurate structures e1 and e2 are indicated as dashed lines.

1.2.3. Mineral Reactions

As already stated, mineral processes tend to reduce the free energy of the system. In order words, the driving forces for changes will be found by considering the thermodynamics of the system. Thermodynamics deal with the beginning and the end state of a process assuming that the minerals are in equilibrium with their environment. Exchange with their environment leads to *reactions* between the different mineral, often involving fluid phases apart from minerals. Changes in the mineral paragenesis and the mineral's compositions are petrological indicators for changing P, T, X conditions. Mineral reactions, such as the simple breakdown reaction albite $\rightarrow$ jadeite + quartz $NaAlSi_3O_8 \rightarrow NaAlSi_2O_6 + SiO_2$ give evidence to deduce the change in conditions to which the minerals have been exposed.

As approaching equilibrium conditions involves exchange between a mineral's bulk structure and its environment, microscopic features such as intracrystalline and intercrystalline atomic diffusion, crystal defects (e.g., dislocations and stacking faults, surfaces, twin, and other domain boundaries) play a major role in determining the characteristics of a transformation mechanism. All these microstructural features often control the timescale and thus the kinetics of the transformation process. The rates of the processes involved are often sluggish and if, for example, the cooling rate is faster than the ability of a mineral to adapt to the changing temperature, deviations from equilibrium would occur. Under these nonequilibrium conditions the behavior of a mineral can be quite different from the stable equilibrium behavior. Microstructural characteristics, such as chemical inhomogenities, mineral zoning, or mineral inclusions, manifest the preserved nonequilibrium and yield information on changing conditions that allow a petrologist P–T–t paths and thus allow a mineral's history to be reconstructed.

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Biographical Sketch

Ronald Miletich was born 1967 in Vienna, Austria. From 1985 to 1990 he studied Mineralogy and Crystallography at the University of Vienna. After his Diploma thesis in 1990 he performed his Ph.D. thesis in the field of Crystallography and Crystal Chemistry and took his degree in 1993. From 1994 to 1998 he was Postdoctoral Research Fellow at the Bayerisches Geoinstitut, University of Bayreuth, Germany. In 1998 he took a position at the Laboratory for Crystallography, ETH Zürich, Switzerland, working as a research assistant in the High-Pressure Group. In 1999 he received the qualification of Lecturer (habilitation) in Mineralogy and Crystallography at the University of Salzburg, Austria. Recently he has accepted a tenure-track position as a Professor for Crystallography at the Mineralogical Institute of the University of Heidelberg, Germany. His scientific research has focused on crystallography, solid-state chemistry, and mineral physics at nonambient conditions. His research projects have involved experimental investigations of microporous materials, high-temperature superconductors, earth materials, and various synthetic inorganic compounds. His most recent research activities have focused on phase transitions at high pressures, elastic properties of materials, and elastic anomalies associated with pressure-induced phase transformations. The construction of new high-pressure devices for *in situ* measurements complete the broad range of his research activities. In 1998 he received the Felix-Machatschki Award from the Austrian Mineralogical Society.