SINGLE-CRYSTAL X-RAY DIFFRACTION IN MINERALOGY: THE END OF A TRADITION?

ARMBRUSTER, TH.

Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestr.3, CH-3012 Bern, Switzerland

»Nowadays, the crystal structures of rock-forming minerals are known. Up to 50 new mineral species are described per year but some of them are already structurally defined by analogy to synthetic compounds, others are either very small in size or complicated twinned and/or intergrown thus escaping from structural investigation by single-crystal methods. Accordingly, the number of scientists active in this field can be drastically reduced compared to decades ago when only few mineral structures were solved«. Such or similar sounds a common statement given at university commissions dealing with reorganizations of geoscience departments. On a first glance, this opinion seems to be confirmed by the development of X-ray equipment and accompanying hard- and software. Whereas, 60 years ago a time span of months was necessary to »roughly« determine the structure of a simple mineral with a fairly small unit cell, the same but much more accurate can be done today within less than 10 hours where the size of the cell becomes rather unimportant. As one consequence of this opinion, X-ray equipment and associated staff positions are frequently shifted from mineralogy to chemistry departments where new compounds are awaiting structural characterization. Only few groups of single-crystal X-ray crystallographers within mineralogy are surviving this period of reorganization and budget cuts. But outsiders and even some geoscientists still ask:

»What are the hundreds of mineralogical crystallographers, working with single-crystal X-ray equipment, actually doing?«.

The answer concerning the new goals of mineralogical crystallography is rather complex and only a strongly simplified and subjective view is given in this paper.

Historical aspects

Most of the early X-ray crystallographers came from the field of solid state physics because they were accustomed to the experimental techniques. The first structures solved were rocksalt, diamond, fluorite, pyrite and calcite. Fascinated by the possibilities provided by X-ray diffraction, they started to analyze the structures of silicates because silicates showed some structural complexity and well formed crystals could be easily obtained (BRAGG, 1932). Already in 1932 the crystal structures of ca. 40 silicates were solved. Only five years later BRAGG (1937) published the book »Atomic Structure of Minerals« and provided a structural classification which is the basis of modern mineralogical crystallography. From todays point of view, the goal of these early structure determinations was to disclose the structural principles like arrangement of atoms in the unit cell, coordinations, and bond lengths. These are actually almost the same goals most chemists, or nowadays protein biologists, are still

aiming for when applying crystal structure methods. It should also be mentioned that at these early times hydrogen escaped from structural localization and was commonly presumed to occur on specific positions based on crystal chemical principles.

Modern aspects of crystallography in geoscience

As soon as the fundamental rules of mineral structures were established, mineralogist became interested in how a structure behaves from the point of its formation at elevated temperature and pressure conditions until the mineral is collected by geologists. Exsolution phenomena, twinning, topotactic transformations etc. became the new subject of investigation, all with a specific geoscientific background (e.g. ROSS et al., 1973).

The early structure refinements, performed at room temperature, may be considered as a snapshot at one arbitrary condition. At room temperature atoms and molecules display significant motional behavior which may mask static disorder phenomena. Thus for an improved characterization of a structure, it must be studied at very low temperatures or even better at different temperatures which enable distinction between dynamic (time averaged) and static (space averaged) disorder (e.g. GEIGER et al., 1992; ARMBRUSTER & GEIGER, 1993; PAVESE et al., 1995; LIBOWITZKY & ARMBRUSTER, 1995, 1996). The same argument of course also holds for structural investigations in chemistry. However, low temperature leads to a decreased unit cell volume, closer packing, and shortening of bonds just as at high pressure (HAZEN & PREWITT, 1977), a condition of specific interest for mineralogists. To obtain preliminary information of a mineral under elevated pressure conditions, it is advisable to study it first at low temperature because such an experiment is easier and delivers much more detailed structural information than a high pressure experiment. Furthermore, diffraction experiments at high temperature provide insight into the mechanisms of thermal expansion and stability of a structure. First useful single-crystal heaters for X-ray experiments were described in the 1960's but until 1972 only four high-temperature structure refinements on minerals were published (BROWN et al., 1973). 1973 the American Mineralogist (Vol. 58, 577-704) provided a special issue on »High Temperature Crystal Chemistry« comprising eleven manuscripts. Since then high temperature research is continued on a rather constant level.

Why are there still so few high temperature studies?

This has various reasons. At moderate temperature conditions the motion of atoms can be treated like a harmonic oscillation. At high temperature these vibrations become increasingly anharmonic which still can be modelled but the refinement requires more vibrational parameters. In other words, the number of unknowns increases. The motion at high temperature leads on the other hand to a decrease of X-ray intensities thus the number of observables and their accuracy strongly decreases and the refined structure is no longer so well defined as at low temperature. In addition to the Bragg reflections, a high temperature X-ray pattern exhibits a more or less diffuse background referred to as »thermal diffuse scattering« which is not treated in a conventional X-ray structure refinement causing an additional uncertainty of the refined structure. Finally, there are various experimental problems keeping a crystal on its exact position at a stable high temperature without lowering the accuracy of the

experiment. For these reasons structural investigations are often restricted to a limited temperature range in order to diminish the problems discussed above. Nevertheless, the results may be extrapolated to higher temperatures to obtain a fairly reliable picture about a structure at a more geologically relevant temperature.

What are the problems with high pressure studies?

In our research group we never performed a single-crystal X-ray experiment at high-pressure, thus I only repeat correspondingly what specialists claim. High pressure single-crystal experiments are commonly performed in diamond-anvil cells where the crystal is squeezed between two diamonds hold together by steal blocks connected by screws (the real setup is actually much more sophisticated). The pressure is increased by fastening the screws and finally measured by the known high pressure property of a small reference crystal also pressed between the diamonds. The in- and out-coming X-ray beam has to travel through the diamond and is considerably absorbed. The spacious high-pressure set up only allows the measurement of a restricted diffraction cone. The measured data are consequently of lower quality but sufficient for a reliable structure refinement with regard to atomic positions. Information concerning the vibrational behavior of atoms is strongly delimited by the low number of available X-ray reflections. The quality of the measurement strongly depends on the skills of the experimentalist. This research field has certainly to be expanded in mineralogy. The main problems of high pressure experiments at high temperature are of course a combination of problems imposed by measurement at only high pressure or only high temperature with the additional problem to keep temperature and pressure stable and homogeneous over the investigated crystal. This aspect is still under development. Reviews on high temperature and high pressure crystal chemistry are provided by HAZEN & FINGER (1982) and ANGEL et al. (1992).

Which information can be gained from minerals not having »end-member« composition?

It is desirable to know the structure of the end-member first to better analyze the distortions imposed by the replacing elements. There are two possibilities to analyze the location of atoms sharing one structural position. They must either be significantly different concerning the number of electrons (e.g. Mg and Fe) or must have different ionic radii (e.g. Si and Al) thus causing different interatomic distances. However, always an average distribution over the whole crystal is obtained. E.g. if one wants to know the exact Mg,Fe distribution on the two octahedral sites in a forsterite-fayalite olivine solid-solution, this information can be obtained with an accuracy of ca. 1%. However, if other elements additionally occur (like Mn or Ca) the problem is much more complex and some assumptions need to be made. In this context the excellent work by the Pavia group has to be mentioned where e.g. the structural aspects of oxidation-and dehydrogenation in staurolite were investigated by crystal-structure refinement of crystals heated in air at a series of temperatures (CAUCIA et al., 1994). The same group also established a crystal chemical data base for garnets comprising structural and chemical data for 281 garnets from various petrogenetic conditions and discuss the chemical and structural relationships (MERLI et al., 1995; UNGARETTI et al., 1995).

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A different aspect of minerals departing from end-member composition was recently resolved by us using single-crystal diffraction methods (ARMBRUSTER et al., 1996). Most of the mineralogists are aware of the problem of »strange« elements determined by electron microprobe analysis in an optically homogeneous mineral. In this example, SiO_2 up to 5 wt.% was analyzed in the Cl-bearing calcium-carbonate defernite. The analyses alone can not answer the question whether SiO_2 is incorporated into the structure or whether submicroscopic SiO_2-rich inclusions exist. A low temperature structure refinement disclosed that in this carbonate two stacked CO_3 groups are partially replaced by a disilicate, Si_2O_7, unit. Thus not only the substitution was confirmed but also the mechanism was resolved.

Are single-crystal X-ray diffraction methods sufficient to characterize a crystalline compound or mineral?

Certainly not! However, the method is so advanced that for an end-member composition without a chemical analysis even a chemical composition may be guessed, provided one major element is known. Even approximate proton positions can be refined in transition-metal hydroxy-oxide structures. In this case not the proton itself is located but the electron bonding the proton to the anion is determined (KOHLER et al., in prep.). In case of minerals with complex composition, the mineralogical crystallographer uses in addition to the X-ray equipment the whole variety of analytical methods based on various spectroscopic and optical techniques (e.g. HAWTHORNE, 1993). Thus he still is a specialist on »his« technique but he has expanded his horizon towards all kinds of analytical methods to obtain a more complete picture of the detailed structure of a mineral. In this sense there are more than enough problems to be tackled by the few hundred specialists on this subject.

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