A century of mineral structures: How well do we know them?

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ABSTRACT

This decade marks the centenary of the discovery of X-ray diffraction. The development of mineralogy as a scientific discipline in which the properties of minerals are understood in terms of their atom-by-atom structures has paralleled the development of diffraction crystallography. As diffraction crystallography revealed more precise details of mineral structures, more subtle questions about mineral properties could be addressed and a deeper understanding of the relationship between the two could be attained. We review the developments in X-ray single-crystal diffraction crystallography over the last century and show how its power to provide fundamental information about the structures of minerals has evolved with the improvements in data quality and the increased technological capacity to handle the data. We show that modern laboratory X-ray diffraction data are of the quality such that mineralogical results are no longer limited by the data quality, but by the physical validity of the refinement models used to interpret the data.

Keywords: Crystal structures, X-ray diffraction, site occupancies, anorthite, feldspars, olivine, Invited Centennial article

INTRODUCTION

Minerals are, by definition, crystalline. Their structures are composed of atoms arranged in periodically repeating patterns. The same atoms in different minerals tend to occupy characteristic local environments with specific coordination geometries and bond lengths. The arrangements of atoms within minerals and the crystal-chemical concepts derived from them successfully explain many of the physical, chemical, and thermodynamic properties of minerals. But how do we know that minerals are built of atoms? More than a century ago, there was no proof of the existence of atoms, although it was clear that gases behaved as if composed of particles that occupied some finite volume. It had been deduced from the regularity of their external form (but not proven) that crystalline materials and especially minerals were probably periodic arrays of “some things”; the common deduction was that crystals were composed of the same “molecular” species that occur in gases, condensed into regular and periodic arrays (Kubbinga 2012). In the first half of 1912 three young men in the Institute for Theoretical Physics of the Ludwigs-Maximilians Universität Muenchen carried out an experiment that would confirm the atomistic view of the chemical and mineral world. Inspired by conversations with P.P. Ewald, Max von Laue had suggested the experiment to two other research assistants, Friedrich Knipping and Walter Friedrich. In May 1912 they submitted a manuscript to the Bavarian Academy for Science that reported the diffraction of X-rays by crystals (Friedrich et al. 1912). It was known from optics and physics that diffraction occurs due to constructive and destructive interference between waves scattered by a periodic array of objects; scattering by resonators was actually the subject of Ewald’s research at the time. Therefore, this single observation of the diffraction of X-rays by crystals proved two things; X-rays can behave as waves, and crystals are periodic arrays of X-ray scatterers. Within a year, the Braggs had used the intensities of the X-ray beams diffracted by crystals to determine the arrangements of the atoms in crystals of simple minerals such as the zinc blende used in the experiments in Muenchen, and NaCl, and showed that they were not molecular compounds (e.g., Gruner 1929). The subsequent development of mineralogy as a scientific discipline in which the properties of minerals are understood in terms of their atomic-scale structures (e.g., Gruner 1931; Kieffer and Navrotsky 1985) has paralleled the subsequent development of diffraction crystallography. As diffraction crystallography revealed more precise details of structures, more subtle questions about mineral properties could be addressed and a deeper understanding of the relationship between the two could be attained. By following the developments over the last century we can understand both the power of diffraction crystallography to provide fundamental information about the structures of minerals, while at the same time appreciating its important intrinsic limitations and how these limitations have changed as the technology supporting X-ray diffraction has developed.

THE DEVELOPMENT OF DIFFRACTION CRYSTALLOGRAPHY

The very first diffraction measurements and structure solutions provided a way for diffraction crystallography to “boot-strap” its own methodology. Bragg showed that the diffracted intensities from crystals of simple structures such as the alkali halides can be explained qualitatively in terms of scattering from point atoms that have a scattering power proportional to their atomic numbers. When the atoms scatter in phase, their scattering power adds together to give strong reflections, when they scatter in antiphase the reflection is weak. This approach is sufficient to establish the basic