A molecular dynamics study of the behavior of sodium in low albite

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ABSTRACT

The structural features of albite (atomic coordinates and distances, thermal displacements) at 25 and 1040 °C, obtained by Molecular Dynamic simulations following the Car-Parrinello approach, were favorably compared with those obtained by single-crystal diffraction experiments. Starting from this basis, it was shown that the marked anisotropy of electron density distribution about the positions of the sodium atoms is due to a time average of highly anisotropic thermal vibrations, and not to a space average of multiple positions occupied by Na. Although the large displacement of Na from its center of gravity results in great variations over time of the individual Na-O distances of the sodium coordination polyhedron, the average distance remains approximately constant, reaching its minimum variation when the 9 nearest O atoms are considered, thus supporting a true 9-coordination of sodium.

INTRODUCTION

Feldspars are by far the most common minerals in the Earth’s crust, constituting more than 50% of it, so that their influence extends into almost all branches of geology. It is consequently of particular interest to determine their structural features and their relationships with the petrologic history of their host rocks.

The feldspar minerals are characterized by (1) an MT4O8 composition where T stands for atoms (normally Si and Al) in tetrahedral coordination with oxygen, and M for a larger cation (usually K, Na, or Ca) and (2) a 4-connected 3-dimensional framework with M cations in the cavities.

Two major features dominate the interpretation of the structural details of feldspars: the (Si, Al) distribution in the tetrahedral sites, and the location and coordination of the extra-framework M sites. The latter feature is particularly interesting in the sodium end-member where, in spite of a large number of structural studies (by X-ray or neutron diffraction), it is still not clear if the Na atoms are characterized by a strongly anisotropic thermal vibration or by a static disorder over two or more distinct crystallographic positions, and whether this behavior is influenced by temperature.

The aim of the present paper is to elucidate this problem by means of molecular dynamics simulations using the Car-Parrinello approach (MD from now on). The recent progress in both experimental and computational mineralogy, and in particular the dramatic increase in available computational resources and the rapid progress of software, allows us to tackle such a problem with an approach impossible only few years ago.

THE CRYSTAL STRUCTURE OF ALBITE

Following Wells (1954, 1977) the crystal structure of feldspar may be described as a 4-connected 3D net where the tetrahedral centers (nodes) are occupied by Si or Al, and the linkages are T-O-T bridges. The basic framework consists of cross-linked “double-crankshaft” chains of SiO4 and AlO4 tetrahedra, alternately parallel and nearly perpendicular to the a axis. These chains are connected through oxygen bridges along the b and c axes.

As noted previously, this paper deals with the Na end-member, whose unit cell content can be expressed as Na8Al3Si3O12. The topological symmetry is monoclinic C2/m, whereas the real symmetry is either monoclinic C2/m or triclinic C1. In monoclinic feldspars there are only two symmetrically non-equivalent tetrahedral sites, T1 and T2, thus complete ordering is prohibited. When the symmetry is reduced to triclinic, T1 and T2 split into T1o and T1m and into T2o and T2m respectively, enabling complete ordering (with Al in T1o). In sodium feldspar both displacive and diffusive transformations occur, which can result in changes of symmetry. Sodium feldspar shows two triclinic C1 structural modifications, which differ in the degree of (Si, Al) order: (1) high albite, which has a disordered (Si, Al) distribution over the 4 tetrahedral sites; (2) low albite, the most common in nature, which presents an ordered (Si, Al) distribution with Al atoms in the T1o site and Si atoms in the other three tetrahedral sites (T1m, T2o, and T2m). Na atoms, which compensate the negative charge of the Al ↔ Si substitution, occupy the interstices of the framework.

THE SODIUM PROBLEM

From the very first structure refinements of low and high albite, performed by Ferguson et al. (1958), the highly anisotropic electron density distribution of the Na atoms was evident in both structures. A possible interpretation made by these authors is that sodium occupies at random one or other of two positions within the feldspar cage.

Ribbe et al. (1969), re-examining the data of Ferguson et al. (1958), suggested that the observed anisotropy of the Na atom in low albite can be explained either as a time average of highly anisotropic thermal vibration, or as a space average of multiple positions occupied by the sodium atoms; in the latter case,