Direct profiling of atom distributions in mica with X-ray standing waves

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Introduction

Phengite contents and other compositional variations at cation sites of muscovite are indicators of the metamorphic conditions during rock formation (Guidotti, 1984). High-resolution, elemental- and impurity-sensitive crystallographic methods, along with valence-sensitive spectroscopies, are required to accurately describe these substitutional cations' structures and chemical states.

New Method

We introduce here a new synchrotron-based X-ray crystallographic method for profiling the atomic-resolution distributions of heavy ions within the crystallographic unit cell of minerals. This method exploits the facts that an atom distribution structure in a crystal can be expanded in a Fourier series of multiple-order components, and that the coefficient of each Fourier component (amplitude and phase) can be obtained from X-ray standing wave data for the corresponding order (see, e.g., Cheng et al, 2000). This method derives atom distributions by means of a direct mathematical inversion, without employing structural modelling or interpret-ations. It has elemental and impurity sensitivities.

From X-ray standing wave measurements made at the Advanced Photon Source (beamline 12ID-D), we acquired the ($00l$) Fourier expansion coefficients (for $l = 2, 4, \ldots, 16$) for cation distributions normal to the basal plane in a dioctahedral ($2M_1$) muscovite (phengite) to a spatial resolution limit of 0.13 nm. We verified the validity of this new method by using it to reproduce the known distributions of lattice cations (K, Al, and Si). We then used it to determine the unknown distribution profiles of substitutional Fe, Mn, and Ti. The results show that Fe and Mn are located exclusively at the octahedral sites, while Ti has a more complex distribution.

References

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Superhigh concentration of REE and strong negative Ce anomalies at the carbonate rock weathering front

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The REE concentration is very low in carbonatite rocks[1]. However, superhigh concentration beds of REE, where the REE concentration can be up to about 31 000 _g/g, are found at the carbonate rock weathering front in Guizhou, China. The strong negative Ce anomalies are also found in those REE enrichment beds, which _Ce can be low to 0.007. The phenomena of lower background, strong enrichment and strong fractionation of REE have some certain universality at the weathering front in karst area of Guizhou[2].

According to mass balance calculation, it is considered that carbonate rocks can supply enough REE sources. The soluble existing states of REE in the parent rocks and enrichment beds are in favor of activation and transportation, which are found by leaching experiments. A sudden change and narrow alkali barrier, which is considered that it is the result of rapid solution of carbonate minerals, exists at the weathering front. The barrier may be the most important factor that causes the REE enrichment[3], because it can preserve REE from carbonate rocks by weathering effectively, and also cause the complexes and/or ions of REE in infiltration water to precipitate and adsorb on clay at the weathering front.

The Ce^{3+} is oxidized to Ce^{4+} and precipitates from solution as very insoluble CeO_2. Consequently, the solution shows a negative Ce-anomaly[4]. However, there is not a weathering profile or a groundwater sample having such strong negative Ce-anomaly as our studied profiles[5]. This imply that the fractionation between cerium and other REEs by oxidization from Ce^{3+} to Ce^{4+} and precipitation from solution can not explain the formation mechanism of the strong negative Ce-anomaly at carbonate rock weathering front entirely. In alkali solution, Ce^{3+} can be oxidized to Ce^{4+} easier, and it has great mobilization (compared with other light REE) results from preferential formation of complexes with carbonate ligands[6], which are released by dissolution of carbonate minerals at weathering front. Therefore, the fractionation between cerium and other REE is not only occur in the upper part of the profile, but also occur at carbonate rock weathering front.

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