

Fe³⁺/Fe^T ratios of amphiboles determined by high spatial resolution single-crystal synchrotron Mössbauer spectroscopy

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ABSTRACT

The Fe³⁺/Fe^T ratios (Fe³⁺/[Fe²⁺+Fe³⁺]) in minerals can be used to understand their crystallization and post-crystallization conditions. However, as natural minerals are often zoned and contain inclusions, bulk techniques, e.g., wet chemistry, may not provide accurate Fe³⁺/Fe^T values for a single phase of interest. We determined Fe³⁺/Fe^T ratios of amphiboles in different crystallographic orientations by single-crystal synchrotron Mössbauer spectroscopy (SMS) in energy and time domain modes from four volcanic localities (Long Valley Caldera, Mount St. Helens, Lassen Volcanic Center, U.S.A., and Mt. Pinatubo, Philippines). The high spatial resolution (as low as 12 × 12 μm spot size) and standard-free nature of SMS allow the detection of intra-grain compositional heterogeneities in Fe³⁺/Fe^T with relatively low uncertainties.

We combine SMS with major element compositions, water contents, and hydrogen isotope compositions to document the Fe³⁺/Fe^T ratios as a function of mineral composition and post-crystallization dehydrogenation. Spectra were fitted with up to five distinct sites: ferrous iron on M(1), M(2), M(3), and ferric iron on M(2) and M(3), consistent with X-ray diffraction studies on single crystals of amphibole. The Fe³⁺/Fe^T ratios range from 0.14 ± 0.03 (Long Valley Caldera), 0.51 to 0.63 ± 0.02 (representing intra-grain heterogeneities, Mount St. Helens) to 0.86 ± 0.03 (Lassen Volcanic Center). The latter grain experienced post-crystallization dehydrogenation, shown by its low water content (0.6 ± 0.05 wt%) and its elevated hydrogen isotope composition (δD = +25 ± 3‰ relative to SMOW). The Fe³⁺/Fe^T ratios of 0.62 ± 0.01 and 0.20 ± 0.01 of two Mt. Pinatubo grains correlate with high-Al₂O₃ cores and low-Al₂O₃ rims and smaller phenocrysts in the sample, respectively. This study shows that SMS is capable of distinguishing two different domains with dissimilar Fe³⁺/Fe^T values formed under different crystallization conditions, demonstrating that SMS in combination with major element, water, and hydrogen isotope compositions allows the interpretation of amphibole Fe³⁺/Fe^T ratios in the context of crystallization and post-crystallization processes.

Keywords: Amphibole, Mössbauer spectroscopy, Fe³⁺/Fe^T ratios, dehydrogenation