

## **Fe<sup>3+</sup>/Fe<sup>T</sup> ratios of amphiboles determined by high spatial resolution single-crystal synchrotron Mössbauer spectroscopy**

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### **ABSTRACT**

The Fe<sup>3+</sup>/Fe<sup>T</sup> ratios (Fe<sup>3+</sup>/[Fe<sup>2+</sup>+Fe<sup>3+</sup>]) 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 Fe<sup>3+</sup>/Fe<sup>T</sup> values for a single phase of interest. We determined Fe<sup>3+</sup>/Fe<sup>T</sup> 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 Fe<sup>3+</sup>/Fe<sup>T</sup> with relatively low uncertainties.

We combine SMS with major element compositions, water contents, and hydrogen isotope compositions to document the Fe<sup>3+</sup>/Fe<sup>T</sup> 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 Fe<sup>3+</sup>/Fe<sup>T</sup> 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 Fe<sup>3+</sup>/Fe<sup>T</sup> ratios of 0.62 ± 0.01 and 0.20 ± 0.01 of two Mt. Pinatubo grains correlate with high-Al<sub>2</sub>O<sub>3</sub> cores and low-Al<sub>2</sub>O<sub>3</sub> rims and smaller phenocrysts in the sample, respectively. This study shows that SMS is capable of distinguishing two different domains with dissimilar Fe<sup>3+</sup>/Fe<sup>T</sup> values formed under different crystallization conditions, demonstrating that SMS in combination with major element, water, and hydrogen isotope compositions allows the interpretation of amphibole Fe<sup>3+</sup>/Fe<sup>T</sup> ratios in the context of crystallization and post-crystallization processes.

**Keywords:** Amphibole, Mössbauer spectroscopy, Fe<sup>3+</sup>/Fe<sup>T</sup> ratios, dehydrogenation