Fe$^{3+}$/Fe$^T$ ratios of amphiboles determined by high spatial resolution single-crystal synchrotron Mössbauer spectroscopy

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ABSTRACT

The Fe$^{3+}$/Fe$^T$ ratios (Fe$^{3+}$/[Fe$^{2+}$+Fe$^{3+}$]) 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$^{3+}$/Fe$^T$ values for a single phase of interest. We determined Fe$^{3+}$/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 Fe$^{3+}$/Fe$^T$ with relatively low uncertainties.

We combine SMS with major element compositions, water contents, and hydrogen isotope compositions to document the Fe$^{3+}$/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 Fe$^{3+}$/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 Fe$^{3+}$/Fe$^T$ ratios of 0.62 ± 0.01 and 0.20 ± 0.01 of two Mt. Pinatubo grains correlate with high-Al$_2$O$_3$ cores and low-Al$_2$O$_3$ rims and smaller phenocrysts in the sample, respectively. This study shows that SMS is capable of distinguishing two different domains with dissimilar Fe$^{3+}$/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 Fe$^{3+}$/Fe$^T$ ratios in the context of crystallization and post-crystallization processes.

Keywords: Amphibole, Mössbauer spectroscopy, Fe$^{3+}$/Fe$^T$ ratios, dehydrogenation

INTRODUCTION

Amphiboles are common minerals in hydrous mafic to felsic arc magmas (e.g., Hawthorne and Oberti 2007; Krawczynski et al. 2012). Due to their common occurrence and stability over wide pressure, temperature, and compositional ranges, the chemistry of amphiboles has been used to infer processes such as magma mixing and recharge (e.g., Kiss et al. 2014; Barnes et al. 2016; Zou and Ma 2020) and to reconstruct the pressure and temperature histories of volcanic and plutonic rocks (e.g., Humphreys et al. 2019; Peters et al. 2017; Mutch et al. 2016; Johnson and Rutherford 1989).

Amphiboles incorporate both ferrous (Fe$^{2+}$) and ferric iron (Fe$^{3+}$) into their crystal structure. Thus, the Fe$^{3+}$/Fe$^T$ ratio has the potential to record the oxygen fugacity of the melt from which they crystallized (e.g., King et al. 2000). However, the use of Fe$^{3+}$/Fe$^T$ ratios in natural amphiboles as potential indicators of magma chemistry requires their accurate determination. Bulk techniques such as wet chemistry and conventional Mössbauer spectroscopy suffer from potentially averaging intra-grain compositional variability and inclusions occurring in natural amphiboles, thus posing a challenge to accurately reflect the conditions during amphibole crystallization. A high spatial resolution technique with low uncertainties is required to understand amphibole Fe$^{3+}$/Fe$^T$ ratios in the context of their magmatic history.

We characterize volcanic amphiboles by single-crystal, synchrotron Mössbauer spectroscopy, an analytical technique that provides the spatial resolution to avoid averaging heterogeneous grains and to detect intra-grain Fe$^{3+}$/Fe$^T$ ratio variations. Furthermore, it uses the physics of nuclear forward scattering on single crystals (e.g., Sturhahn and Gerdau 1994; Sturhahn 2000, 2004), and therefore it does not require reference spectra for data interpretation as required for other techniques determining Fe$^{3+}$/Fe$^T$ ratios (e.g., X-ray absorption near edge structure spectroscopy; Dyar et al. 2016). Moreover, synchrotron-based Mössbauer spectroscopy is time-efficient compared to conventional Mössbauer spectroscopy. Herein, we investigate calcic