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Gas-mediated trace element incorporation into rhyolite-hosted topaz: A synchrotron microbeam XAS study

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Abstract

Magmatic gas exsolving during late-stage cooling of shallow magmas has been considered an important facilitator of low-pressure alteration and metal transport. However, the chemical properties of such gas, particularly its metal transport mechanisms and capacity, remain elusive. Trace elements in minerals produced by gas-mediated surface reaction or precipitation from gas capture details of gas composition and reaction pathways. However, interpretation of mineral trace element contents is dependent on understanding crystallographic controls on gas/mineral partitioning. This work investigates the structural accommodation of As, Mn, Ga, Ge, Fe, and Ti in vapor-deposited topaz of vesicular topaz rhyolite from the Thomas Range, Utah, through single-crystal synchrotron microbeam X-ray techniques on picogram quantities of those trace elements. X-ray absorption near edge structure (XANES) data indicates that these elements are incorporated into topaz as As^{5+}, Fe^{3+}, Mn^{3+}, Ti^{4+}, Ga^{3+}, and Ge^{4+}. Extended X-ray absorption fine structure (EXAFS) analysis for these trace elements, compared to EXAFS of structural Al and Si, reveals that As^{5+} and Ge^{4+} are incorporated directly into the tetrahedral site of the topaz structure, with the octahedral site accommodating Mn^{3+}, Fe^{3+}, Ga^{3+}, and Ti^{4+}. For As^{5+} and Fe^{3+}, the structural impact of substitution extends to at least second neighbors (other elements were only resolvable to first neighbors). Further interpretation of the EXAFS results suggests that the substitution of Ti^{4+} results in increased distortion of the octahedral site, while the other trace elements induce more uniform expansion correlating in magnitude to their ionic radius. Comparison of quantified X-ray fluorescence (XRF) data for two topaz crystals from this rhyolite reveals variable trace element concentrations for As^{5+}, Fe^{3+}, Ga^{3+}, and Ti^{4+}, reflective of a source gas undersaturated in these trace elements changing in concentration over the period of topaz deposition. The identical Ge^{4+} content of the two topaz crystals suggests that Ge^{4+} in the gas was buffered by the growth of another Ge^{4+}-bearing phase, such as quartz. The very low Mn^{3+} content in the topaz crystals does not reflect the abundance of Mn^{3+} in the gas (saturation of Mn is evidenced by coexisting bixbyite). Instead, it suggests a strong Jahn-Teller inhibitory effect to the substitution of Mn^{3+} for Al^{3+} in the distorted octahedral site of topaz. It is proposed that exsolution of an HF-enriched gas from cooling rhyolitic magma led to local scouring of Al, Si, and trace metals from the magma. Once topaz crystals nucleated, self-catalyzed reactions that recycle HF led to continued growth of topaz.

Keywords: Crystal structure, EXAFS, igneous rocks, magmatic gas, rhyolite, silicates, single-crystal EXAFS, topaz, trace elements, vapor phase, X-ray absorption spectroscopy; Experimental Halogens in Honor of Jim Webster