Smoking gun for thallium geochemistry in volcanic arcs: Nataliyamalikite, TlI, a new thallium mineral from an active fumarole at Avacha Volcano, Kamchatka Peninsula, Russia

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Abstract

This paper describes the new mineral nataliyamalikite, the orthorhombic form of thallium iodide (TlI), from high-temperature fumaroles from the Avacha volcano, Kamchatka Peninsula, Russia. We also present some chemical analyses showing extreme enrichment of Tl in the volcanic gases at the Avacha volcano, and a review of thallium geochemistry that highlights the fascinating processes that led to the formation of nataliyamalikite.

Nataliyamalikite occurs as pseudo-cubic nanocrystals (≤0.5 μm) within vacuoles in an As-(Te)-rich amorphous sulfur matrix and rarely as irregularly shaped aggregates up to ~50 μm in diameter within the amorphous sulfur matrix. Associated minerals include an unidentified Tl-As-S mineral, barite, and rare inclusions of a Re-Cu-bearing phase. The mean empirical composition based on four EDS analyses is $Tl_{1.00}(I_{0.95}Br_{0.03}Cl_{0.02})$, corresponding to the ideal formula TlI. Nataliyamalikite crystallizes in the orthorhombic system, space group *Cmcm*, which is consistent with the low-temperature (<175 °C) synthetic TlI polymorph. EBSD data reveal that some grains retain the cubic symmetry ($Pm\overline{3}m$) of the high-temperature polymorph, although most analyzed grains display the orthorhombic symmetry. Single-crystal X-ray studies of material extracted by the focused ion beam-scanning electron microscopy (FIB-SEM) technique, and carried out on the MX2 macromolecular beamline of the Australian Synchrotron, determined the following cell dimensions: $a = 4.5670(9)$, $b = 12.803(3)$, $c = 5.202(1)$ Å, $V = 304.2(1)$ Å^3, and $Z = 4$. The six strongest calculated X-ray reflections and their relative intensities are: 3.31 (100), 2.674 (73), 3.20 (43), 2.601 (28), 2.019 (21), and 2.284 Å (19). The combination of EBSD analysis (providing an efficient test of the crystallinity and crystal symmetry of a population of micrometer-sized grains) and synchrotron single-crystal X-ray micro-diffraction (beam size ~7.5 μm) on micro-aggregates extracted using FIB-SEM opens the way to the characterization of challenging specimen—in this case, the sulfur matrix is highly beam sensitive, and the nataliyamalikite grains could not be isolated using optical microscopy.

The high-temperature (>600 °C) sulfidic (~1.2 wt% S) vapors at Avacha are extremely enriched in thallium; with 34 ppm, they contain an order of magnitude more Tl than the richest volcanic gases analyzed to date and ~100× more Tl than most metal-rich fumarolitic fluids associated with volcanic arcs. The formation of nataliyamalikite illustrates the complex processes that control thallium geochemistry in magmatic arc systems. Thallium minerals have now been reported in andesitic (Avacha), basaltic (Tolbachik, Kamchatka), as well as rhyolitic (Vulcano, Eolian Islands, Italy) volcanoes. Ultimately, these thallium minerals result from the transfer of thallium from subducted sediments to volcanic gases in arc volcanoes. We suggest that the extremely thallium-enriched vapors from which nataliyamalikite formed result from complex and transient interactions between Tl-rich sulfosalt melts and magmatic vapors, a process that may be important in controlling metal distribution in boiling epithermal systems.

Keywords: Nataliyamalikite, new mineral, thallium, fumaroles, vapor transport, Avacha Volcano, Kamchatka Peninsula, Russia