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Trace element contents of sulfur spherules in acid crater lakes: signals of volcanic activity

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Interaction between molten sulfur pools at the bottom of active crater lakes and volcanic gas leads to the formation of sulfur spherules (1-5mm in diameter) that have been observed floating on the surface of acid crater lakes worldwide. Eruptions occasionally eject solid sulfur pieces from a disrupted subaqueous sulfur layer out of the crater, yielding pyroclastic sulfur. Elemental sulfur also occurs in banded lake sediments on lakeshores that have been interpreted as remnants of ancient bottom deposits. Sulfides (mainly pyrite) are frequently present as inclusions in the sulfur matrix. In contrast, fumarolic sulfur deposited around subaerial vents appears to be pure, as sulfide sublimates would form at much higher temperatures than sulfur.

Native sulfur can be formed in crater-lake environments under a wide range of conditions, which largely depend on the degree of volcanic/hydrothermal activity. At some lakes, e.g. Noboribetsu (Japan), sulfur is formed mainly by bacterial and inorganic H_2S oxidation, whereas at highly active lakes such as Póas (Costa Rica) and Kawa Ijen (Indonesia) disproportionation of magmatic SO_2 and sulfitolysis of polythionate anions are the mechanisms responsible for sulfur deposition. Such differences in the origin of the native sulfur should affect its trace element contents. Aiming to explore the potential of trace metal contents in sulfur as records of (1) subaqueous volcanic/hydrothermal activity and (2) volcanic emission of environmentally sensitive chemicals, we studied a diverse suite of samples, concentrating on a highly toxic and poorly studied group of elements: As, Se, Te, Hg, Sb, Cd, Tl and Sn.

Sulfur spherules, molten sulfur, pyroclastic sulfur, banded sulfur sediments as well as fumarolic sulfur from 9 subduction-related active volcanoes were analysed (Póas, Costa Rica; Kawa Ijen, Dempo and Merapi, Indonesia; Kusatsu and Noboribetsu, Japan; Bannoe, Maly Semiachik and Mutnovsky, Kamchatka). Inclusions were separated from native sulfur hosts, and their nature was determined by SEM-EDS and X-ray microdiffraction (GADDS). Native sulfur and sulfide inclusions were separated, dissolved and analysed for trace metal elements by ICP-MS. Trace element contents of both fractions was also determined *in situ*, using Laser Ablation ICP-MS techniques.

Pyrite inclusions determine the colour of their sulfur hosts, which varies from black (5-16%) to grey (1-2%) and yellow ($<$1%). Marcasite and magnetite were only observed at Bannoe and Noboribetsu lakes, which show relatively low activity. Spherules from these lakes display the highest As (300ppm-1%) and Hg (17-70ppm) contents, which are preferentially incorporated in the sulfide fraction. These elements as well as Sb (0.5-80ppm) and Te (5-230ppm) appear to be associated with Pb, Cu and Zn in the sulfides at all of the sites studied. Selenium (6–183ppm) is only incorporated in the native sulfur and displays higher contents at the more active volcanoes, showing the most conspicuous enrichments in samples collected at high activity periods (121ppm, Póas 1979; 183ppm, Kawa Ijen 1993). Molten and pyroclastic sulfur is systematically enriched in Fe and sulfide-associated elements compared to sulfur spherules collected at the same site and in the same period.