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Identification of Metal Sulphides in Sulphur Spherules from the Hyper-acidic Crater Lake of Poás Volcano (Costa Rica) by Laser Ablation-ICP-MS

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Novel aspect: Laser-ablation ICP-MS analysis of sulphur spherules from the acidic volcanic lake of Poás volcano provides the opportunity to estimate the magmatic output of a poorly studied group of trace elements including Se, Te, Sb, as well as to get better insights on other magmatic-hydrothermal processes.

The acidic volcanic lake of Poás volcano presents at its surface buoyant spongy yellow masses that consist of an aggregate of sulphur spherules. The spherules have been also observed at other volcano-hosted acid lakes and they are mostly composed of elemental sulphur with a yellow colour although some of them are grayish-black with a metallic lustre. They are spherical in shape with diameters up to 4-5 mm, and with a striated porous surface. They are formed when gas bubbles detach from a hot-liquid sulphur mass present on the lake bottom carrying a shell of sulphur around them when moving to the surface of the lake.

Analysis of the spherules by Laser-Ablation ICP-MS¹ has provided chemical data of a variety of rare trace metals including As, Bi, Te, Sn, Tl, Cu, Ni, Se, Sr, Zr, Mo, Cd, Hg, Sb, Pb and Fe. These elements are associated to abundant metal-bearing

sulphidic inclusions present in the spherules' matrix such as pyrite (FeS_2), enargite (Cu_3AsS_4) than can be Sb-rich, bismuthinite (Bi_2S_3), stannite ($\text{Cu}_2\text{FeSnS}_4$), and other sulphides² of these elements Cu, Fe, Mo, Sb, As, and Bi appear to be preferentially concentrated in the inclusions as indicated by poor signal stability and non consistent relative signal intensities whereas Se, Sb, As and Te showed good signal stability and consistent relative intensities indicating homogeneous distribution of these elements within the native sulphur matrix of the spherules. On the other hand, certain elements (e.g., Sn) were detected only in some of the sulphide inclusions. These observations point to a systematic distribution of trace elements among the solid phases and suggest the existence of sulphide grains with distinct chemical properties.

While the spherules are enriched in Fe (average concentration 8785 ppm with a standard deviation of ± 8470 ppm), Se (10866 ± 1410 ppm), Te (1644 ± 269 ppm), As (164 ± 59 ppm), Hg (107 ± 38 ppm), Sb (1.9 ± 0.7 ppm), Bi (1.5 ± 0.9 ppm) and Cd (less of 3 ppm), the waters of the Poás hyperacid crater lake are depleted in most of these elements (e.g. the lake waters collected between January 1996 and May 2002 yielded 776 ± 284 ppm Fe, 0.027 ± 0.009 ppm Se, 0.8 ± 0.4 ppm As, 0.003 ± 0.002 ppm Sb, 0.005 ± 0.004 ppm Bi, and 0.03 ± 0.01 ppm Cd).

Analysis of the spherules presents a new opportunity to estimate the magmatic output of a poorly studied group of trace elements including Se, Te, As, Sb and Hg that are usually difficult to analyse in aqueous solutions, and often represent a major environmental hazard in volcanic areas and also provide information on fluid-lake water interaction.

References

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