Long-term changes in water chemistry of crater lakes of Kusatsu-Shirane volcano, Japan

Y. KIKAWADA, A. INOUE, K. IKEHATA AND T. OI

Faculty of Science and Technology, Sophia University, Tokyo, Japan (y-kikawa@sophia.ac.jp; inoue-a@sophia.ac.jp; t-ooi@sophia.ac.jp)

Kusatsu-Shirane volcano is located at central Japan and has three crater lakes named Yugama, Mizugama and Karagama on its summit. Yugama, the largest and the most acidic (around pH 1) among the three, is well known as an active crater lake. Volcanic fluids are discharged constantly into Yugama from its bottom, and thus chemistry of Yugama water reflects the volcanic activity of Kusatsu-Shirane volcano. Therefore many researchers have studied its water chemistry as an indicator of the volcanic activity of the volcano. To the contrary, very few researchers note the other two crater lakes, because their acidity (around pH 3) is lower than that of Yugama, and volcanic fluids directly discharged into them have not been observed. Those two are thus recognized as non-active crater lakes at present. Recently, however, we have grasped some evidence that their water chemistries also reflect the volcanic activity of Kusatsu-Shirane volcano. In this study, we have discussed the long-term changes in water chemistry of the crater lakes of Kusatsu-Shirane volcano accompanying its volcanic activity.

Five phreatic eruptions had occurred at the edge of Yugama in 1982-83. A remarkable increase in concentrations of dissolved components of Yugama water was observed after the eruptions, which has been considered to be due to the influx of highly-concentrated fluids into Yugama water. Secular change in water chemistry of Mizugama resembles that of Yugama, although the absolute concentrations of the former are much lower than those of the latter. A similar trend in secular change is also observed for Karagama and Yumi-ike, a marsh embracing the old crater beside the pyroclastic corn. It was thus possible that the same fluid that was discharged into Yugama was also supplied to the other lakes during the eruptions. In addition, the concentration of the chloride ion had increased in Mizugama, Karagama and Yumi-ike waters immediately after the 1982-83 eruptions. Since the influx of the chloride ion generally suggests the existence of volatiles from the magma, those observations must be an evidence that their water chemistry reflects the volcanic activity. On the other hand, such as increase in the concentration of the chloride ion after the eruptions had not been observed in Yugama. This may be interpreted as follows. The influx of the volatiles could not change the water chemistry of Yugama because its water always kept high salinity, and consequently was insensitive to the influx of the volatiles unlike the other lakes. Thus, the waters of Mizugama, Karagama and Yumi-ike may be more sensitive indicators for the volcanic activity of Kusatsu-Shirane volcano compared with Yugama.

Particle size effects on heavy metal distribution, speciation, and correlations in mine wastes

C.S. KIM[1] AND J.J. RYTUBA[2]

[1]Department of Chemistry, Chapman University, Orange, CA USA (cskim@chapman.edu)
[2]U.S. Geological Survey, Menlo Park, CA USA

Centuries of mining have left a legacy of metal-contaminated mine wastes across the world's mineralized regions. These wastes often contain highly elevated levels of many hazardous metals in addition to the primary ore metal. Characterizing trends in metal concentrations, metal speciation (the dominant chemical form of the metal), and correlations between metals as a function of particle size can provide insight into the mechanical and chemical processes that distribute metals in the environment and impact their availability to living organisms. A combination of physical size separations, bulk chemical analyses, X-ray spectroscopic methods, and empirical leach tests aids the identification of such trends as well as the pathways that control metal transport from mine impacted sites.

Samples of both mine wastes and background soil samples from mine sites throughout California were collected and weighed prior to particle size separation using stainless steel sieves to generate 11 size range-specific fractions (from >2830 μm down to <20 μm). Each fraction was weighed and analyzed using ICP-MS to determine the bulk concentrations of a standard suite of 48 elements. Results of elemental concentrations as a function of particle size were plotted and categorized based on their size-dependent behavior, resulting in groupings of elements that share similar trends and therefore possible geochemical associations.

Bulk and microspectroscopic methods were then applied to selected size fractions of mine wastes, utilizing X-ray fluorescence (XRF), extended X-ray absorption fine structure (EXAFS) spectroscopy, and X-ray diffraction (XRD) to assess the speciation, distribution, and correlation of metals of interest. The microspectroscopic methods in particular can allow the analysis of samples previously inaccessible by bulk spectroscopic techniques due to sample concentration limitations.

Results from bulk concentration analyses demonstrate that many heavy metals are concentrated in the finer grain size fractions, sometimes by over an order of magnitude, increasing their mobility and potential availability by ingestion or inhalation. However, changes in metal speciation corresponding to preferential weathering of more soluble phases may offset the potential toxicity of such metals in fine-grained fractions; this is tested through selective leach extractions. Consistent correlations between certain metals, such as iron and arsenic, were identified and further investigated with XRF, where specific As:Fe ratios could be associated with discrete phases. Such species appeared to increase in diversity with decreasing particle size, suggesting secondary mineralization or sorption processes.