

Chlorine isotope variations in the hyper-acid lake system of Poás volcano, Costa Rica

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Chlorine is the most abundant halogen in volcanic systems. Its presence in interacting magmas, hydrous fluids and gases, together with its conservative behaviour, makes this element a convenient tracer of near-surface processes in active magmatic-hydrothermal settings. Available results of d37Cl analyses of fumarolic gases, crater lakes and geothermal waters from volcanoes worldwide are limited and commonly represent single or infrequent sampling at a given location. This absence of time-series data for individual volcanoes may hamper the interpretation of isotopic signatures of the fluids and their potential response to changes in activity.

We collected d37Cl time-series data for the hyper-acid crater lake of Poás volcano (Laguna Caliente) and for gas condensates from fumaroles from the composite pyroclastic cone (CPC), which are supposed to be equivalent to the gas influx into the lake-water body. The samples from Laguna Caliente cover an extended period (1985-2012), which is marked by conspicuous changes in activity and properties of the lake. New and published data from the CPC fumaroles, representing intermittent sampling between 2001 and 2012, cover periods when gas temperatures showed strong temperature differences (ca. 100 to >800 °C).

The d37Cl data from Laguna Caliente show a restricted range between -0.03 and 0.69‰(SMOC). Relatively positive values mark the samples taken during an interval of peak activity of the lake (1980-1986), when Cl concentrations (<73100 ppm) and temperatures (<65 °C) were high, pH values were <0, and its volume was strongly reduced. This elevated d37Cl is attributable to a preferential depletion of light Cl due to evaporation of HCl, or to a distinctive input flux into the lake. The fumarole condensates show a remarkable variability in d37Cl from -0.48 to 13.43‰, while even higher values were reported in a previous work. These d37Cl results exhibit an inverse relationship with Cl concentration and fumarole temperature. Near-zero or slightly negative d37Cl values at the highest temperature (763 °C) correspond to mantle values and are consistent with direct derivation of the gas from a shallow magma body. The strongly positive d37Cl at much lower gas temperatures reflects interaction with subsurface water bodies that preferentially remove and dissolve ³⁵Cl (cf. Sharp et al., 2010).

We infer that the observed chlorine isotope trends reflect temporal changes in water-gas interaction in the two-phase hydrothermal system below the lake. Although better constraints of magnitudes and controls of isotopic fractionation are necessary for detailed interpretations, the excellent correspondence between the Cl isotope signatures and independently derived fluctuations in the lake activity highlights their potential for monitoring purposes.