

Ejection of trace metals from volcanoes

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Investigation of trace element content of snow which fell through the pyroclastic ejecta of the Hekla, Iceland eruption of 1991 revealed elevated concentrations of a variety of elements. Laboratory rinses of pristine tephra and lava show similar concentrations as the snow when the water/rock ratio is 12.5. Many metals have concentrations higher than 100 ppb (Ti, Mn, Fe), between 10-100 ppb (Cu, Zn), and between 1-10 ppb (Sc, V, Cr, Co, As, Se, Sn, La, Sm) in the snow and tephra rinses. The light *REE* (*LREE*), that have the highest chondritic abundances, contain greatest values in the snow. The metals depict a positive correlation with Cl^- . No *REE* fractionation occurs during volatilization from the magma. It is proposed here that the metals are evaporated as chlorides during devolatilization of the magma in the eruption cloud. The metals form solid sublimates on the surface of the tephra and lava upon cooling. These halides are very soluble and are dissolved upon contact with the first rain that falls on the erupted solids.

Introduction

The Hekla volcano in Southern Iceland erupted for eight weeks in the beginning of 1991 producing andesitic lava of the volume of 0.15 km^3 (Gudmundsson *et al.*, 1992). The eruption had an initial plinian phase, that reached 11.5 km height in 10 min, giving rise to 0.02 km^3 of tephra. During this phase snow fell through the eruption cloud. The snow was collected from the flanks of the volcano using clean equipment, brought to the laboratory and immediately melted, filtered, and acidified to 0.5% with HNO_3 .

Results

The melted snow contained elevated concentrations of a variety of metals. In order to investigate

the origin of the elevated metals in the snow two tests were undertaken in the laboratory. They included rinsing of four tephra samples of size fraction 1-3 mm and crushing and rinsing of four lava samples to a size fraction 125-250 μm . All rinsing tests of lava were undertaken with 4g of solids, rinsed with 50 ml of water (pH 6 and 3), i.e. a water/rock ratio of 12.5.

The rinses of one lava and one tephra contained elevated concentrations of metals, similar to the concentration in the snow. Varying the pH of the rinsing water made no difference to the metal concentrations of the rinses. The metals that have higher concentrations than 10 ppb include Ti, Mn, Fe, Cu and Zn. The concentration of the light *REE*, reaches as high values as 8 ppb in the snow and rinses. No *REE* fractionation appears to have occurred in the devolatilization process. The *REE* depict a positive correlation with Cl and less convincingly with F. The samples that gave off high concentrations of metals were collected immediately upon eruption and are termed here pristine. The other solid samples were collected after rainstorms and did not give off measurable metal concentrations upon rinsing. Note also that a second rinse of the pristine samples resulted in much lower concentration of metals. Major elements also show high concentrations in the snow (> 1ppm), including fluorine, chlorine, phosphorus sulphur, silicon, and aluminium as well as a low pH (3) (Gislason *et al.*, 1992; Oskarsson, 1992).

Magma degassing

Several workers have shown that halides occur with metals in volcanic sublimates (e.g. Oskarsson, 1981), lava incrustations (White and Hochella, 1992) and volcanic gases (Miller, 1991). Metals have also been measured after laboratory devolatilization of man-made melts (Dunbar,

1992). These observations as well as thermodynamic modelling (e.g. Quisefit *et al.*, 1989) indicate that halides may play a role in metal transport during devolatilization of magmas. No such modelling is to date available for the REE.

When magmas are degassed at the depth of a few hundred metres HF, HCl and H₂S are the most likely gases to play a role in metal transport. We believe that the rapid dissolution of the metal bearing phases into the snow and water in the laboratory indicates that the metals were primarily contained in chlorides (e.g. LaCl₃(s)) which have a much higher solubility than fluorides (i.e. LaF₃(s)). We propose that the metals are on the form of volatile chlorides in the eruption column (e.g. LaCl₃(g)). The metals escape from the magma and precipitate onto the surfaces of the tephra grains, forming soluble sublimates. Upon contact with the first water, the metals are released into the hydrosphere.

Conclusions

A variety of metal halides are found on the surfaces of erupted solids immediately upon eruption. The metal halides are soluble and dissolved into the snow falling through the eruption cloud (and laboratory rinsed pristine tephra surfaces). An estimate of soluble metals which enter the hydrosphere can be done assuming that the devolatilization process is uniform, and that all the tephra is coated with the same concentration of metal-halides as reported here. The calculations reveal that for each km³ of volcanic ejecta the metal pollution from an andesitic eruption is 1.5×10^8 kg. Such input of metals could have an adverse effect on living organisms, especially if the tephra or lava falls

onto a small area of highly populated land. Volcanic eruptions, therefore, cause vast heavy metal pollution which has hitherto not been investigated. The metals could have a poisonous effect on the biota. Are we any closer to understanding mass extinctions?

References

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