

## Enhanced sulfur solubility in chlorine-bearing rhyodacitic melt – a key to the excess sulfur problem?

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The solubility of volatiles in silicate melts in equilibrium with mixed fluids is of increasing interest in volcanology and petrology because such fluids are closer to natural ones. Interaction of volatile components in the melt and in the fluid may strongly effect the solubility behavior of these components in the melt. In this study we report new results on the solubilities of S and Cl in a rhyodacitic melt (groundmass composition of recently erupted magma of Unzen volcano, Japan) equilibrated with an aqueous Cl-S-bearing fluid. Experiments were performed at T=850°C, P=200 MPa, and  $f_{O_2}=NNO$  using conventional cold seal pressure vessels.

The experimental results show complex behavior of volatile components. At low Cl/H<sub>2</sub>O molar ratios in the fluid phase (<0.02), the addition of sulfur affects negligibly Cl solubility in the melt. At higher Cl/H<sub>2</sub>O ratios, increasing the S content in the fluid up to 18 mol% reduces slightly the Cl solubility (by a factor of 0.7). Such a behavior of Cl can be explained by the dilution of the fluid phase, changes in the activities of volatiles, and an increasing non-ideality of mixing in the fluid.

The solubility of S in the Cl-free silicate melt increases only slightly (from 60 to 100 ppm) with increasing S/H<sub>2</sub>O molar ratio in equilibrium fluid phase (from 0.03 to 0.12) mostly due to the buffering effect of phyrrotite crystallization. In contrast, the first small amounts of added Cl to the system dramatically enhance S solubility in the melt by a factor of 2-3. Further additions of Cl to the fluid phase at constant S/H<sub>2</sub>O ratios have almost no effect on S solubility. Such a behavior of S cannot be explained by the dilution of the fluid phase by Cl because the activities of the other components are lowered. Furthermore, this effect cannot be attributed to changes in FeO content of the melt or to a decrease in oxygen fugacity in the system. We suggest that Cl and S may form complexes in the melt changing the speciation of both components in the silicate liquid and increasing their solubilities. Since the S content in the melt is lower by about 1-2 orders of magnitude than the Cl concentration, such S-Cl complexes will affect predominantly the S solubility and to a lower extent the Cl solubility.

The obtained results indicate that the problem of “excess sulfur” in recent eruption of Unzen volcano can be attributed to the enhanced sulfur solubility in Cl-bearing melts and concomitant degassing of Cl- and S-bearing species.

## *In situ* U-Pb zircon dating using laser ablation-multi ion counting - ICPMS (LA-MIC-ICPMS)

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U-Pb dating of zircons using ion probe SIMS instruments which provide high spatial resolution (20 µm) has been highly successful. Laser ablation combined with ICPMS has been proposed as an alternative analytical technique. Because the laser ablation process produces rather erratic transient signals, multicollection is an absolute requirement if high precision is to be obtained. Because smaller sample sizes lead to decreased signal intensities, the noise in the detection system joins the analytical blanks as a limiting factor for the attainable precision.

We have developed specialized miniaturized ion counters, identical in size to and interchangeable with the standard Faraday detectors of the ThermoFinnigan NEPTUNE MC-ICPMS, which can be used in a true multicollector array. In total, up to 9 Faraday Cups plus 8 MIC channels can be installed simultaneously. The dispersion of the variable multicollector array is sufficiently large that simultaneous static multicollection at unit mass separation of the U isotopes and all of the Pb isotopes can be effected. As a consequence, the NEPTUNE can be used with a pulsed focused UV laser beam for *in situ* U-Pb analysis of single zircons. Here, first results of measurements on zircon standards and real samples will be presented and analytical and instrumental challenges relating to the laser ablation process, the plasma interface and the MIC detectors will be discussed.