The fate and transport of magmatic volatiles in the Yellowstone hydrothermal system

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The transport of volatiles between magma and the ground surface depends mainly on their initial abundances, their solubility in water, their reactivity with rocks, and ultimate transport along permeable pathways. Episodic fluid flow from the high pressure ductile region surrounding partially molten magma to the hydrostatically pressured brittle crust results in boiling and phase separation. At Yellowstone, the more water-soluble volatiles, chlorine and fluorine are transported by groundwater to the relatively low-elevation areas in the Firehole River and Gibbon River geyser basins where they are discharged. Steam and less soluble gases (CO_2 H_2S, H_2, CH_4, He) are exsolved from the thermal waters, and discharged at the high-elevation, "acid sulfate" areas, typically near the eastern margin of the Yellowstone Caldera, where the seismically imaged partially molten magma appears to be shallowest. Although reaction of HCl and SO_2 with crustal rocks may occur at near-magmatic temperatures, most of the reaction of CO_2 occurs at temperatures <270°C, manifested by higher HCO_3^- concentrations in thermal waters. In the shallow hydrothermal system, sulfur speciation is complex because it is a key redox element that supports different microbial populations through a series of energetically favorable reactions. Measurements of dissolved volatiles discharged from the Yellowstone hydrothermal system through rivers have been carried out since 2002. Riverine volatile discharge decreases in the following order, CO_2 (as HCO_3^-)> Cl^- > S (as SO_4^{2-}) >F^- . Diffuse CO_2 flux measurements in thermal areas made since the late 1990s suggest a total emission rate of 20-50 kt/d. The significantly different Cl/F dissolved in glass melt inclusions (~0.5 by mass) compared with the ratio in the thermal discharge (~8) implies a major fluorine sink in the hydrothermal system, which is likely controlled by the solubility of fluorite (CaF_2).