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Geochemical processes governing the compositional features of the crater fumarolic field at Mt. Etna

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Mt Etna is one of the most-active volcanoes in the world. It is characterized by major eruptions, frequent Strombolian activity, and ash emissions. The volcano summit consists of the central crater of Voragine surrounded by the three active cones of the North-East Crater, Bocca Nuova, and the South-East Crater. They are characterized by very fractured and unstable edges. Under these conditions most of the fractures represent preferential degassing pathways for volcanic fluids, so that the main fumarolic fields develop in such fractured areas. The geochemistry of the fumaroles at the summit area of Mt. Etna was investigated. Fumarolic samples were collected between June 2008 and August 2009. Gas samples were usually collected as “dry gas” and analyzed for the concentrations of He, H_2, O_2, N_2, CO, CH_4, and CO_2. Fumarolic gases were also sampled a few times using the classical Giggenbach bottles and Giggenbach-type bottles filled with ammonia and silver nitrate in order to determine the SO_2/H_2S ratio. In addition a novel method was employed in order to sample fumaroles characterized by high content of atmospheric gases. Two types of fumaroles were identified: low-temperature fumaroles, which are dominated by CO_2 with minor amounts of SO_2 and H_2S, and negligible halogen contents, and high-temperature fumaroles, which are strongly air-contaminated and characterized by appreciable amounts of volcanogenic carbon, sulfur, and chlorine. Our data clearly indicate that secondary processes modify the composition of the fluids once they leave the magma body. A model based on thermodynamic data is proposed to explore such postmagmatic processes. We computed the equilibrium composition of magmatic gases that cool starting from magmatic temperatures under several pressure conditions. The model, which uses Etnean plume geochemistry as starting composition of fluids exsolved from magma, shows that SO_2 and H_2S control the redox conditions of the gas mixture during the cooling, until the reactions involving CO/CO_2 and H_2/H_2O ratios are fully quenched. The scrubbing processes occurring subsequent to condensation and gas–liquid water interaction allow total removal of HCl and partial removal of sulfur species. During the ascent toward the surface, the concentration of CH_4 increases in all fumaroles due to a modest contribution from hydrothermal fluid. A geochemical model for the interaction of pristine magmatic fluids with shallower systems is proposed. The model explains geochemical changes at the crater fumaroles in terms of variable hydrothermal and magmatic contributions, and modified thermodynamic conditions.