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Numerical modelling of gas-water-rock interactions in volcanic-hydrothermal environment: the Ischia Island (Southern Italy) case study.

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Hydrothermal systems hosted within active volcanic systems represent an excellent opportunity to investigate the interactions between aquifer rocks, infiltrating waters and deep-rising magmatic fluids, and thus allow deriving information on the activity state of dormant volcanoes. From a thermodynamic perspective, gas-water-rock interaction processes are normally far from equilibrium, but can be represented by an array of chemical reactions, in which irreversible mass transfer occurs from host rock minerals to leaching solutions, and then to secondary hydrothermal minerals. While initially developed to investigate interactions in near-surface groundwater environments, the reaction path modeling approach of Helgeson and co-workers can also be applied to quantitative investigation of reactions in high T-P environments.

Ischia volcano, being the site of diffuse hydrothermal circulation, is an ideal place where to test the application of reaction-path modeling. Since its last eruption in 1302 AD, Ischia has shown a variety of hydrothermal features, including fumarolic emissions, diffuse soil degassing and hot waters discharges. These are the superficial manifestation of an intense hydrothermal circulation at depth. A recent work has shown the existence of several superposed aquifers; the shallowest (near to boiling) feeds the numerous surface thermal discharges, and is recharged by both superficial waters and deeper and hotter (150-260°C) hydrothermal reservoir fluids.

Here, we use reaction path modelling (performed by using the code EQ3/6) to quantitatively constrain the compositional evolution of Ischia thermal fluids during their hydrothermal flow. Simulations suggest that compositions of Ischia groundwaters are buffered by interactions between reservoir rocks and recharge waters (meteoric fluids variably mixed - from 2 to 80% - with seawater) at shallow aquifer conditions. A CO_2 rich gaseous phase is also involved in the interaction processes (fCO_2 = 0.4-0.6 bar). Overall, our model calculations satisfactorily reproduce the main chemical features of Ischia groundwaters. In the model runs, attainment of partial to complete equilibrium with albite and K-feldspar fixes the Na/K ratios of the model solutions at values closely matching those of natural samples. Precipitation of secondary phases, mainly clay minerals (smectite and saponite) and zeolites (clinoptilolite), during the reaction path is able to well explain the large Mg-depletions which characterise Ischia thermal groundwaters; while pyrite and troilite are shown to control sulphur abundance in aqueous solutions. SiO_2(aq) contents in model simulations fit those measured in groundwaters and are being buffered by the formation of quartz polymorphs and Si-bearing minerals. Finally, our simulations are able to reproduce redox conditions and Fe-depletion trends of natural samples. We conclude that reaction path modelling is an useful tool for quantitative exploration of chemical process within volcano-hosted hydrothermal systems.