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Fluoride circulation from geothermal fluids to surface waters and in volcanic rocks of the Aluto Volcanic Complex (Ethiopia)

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Fluoride-enriched waters frequently occur not only in the deep geothermal waters but also in the ground and surface waters in many areas along the East African Rift, where they represent a major health risk for the population. This study determines the migration and accumulation pathways of fluoride in this region. Rock-, gas, water-, soil-, and plant samples were collected from the area within and close by the Aluto Volcanic Complex, which is part of the Main Ethiopian Rift. Most analysed waters showed fluoride concentrations above the drinking water limit (> 1.5 mg/L) with the highest values in hot springs (up to 70 mg/L) and the geothermal well (76 mg/L). In the solid phase, a high fluoride content was found in acid volcanic rocks (ignimbrite: 4,391 ppm; rhyolite: 3,248 ppm) as well as in pumice (up to 1,955 ppm). The fluoride content of soil samples collected within the volcanic complex varied between 82 and 1,036 ppm. The highest fluoride content was measured in lake sediments (8,171 ppm).

Identified fluoride-rich minerals are beside fluorite (CaF_2) itself, various amphiboles and fluor-apatite (both with about 3 wt. % F^-), minerals of the fluor-caphite group (about 5 wt.-% F^-) and parisite (up to 9 wt.-% F^-). Elevated fluoride concentrations were also measured in some gas (up to 50 ppm) and few plant (up to 65 ppm) samples. Leaching experiments of solid samples with deionised water demonstrated that fluoride can easily be mobilized from pumice and sediments but hardly from consolidated rocks. Fluoride release increased with temperature and correlated roughly with dissolved silica indicating the binding of some fluoride to the amorphous or weakly crystalline silica fraction.

It was concluded that both pathways play a role for fluoride enrichment in the waters: (1) fluoride partially leaches out by weathering from the glassy rock fraction and (2) it derives from deep magmatic intrusions and migrates as gas and liquid along fault zones towards the surface. The good correlation between bicarbonate (deriving from dissolution of magmatic CO_2) and fluoride content in all analysed water samples confirm this assumption.