Goldschmidt 2024 Abstract
https://doi.org/10.46427/gold2024.23111

Nitrogen Isotope Signature of Minerals and Water from a Steam-Heated Environment

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Isotopic values of rare constituents of minerals can record unique formation mechanisms existing throughout the earth's crust. There can be large fractionations between species (i.e. ammonium) in the mineral, liquid, and vapor phase recording how the species is transported through the crust and its thermal history. In this study, we analyzed samples from Sulphur Bank Mercury Mine, a formerly mined site in California with an active geothermal steam-heating zone. The site is located about 20 km north of Cobb Mountain and is part of The Geysers-Clear Lake geothermal region. Values of $\delta^{18}O$ and $\delta^{2}H$ in water and minerals from the site record the influence of both meteoric water and "hydrothermal" water that has higher values of $\delta^{18}O$, indicating exchange with host rocks or magmatic (or metamorphic) water from depth, consistent with other hydrothermal systems. In contrast, the nitrogen isotopes in the same samples record a different mechanism. Here we measured values of $\delta^{15}N$ in ammonium-bearing alunite, an aluminum-sulfate mineral formed in altered host rocks within this steam-heated environment with nitrogen contents from 0.1-1 weight percent. The samples have a range of very depleted nitrogen isotope values which are some of the lowest values ever recorded in the literature with a minimum of -21‰, and average -16.8‰ for 9 samples analyzed. Proximal to these samples, a flooded mine pit (Herman Impoundment) has elevated ammonium concentrations (approximately 450 mg/L) with $\delta^{15}N$ values that are also quite depleted, around -10 ‰. Due to the geologic context and isotopic values, we hypothesize that these results indicate depleted ammonium from a vapor phase rising in this steam environment recorded in the mineral phase. We predict that this signature may occur in other vapor rich environments. These observations could determine whether ammonium is being transported in the vapor or liquid phase, helping to determine the thermal and fluid structure of the environment at the time of mineral precipitation and ore formation.