Mass anomalous fractionations of sulfur isotopes in the Talvivaara Ni deposit, Finland - evidence for hydrothermal input

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Talvivaara black shale-hosted Ni deposit

The Talvivaara deposit contains 1 550 Mt of Ni-Cu-Co-Zn-Mn-U ore and was deposited in a stratified marine basin ca. 2 Ga ago. The deposit is characterized by high C_{org} and S concentrations with median values of 7.6% and 9.0%, respectively, and the occurrence of layers with Mn ≥ 0.8%. Pyrite, pyrrhotite, chalcopyrite, sphalerite, alabandite and pentlandite occur both as fine-grained disseminations and as coarser grains in quartz-sulfide veins.

The median $\delta^{34}S$ values of both pyrite and pyrrhotite are -3‰ in the Ni-rich black shales. In the black shales with Ni < 0.1% the $\delta^{34}S$ values are -4‰ in pyrite and -5‰ in pyrrhotite [1, 2]. Both thermochemical and biogenic sulfate reduction were important for the generation of reduced S as has been reported from the Sullivan Pb-Zn-Ag deposit in Canada [3] where $\delta^{34}S$ patterns resemble those at Talvivaara.

The black shales have undergone medium grade regional metamorphism but spheroidal pyrite with grain size < 0.01 mm and containing up to 0.7% Ni is still preserved in places.

Results

Sequentially extracted S fractions analyzed for 27 Talvivaara samples show mass anomalous $\Delta^{33}S$ values for spheroidal pyrite. For example, in one drill core sample (map sheet 3433, drill core 305, depth 150.89 m in the drill core), the values for spheroidal pyrite range between -2.27‰ to -7.73‰ for $\delta^{34}S$, -0.60 to -4.38‰ for $\delta^{33}S$ and 0.57 to -0.40‰ for $\Delta^{33}S$.

Values for recrystallized pyrite and pyrrhotite in the same sample range from -3.09 to -6.25‰ for $\delta^{34}S$, -1.57 to -3.20‰ for $\delta^{33}S$ and 0.01 to 0.05‰ for $\Delta^{33}S$.

Conclusions

Previous MIF sulfur anomalies have been reported for rocks older than 2.4 Ga. However, anomalous S isotope signatures may also result from reactions between organic matter and S-bearing aqueous solutions under hydrothermal conditions [4] which is the most likely case at Talvivaara. The uniform distribution of Ni in the extensive black shale unit indicates mixing between seawater and Ni-rich fluids.

[1] Loukola-Ruskeeniemi & Heino (1996) *Econ. Geol.* **91**, 80-110. [2] Loukola-Ruskeeniemi (1995) *Geological Survey of Finland, Special Paper* **20**, 31-46. [3] Taylor (2004) *Chem. Geol.* **204**, 215-236. [4] Lasaga et al. (2008) *Earth and Planetary Science Letters* **268**, 225-238.

Dating old groundwater by multiple tracers including Krypton 81

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The Great Artesian Basin (GAB) of Australia is one of the largest groundwater basins in the world and contains the largest storage of potable groundwater in the Australian continent. Because of its vast size and the potential for large regional flow systems to occur, the GAB has been considered an ideal basin to test emerging groundwater dating techniques such as Cl-36 and He-4. However both of these techniques are subjected to large degrees of uncertainty, as they require a detailed understanding of different sources and sinks of these two isotopes. Contrasting this Kr-81 is considered to be an ideal tracer as it contains only one source, the atmosphere with no or at most minimal sub surface production. Our study area is focused on the western margin of the GAB between the Finke River system in the Northern Territory and the iconic Dalhousie springs in South Australia. This represents the direction of groundwater flow from recharge to discharge through the Dalhousie spring complex. For the first time we have provided a comprehensive suite of analyse not only of Cl-36, He-4, C-14, Ar-39, stable isotopes of the water molecule and noble gases but also, Kr-85 and Kr-81. Our preliminary results indicate a spectrum of "tracer groundwater ages" ranging from modern as indicated by C-14 and Ar-39 up to hundreds of thousands of years as indicated by Kr-81, Cl-36 and He-4. We suggest that this groundwater flow transect may represent an ideal type section for understanding different isotope systematic in order to obtain a greater knowledge of regional groundwater flow.