Radiogenic ^{26}Al chronometry of evaporites

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Radiogenic production of ^{26}Al in Na rich evaporites can potentially be used for chronometry over several million years. This can be a tool for dating paleoclimate conditions in arid environments. Measurable quantities of ^{26}Al are present in material with either high concentrations of alpha emitters (principally U and Th) or high concentrations of target nuclei. Significant quantities of ^{26}Al are recorded in U and Th ores, and the primary mechanism of this production is the ^{23}Na (α, n)^{26}Al reaction (Sharma and Middleton, 1989). Measurable quantities of ^{26}Al should, therefore, also be present in material with modest concentrations of U and Th, but high concentrations of Na. To test this potential geochronometer, a review of the available cross-sectional data for this reaction, as well as the U.Th, and Na composition of various evaporites was done. We will present preliminary data testing the feasibility of this method.

The ^{238}U and ^{232}Th decay chains are the dominant natural alpha sources, with a total of 8 alpha particles emitted in the ^{238}U decay chain and 6 from ^{232}Th decay. The range of alpha particles in rocks is generally less than a few tens of microns, and the alpha-emitters contained within the evaporite minerals themselves are the principal mechanism of radiogenic ^{26}Al production. Since U is soluble in water, and Th is largely insoluble, many evaporite deposits have high U/Th. Disequilibrium in the U-series decay chain occurs in sub-aqueous deposits over the time range of this potential chronometer, and excess of ^{234}U over ^{238}U in evaporites will result in higher ^{26}Al production.

Saline minerals, which are common in marine, lacustrine, hydrothermal, and soil deposits are high in Na and low in Al. Calculated ^{26}Al production rates for U in secular equilibrium is ~10 atoms/gramNa/ppmU, and minerals such as halite, glauberite, and trona are 30 to 40 weight percent Na. The range of measured and previously reported U concentration in salts varies from a few ppt to several ppm. Exceptionally pure salts incorporates less U, but also contain less stable Al. Al concentrations in salts range from 1.5-150 ppm. At these concentrations, production rates are comparable to cosmogenic ^{26}Al at the surface. A salt with 10 ppm Al and 1 ppm U should contain detectable ^{26}Al in less than a century.

Reference

Sharma, P. Middleton, R., 1989, *Geochem. Cosmochem. Acta* **53,** 709-716.

Importance of thioarsenates for arsenic redox processes along geothermal drainages, Yellowstone National Park

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Thioarsenates were found to play an important role in arsenic speciation and the mechanism of arsenic oxidation in sulfidic hot spring discharges in Yellowstone National Park. Previous studies, using hydride-generation atomic absorption spectrometry (HG-AAS) [1], reported arsenite predominance at the geothermal source, followed by rapid oxidation to arsenate in the discharge channels, however, HG-AAS is not designed to measure thioarsenates. We used anion-exchange chromatography inductively-coupled plasma-mass-spectrometry to study arsenic speciation along the drainage channel of the sulfidic Ojo Caliente hot spring (pH 8) and a near-by geyser (pH 9.1).

At the geothermal sources, we detected trithioarsenate, not arsenite, as the predominant species. Its formation is presumably caused by the presence of S^0-donors such as polysulfides or thiosulfate (0.6 mg/L at the source of Ojo Caliente). Along Ojo Caliente drainage channel the major initial product of trithioarsenate conversion was arsenite. Arsenate only formed from arsenite as a secondary product once all thioarsenates disappeared. Compared to Ojo Caliente, the discharge at the geyser was more vigorous, the drainage channel steeper and the flow faster. Under these conditions, trithioarsenate was found to transform to di- and monothioarsenate with arsenate as final end product. Arsenite concentrations did not increase significantly.

Preliminary laboratory studies show that trithioarsenate converts to arsenite without significant increase of arsenate, mono- or dithioarsenate if the solution is purged with nitrogen or air and sulfide is volatilized from solution or partially oxidized to thiosulfate but the oxidation rate is too low for complete oxidation to sulfate. By adding H_2O_2, thiosulfate is oxidized to sulfate and trithioarsenate undergoes ligand exchange to thioarsenate species with a successively lower number of SH-groups to finally yield arsenate without formation of significant amounts of arsenite.

Reference

[1] Nordstrom D. K., Ball J.W., McCleskey, R. B. (2005), In *Geothermal Biology and Geochemistry in Yellowstone National Park*; Inskeep, W., McDermott, T. R., Eds.; Thermal Biology Institute, Montana State University: Bozeman, Montana, 73-94.