

The role of groundwater in the formation of the giant nitrate deposits of Atacama: Iodine-129 and stable chromium isotopic evidence

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The nitrate deposits of the hyperarid Atacama Desert are a complex mineral association of nitrates, chlorides, sulfates, perchlorates, iodates and chromates. Recent studies have focused mainly on the nitrate, sulfate and perchlorate components and despite the fact that the atmospheric influence is indeed recognized, the formation of these extensive deposits still remains highly controversial.

Here we focus on the so far poorly studied iodine and chromium components of nitrates, and we present the first iodine-129 (¹²⁹I) and stable chromium isotopic ($\delta^{53/53\text{Cr}}$) data for these deposits. Stable iodine in the nitrates is high (10's of ppm to >2000 ppm), exceeding the iodine content of the average continental crust by 3 to 4 orders of magnitude. Furthermore chromium is enriched in the nitrate deposits in its oxidized state Cr(VI), forming chromate minerals, a rare phase of chromium under natural and surficial conditions. Iodine isotopic ratios of nitrate samples are generally low ($^{129}\text{I}/^{127}\text{I} \sim 200\text{-}600$) and similar to deep marine sediment reservoirs and shales. Stable chromium isotopes of nitrates have positive and highly fractionated values ($\delta^{53/52}\text{Cr} \sim +1$ to $+3\text{‰}$), showing that the chromium signal is highly distinct compared to most chromium terrestrial reservoirs.

The isotopic signatures of iodine and chromium in the nitrates is consistent with a groundwater source rather than an atmospheric one. Therefore, and considering that: (i) low iodine-129 ratios are indicative of deep sedimentary sources and (ii) chromium data reveal significant redox-cycling, most probably related to groundwater transport, we suggest a genetic model where iodine, chromium and eventually other chemical components (e.g. part of the nitrate and sulfate) were sourced from Jurassic marine shales found upstream in the Precordillera. The formation of nitrate deposits would then be the result of a unique combination of multiple sourcing, groundwater transport processes, and wet and dry (atmospheric) deposition under conditions of increasing desiccation.

Isotopic fractionation of Cu in biofilms from a historic mining site

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The environmental development of historical mine sites offers a good opportunity to study the metal cycle processes within the system. One of those sites is the spoil heap area of Schwarzwand in Salzburg, Austria. In this location a constant bluish precipitation -composed of Cynaobacteria and secondary copper minerals- in the creeks is present. In this study, the Cu concentration and isotope composition ($\delta^{65}\text{Cu}$) in selected samples from biofilm, stream water and heap rocks from Schwarzwand was measured.

Results show a variability towards the heavier Cu isotope from rocks, to water to biofilm samples. An interesting observation is the fact that regardless the Cu concentration in the biofilm that ranges from 100 ppb to 5%, its isotopic signature remains constant, with values from 0.3435‰ to 0.6984‰. Contrary to the expected behaviour of bacterias to be a sink for the lighter Cu isotope [1], the biofilm has a heavier Cu isotope signature compared to the rock and stream water from the site. This biofilm comprises several species of *Phormidium* (Cyanobacteria) embedded in a matrix of organic polymers and detritus. This result implies that in a bulk result the processes that occur in the matrix such as mineral precipitation and adsorption can count in a larger extent to the total Cu isotope in the biofilm system. In addition, the presence of plants such as copper mosses (*Pohlia* spp.) in the biofilm can also isotopically fractionate the Cu available to the biofilm, as it has been seen before in plant systems [2].

The results shown can be of importance in the potencial use of such metal-tolerant biofilms for remediation purposes by pointing out the main processes that can cause a fractionation of metals such as Cu and Fe.

[1] Navarrete *et al* (2011) *Geochim. Cosmochim. Acta* **75**, 784-799. [2] Weinstein *et al* (2011) *Chem. Geol.* **286**, 266-271.