

The origin of the nitrate ore fields from the Atacama Desert revisited: New insights from the iodine-129 and stable chromium isotopic systems

Alida Pérez Fodich^(1,2), Fernanda Álvarez^(1,2), Martin Reich^(1,2), Glen Snyder⁽³⁾, Ronny Schönberg⁽⁴⁾, Gabriel Vargas^(1,2), Carlos Palacios⁽¹⁾

(1) Departamento de Geología, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile

(2) Centro de Excelencia en Geotermia de los Andes, Universidad de Chile, Santiago, Chile

(3) Department of Earth Science, Rice University, Houston, Texas, USA

(4) Fachbereich Geowissenschaften, Eberhard Karls Universität Tübingen, Tübingen, Germany

*E-mail: aliperezfodich@gmail.com

Abstract. Iodine is strongly depleted in the continental crust, and due to its large ionic radius it is not incorporated into minerals remaining in the aqueous phase much longer than other halogens. In the nitrate ore fields of the Atacama Desert of northern Chile, iodine is highly enriched forming one of the largest reservoirs of iodine in the Earth's continental crust. However, its occurrence in these deposits is poorly understood and remains unconstrained.

In this study, we couple iodine-129 (¹²⁹I) isotopic with stable chromium isotopic ratios (⁵³Cr/⁵²Cr) in chromate-bearing, iodine-rich nitrate samples. Preliminary data show that ¹²⁹I/I ratios from nitrate samples range between 148 and 446 [$\times 10^{-15}$ at/at]. These results make it unlikely that the source for iodine in the nitrates is atmospheric. Moreover, they suggest that the iodine in the nitrates came from waters originally derived from organic-rich marine sediments. The $\delta^{53}\text{Cr}/^{52}\text{Cr}$ values are highly fractionated and range between +0.711 to +1.233 per mil. When coupled with I-129 data, the $\delta^{53}\text{Cr}/^{52}\text{Cr}$ data provide evidence of an intensive redox cycling (e.g. oxidation of reduced Cr) involved in the genesis of the iodate and chromate minerals.

Keywords: Iodine, nitrate, Atacama, ¹²⁹I, chromium, stable isotopes, groundwater.

1 Introduction

The presence of iodine in the continental crust is uncommon, since iodine is a strongly biophilic element and its distribution is dominated by the marine system. Because of its large ionic radius, iodine is rarely incorporated into mineral phases and remains in the aqueous phase much longer than other halogens such as chlorine or bromine (Snyder & Fehn, 2002; Fehn et al., 2007).

The nitrate ore fields from the Atacama Desert (Figure 1) are considered one of the largest iodine reservoirs in the continental crust, with average iodine concentrations of 50 ppm in soils and 900 ppm in high grade nitrate ore, compared to the low, ~100 ppb average iodine in the continental crust (Muramatsu & Wedepohl, 1997). The nitrate deposits are also unique because trace amounts of chromium are widespread in rare Cr-bearing minerals in the nitrate ore, and can reach concentrations up to 70 ppm. The preservation of the anomalous iodine and chromium in

the nitrates and soils are the result of the prevalent hyperarid climate conditions of the Atacama Desert, with average rainfall rates of less than 10 mm/yr in the last ~3 Ma (Vargas et al., 2006; Garreaud et al., 2010).

The nitrate deposits have been studied in detail for decades, and several hypotheses have been proposed for their origin (marine, atmospheric, organic, hydrothermal, etc), (Ericksen, 1981; 1983 and references therein). However the occurrence of iodine and chromium in these deposits is enigmatic, and has been overlooked by most of these studies, which have mostly focused on the nitrogen and sulphur components (Böhlke et al., 1997; Michalski et al., 2004).

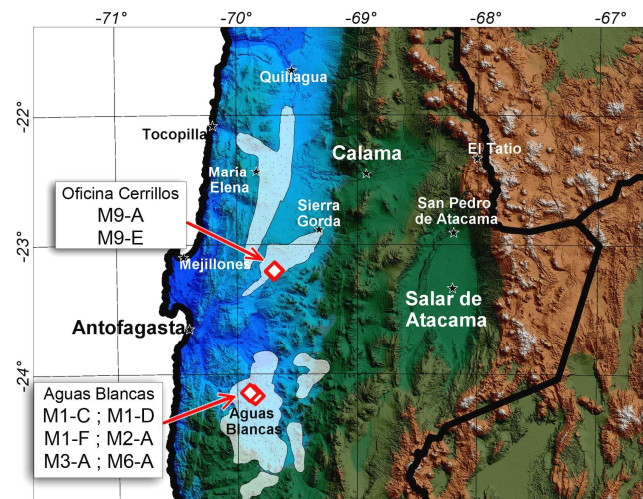


Figure 1. Digital elevation map (SRTM 90m) of the Antofagasta area in the Atacama Desert in northern Chile. Showing sample sites in the nitrate ore fields from Oficina Cerrillos and Aguas Blancas.

In this report, we present new geochemical and isotopic data from nitrate samples from the Antofagasta region of the Atacama Desert, providing new insights into the origin of the nitrate deposits. Isotopic data from the iodine-129 (¹²⁹I) system are used to trace the source(s) of iodine, while stable isotopes of chromium ($\delta^{53}\text{Cr}/^{52}\text{Cr}$) values are used as a proxy to evaluate the contribution of redox processes during the formation of iodine and its associated chromium-bearing minerals.

2 Geologic setting, Samples and Methods

2.1 Geologic setting and sampling

The Chilean nitrate deposits consist of water-soluble saline minerals (nitrates, sulphates, chlorides, perchlorates, iodates, chromates) that occur as cement in unconsolidated gravels and as impregnations and veins in bedrock. In these deposits, iodine is present as iodate minerals (I valence +5) such as lautarite ($\text{Ca}(\text{IO}_3)_2$) or bruggenite ($\text{CaIO}_3 \cdot \text{H}_2\text{O}$), and chromium is present as chromate and dichromate minerals (Cr valence +6), like tarapacaite (K_2CrO_4) and lopezite ($\text{K}_2\text{Cr}_2\text{O}_7$) respectively (Ericksen, 1981; 1983).

The nitrate ore fields are located in the hyperarid core of the Atacama Desert, from latitudes $19^\circ 30'$ to 26°S , mostly east to the Coastal Cordillera and in the western part of the Central Depression (including portions from both domains). Neogene gravels infill the central basin that hosts the nitrate ore fields. The Central Depression is bounded to the west by the Coastal Cordillera, which is formed by Jurassic to Lower Cretaceous intrusives and volcanics and its eastern border is composed by Jurassic marine back-arc sequences (Amilibia et al., 2008).

Nitrate samples were obtained in active and abandoned nitrate mines in the Antofagasta and Tarapacá regions. Sampling locations are shown in Figure 1 (only from Antofagasta). In the studied samples, iodine and chromium bearing minerals were identified using X-ray fluorescence (XRF-EDS) and X-ray diffraction (XRD).

2.2 Analytical Methods

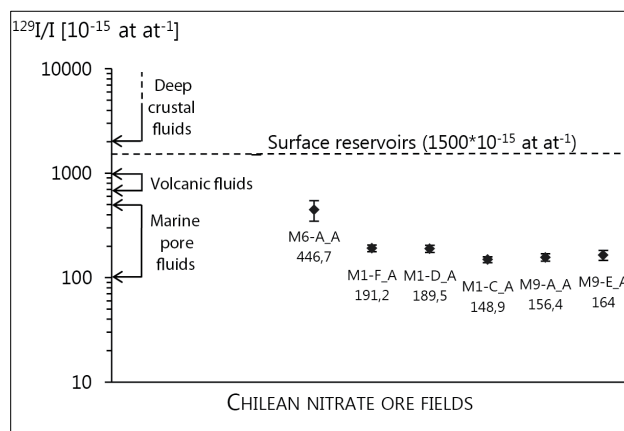
To determine the $^{129}\text{I}/\text{I}$ ratios from nitrate and soil samples, iodine was separated from powdered samples to an aqueous solution. About 30 to 50 g of every sample were diluted in 100 mL of water to release iodine as IO_3^- , then I was extracted for ^{129}I analysis at the Geochemistry Laboratory, Rice University, following the methods by Fehn et al. (1992). Iodine was extracted into carbon tetrachloride, then back-extracted with a sodium bisulfite solution and precipitated as a ~ 2 mg AgI target. The $^{129}\text{I}/\text{I}$ ratios were measured using the accelerator mass spectrometry (AMS) facility at PRIME Laboratory, Purdue University (Sharma et al., 2000).

To obtain $\delta^{53}\text{Cr}/^{52}\text{Cr}$ values for the nitrate and rock samples, Cr was separated from the other solid materials, following established anion exchange chromatography technique (Ball & Basset, 2000; Frei & Rosing, 2005; Schoenberg et al., 2008). Chromium isotope measurements were performed using thermal ionization mass spectrometry (TIMS) at Fachbereichs Geowissenschaften, Universität Tübingen, following the procedures reported by Schoenberg et al. (2008).

3 Results and Discussion

3.1 $^{129}\text{I}/\text{I}$ ratios

Preliminary I-129 data for samples taken from the Aguas Blancas district and Oficina Chacabuco show a significant deviation from pre-anthropogenic atmospheric/meteoric isotopic ratios. The $^{129}\text{I}/\text{I}$ ratios range between 148 and 446 [$\times 10^{-15}$ at at^{-1}], indicating that iodine is most likely derived from a deep, non-meteoric pore fluid reservoir of marine



origin (Figure 2).

Figure 2. $^{129}\text{I}/\text{I}$ ratios for nitrate ore samples of the Atacama Desert. Source ranges from Snyder & Fehn (2002) and Fehn et al. (2007).

Based on these results, we propose that the sedimentary rocks from the Jurassic-Cretaceous marine basement in the region are the most probable source for iodine in the nitrate ore fields, contrasting with the organic, marine or atmospheric geneses previously proposed. Diverse deep sources of fluids (groundwater, pore fluids, volcanic and hydrothermal fluids) are involved in the genesis of the iodine rich nitrate deposits.

3.2 $\delta^{53}\text{Cr}/^{52}\text{Cr}$ values

The preliminary $\delta^{53}\text{Cr}/^{52}\text{Cr}$ values for 5 nitrate ore samples range between 0.711 and 1.232‰, showing a strong enrichment in the heavier Cr isotope compared to Earth materials mean values (Figure 3). The stable Cr-isotope results are similar to hydrothermal crocoites from Russia and Germany reported by Schoenberg et al. (2008).

The heavy Cr isotope composition of the nitrate ore samples reveals a significant fractionation from the mean values (-0.151 to -0.032‰), suggesting that an extensive redox process is involved in the formation of chromates and iodates (e.g. oxidation from Cr(III) to Cr(VI), and from I^- to I^{+5}). However, it is most likely that the heavy Cr isotope composition of the nitrate samples is the result from repeated redox processes rather a unique, extensive oxidation event (Schoenberg et al., 2008).

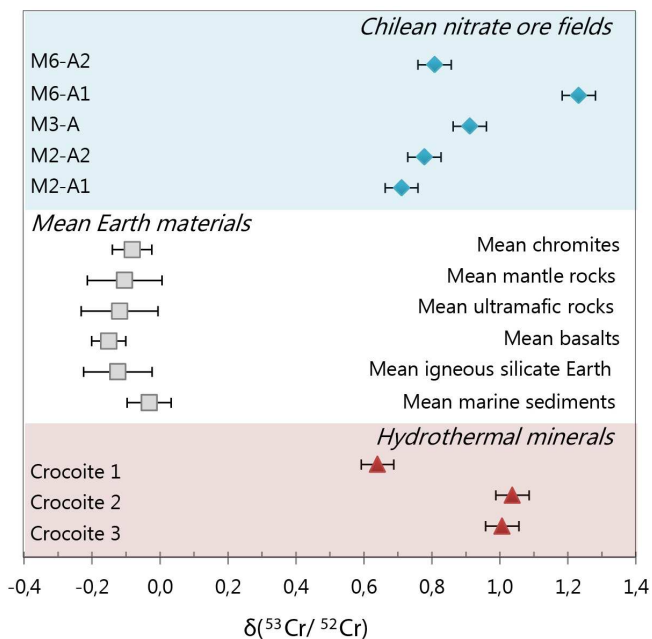


Figure 3. $\delta^{53}\text{Cr}/^{52}\text{Cr}$ values for nitrate ore samples from the Atacama Desert, compared to mean Earth materials and hydrothermal crocoites from Russia and Germany (Schoenberg et al., 2008).

4. Conclusions

The new I-129 and stable Cr isotope data presented in this report provide new insights into the origin of the nitrate deposits of Atacama. The isotopic analysis of iodine and chromium, two largely ignored and abundant components of nitrate deposits, points towards a multiple-source origin for these enigmatic deposits, where the repeated, near-surface oxidation of deep and old groundwater might play an unforeseen role.

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