



## Arsenic speciation in sinter mineralization from a hydrothermal channel of El Tatio geothermal field, Chile



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### SUMMARY

El Tatio geothermal field is the principal natural source of arsenic for the Loa River, the main surface water resource in the hyper-arid Atacama Desert (Antofagasta Region, Northern Chile).

Prior investigations by bulk X-ray absorption spectroscopy have identified hydrous ferric oxides as the principal arsenic-containing phase in sinter material from El Tatio, suggesting sorption as the main mechanism for arsenic scavenging by the solid phases of these hot spring environments. Here we examine siliceous sinter material sampled from a hydrothermal channel using synchrotron based X-ray micro-probe techniques, including As and FeK $\alpha$  X-ray fluorescence ( $\mu$ -XRF), As K-edge X-ray absorption near edge structure ( $\mu$ -XANES), and X-ray diffraction ( $\mu$ -XRD). Least-squares linear fitting of  $\mu$ -XANES spectra shows that arsenic is predominantly present as arsenate sorbed on hydrous ferric oxides (63% molar proportion), but we also identify nodular arsenide micro-mineralizations (37% molar proportion) similar to loellingite (FeAs<sub>2</sub>), not previously detected during bulk-scale analysis of the sinter material. Presence of arsenide mineralizations indicates development of anoxic environments on the surface of the siliceous sinter, and suggests a more complex biogeochemistry for arsenic than previously observed for circum-neutral pH brine hot spring environments.

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### 1. Introduction

El Tatio geothermal field (TGF) is recognized as the principal natural source of arsenic (As) to the Loa River, the main surface water resource for the Antofagasta Region in northern Chile (Romero et al., 2003; Smedley and Kinniburgh, 2002). The Loa is the longest river from Chile (Rudolph, 1927), traveling approx. 4.400 m from the Andes to the coast across the hyper-arid Atacama Desert (Houston and Hartley, 2003). Such attributes provide a unique relevance to the Loa River, since it supports the development of ecosystems and human activities in one of the driest places on Earth. However, high concentration of arsenic compromises the use of scarce surface waters in the region for drinking and agricultural purposes, particularly for rural communities (Flynn et al., 2002; Queirolo et al., 2000; Smith et al., 2000).

Geothermal systems usually contribute as natural sources of arsenic in groundwater (Smedley and Kinniburgh, 2002) and surface streams (Ballantyne and Moore, 1988). TGF is an example of the latter, with hydrothermal discharges containing up to 600  $\mu$ M total

As (Ellis and Mahon, 1977). Human health consequences of using waters tainted with arsenic for drinking purposes have been recognized for decades: diseases such as bladder and lung cancer (Smith et al., 1998), along with elevated infant mortality rates (Hopenhayn-Rich et al., 2000) in the Antofagasta Region have been related to chronic exposure to arsenic in drinking waters. The well-defined period of exposure of the population of the city of Antofagasta to high concentrations of arsenic in drinking water ( $\sim$ 12  $\mu$ M) from 1959 (change to an As-rich water source) to 1970 (arsenic removal plant starts operation) has given ample evidence of the increase in mortality rate due to early-life exposure to arsenic (Smith et al., 2012). Despite the construction and operation in 1969–1970 of drinking water treatment facilities for the Calama and Antofagasta cities, scattered rural communities are still depending on arsenic enriched waters for their drinking and irrigation needs, with development of skin lesions and keratosis (Smith et al., 1998).

On the other hand, TGF is a complex and scientifically interesting natural system, with hot springs and hydrothermal discharges supporting the development of archaea and mat-forming microbial communities which thrive under unique environmental conditions of siliceous sinter precipitation and dissolution, high temperature ( $\sim$ 86 °C, local water boiling temperature at TGF altitude, approx.

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4300 m) and intense UV light radiation, and high concentration of metals and metalloids (Phoenix et al., 2006). Hydrothermal discharges of TGF are particularly well suited to study the principal mechanisms controlling arsenic and antimony mobility and fate at the solid–water interphase, owing to high concentration of these elements in its waters (Landrum et al., 2009).

Mobility and fate of contaminants in natural systems is governed by the interaction of physical and biogeochemical processes, including advective–diffusive transport, redox reactions, surface adsorption/desorption, precipitation and dissolution of minerals, and biological catalysis (Brown et al., 2008). Thus, understanding the chemical forms present in natural solid matrices is needed to assess the mechanisms controlling chemical speciation, mobility and potential bioavailability of arsenic in hot spring environments.

Scientific research at TGF formally began in the early 1970s, as part of a United Nations Development Project conducted by the Chilean Government to investigate feasibility for geothermal energy generation in the Andes region of the country (Healy and Hochstein, 1973; Lahsen and Trujillo, 1976). Despite early investigations, research on arsenic speciation in the solid phases of hydrothermal channels of TGF has only been conducted in the last decade: Romero et al. (2003) performed multi-step sequential extraction analyses on stream sediment samples from the Loa river basin (including TGF), concluding that arsenic is mainly associated with Fe/Mn oxy-hydroxides and residual phases, with approx. 20% readily available from the exchangeable and carbonate phases. Although calcite has been found to sorb/coprecipitate arsenic (Bardelli et al., 2011; Roman-Ross et al., 2002, 2006), no significant calcite content in the sediments studied here was observed (Landrum et al., 2009). Further sequential extraction analyses performed specifically on stream sediments from TGF (Landrum et al., 2009) showed that arsenic is mainly present as a tightly sorbed species on Fe/Mn oxy-hydroxides, and species strongly associated with amorphous Fe/Mn oxides, although some samples also showed availability from the exchangeable fraction.

The study of arsenic speciation in natural solid matrices is a challenging task, especially considering the often diluted concentration of metalloids, presence of numerous chemical species, and presence of hydrated (and often poorly crystalline) minerals, all features that interfere with the correct identification of arsenic coordination chemistry in the solid phase. Among the analytical tools available to study arsenic speciation in solid matrices, X-ray absorption spectroscopy (XAS) stands out as a particularly suitable and versatile technique, since it is element-selective, sensitive to concentrations in the range of parts per million, and capable to probe hydrated matrices (Brown et al., 2008; Gaillard et al., 2001). In particular, XAS has been successfully employed to investigate arsenic speciation in environmental matrices, including soils, mineral assemblages, mine tailings, and vascular plants (Arai et al., 2006; Foster et al., 1998; Sahai et al., 2007; Webb et al., 2003).

As K-edge XAS studies conducted on bulk-scale stream sediments and co-occurring microbial mats from a hydrothermal channel of TGF consistently identified arsenate (As(V)) as the main oxidation state for arsenic in the solid phase (Alsina et al., 2008). Further, non-linear least squares fitting of the Extended X-ray Absorption Fine Structure (EXAFS) spectra was consistent with a model structure consisting of a first coordination shell of 4 oxygen atoms at a distance of 1.69 Å from the central As atom, together with a second shell of 2Fe atoms at a distance of 3.23 Å. The latter was interpreted as arsenate sorbed onto hydrous ferric oxides (HFO) via inner-sphere bidentate surface complexes (Alsina et al., 2008).

Although consistent evidence supports arsenate sorption on HFO as the main mechanism for arsenic incorporation into the

solid phase of hydrothermal channels of TGF, several issues need to be addressed regarding this conclusion. First, HFO precipitation at the hydrothermal channels of TGF occurs in presence of silicic acid (3 mM  $\text{Si}(\text{OH})_4$ ), likely favoring formation of siloxane linkages (Si–O–Si) on the surface of HFO, leading to polymerization of silica ( $\text{SiO}_2$ ), and hence potential inhibition for arsenic adsorption in some cases (Carlson and Schwertmann, 1981; Swedlund and Webster, 1999) or in other cases increased reactivity due to smaller particle size and increased structural disorder (Cismasu et al., 2011). In addition, the content of arsenic in the siliceous sinter of TGF is estimated by bulk chemical analyses in 0.45 mol As per mole of Fe (Alsina et al., 2008), a value that doubles the estimated adsorption capacity of arsenate on pure HFO of 0.2 mol As per mole of Fe (Dixit and Hering, 2003). Although pure HFO reactivity could be altered to some extent by silicic acid, there are still doubts on the availability and capability of HFO to conclusively account for arsenic presence in the solid matrix, and foster research over additional mechanisms responsible for arsenic incorporation into the solid phase characteristic of TGF hydrothermal channels.

Composition of TGF hydrothermal waters –enriched with metals and metalloids– forces competition of the dissolved arsenic species for available complexation and/or nucleation sites on reactive surfaces, leading to potential formation of structurally heterogeneous and spatially distributed arsenic phases within the solid matrix. Hence, it is important to consider that elemental and structural heterogeneities within the sample may be occurring at the micro-scale, and thus spectroscopic techniques aimed at this resolution are required to identify both minor and scattered arsenic solid phases within the solid matrix.

In order to further explore the mechanisms for arsenic incorporation into solid phases of hot springs and hydrothermal channels of TGF, this work examines the spatial distribution and speciation of arsenic in siliceous sinter deposits by means of X-ray microprobe techniques, including XAS, X-ray fluorescence mapping, and X-ray diffraction.

### 1.1. Site of study

TGF is located within the Andes mountain chain, at the north-west end of the Antofagasta Region, approximately 100 km east of the city of Calama, at an altitude of approx. 4300 m.a.s.l. (22°20'S; 68°01'W, Fig. 1A). Hydrothermal manifestations of TGF are scattered in three major zones, the Upper, Middle and Lower Basins, occupying an area of approximately 30 square km (Glennon and Pfaff, 2003). Documented thermal activities at TGF include geysers, perpetual spouter geysers, hot springs, fumaroles, mud ponds, and sinter terraces (Lahsen and Trujillo, 1976). TGF lies in the Altiplano–Puna volcanic complex of the central Andes, a major and still active volcano-tectonic province, resultant of an intense episode of ignimbrite volcanism during the late Miocene period (de Silva, 1989).

According to isotopic and geochemical studies, the hydrothermal discharges from TGF are controlled by water–rock interaction processes and several types of mixing, (i) from both meteoric and local groundwater sources, giving rise to variation in chloride contents, (ii) with carbon dioxide ( $\text{CO}_2$ ) or hydrogen sulfide ( $\text{H}_2\text{S}$ ) gases (Giggenbach, 1978), giving rise to acidic waters, and (iii) and mixing with hydrocarbon-rich magmatic fluids (Tassi et al., 2005).

Several water chemistry analyses have been conducted on TGF hot springs (Cusicanqui et al., 1976; Ellis and Mahon, 1977; Fernandez-Turiel et al., 2005; Landrum et al., 2009; Romero et al., 2003). In general, hydrothermal waters from the Middle Basin are discharged at 86 °C, with circum-neutral pH (6.77), and are dominated by sodium chloride (130 mM Na; 160 mM Cl), boric acid (13.3 mM), calcium (6.8 mM), potassium (4.2 mM), lithium

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