Were Chinchorros exposed to arsenic? Arsenic determination in Chinchorro mummies' hair by laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS)

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Abstract

Chinchorros, a fishermen culture, who lived about 7000 years ago in the coastal region of the Atacama Desert in the northern outpost of present-day Chile, practiced an intricate system of mummification of their dead. The drinking water in this region is rich with arsenic, and the mummies were found in these arsenic endemic areas. Well preserved mummy hair samples provided a unique opportunity to explore the ancient arsenic exposure of the Chinchorros by laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) using a single hair strand without any elaborate sample preparation. Forty-six hair samples from mummies found in five burial sites around the Atacama Desert, Chile, were used for this study. After cleaning, hair strands were placed on mounting tape and ablated using a Nd:YAG UV laser coupled to ICP-MS. A suite of contemporary human hair from the same region with known arsenic concentrations was used for calibration of LA-ICP-MS. Satisfactory linear calibration functions were obtained for arsenic in hair. The method detection limit was 0.8 μg/g and the sample throughput for this method is ∼10 samples per hour. It appears that mummies from the Morro (Arica), Iquique and Camarones had the elevated concentration of arsenic in hair (AsH>10 μg/g) in this sub-set of samples, where Morro had the broad distribution of As concentrations.

1. Introduction

Chinchorros, an ancient culture who lived about 7000 years ago in the coastal region of the Atacama Desert in the northern tip of present-day Chile, practiced an intricate system of mummification of their dead [1–5]. The natural water in this region is rich with arsenic [6,7], and the mummies were found in these arsenic endemic areas. The Atacama Desert in Northern Chile has elevated levels of arsenic, copper and several other toxic metals [8–11]. These metalloid and metal containing minerals are ubiquitous in the arid desert bedroock and volcanic slopes bordering the Andean altiplano. As the winter snow melts, trace metals in these minerals leach into Andean mountain springs, finally flowing to rivers that run through the narrow valleys in Atacama, thereby contaminating the scarce fresh water sources in the region. It is very likely that the peoples of this region, both historical [6] and contemporary [9,12], have been exposed to these toxic elements through water, food, and direct contact with soils.

Arsenic has been a well known toxic element since antiquity. This metalloid is typically found as a chalcophilic mineral, such as realgar (As₄S₄), orpiment (As₂S₃), arsenolite (As₂O₃), or bound to iron (siderophilic) as arsenopyrite (FeAsS) or enargite (Cu₃AsS₄) [13]. Arsenopyrite and enargite are the most common naturally occurring chalcophilic minerals in Chile. Arsenic in these sulfide mineral veins is readily soluble in water and the majority of present-day arsenic exposure comes from contaminated drinking water [9,10,14]. It is typically found as an oxyanion in natural aqueous environments. The arsenate form is common [As(V)] in oxic conditions while arsenite [As(III)] species, which are more toxic, occur under reducing conditions [15,16]. As an oxyanion, arsenic’s solubility is less affected by the neutral pH of water. Many toxic trace metals form divalent cations (such as Pb²⁺, Ni²⁺, Cd²⁺) present in acidic solutions. These cations become less soluble as the pH reaches the neutrality of natural waters. By contrast because of this anionic nature, arsenic can be found in relatively greater concentrations in aqueous environments than divalent trace metals [13]. Arsenic is most soluble in high pH which is present in arid environments such as the Atacama Desert [13]. Dissolved arsenic levels are highly elevated in the Camarones River and reach >1000 μg/L near the village of Illapata [6,9], which is ∼100