Effect of iron redox transformations on arsenic solid-phase associations in an arsenic-rich, ferruginous hydrothermal sediment

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Abstract

Well-constrained laboratory incubations of a ferruginous marine hydrothermal sediment from Santorini, Greece, were used to elucidate the effect of microbially induced redox transformations on arsenic speciation and mobility. Despite naturally high arsenic concentrations ($\sim$400 mg/kg), the sediment has a low As:Fe ratio (1:1000 wt/wt). Acetate-amendment of sediment, extracted from the naturally-occurring suboxic–anoxic (Eh -60 to -138 mV) transition zone, promoted Fe(III) reduction, and increased the concentration of Fe(II) from $\sim$40% to $\sim$60% in the bulk sediment. Sulfate, which was present at lower concentrations, was also reduced. Phylogenetic 16S rRNA and *dsr* gene analysis suggested that Fe(III) and sulfate were reduced by bacteria related to *Malonomonas rubra* and *Desulfosarcina variabilis*, respectively. Arsenic remained predominantly as arsenic trioxide (As_2O_3) throughout the amendment experiment. However, the percentage of total arsenic present within poorly-crystalline iron oxides decreased from $\sim$69% to $\sim$32%, while the percentage incorporated within crystalline iron-containing minerals or sorbed to surfaces *via* inner-sphere complexes increased significantly (to 22% and 30%, respectively). Re-oxidation of the system with nitrate resulted in incomplete reduction of the nitrate pool, and partial re-association of arsenic with the poorly-crystalline iron fraction. Exposure to air led to virtually complete reversal of the arsenic partitioning, and oxidation of 71% As(III) to As(V). During aeration, oxidation of sediment-bound sulfur/sulfide occurred, alongside an observed $\sim$63% decrease in arsenic bound to this minor component. Analogous trends in arsenic-sediment associations were observed in the natural, unamended sediment depth-profile, whereby a greater proportion of arsenic (34% As(III), 66% As(V)) was bound within poorly-crystalline iron oxides at the sediment–water interface. Arsenic (96% As(III)) was increasingly incorporated within well-crystallized forms of iron with depth and decreasing Eh values. At the greatest depth sampled (35 cm) arsenic increased substantially within the sulfide/organic fraction. Results here contribute to existing evidence that arsenic is not necessarily released from iron-rich sediment systems under conditions of anoxia, but that Fe(II)-bearing minerals forming concomitantly can immobilize arsenic in the solid-phase. Such results may have implications for other systems with high Fe:As ratios.
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1. INTRODUCTION

Arsenic occurs naturally at elevated levels in a range of environments, including aquifer groundwater and sediment (e.g. Polya et al., 2005; also see reviews by Smedley and Kinniburgh, 2002; Welch et al., 2006), lake sediments (e.g. Belzile and Tessier, 1990), terrestrial geothermal or geothermally affected systems (Anderson and Bruland, 1991; Kneebone and Hering, 2000; Planer-Friedrich et al., 2007) and marine hydrothermal sediments (e.g. Pichler and Veizer, 1999; Schaller et al., 2000; Rancourt et al., 2001; McCarthy et al., 2005), as well as in systems involving anthropogenic contamination (e.g. Sánchez-Rodas et al., 2005; Wilkin and Ford, 2006). The predominant forms of arsenic in the environment are inorganic arsenate, As(V), and arsenite, As(III), and, to a lesser extent, organic methylated arsenic (Smedley and Kinniburgh, 2002; Vaughan, 2006). In general, As(III) is considered to be more mobile in sediments than As(V); however, As(III) also has the potential to sorb effectively onto hydrous ferric oxides (HFO), and sorption can be similar to, or greater than, that of As(V) at circum-neutral pH, and even greater at more alkaline pH levels (Manning et al., 1998; Raven et al., 1998; Goldberg and Johnston, 2001; Bostick and Fendorf, 2003).

The range of microbially and abiotically mediated processes affecting arsenic retention or release from sediments is complex (Smedley and Kinniburgh, 2002; Welch et al., 2006). Both field and laboratory studies to date have indicated that the processes relating to microbially-mediated and inorganic arsenic capture and release are highly dependent upon a number of factors, such as: Eh, pH, arsenic speciation, and host mineral crystallinity, surface area or concentration (Moore et al., 1988; Roden and Zachara, 1996; Raven et al., 1998; Farquhar et al., 2002; Genç-Fuhrman et al., 2004; Richmond et al., 2004; Islam et al., 2005b; Burnol et al., 2007). In particular, the nature of As(V) and As(III) co-precipitation/sorption response is heterogeneous over a range of iron and sulfide mineralogies (e.g. Farquhar et al., 2002; Bostick and Fendorf, 2003; O'Day et al., 2004; Islam et al., 2005b).

The mechanisms of the binding of arsenic to iron minerals and of its release have received a great deal of attention, owing to the prevalence of HFO in the natural environment and their strong affinity and uptake capacity for arsenic (Ferguson and Anderson, 1974; Fuller et al., 1993; Raven et al., 1998). In circumneutral oxidizing environments, where HFO are stable, they provide an important sink for arsenic immobilisation (e.g. Price and Pichler, 2005). Conversely, under reducing conditions the microbial respiration and dissolution of Fe(III) to aqueous Fe(II) can liberate arsenic from sediments, or more specifically from iron minerals (e.g. Cummings et al., 1999; Islam et al., 2004). Numerous studies have also demonstrated that ecologically and phylogenetically diverse bacteria and archaea are capable of enzymatically transforming arsenic oxyanions from As(V) to As(III) and vice versa (reviewed by Oremland and Stolz, 2003; Lloyd and Oremland, 2006; Stolz et al., 2006). Arsenate-respiring bacteria are also capable of promoting the release of arsenic as As(III) sorbed to sediment even in the absence of host mineral dissolution (Ahmann et al., 1997; Zobrist et al., 2000).

Nonetheless, oxidation state alone cannot be relied upon to determine arsenic mobility or retention. The idealized trend of arsenic capture and release can also operate in reverse; for example, via the oxidative dissolution of arsenic-bearing sulfide minerals, which can be responsible for arsenic discharge from sediments (e.g. Nickson et al., 2000). Alternatively, the transition between oxidizing and reducing sediments can be accompanied by a solid-phase change in the minerals carrying arsenic. Accordingly, arsenic may be adsorbed onto, or co-precipitated with, a variety of Fe(II)-bearing minerals or sulfides where conditions become reducing (e.g. Bostick and Fendorf, 2003; Kirk et al., 2004; O'Day et al., 2004; Islam et al., 2005a,b; Wolthers et al., 2005; Kocar et al., 2006; Root et al., 2007). Further to this, the trend of arsenic solubility with depth in sediments can also be uncoupled from distinct redox boundaries owing to ongoing changes in reduced host minerals (Root et al., 2007).

Previous investigations of hydrothermal sediments from Nea Kameni Island at Santorini have identified abundant HFO, and sediment that was depleted in levels of most trace metals typical of hydrothermal systems (e.g. Mn, Cu, Ni, Zn, V), but highly enriched in arsenic (Bostrom and Widenfalk, 1984; Varnavas and Cronan, 1988; Cronan et al., 2000). The sediment underlies shallow (<1 m deep) circum-neutral pH marine water, warmed by rising hydrothermal fluids (maximum reported temperature, 40 °C; Bostrom and Widenfalk, 1984). Analyses of this sediment have revealed that it is biogeochemically stratified, and host to a diverse bacterial community capable of redox cycling of iron, nitrogen, sulfur and arsenic species (Holm, 1987; Handley et al., 2010). In a similar ferruginous environment (Tutum Bay, Papua New Guinea) with high arsenic concentrations, up to 6% (Fe:As ≈ 6), arsenic was found to be almost entirely captured within HFO (Pichler and Veizer, 1999). Examination of arsenic partitioning in the surface layer of the Tutum Bay sediment showed that arsenic was predominantly (>98%) associated with an oxalate-extractable poorly-crystalline iron oxide fraction, with comparably minor quantities of arsenic present in carbonates, as easily exchangeable outer-sphere complexes, or in residual phases (Price and Pichler, 2005). The effect of microbial respiration on arsenic partitioning within either of these sediments has not previously been studied, although it is anticipated to have a significant effect on iron mineralogy and hence the nature of arsenic-iron associations.

In the present study, laboratory experiments were undertaken in order to investigate the effect of anaerobic microbial respiration on arsenic-cycling in iron-rich hydrothermal sediment from the Nea Kameni site, Santorini, and also the impact of re-oxidation on arsenic speciation. The arsenic- and iron-rich nature of the sediment made it possible to use techniques, such as XANES and EXAFS, to study arsenic speciation and coordination environments, which is not possible with lower arsenic concentrations more typically found in sediments. The fate of arsenic under reducing conditions was determined by stimulating Fe(III) and sulfate respiration in the indigenous microbial