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Arsenic distribution and speciation in the bauxitic Fe-Ni-laterite ore deposit of the Patitira mine, Lokris area (Greece)

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ABSTRACT

Bauxitic Fe-Ni-laterite ore from the Patitira mine in Lokris area (Greece) contains assemblages of unusual As-bearing goethite-type phases in samples with significant organic matter. The material was initially characterized by bulk ICP-MS and SEM-EDS. Furthermore, the distribution and speciation of As were studied by Synchrotron Radiation (SR) spectroscopic techniques, for first time in the literature. The SR μ-XRF elemental maps and the As *K*-edge μ-XAFS spectra revealed that As is exclusively correlated to Fe, occurring as As^{5+} in the form of arsenate anions (AsO_4^{3-}). However, the arsenate anions, being considered as sorbed species on goethite-type phases, exhibit -at molecular scale- a disordered structural environment, resembling locally to the configuration of such anions in natural hydrated Ni arsenates (annabergite) rather than to natural hydrated ferric arsenates (scorodite). The metalloid element in study, possibly derived from As-mineralizations or volcanic rocks, has been transferred in the environment of the laterite re-deposition, where arsenates could interact with the aforementioned Fe-phases.

1. Introduction

The metalloid element arsenic (As) has an excess of electrons and unfilled orbitals that stabilize formal oxidation states from 5+ to 3- and has the ability to readily change oxidation state and bonding configuration. Although As can be combined with many other elements to form covalent compounds, it most commonly bonds to O and S in the nature. In aqueous solutions, As forms the oxo-anions arsenite, $H_3As^{3+}O_3$ [or, commonly, written as $As^{3+}(OH)_3$] and arsenate, $H_3As^{5+}O_4$. Arsenic oxo-anions have diverse chemical behavior in nature due to their redox potential. While arsenite is expected to be the stable aqueous form under moderately reducing conditions, arsenate is stable in oxidized aqueous solutions (O'Day, 2006 and references therein). Currently, much research interest has been focused on the microbial mobilization of ferric Fe, related to enzymatic reduction of Fe (III) to Fe(II), and Fe-oxidizing bacteria that use the energy from the oxidation of Fe(II) to Fe(III) for carbon assimilation. This is due to their importance in the global Fe cycle and their potential to mobilize metals contained in ores (Lowenstam and Weiner, 1989; Taylor and Curtis, 1995; Konhauser, 1998; Posfai et al., 1998; Donald and Southam, 1999; Taylor and Macquaker, 2000; Schippers and Jørgensen, 2001; Rawlings, 2005; MacLean et al., 2007; Gong et al., 2008; Hedrich et al., 2011; Taylor and Macquaker, 2011). Recent studies have also pointed out the controlling role of Fe and S in influencing As uptake and release from solution and the complex interplay among adsorption and precipitation processes, changes in oxidation states and mineral stabilities, and the rates of these processes as mediated by microbial activities in surface and subsurface environments (O'Day, 2006 and references therein).

A review concerning the geological sources of As in Greece has been presented (Gamaletsos et al., 2013). While the As content seems to be negligible in the majority of the Fe-Ni-laterite ore deposits of the Balkan Peninsula and Eastern Turkey, elevated As concentrations, reaching bulk values up to 0.26 wt% and 1.94 wt% in Lokris (central Greece) and Gordes (western Turkey) deposits, have been recorded (Çolakoglu, 2009; Eliopoulos et al., 2012). The advantages of the application of Synchrotron Radiation (SR) spectroscopic techniques, to the investigation of As distribution and speciation in various geological materials, including goethite-type phases (in fact Fe^{3+}-(hydrated)-oxyhydroxide), have been well-established (e.g., Hattori et al., 2005; Majzlan et al.,

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2007; Costagliola et al., 2013; Das et al., 2014; Foster and Kim, 2014; Godelitsas et al., 2015; Liu et al., 2017). It is noteworthy that in a very recent study, Fe *K*-edge and Ni *K*-edge μ-XAFS data were obtained with regard to laterite ore deposits from Dominican Republic (Roqué-Rosell et al., 2017). However, As *K*-edge μ-XAFS investigation in laterites has never been presented in the literature. In the present work, a combination of SR μ-XRF and As *K*-edge μ-XAFS is applied, for first time, concerning the nature of As in the bauxitic Fe-Ni-laterite mined in Patitira, Lokris area (Greece). Among others, the studied material has been reported to contain assemblages of As-bearing goethite-type phases (Kalatha and Economou-Eliopoulos, 2015; Kalatha et al., 2017), in samples with significant organic matter (Eliopoulos et al., 2012; Kalatha and Economou-Eliopoulos, 2015; Kalatha et al., 2017).

2. Geological setting

According to the literature, Fe-Ni laterite ores in Central Greece were formed during Early Cretaceous, by intense weathering of ultramafic rocks, and they have been transported, re-deposited as marine sediments (mixed in some cases with weathering material derived from non-ultramafic protoliths) and buried by later transgressive Upper Cretaceous limestones (Albandakis, 1980; Rosenberg, 1984; Valeton et al., 1987; Maksimovic et al., 1993; Alevizos, 1997; Skarpelis, 2006; Eliopoulos et al., 2012). The mining area of Aghios Ioannis (Lokris area, central Greece) includes the Nissi area deposits (located SSW of the Aghios Ioannis deposit) (Fig. 1; see: Baker et al., 2011). Evidence of the allochthonous origin of the Aghios Ioannis and Nissi deposits through marine transgression with associated re-working and deposition in a shallow marine environment (Skarpelis and Zampetaki-Lekka, 1998) as well as diagenetic and post-diagenetic processes has been reported in previous works (Albandakis, 1980; Rosenberg, 1984; Valeton et al., 1987; Maksimovic et al., 1993; Alevizos, 1997; Maksimovic, 2004; Eliopoulos et al., 2012). The Nissi area deposits are allochthonous lying on karstified Triassic–Jurassic limestones. Moreover, they are conformably overlain by Upper Cretaceous limestones and have been affected by faulting (Albandakis, 1980; Valeton et al., 1987; Alevizos, 1997;Economou-Eliopoulos et al., 1997; Arnisalo et al., 1999; Eliopoulos and Economou-Eliopoulos, 2000; see: Fig. 1).

The Nissi area deposits comprise a series of lenses occurring either as isolated typical Fe-Ni-laterite or as bauxitic laterite ores. Besides, this series is also present as an association of Fe-Ni ore at the lowest part of the deposit followed by bauxitic laterite towards its upper part (i.e., the case of the Patitira deposit located at the eastern part of the Nissi area; see: upper image of Fig. 1). A detailed geochemical and mineralogical study of the Fe-Ni ores and bauxitic laterite ores from the Nissi deposits have shown the existence of transitional zones between a typical brown-red Fe-Ni ore, gradually grading to gray-white, gray-black, pinkish white and pale green zones, towards to the overlying and underlying limestone and carbonate units, respectively. These multicolor transitional zones (see lower image of Fig. 1) are mainly characterized by multistage changes in Fe-mineral assemblages (Fe-sulfides and Fe-oxides) associated with framboidal pyrite and assemblages of As-bearing goethite-type phases (Kalatha and Economou-Eliopoulos, 2015; Kalatha et al., 2017), in samples with significant organic matter (Eliopoulos et al., 2012; Kalatha and Economou-Eliopoulos, 2015; Kalatha et al., 2017).

3. Materials and methods

The bulk geochemistry (major and trace elements) of the bauxitic Fe-Ni-laterite ore samples was determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analyses. The samples were dissolved using (a) hot Aqua Regia digestion and (b) a strong multi-acid (HNO_3–$HClO_4$–HF) digestion and the residues dissolved in concentrated HCl. The moisture content was determined by drying the samples at 105 °C and the organic matter content by igniting the oven-dried samples (from moisture content determination) in a muffle furnace at 440 °C for 3 h (ASTM, 2000). The organic matter content (Table 1) was calculated as the difference between the initial and final sample weight divided by the initial sample weight and multiplied by 100 to yield the wt% fraction (ASTM, 2000).

The mineralogy was initially checked by optical microscopy and Scanning Electron Microscopy combined with Energy Dispersive Spectroscopy (SEM-EDS), using a Jeol JSM 5600 SEM equipped with an ISIS 300 Oxford EDS detector. Analytical conditions were 20 kV accelerating voltage, 0.5 nA beam current, < 2 μm beam diameter and 50 s dwell time. The following x-ray lines were used: As*L*α, Fe*K*α, Ni*K*α, Co*K*a, Cu*K*α, Cr*K*α, Al*K*α, Ti*K*α, Ca*K*α, Si*K*α, Mn*K*α, Mg*K*α, Cl*K*α. Standards used were pure metals for the elements Ni, Co, Cu, Cr and Ti as well as corundum variety ruby (Al_2O_3) for Al, wollastonite ($CaSiO_3$) for Ca & Si, rhodonite ($MnSiO_3$) for Mn, periclase (MgO) for Mg, tugtupite ($Na_4AlBeSi_4O1_2Cl$) and pyrite (FeS_2) for S and Fe, respectively. Indium arsenide (InAs) was utilized as standard for As using 300 s dwell time, while the presence of arsenic was confirmed in the X-ray emission spectra.

A representative ore sample from the Fe-Ni laterite Patitira deposit, with remarkably high As concentration (up to 350 ppm in bulk), was selected for Synchrotron Radiation (SR) investigation. The SR micro-X-ray-Fluorescence (μ-XRF) elemental mapping and micro-X-ray Absorption Fine Structure (μ-XAFS) spectra were both obtained in the X-ray beamline of the Laboratory for Environmental Studies (SUL-X) of the ANKA Synchrotron Radiation Facility (Karlsruhe Institute of Technology/KIT, Germany). For this purpose, solid fragments of the ore were embedded into resin and polished, whereas powders of reference minerals and compounds were pressed with cellulose to pellets (Göttlicher et al., 2006). Three representative mm-sized regions on polished section, regardless of the SEM-EDS examination, were X-ray scanned in order to locate As-rich micro-areas (by SR μ-XRF) -and also other elements-, in order to proceed to acquisition of μ-XAFS spectra. Natural minerals of known As oxidation state, i.e. As^{1-} and As^{5+}, such as arsenopyrite (FeAsS), orpiment (As_2S_3), annabergite ($Ni_3(AsO_4)_2*8H_2O$) and scorodite ($FeAsO_4*2H_2O$), as well as synthetic As^{3+} compounds such as As_2O_3 and $NaAsO_2$, were used as reference materials (e.g., Helz et al., 1995; Foster et al., 1998; Savage et al., 2000; Takahashi et al., 2003; O'Day et al., 2004; Hattori et al., 2005; Lee et al., 2007; Burton et al., 2013; Chen et al., 2013; Handley et al., 2013; Godelitsas et al., 2015). Spectra were measured at the As *K*-edge (11,867 eV). Energy was calibrated for the As *K*-edge XAFS measurements to 11,919 eV (1st derivative of the Au L_3-edge, Au metal foil). The spectra were processed using the ATHENA software package (Ravel and Newville, 2005).

4. Results and discussion

4.1. Geochemical and mineralogical characteristics

The bauxitic Fe-Ni-laterite ore from the Patitira deposit contains significant amount of organic matter (O.M.: 4.6 wt% in bulk) and exceptionally high As content (up to 350 ppm) compared to 13 ppm in average shale (Krauskopf and Bird, 1994) and to the 4.8 ppm referred to the Upper Continental Crust/UCC (Rudnick and Gao, 2003). Besides, the content in Cr (4540 ppm), Zn (680 ppm) and Co (240 ppm) is remarkably elevated compared to the average shale (90 ppm, 95 ppm and 19 ppm, respectively). The Y and U bulk contents are also relatively high (240 ppm and 27 ppm respectively, compared to 26 ppm and 3.7 ppm in average shale), while the Th content seems to be normal, i.e. 14 ppm compared to 12 ppm average shale. The La/Ce ratio is calculated to be > 1.95 (Table 1). However, it should be noted that lower As