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Uranium accumulation in modern and ancient Fe-oxide sediments: Examples from the Ashadze-2 hydrothermal sulfide field (Mid-Atlantic Ridge) and Yubileynoe massive sulfide deposit (South Urals, Russia)

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ABSTRACT

Fe-oxyhydroxide sediments (gossans) from the Ashadze-2 hydrothermal sulfide field (Mid-Atlantic Ridge) and hematite–carbonate–quartz rocks (gossanites) from the Yubileynoe Cu-Zn VHMS deposit (South Urals) are characterized by anomalously high U contents (up to 352 ppm and 73 ppm, respectively). In gossans from the Ashadze-2 hydrothermal sulfide field, rare isometric anhedral uraninite grains (up to 2 μm) with outer P- and Ca-rich rims, and numerous smaller (<1 μm) grains, occur in Fe-oxyhydroxides and sepiolite, associated with pyrite, isocubanite, chalcopyrite, galena, atacamite and halite. In gossanites from the Yubileynoe deposit, numerous uraninite particles (<3 μm) are associated with apatite, V-rich Mg-chlorite, micro-nodules of pyrite, Se-bearing galena, hessite and acanthite in a hematite–carbonate–quartz matrix. Small (1–3 μm) round grains of uraninite, which locally coalesce to large grains up to 10 μm in size, are associated with authigenic chalcopyrite. The similar diagenetic processes of U accumulation in modern and ancient Fe-oxyhydroxide sediments were the result of U fixation from seawater during the oxidation of sulfide minerals. Uraninite in gossanites was mainly deposited from diagenetic pore fluids, which circulated in the sulfide–hyaloclast–carbonate sediments.

1. Introduction

Despite a wealth of research on modern hydrothermal seafloor massive sulfide deposits and their ancient equivalents (volcanic-hosted massive sulfide/VHMS deposits), little attention has been paid to radioactive elements such as uranium. The hydrothermal fluids venting at the seafloor are depleted in uranium and consequently the sulfides derived from these fluids are also U-poor (Hegner and Tatsumoto, 1987; Butler and Nesbitt, 1999; German et al., 2002). However, the average U contents of massive sulfides from the Mid-Atlantic Ridge (MAR) are highly variable (<0.5–14 ppm), reaching 40 ppm in samples from the Ashadze-2 hydrothermal field associated with ultramafic rocks (Fouquet et al., 2010). Extremely high U contents (1560 ppm) also have been reported for one sample of massive sulfide from the Logatchev-2 hydrothermal field, again related to ultramafic rocks of the Mid-Atlantic Ridge (Torokhov et al., 2002).

Modern marine Fe-oxyhydroxide sediments from different geodynamic settings are characterized by higher U concentrations than massive sulfide deposits, up to: (i) 18.7 ppm in the Lilliput low-temperature field, MAR (Dekov et al., 2010); (ii) 20 ppm in the TAG massive sulfide field, MAR (Mills et al., 1994), and East Blanco Depression low-temperature hydrothermal field, Blanco Fracture Zone, Northeast Pacific (Hein et al., 2008); and (iii) 30 ppm in the Endeavour segment of the Juan de Fuca Ridge, Pacific Ocean (Hrischeva and Scott, 2007), and PACMANUS hydrothermal field, Eastern Manus basin (Zeng et al., 2012). Within these hydrothermal fields, Fe-oxyhydroxide sediments (gossans, cf. Hannington et al., 1988) generally overlie the sulfide mounds (Petersen et al., 2000). Partially or completely oxidized sulfide minerals are present due to the interaction between sulfides and ambient seawater (Hannington et al., 1988; Herzig et al., 1991; Hannington, 1993). The enrichment of U in these sediments has therefore been attributed to the fixation of seawater derived U during the oxidation of iron sulfides, possibly through microbially mediated reactions (e.g., Mills et al., 1994).

Due to their excellent state of preservation, Paleozoic VHMS deposits of the South Urals are among the best examples of seafloor massive sulfide deposits preserved in the rock record (Herrington et al., 1998; Maslennikov et al., 2017b). Key features include fragments of black smoker chimneys, fossils, sulfide breccias, sulfide turbidites, and Fe-rich ferruginous rocks which occurred prior to sedimentation and

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extrusion of the overlying lavas (Maslennikov et al., 2012, 2017a, 2017b; Ayupova et al., 2017a). These ferruginous rocks exhibit a variety of lithological associations, mineral phases, and textures.

In the Urals, Fe-rich gossan-derived unmetamorphosed ferruginous rocks have been termed "gossanites" (Maslennikov et al., 2012). Gossanites generally comprise oxidized clastic sulfides mixed with hematitized carbonate and/or hyaloclastic material, almost entirely replaced by hematite, silica, and chlorite. Locally they form dispersion halos around eroded sulfide mounds, covering an area twice to several times that of the orebodies themselves (Maslennikov et al., 2012; Ayupova et al., 2015). The formation of gossanites has been attributed to seafloor weathering of clastic sulfide sediments or plume settled sulfide particles, which were mixed with background sediments (i.e., hyaloclastites and/or their calcareous varieties) (Maslennikov et al., 2012). In the Uralian VHMS deposits, massive sulfide ores are generally characterized by low U contents (<0.50 ppm, unpublished data). The highest U contents (up to 9.10 ppm) were detected in gossanites from the Molodezhnoe, Talgan, and XIX Parts'ezda deposits of the South Urals. The U enrichment of these rocks is related to U-bearing (up to 22.59 ppm) pseudomorphic hematite, which replaces sulfide clasts, and hematitized tube microfossils (up to 11.67 ppm U) (Ayupova et al., 2017b).

In this paper, we compare U-rich gossans (the precursors of gossanites) from the Ashadze-2 hydrothermal sulfide field of the Mid-Atlantic Ridge, to U-rich gossanites from the well preserved Yubileynoe Cu-Zn VHMS deposit of the South Urals. We reveal the source of U in these rocks, the reasons for its enrichment, and track its evolution from seawater to precipitation as a solid phase and further remobilization during the course of post-sedimentation processes.

2. Geological background

2.1. Ashadze-2 hydrothermal field

The Ashadze-2 hydrothermal field (12°99′ N, 44°91′ W) of the Mid-Atlantic Ridge is part of the Ashadze hydrothermal cluster, which consists of four hydrothermal fields located between the Fifteen Twenty and Marathon fracture zones (Fig. 1a). The Ashadze-1 hydrothermal field was discovered in 2003 by the Polar Marine Geosurvey Expedition (St. Petersburg, Russia) (Beltenev et al., 2003). The Ashadze-2 hydrothermal field is located 4.3 km west of the Ashadze-1 field in the western wall of a rift valley, at a depth of 3100–3350 m (unpublished report of PGME, 2007; Cherkashev et al., 2013) and is associated with gabbros and ultramafic rocks (Beltenev et al., 2003).

Black smokers of the Ashadze-2 field occur in a narrow (about 70 m) N-S trending graben-like trough bounded to the east by a faulted gabbroic body (Ondreas et al., 2007). To the west, it is limited by a narrow N-S trending ridge, 20 to 50 m high that bears numerous extinct hydrothermal chimneys. A high resolution (up to 30 cm) topographic survey in the Ashadze-2 field revealed a chain of hydrothermal mounds and a crater shaped structure 20–25 m in diameter and 1–3 m deep (Fouquet et al., 2008). Subsequent visual observations revealed black smokers on the crater bottom, indicating recent hydrothermal activity. Five massive sulfide bodies were found within the Ashadze-2 hydrothermal field (Fig. 1b), most of which is covered by sediments (unpublished report of PMGE, 2007). The largest orebody (number I) is approximately 125 by 335 m in size. Massive sulfide bodies in the south (numbers III and IV) are mostly composed of Fe-sulfides (pyrite and marcasite), whereas those in the centre and far north (numbers I, II, and V) contain significant amounts of Cu and Zn sulfides.

Samples of gossans from the Ashadze-2 hydrothermal field were collected in 2007 during the 30th cruise of the R/V *Professor Logatchev* using a TV grab at stations 30L217, 30L220, 30L221, 30L227, 30L228, and 30L238 (hereafter, st 217, 220, 221, 227, 228, and 238, respectively) (Table 1) (unpublished PMGE report, 2007). All of the TV grabs were positioned within the contours of massive sulfide bodies, distinguished according to electric sounding (Fig. 1b). Four TV grabs collected samples from the top parts of massive sulfide bodies (Fig. 1b). Within orebody number IV, several specimens of Fe-oxyhydroxide sediments (~25 ×20 × 10 cm in size) were recovered from st 217. The st 220 within orebody no. III contained ~90% of strongly oxidized Fe-rich massive sulfides and ~10% of Fe-oxyhydroxide sediments. Samples of st 221 included 50% of strongly oxidized Fe-rich massive sulfides, 30% of stringer-disseminated massive sulfides, and 20% of Fe-oxyhydroxide sediments. Samples of st 228 within orebody number II and st 238 in the northern flank of orebody number I were exclusively composed of Fe-oxyhydroxide sediments. Grab samples from st 227, which is located between orebodies numbers II and III, included atacamite-bearing Fe-

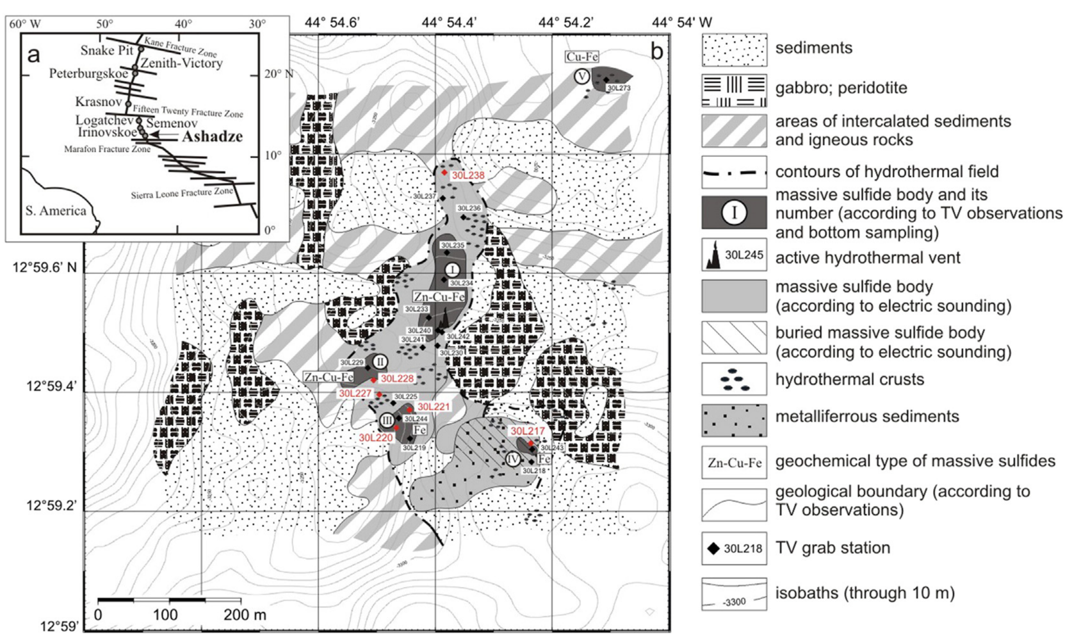

Fig. 1. (a) Location of the Ashadze hydrothermal cluster in the Central Atlantic (Mid Atlantic Ridge) and (b) the schematic structure of the Ashadze-2 hydrothermal field (b), simplified after an unpublished report by PMGE (2007). TV grab stations studied are typed in red.