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Investigation on the role of microorganisms in manganese mineralization from Abadeh-Tashk area, Fars Province, southwestern Iran by using petrographic and geochemical data

Mohammad Ali Rajabzadeh [a,*], Fatemeh Haddad [a], Márta Polgári [b,c], Krisztián Fintor [d], Heléna Walter [d], Zsombor Molnár [e], Ildikó Gyollai [b]

[a] *Department of Earth Sciences, College of Sciences, Shiraz University, Shiraz 7146713565, Iran*
[b] *Research Center for Astronomy and Geosciences, Geobiomineralization and Astrobiological Research Group, Institute for Geology and Geochemistry, Hungarian Academy of Sciences, 1112 Budapest, Budaörsi út. 45, Hungary*
[c] *Eszterházy Károly College, Department of Natural Geography and Geoinformatics, Leányka str. 6, 3300 Eger, Hungary*
[d] *Szeged University, Department of Mineralogy, Geochemistry and Petrology, Egyetem str. 2-6, 6702 Szeged, Hungary*
[e] *Eötvös University, Department of Petrology and Geochemistry, 1117 Budapest, Pázmány P. s. 1/c., Hungary*

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ABSTRACT

Hydrothermal manganese and ferromanganese deposits associated with Neyriz ophiolite colored mélange occurred as small ore deposits in the Abadeh-Tashk area, SE of Fars Province, SW Iran. The deposits are found in three types: a) banded syngenetic ores, b) massive boudin and lens shaped diagenetic ores and c) vein and veinlet epigenetic ores. Microtextural, geochemical and mineralogical data associated with petrographic Raman, FTIR and SEM studies indicated that the primary Fe compounds formed series of microbially mediated biomats and Mn compounds were precipitated as an amorphous oxide on an active oxide surface accompanying silica gels. Field relationships between ore and host rock, high Mn/Fe ratio (17.43 to 40.79), ΣLREE, positive Eu and negative Ce anomalies in syngenetic ore types reveal that the ores were formed by hydrothermal fluid in an oceanic floor environment. Manganese was fractionated from iron due to physicochemical changes as well as microbial activities in the sedimentary environment. Microbial remains as filamentous beads with regular circular shapes, vermiform structures, series of Fe-rich biomats, traces of embedded organic material besides trace metals and REE concentrations in Mn ores emphasize the role of microorganisms in Fe and Mn precipitation. Syngenetic mineralization took place under suboxic neutrophilic conditions, while diagenetic processes resulted in variably reduced Fe- and Mn-oxides via organic matter decomposition, forming rhodochrosite as the end product. Braunite formation occurred most probably as a biogeochemically mediated early diagenetic product. Diagenetic and epigenetic Mn ores were formed when primary Mn deposits underwent subsequent diagenetic and remobilization–redeposition events respectively.

1. Introduction

By the mid-19th century Mn metal was an essential component in steel making as a deoxidizer and desulfurizing agent. Manganese demand grows with increasing hard-steel alloy production, especially in developing countries such as Iran. Mn oxides are the predominant ore minerals in most of today's commercially important Mn deposits. Sedimentary and hydrothermal Mn ore deposits in modern and ancient geological environments as the most important Mn reservoirs were described by Roy (1997). The stratiform sedimentary deposits that attain huge sizes reservoirs with hundreds of million tons, were developed as oxide–carbonate phases in organic-rich sediments on continental shelves during transgression–regression in a greenhouse–icehouse climate, e.g. Chiatura (Georgia) and Nikopol (Ukraine) (Roy, 2006). In contrast, stratabound hydrothermal deposits are of small size and occur as irregular bodies in the marine environment, proximate to the spreading centers or in subduction-related island arc settings (Heshmatbehzadi and Shahabpour, 2010). The origin of hydrothermal Mn deposits in marine environments is a matter of debate. In proposed schemes, the role of biogenetic agents (e.g. manganese oxidizing bacteria and fungi) in different environments was explained by many authors (e.g. Palmer et al., 1986; Chandramohan et al., 1987; Bolton et al., 1988; Okita

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* Corresponding author.
E-mail addresses: rajabzad@susc.ac.ir (M.A. Rajabzadeh), hadad_fa@yahoo.com (F. Haddad), rodokrozit@gmail.com (M. Polgári), efkrisz@gmail.com (K. Fintor), walterhelena88@gmail.com (H. Walter), molnarzs1994@gmail.com (Z. Molnár), gyildi@gmail.com (I. Gyollai).

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et al., 1988; Roy, 1992; Konishii and Asai, 1995; Hein et al., 1997; Shah and Khan, 1999; Valix et al., 2001; Ehrlich, 2002; Maruthamuthu et al., 2002; Acharya et al., 2004; Tang and Valix, 2006; Wanger et al., 2008; Mehta et al., 2010; Oksuz, 2011; Polgári et al., 2012a).

The Neyriz ophiolite in the Abadeh-Tashk area is comprised mainly of ultramafic rocks and indicates a well-developed mid-oceanic to supra subduction ophiolite complex of Cretaceous age (Rajabzadeh et al., 2013). The geologic context and ore–host rock relationship are similar to those of the Waziristan ophiolite in Pakistan (Shah and Moon, 2004, 2007), the Artova ophiolite in Turkey (Öksüz and Okuyucu, 2014) and the Baft ophiolite in Iran (Heshmatbehzadi and Shahabpour, 2010). Radiolarian cherts and metacherts outcropped in SSW and NE of the ophiolite are intensely fractured or folded. The cherts are found in a variety of colors ranging from white and greenish white, light to dark red and then to brown. Those of brown and dark red contain small Mn deposits of banded, lens- and vein-types. Although most of the Mn deposits in Abadeh-Tashk are small with changing grade and periodically examined as a potential source for Mn ore, no detailed study on the mineralization had been performed. The aim of this paper is to discuss the genesis of different Mn ore types and the role of microorganisms in Fe–Mn precipitation in the Abadeh-Tashk area. This paper reports, for the first time, fossil-bacteria relicts for Fe–Mn biomineralization in ophiolite related manganese deposits in Iran.

2. Geological setting and field description

Most of the Iranian ophiolites are part of the Middle Eastern NeoTethyan Ocean of the Mesozoic that geographically were divided into four groups: (1) ophiolites of N Iran, along the Alborz range; (2) ophiolites of NW-SE Iran, along the Zagros Suture Zone; (3) ophiolite colored mélanges of Central Iran; and (4) ophiolites of SE Iran in the Makran Zone, S of the Jazmurian depression (Fig. 1A). They are linked to other Asian ophiolites, such as those of Pakistan in the E and to the ophiolites in the Mediterranean region, such as Turkey, Troodos, and East Europe in the W (Arvin and Robinson, 1994; Shaker Ardakani et al., 2009). The ophiolites of NW-SE Iran were outcropped parallel to the Zagros Fold-Thrust belt, developed due to collision of the Arabian continent and the Iranian microcontinent (Alavi, 2004). The Neyriz ophiolite as remnants of the NeoTethyan Oceanic crust was emplaced along the SW part of the Zagros Fold-Thrust belt, SW Iran. It is regarded as part of the 'Croissant ophiolitique' after Ricou (1971), which extends over 2000 km eastward through Turkey and Iran to Oman.

The Neyriz ophiolite at its NW part in the Abadeh-Tashk area comprise of four major separated ultramafic massifs constituting mainly of harzburgite, dunite and pyroxenite, in an area 12.5 km long and 10 km wide between the Bakhtegan depression to the SW and high mountains of the Zagros Suture Zone to the NE. The gabbro sequence is absent from the ophiolite complex in the study area. The Neyriz ophiolite was thrusted over the Banguestan Formation (massive limestone) of the Early Cretaceous along its W margin and is conformably overlayed by the Asmari-Jahrom Formation (shallow-water marly limestone) of the Early Tertiary along its NE border. The Abadeh-Tashk area as a small mining district contains several chromium (hosted by dunite), and manganese (hosted by chert) ore deposits that are actively exploited (Fig. 1A). Manganese ore deposits of small size (<1000 tons) are continuously hosted by widespread cherts and metacherts in S-SW and NE of the ultramafic outcrops. The cherts are found in different colors: white and greenish white, light to dark red and brown that often overlay serpentinized ultramafics and are covered by pelagic limestone. The Mn ores occur in three various types: syngenetic, diagenetic and epigenetic ores in association with red and brown cherts. No stratigraphic correlation can be made because of intense folding, faulting and the exotic nature of the rocks (Fig. 1B).

Primary Mn compounds in syngenetic deposits are found as alternative bands with amorphous silica and quartz in dark red to brown cherts, indicating sedimentary origin (Fig. 2A). The second ore type occurs in boudin and lens shaped bodies, showing a diagenetic type of mineralization. The diagenetic ores hosted by dark red cherts are found in fold hinges. The contact between Mn ores and the host cherts is nearly sharp. The Mn-bearing lenses are usually pinching out into the thin-bedded cherts. The thickness of these lens shaped bodies varies from several centimeters to several meters (average 2 m) with the length ranging from a few decimeters up to 20 m. Manganese compounds in epigenetic deposits were formed during remobilization and re-precipitation of Mn phases as open space fillings (cockade and comb structures with fine-grained minerals on the walls of the cavities and those coarser in the center) in hydrothermal light red cherts. The host cherts were highly fractured and cut by a dense network of veinlets ranging from several centimeters to micrometer size in diameter. These cherts are found in the upper part of the chert column. Field relationships show that the Mn dioxides (generally pyrolusite) are followed by white microcrystalline quartz. The origin of the late fluids is not determined but it is evident that the epigenetic mineralization should have occurred much later (Fig. 2B). Some white and greenish white cherts are located far from the ore deposits (Fig. 2C).

3. Sampling and analytical methods

Systematic sampling was done along seven cross sections perpendicular to ore trending in order to sample all chert and ore types. A brief information on the studied samples was summarized in Table 1. To assess the geochemical characteristics and the presence of microorganisms in the samples, eighty samples were collected. All samples were studied in thin, thin polished and polished sections using conventional transmitted and reflected microscopic methods at Shiraz University, Iran. Supplementary petro-textural studies were undertaken on ten thin sections using a Nikon ECLIPSE 600 optical petrographic microscope (OM) in Budapest, IGGR-RCAES-HAS, Hungary (samples 1/E, 1/F, 2/D, 2/E, 3/D, 3/E, 4/E, 4/F, 5/D, and 6/D).

Samples containing putative microbial remnants have been examined under the scanning electron microscope (SEM) model JEOL-JSM-6400 at 20 kV with an energy dispersive X-ray facility Thermo-Noran Pioneer with a Si–Li detector at the Materials and Metallurgical Engineering Department of Shiraz University, Iran. Fifteen representative ore and chert samples (least fractured and altered) examined for major elements (Al, Fe, Mn, Mg, Ca, Na, K, and Na) by atomic absorption spectrometry (AAS) and SiO_2 was determind using the Washington gravimetery method at the Department of Earth Sciences, Shiraz University, Iran. Inductively coupled plasma-mass spectrometry (ICP-MS) at ACME Analytical Laboratories, Vancouver, Canada was also used in the determination of rare earth elements (REE) and other trace metals (Ti, P, Ba, Sr, Cu, Ni, Zn, Co, and Pb). X-ray microdiffractometric analyses were also carried out on seventeen ore and chert samples using Cu Kα with a graphite monochromator, 40 kV, 30 mA, Bruker, GADDS bi-dimensional detector Histar at the Department of Physics, Shiraz University, Iran.

Fourier transform infrared spectroscopy (FTIR) for in situ micromineralogy and organic material determination was used on one representative thin section No. 1/E (10 measuring areas, 124 spectra acquired), in Budapest, IGGR-RCAES-HAS, Hungary. The IR measurements were performed on a Bruker VERTEX 70 FTIR equipped with a Bruker HYPERION 2000 microscope with a 20× ATR objective and MCT-A detector. During ATR analysis, the samples were contacted with a Ge crystal (0.5 μm) tip on the selected 1 N pressure. The measurement was conducted for 32 s in the 600–4000 cm^{-1} range with 4 cm^{-1} resolution. Opus 5.5 software was used to evaluate the data. For Mn oxide determination the equipment couldn't be used, as those peaks occur in the <600 cm^{-1} range. The contamination effect of epoxy glue and glass were taken into consideration.

Detailed, high resolution in situ micro-Raman spectroscopy investigation for micro-mineralogy and organic material determination was made on two selected representative thin sections (No. 1/E, 2/D). A