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Cu–Mn–Fe alloys and Mn-rich amphiboles in ancient copper slags from the Jabal Samran area, Saudi Arabia: With synopsis on chemistry of Fe–Mn(III) oxyhydroxides in alteration zones

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ABSTRACT

In the Jabal Samran area (western Saudi Arabia), secondary copper mineralization in a NE-trending shear zone in which the arc metavolcanic host rocks (dacite–rhyodacite) show conjugate fractures and extensive hydrothermal alteration and bleaching. The zones contain frequent Fe–Mn(III) oxyhydroxides (FeOH–MnOH) that resulted from oxidation of pyrite and Mn-bearing silicates. In the bleached part, the groundmass is represented by Fe-bearing interstratified illite–smectite with up to 4.02 wt% FeO^t. FeOH–MnOH are pre-weathering phases formed by hydrothermal alteration in a submarine environment prior to uplifting. Five varieties of FeOH are distinguished, four of them are exclusively hydrothermal with ~20 wt% H_2O whereas the fifth contains ~31–33 wt% H_2O and might represent reworking of earlier hydrothermal FeOH phases by weathering. FeOH fills thin fractures in the form of veinlets and crenulated laminae or as a pseudomorph for pyrite, goethite and finally ferrihydrite, and this oxyhydroxide is characterized by positive correlation of Fe_2O_3 with SiO_2 and Al_2O_3. On the other hand, MOH shows positive correlation between MnO_2 and Al_2O_3 whereas it is negative between Fe_2O_3 and SiO_2. Paratacamite is the most common secondary copper mineral that fills fractures and post-dates FeOH and MnOH. It is believed that Cl^- in the structure of paratacamite represents inherited marine storage rather than from surfacial evaporates or meteoric water.

The mineralogy of slags suggests a complicated mineral assemblage that includes native Cu prills, synthetic spinifixed Mn-rich amphiboles with 16.73 wt% MnO, brown glass and Ca–Mn–Fe phase close to the olivine structure. EMPA indicate that the some Cu prills have either grey discontinuous boarder zone of S-rich Mn–Cu alloy (with up to 21.95 wt% S and 19.45 wt% Mn) or grey Cu–Mn–Fe alloy (with up to 15.9 wt% Cu, 39. 12 wt% Mn and 61.64 wt% Fe). Mn in the Cu prills is expelled inward as Cu–Mn–Fe alloy inclusions whereas S is expelled outward as S-rich Mn–Cu alloy crust. Remains in the Samran smelter sites suggest the use of charcoal as a source of energy, quartzite as a flux and an air-cooling technique was used.

1. Introduction

The Jabal Samran area is known for its secondary copper mineralization and heaps of ancient slags that belong to the Abbasid Caliphate (750–1258 A.D.) in the Arabian Peninsula (Sabir, 1999; Sahl et al., 1999). The miners and smelters of the Abbasid Caliphate mined and extracted considerable amounts of copper that was needed for coinage and manufacturing tableware, shields and weapons. Their activities left behind several heaps of slags and antique houses that were used as shelters for workers at the same sites of their primitive small-scale mines. Such wastes and ruins are still kept partially in some localities, for example Samran, Kutam, Ash Shizm and Umm ad Damar that all include secondary copper mineralization as a result of oxidation of hidden late Neoproterozoic volcanic massive sulphides (VMS). Ore reserves in the Kutam and Samran deposit are the highest and lowest (4.5 and 0.9 million tons, respectively), and their grade averages 2% Cu but it reaches up to 2.92 at the Ash Shizm deposit (Fadol, 2002). Generally, the Arabian Shield in western Saudi Arabia includes some hundreds of copper mineral deposits and occurrences. Three copper districts are known in the shield, namely northern, central and southern (Collenette and Grainger, 1994). The Samran and the nearby Abu Mushut occurrences, in addition

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to the Khnaiguiyah are confined to the so-called "Samrah Belt". On the other hand, the northern and southern districts contain high-grade ore of marginally commercial sizes such as those of Jabal Sayid-Nuqrah and Kutam-Al Masane, respectively.

In the framework of tectonism, the VMS mineralization in the Arabian Peninsula and northeast Africa was developed in association with calc-alkaline subaerial volcanism that characterizes island-arc setting during the late Neoproterozoic (Johnson and Vranas, 1984; Roobol, 1989; Volesky et al., 2003; Al-Shanti, 2009; Johnson et al., 2011; Haldar, 2013; Legault et al., 2013). The site of secondary copper mineralization at the Jabal Samran area overlies subsurface VMS (Liddicoat, 1966). The Cu-rich VMS of Jabal Samran and the gold-rich VMS of the Shayban prospect are the eastern extension of the famous Ariab deposit with economic cupriferous pyrite in northern Sudan. All of them show confinement to the so-called "Ariab-Samran-Shayban" greenstone belt extends for a distance of almost 1000 km from the Nile Valley in Sudan north-eastwards across the Red Sea to Mahd adh Dhahab in Saudi Arabia (Dolbear, 2007). This VMS-rich greenstone belt has an average width of about 50 km and many of them are capped by gold-rich oxide-hydroxide "gossans" to depths of 20–50 m.

The current work presents the detailed mineralogy and microchemical analysis of both slags and secondary copper mineralization at the Jabal Samran area. A possible scenario for the extraction of copper from the ore is suggested based on mineralogy and the anthropological relics found at the sites of smelting.

Also, the current work presents some new mineralogical and geochemical data about the Fe–Mn(III) oxyhydroxides in the "bleached" intermediate to acidic metavolcanics at the Jabal Samran area where significant information about Fe–Mn(III) oxyhydroxides are lacking in the literature. A few mineralogical data about Fe–Mn(III) oxyhydroxides formed in soil and laterites or in seamounts and mid-ocean ridges were presented (Varentsov et al., 1991; Boughriet et al., 1996; Braun et al., 1998; Duzgoren-Aydin and Aydin, 2009). Their origin is still a matter of ambiguity but in general it is accepted that either hydrogenetic or hydrothermal (Bonatti, 1975). Some recent studies (Merinero et al., 2008; Zeng et al., 2012) did not neglect the possible role of metal oxidizing bacteria and hydrocarbons in submarine chimneys in the formation of such hydrous phases in the proper marine environment. Whether it is hydrogenetic or hydrothermal, the Fe–Mn(III) oxyhydroxides coating marine sediments are authigenic (Bayon et al., 2004; Gutjahr et al., 2007; Charbonnier et al., 2012). In addition, an account about the formation condition of paratacamite is given for natural geologic materials talking in consideration that such phases are essential components of the so-called "bronze disease" that forms as rust for copper tools, alloys and statues (Scott, 2000; Frost et al., 2002; Zhang et al., 2013).

2. Methodology

The rock samples were systematically selected from secondary mineralization and slags area to represent mineralized veins, oxidation and alteration zones of Jabal Samran area. In order to study mineral composition and textures, twenty-four polished sections in addition to sixteen polished mounts were prepared from the selected rock samples. The sections were studied in both transmitted and reflected light for their silicates and ore mineralogy.

The quantitative electron microprobe analyses (EMPA–WDS) of the oxyhydroxides and silicate phases both in secondary mineralization zones and slags were conducted using a Jeol JXA8200 instrument. It is housed at the Faculty of Earth Sciences, King Abdulaziz University in Jeddah, Saudi Arabia. Operating conditions were 15-kV accelerating voltage, 20 nA probe current, 3 μm beam diameter and 20 s counting time for each element. The following standards were used: hornblende for Si and Al, eskolaite for Cr (99.99 wt% Cr_2O_3), periclase for Mg, wollastonite for Ca, fayalite for Fe, nickel oxide for Ni (99.99 wt% NiO), barite for Ba, $KTiPO_5$ for K & Ti, jadeite for Na and manganosite for Mn. The ore minerals (native Cu and metal alloys) in the slags were also analyzed by the electron microprobe for Fe, S, Cu, Au, Ag, Zn, Pb, Co, Ni and As. Analytical conditions were 20-kV accelerating voltage, 20-nA probe current, 3 μm beam diameter and the counting time was 20 s for each element except for Au and Ag which were 50 and 30 s, respectively. The standards used were pyrite for Fe and S, pure metals for Cu, Au, Ag, Zn, Pb, Co and Ni, and gallium arsenide for As.

Some XRD analyses, mineral spectra and back-scattered electron (BSE) images were obtained. The latter were produced using a (SEM–EDX) Philips XL 30 at the Central Laboratories of the Egyptian General Authority of Mineral Resources in Dokki, Egypt. The obtained data were in the form of spot semi-quantitative microanalyses of some ore minerals and non-opaque minerals in the investigated samples. In Fe oxyhydroxide (FeOH), Mössbauer spectra were obtained to investigate accommodation of either Fe^{2+} or Fe^{3+} in the structure. In order to test crystallinity of the Fe–Mn oxyhydroxides (FeOH–MnOH) phases in the alteration zones, some XRD runs were carried out that help to decide whether they are crystalline or amorphous.

3. General geology of Jabal Samran area

The Jabal Samran area is an island-arc terrane that comprises a variety of late Neoproterozoic rock assemblages that are dominated by volcanics and volcaniclastic rocks (Figs. 1 and 2a) that undergone regional metamorphism mostly in the greenschist facies condition (Nebert, 1969; Ba-battat, 1982; Ba-battat and Hussein, 1983). The metamorphosed volcanic association is interrupted by some marble bands, and the entire succession is intruded by gabbro and granitoids. According to Ba-battat and Hussein (1983), the metavolcanic–metavolcaniclastic succession is of calc-alkaline to slightly tholeiitic composition and comprises of three volcanic cycles in which the first two are metamorphosed metatuffs of andesitic to rhyolitic composition whereas the third cycle is represented by non-metamorphosed flows of andesite.

From the lithostratigraphic point of view, the layered rocks (metavolcanic–metavolcaniclastic succession and the marble bands) at the Jabal Samran are believed to correlate with the Hulayfah Group of the Arabian Shield (Ba-battat and Hussein, 1983; Johnson et al., 2011). The first nomenclature of the so-called "Samran Series", was suggested by Nebert (1969) to assign an andesitic-dominated volcanic section at the Jabal Samran area. Later on, Skiba and Gilboy (1975) used "Samran Group" instead of "Samran Series". Schmidt et al. (1973) presented the stratigraphy of the Jeddah Group in which its metabasalt to meta-andesite Qirshah Formation can be correlated with the "Samran Series". The "Samran Series" is also termed as the Samran Group (Smith and Kahr, 1966; Skiba, 1980). The Jeddah Group itself represents a part of the early episode of mafic-intermediate volcanism and sedimentation of the Hijaz tectonic cycle (Greenwood et al., 1973). The Jeddah and Samran Groups are similar to the greenstone rocks (metabasalt, meta-andesite and graphitic schists) of the Baish–Bahah Groups that have been formed during the early Hijaz cycle, and are believed to have accumulated in subareial to shallow marine environments and were metamorphosed to upper greenschist facies condition (Blodget and Brown, 1982). The age of the Jeddah–Samran–Baish–Bahah Groups is uncertain due to re-setting by the subsequent Ablah orogeny at 763 M.a. (Brown et al., 1989). Older ages of the Jeddah Group and its equivalents are obtained including 720–800 M.a. K–Ar ages of separated mica crystals and a remarkably higher whole-rock age of 965–1025 M.a by the Rb/Sr method (Aldrich et al., 1978). Johnson (2006) assumed