SYNCHROTRON BASED MICRO-MAPPING AND XAFS INVESTIGATION OF Fe-Mn AND EPIGENETIC INTERGROWTH WITHIN THE CAMBRIAN SHALLOW MANGANESE DEPOSITS, SOUTH JORDAN

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**ABSTRACT**

The current work investigates the Cambrian Manganese ore deposits from Wadi Dana at central Wadi Araba region. This investigation aims to unravel the chemistry and micro-textures of the mineral paragenetic sequence for these manganese ore deposits. Particularly the Fe–Mn intimate intergrowth micro texture and the epigenetic Mn mineralization associated with Cu minerals. The combination of the synchrotron-based X-ray fluorescence (syn-XRF) micro-mapping and X-ray absorption fine structure (XAFS) techniques were used. They provide a clear picture of the elemental distribution of Mn, Fe, Cu, and Pb and other elements presented within the ore micro textures. Besides, it determines the exact elemental speciation. The results obtained gave a better understanding of the elemental atomic structures and eventually the depositional environment. Particularly, the syn-XRF micro-mapping reveals the existing of many successive evolution stages in the Mn ores. Besides, the X-ray Absorption Near Edge Structure (XANES) results showed that the micro-rhythmic texture is changing from Mn$^{4+}$ (Pyrolusite) into Fe$^{3+}$ (Hematite). This is evidence for the role of Eh as the main controlling factor during the ore formation. Eventually, indicating tentatively the paleoceanography setting of the Mn deposits. This is related to the continuous transgression-regression on the sea level in a semi-closed sea.

Keywords: Cambrian; Shallow Manganese; Pyrolusite; Hematite; Synchrotron-Based X-Ray Fluorescence Micro-Mapping; Eh-pH
INTRODUCTION

The main manganese deposit outcrops at Wadi Dana area, at the central Wadi Araba region (Fig. 1). Manganese is hosted in the middle Cambrian Dolomite Limestone Shale Unit (DLSU). This formation consists of the lower calcareous part and upper siliceous part. The manganese ores are found as disseminations, thin intercalations, lenses, concretions, and bands (El-Hasan et al. 2001a). Since the manganese of Wadi Dana area is the larger manganese deposit in Jordan, it was studied by many authors (Khoury, 1986; Shaltoni, 1988; El-Hasan, 1999; El-Hasan and Lataifeh, 2001; El-Hasan et al., 2000, 2001b & 2008). Wadi Dabbah ore body is composed of massive bands of 2–3 m thickness with a limited lateral spread. The mineral constituent is very complicated and shows intimate growth of Cryptomelane, Hollandite, Psilomelane, Pyrolusite, and Hematite. Additionally, a significant concentration of Cu, K, and Ba were detected, as well as traces of Zn, Ni and Co. Hematite is the main gangue mineral. It is a common mineral in supergene Mn deposits, (Ghosh, and Dean, 1980). In previous studies, hematite was identified by ore microscopy and XRD, to be associated with Pyrolusite.

High Mn ore deposits typically present intergrowth of Fe and Mn, ranging from Fe-Oxide (i.e. Hematite) to Mn-Oxide (i.e. Pyrolusite) in a fish-scale or wave-like texture (Fig. 2). This is a unique phenomenon which might be attributed to various reasons and complex processes during ore formation, which is mainly related to the Eh-pH conditions. This hypothesis was not examined in depth by using conventional SEM and EPMA techniques (El-Hasan et al., 2001b).

The synchrotron applications, particularly XRF and XAFS techniques are ideal for mineral chemistry studies because bulk XAFS shows limitation to determine the Mn species in heterogeneous systems. It probes a volume of several square millimeters, thereby averaging over all the atoms of a certain atomic number in the system under study, regardless of their chemical state. However, when Mn is present in multiple phases, the atomic shells from the different species overlap and cannot be distinguished when there is a mixture. However, using a coarse spatial resolution beam (~220x110 μm²) to perform coarse elemental fluorescence mapping on the sample will help to identify the different phases and thus select target zones of interest achieve XAFS data measurements. By using a relatively focused beam it is possible to access the small domain, which allows to track spatial changes in the composition and to differentiate the multiple phases. Thus, a combination of XRF and XAS using small beam is an ideal tool for the analysis of extremely heterogeneous materials in general and will give us a clear image and indications about the determining factor in developing the intimate Mn growth, through tracing the oxidation valences changes for both Fe and Mn ions.
Therefore, synchrotron based X-ray Absorption Fine Structure (XAFS) (i.e. XANES) is a technique that can provide detailed chemical and structural information about a specific element with minor or no pre-treatments (Hunter and Bertsch, 1998). X-ray Absorption Spectroscopy (XAS) has become the method of choice for probing the local structure at the short and medium range order in particular when the structure is disordered. The XANES has been successfully used for the discrimination of different oxidation states in chromium in treated wood (Strub, 2008), in addition to glass samples (Görner, 2006). Many previous workers have used the synchrotron radiation in mineralogical and geochemical applications, such as Buehn et al. (1999), they had determined the elemental composition of Burbankite was determined by a combination of SEM-EDX on opened inclusions and synchrotron-XRF analysis on unopened wafers. Moreover, Synchrotron radiation-induced X-ray fluorescence (SR-XRF) analysis was used to study the chemical composition of precious renaissance silverpoint drawings (Reiche et al., 2004). Its use has demonstrated the variable reactivity and speciation of elements in different structural systems. XANES spectroscopy has shown to be extremely useful for a quantitative, fast and reliable determination of the oxidation state in the soils (Peterson et al., 1997). The XANES techniques were used successfully in determining the Cr (VI)/Cr (III) within oil shale ash (El-Hasan et al. 2011). Recently, EXAFS techniques were used for determining the Cr-host mineral matrix in the solidified oil shale ashes (El-Hasan et al., 2019). Pre-edge features in the XANES area due to a bound-state transition contain information about the geometry of the photo-absorber, for instance, in the case of Mn and Fe will represent a clear fingerprint of the redox of this environmentally related element. Therefore, the use of powerful synchrotron-based XRF and XAFS techniques will allow us to estimate the elemental speciation of Mn-ore mineral, to determine the redox state of the Mn and Fe and to explore, at the atomic level, the local structure behavior around these two elements. Moreover, the high level of monochromaticity and tunability of the X-ray beam is required to probe the chemical speciation and the local arrangements of the atoms of the selected elements. Previously; El-Hasan (1999) has identified fish-scale texture using SEM. It is a prerequisite to our experiment and it is a feature offered only by synchrotron facilities. However; it qualitatively identified the total Fe and total Mn without identifying their valances, which cause the use of the Eh-pH diagram uncertain. Therefore, the main incrimination in this current work is providing us with exact Fe and Mn speciation that sharply pinpoints for the exact Eh-pH conditions during ore formation and the events that cause the formation of this texture. Therefore, this study aimed to execute several XRF mapping and XANES measurements for high and low grade Mn-ores from Wadi Dana deposits, to clarify the paleo-oceanographic and paleo-environmental setting dominating
during the ore formation. Moreover, to confirm the mineralogical paragenetic sequence and ore evolution stages.

**METHODOLOGY AND MATERIALS**

The samples of this study were brought from the high-grade ore outcropping at Wadi Dabbah (Db) which have an average ore grade 26.1 (Vol. % of Mn) and low-grade ore outcropping at Wadi Khaked (Kh) (Fig. 1). The Mn ore samples were polished thin section impregnated into resin base and with very smooth polished faces by very fine silicon carbide spray. The area of ore polish faces is about 1.5 X 2 cm in diameter, while the total resin sections are from 2 –2.5 cm in diameter. The use of conventional methods such as XRF and XRD was neither able to give a clear answer about the micro texture of Mn, Fe and Cu minerals nor their oxidation state (El-Hasan, 1999).

An experiment was carried out at the X-Ray Fluorescence beamline at Elettra. XRF and XAFS data were collected at the K-edges of Mn (6.539 keV), Fe (7.112 keV) and Cu (8970 keV) (Jerk et al., 2014). The selected high-grade Mn ores samples were used to improve the quality of mapping and XAFS measurements. Reference samples were used for the redox comparison such as compounds with Mn(II), Mn(III), Mn(IV), Fe(II), Fe(III) or Fe (IV) species. The analysis was accomplished with 15 shifts used to collect high quality XAFS data up to k=13 Å⁻¹. Assuming a minimum of 3 scans per sample for statistics, we end up with 6 hours per sample.

The beam settings are as follows: for the mapping: - step size of 200 microns horizontally, and 80 microns vertically. The excitation energy of 10500 eV. The EDXRF detector at 10 to 20 mm from the sample (depending on the sample), and with a shaping time <90 kcps. As for the XANES: step size of 0.5 EV (i.e. 501 points in each spectrum), the integration time of 3s/ point usually the spectra were repeated at least twice to ensure a good S/N ratio. The EDXRF detector at 10 to 30 mm from the sample plane, with a shaping time < 130 kcps. The energy resolution is one intrinsic to the Si (111) pair of crystal, at the energy of excitation considered; with up to 1eV above for the Mn, Fe and Cu edges for the investigated samples.

The selected samples underwent comprehensive and details elemental mapping at the first step. Then, based on the mapping hot spots were targeted by syn-XRF micro mapping and XANES measurements at K-edges of Mn, Fe and Cu. The samples were categorized according to ore bodies in terms of Mn ore grade as follows: 1- Low-grade ores (KH2) and 2- High-grade ores (Db9 and Db13).
Fig. 1: Study area map and the location of studied samples (after El-Hasan, 1999)

RESULTS

High-grade Mn Ores
The previous SEM investigations of these samples had revealed the presence of fish-scales texture within the high grade Mn-ores at Wadi Dabbah (e.g. Db9 & Db 13). The rhythmic nature of this wave-like texture that ranges from continues cycles from pure Mn to pure Fe ends. This structure and mineral changes need to be clarified by identifying the metal valences by executing the XANES measurements for several points taken in cross-section from Mn-end into Fe-end. The mapping results confirmed the cyclic nature of both Fe and Mn. Moreover, the syn-XRF micro-mapping confirmed the presence of secondary Pb-phase as epigenetic veinlets (Fig. 2).

After allocating the best cross-section, Syn-XRF elemental mapping, which helped in allocating the Mn and Fe XANES results reveals the changing from Mn (IV) (e.g. Pyrolusite MnO₂) to Fe(III) (e.g. Hematite Fe₂O₃), as shown in Figure (3). The implication for this finding is essential for determining the paleo-oceanographic conditions in terms of dominating Eh-pH for the lower- middle Cambrian shallow marine manganese ores.
Fig. 2: Synchrotron XRF micro-mapping for Samples from high-grade Mn ores bodies (a) DB9 and (b) DB13; shows epigenetic Pb-Mn oxide veinlets

Fig. 3: XANES for Mn, Fe and Pb for samples from high-grade ores (Db9 and Db13)

Low-grade Mn Ores

The results of Syn-XRF micro mapping of the low-grade Mn ores from Wadi Khaled (e.g. KH2) representing the ideal epigenetic type of mineralization. The mapping included Mn, Fe, Cu, and Pb. The obtained results were very important in tracing the various syngenetic and epigenetic manganese ore mineralization (Fig. 4). To determine the mineral phases a selected hot spot was analyzed. The results of Syn-XRF micro-mapping reveal the presence of Pb-Mn oxide (Coronadite) as epigenetic phase intruding the primary supergene Cu- Carbonate
mineral (Chryscolla), Fe was also associated with Mn, which is presented in the solid solution phase (Hollandite) (El-Hasan, 1999, El-Hasan and Al-Malabeh, 2009) (Fig. 5). Furthermore, the XANES measurements of the Cu and Mn show that they are found in higher oxidation states i.e. Mn (IV) and Cu(II)) as showing in Figure (6). Such phases indicate highly oxidizing conditions that provide evidence for the epigenetic type of mineralization, which might be attributed to descending meteoric water effect.

Fig. 4: KH2 hand specimen samples and reflecting microscope photo; showing the manganese epigenetic phase (Coronadite) introducing into the Cu- mineral (Chryscolla)

Fig. 5: Synchrotron micro-mapping of Fe, Mn, Cu and Pb, showing epigenetic Pb-Mn oxides (Coronadite) intruding the supergene Cu-mineral (Chryscolla)
DISCUSSION

The intergrowth of Fe and Mn is considered a valuable tool for tracing the paleo-environmental depositional conditions of Mn ore formation, as it identifying the paleo-oceanography settings. The results elucidate the exact Eh-pH conditions during formation, and thus lead to determine the precise phase diagram of the system Fe-Mn-O within the shallow marine environment. The high-grade Mn-ores are also rich in Fe, forming a unique intergrowth between Mn and Fe oxides. This intergrowth was recognized by the changing from Fe-oxide into Mn-oxide in a fish-scale or wave-like texture (Fig. 2). The fish-scale and rhythmic nature of this intergrowth might be attributed to the continuous changing in sea-level status during Mn ore deposition (El-Hasan, 1999). This sea-level change will cause a continuous change in the Eh-pH conditions of the depositional environment; as mentioned in (Brookings, 1988). This hypothesis was roughly recognized using conventional SEM and EPMA methods (El-Hasan, 1999; and El-Hasan et al., 2001a). However, the Synchrotron XANES analysis provided precise identification of both existing Fe & Mn oxidation states within this intergrowth. Through XANES measurements for Fe and Mn, this was carried out in form of spot or traverses within a complete fish scale texture cycle. XANES results confirm exactly that the controlling factor was the change in Eh rather than pH. This might have attributed to the cyclic change in sea level during shallow sea-level more oxygen can reach.
the water that contain Mn ore and causing higher Eh values, causing Mn oxide to form. But during high sea-level periods thick water column prevents oxygen to penetrate to the ore causing lower Eh values, thus Fe oxide more preferably formed. As shown in Figure (7); higher Mn oxidation state mineral Mn(IV) (e.g. Pyrolusite) are start forming at Eh0.7 (V), whereas higher Fe oxidation such as Fe(III) (e.g. Hematite) starts at lower Eh=0.1 (V), if we consider constant pH=7 as normal seawater. Therefore, at shallow periods (i.e. low Sea-level) Pyrolusite (MnO₂) formed as a more oxidized environment is prevailing. Meanwhile, at thicker water periods (i.e. high sea-level) Hematite (Fe₂O₃) would form in less oxidized environment.

Fig. 7: Eh-pH stability diagrams for (a) Mn and (b) Fe species (Diagrams after Brooking, 1988; Force and Cannon, 1988)

The bulk mineral assemblage is typically of supergene manganese ore type. The microscopic and field observations indicate the presence of the three genetic stages. Primary ore stage, dominating the lower Cambrian, the ore was formed by sedimentary accumulation under a shallow marine environment. Followed in the middle Cambrian by the supergene enrichment stage, which was the dominant, and thus it is overprinting totally the primary ore features. Finally, the ore was affected by the epigenetic mineralization stage mainly affects the upper part of the main mineralized horizon (El-Hasan, 1999). Therefore, the projection on mineralization evolution stages indicates a semi closed seas environment. As well a continuous transgression -regression on the sea level. This can explain the changing in Eh
values due to change in sea level. Similar depositional environment of shallow manganese deposits of Groote Eylandt (Australia) was proposed by Bolton and Frakes (1984).

CONCLUSIONS

Synchrotron XRF micro-mapping and XANES analyses were an ideal tool in providing detailed mineral micro-textures and precise identification of Mn, Fe and Cu oxidation states. Moreover, from geochemical point of view, it is important to elucidate the exact prevailing Eh-pH conditions, eventually determining the paleo-oceanographic settings and ore depositional environment. The rhythmic wave – like micro texture changing from Hematite Fe (III) into Pyrolusite Mn(IV) is controlled mainly by Eh changing rather than pH. The Eh was changing from (0.7 to 1.0 V), caused by the change in sea level, indicating continuous transgression-regression of semi-closed sea environment. This would indicate the nature of the prevailing oceanography setting as semi closed seas. The Syn-XRF micro-mapping and XANES measurements provides a more logical explanation for the Mn ore evolution stages, and in particular the epigenetic Pb-Mn oxide (Coronadite) intrusion into the primary Cu-carbonate mineral (Chryscolla).

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