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EELS Characterisation and Valence Determination of Mn Minerals from the Kalahari Manganese Field in South Africa.

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Abstract. Preliminary EELS analyses of range of rare Mn-bearing ore minerals from the N'chwaning II mine in the Kalahari Manganese field have been undertaken. The EEL data reveal a range of Mn oxidation states which reflect the oxidation changes due to post-sedimentary and early metamorphic changes. Further detailed investigation and quantification of the various Mn-valences, will be used to track oxidation changes within these geochemical significant deposits.

1. Introduction

The Kalahari Manganese field of South Africa is of interest both for economic reasons, and also as a record of significant geochemical changes within the Proterozoic lithosphere. These deposits date from ~2.2Ga and are interbedded with banded iron formations (BIF), which are also geologically significant. The Mn deposits form part of the Hotazel formation, the main Mn minerals are a Braunitelutite assemblage, which has been oxidised during the Wessels alteration event (1-1.23Ga) to Hausmannite [1]. The development of these ore deposits has been linked to an inferred Paleoproterozoic snow-ball Earth event [2] and appears to represent a transition in the oxidation state of the Earth's Ocean. Current research [2] suggests isolation of the oceans along with continued sea-floor vulcanism and the lack of photosynthesis produced a metalliferous and reducing ocean chemistry.

There are a number of papers in the literature that cover fingerprinting of Mn-compounds [3, 4 and 5], however they do not include the rarer hydroxide phases analysed in this study. Here we present work on some rare Mn-bearing minerals from the N'chwaning II mine in the hydrothermally altered area of high-grade Mn ore to the NW of the Kalahari ore deposit, including co-ordination fingerprinting; and valence determination.

2. Experimental

EELS analyses were made using a Gatan Imaging Filter (GIF) attached to a FEI CM200 FEGTEM operated at 200keV (at the University of Leeds). The mono-mineralic samples were prepared by crushing in an agate mortar and pestle and dispersed in acetone onto a holey carbon film. All EELS measurements were made in CTEM diffraction mode (image coupling to spectrometer) on ultra thin (<30nm) crystalline areas of dimension ~ 0.1µm. All spectra were corrected for dark count and detector gain. Ultra thin areas ($t/\lambda \leq 0.3$) were chosen to avoid the need for deconvolution. For each mineral, 10 Mn L_{2,3}-, O K-edges and associated lowloss spectra were collected, with total integration times of 10-20 seconds for Fe L_{2,3}-edges and 20-25 seconds for O K-edges at an energy dispersion of

0.1eV/pixel. The 0.6mm EELS entrance aperture was used, giving a collection angle β of 4.6mrad at the cameral length used. The energy resolution for all measurements was 0.7-0.8eV.

The energy resolution for all measurements was 0.8eV. All spectra were energy calibrated by collection of a 0.3eV dispersion spectrum containing the C K-edge (calibrated at 285eV), Ca L_{2,3}-edge and the O K-edge. Finally, the spectra presented here have been background subtracted, using a power law function and intensity normalised for ease of comparison.

3. Results and Discussion

3.1 Mn L_{2,3}-edges

Figure 1 shows the Mn-L_{2,3}-edges for the Mn-minerals listed in table 1 below. The edges for both the pyrochroite samples and that of braunite II are similar, in having the suggestion of shoulders on the low energy-loss side of the main L₃-peak. The shoulder on the second sample of pyrochroite is higher, almost suggesting the start of a second peak. The L₃ -peak of hausmannite shows clear splitting of 6eV, this is also shown to a lesser degree by the L₂ -peak. The L₃-peak for poldervaartite is much broader than any of the other Mn-minerals and shows little NES, except the suggestion of a slight shoulder to the high energy side. The edge for the unknown Mn-silicate shows a L₃-peak with a well defined shoulder on the higher energy-loss side.

3.2 O K-edges

Figure 2 shows the O K-edges for the Mn-minerals analysed. On the whole they comprise a pre-peak, at the edge threshold, followed by a broader peak around 10eV after this. In general the observed pre-peaks show a doublet structure, with that of the hausmannite and the first pyrochroite sample showing clear evidence of peak splitting. For hausmannite, this splitting is in the order of 6 eV and matches that of the Mn L_{2,3}-edge. The braunite II O K-edge also shows evidence of splitting in the pre-peak (1.5eV) with a shoulder to the high energy-loss side and is similar to that of the Fe³⁺ oxide hematite [6]. The second sample of pyrochroite does not show the second peak, but has a suggestion of a shoulder to the high energy-loss side. The O K-edge for the poldervaartite sample has a low intensity pre-peak with the suggestion of a shoulder and the O K-edge for the unknown Mn-silicate shows no evidence for a pre-peak, but the second broader peak does show a doublet.

Mineral	Formula	Mn Valence	Ref Number	Source
Braunite II	Ca(Mn,Fe) ₁₄ SiO ₂₄	Mn ³⁺	1076	N'chwaning II Mine
Hausmannite	Mn ₃ O ₄	Mn ²⁺ Mn ³⁺	937	N'chwaning II Mine
Poldervaartite	(CaMn) ₂ (SiO ₃ OH)(OH)	Mn ²⁺	1432	N'chwaning II Mine
Pyrochroite	Mn(OH) ₂	Mn ²⁺	1418	N'chwaning II Mine

Table 1: Mn-minerals analysed

From the observed Mn L_{2,3}-edges it is clear that the pyrochroite sample is not Mn²⁺. The first sample appears to be a mixture of Mn²⁺ and Mn³⁺ similar to that of the mixed valance oxide hausmannite, whereas the second sample appears to be almost pure Mn³⁺, although there are some subtle differences between this sample and that of the pure Mn³⁺ sample of braunite II.

3.3 Interpretation of the O K-edges

The O K-edge pre-peak can be assigned to transitions of O 1s electrons to O 2p-states strongly hybridised with Mn 3d-states. The pre-peak structure is present in all the oxides and is strongest in the second pyrochroite sample and weakest in poldervaartite, where O is in 8 fold co-ordination with Mn. The hausmannite O K-edge matches well with published data [3 & 4] as does the second pyrochroite

edge if the sample is considered to be completely oxidised to Mn^{3+} . If ligand field/MO orbital theory is considered, then the presence and intensity of peak A can be described in terms of the formation of hybrid bonds and can be related to the amount of $O\ sp^2$ - $Mn\ 3d$ hybridisation in the mineral. For Mn in

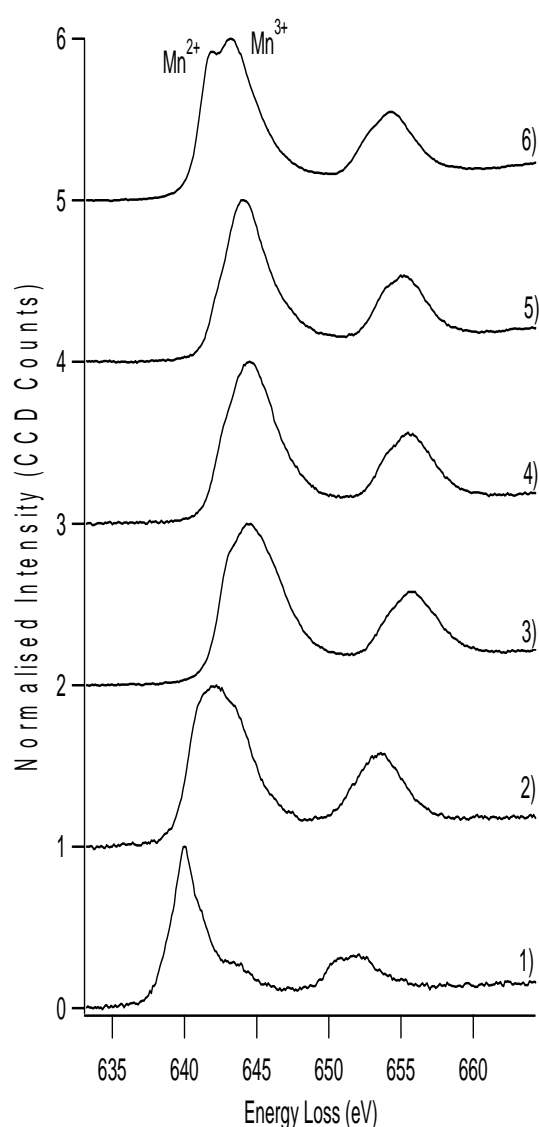


Figure 1 Mn $L_{2,3}$ - edges for 1) Unknown Mn^{2+} silicate; 2) Poldervaartite; 3) and 4) Pyrochroite ; 5) Braunite II and 6) Hausmannite

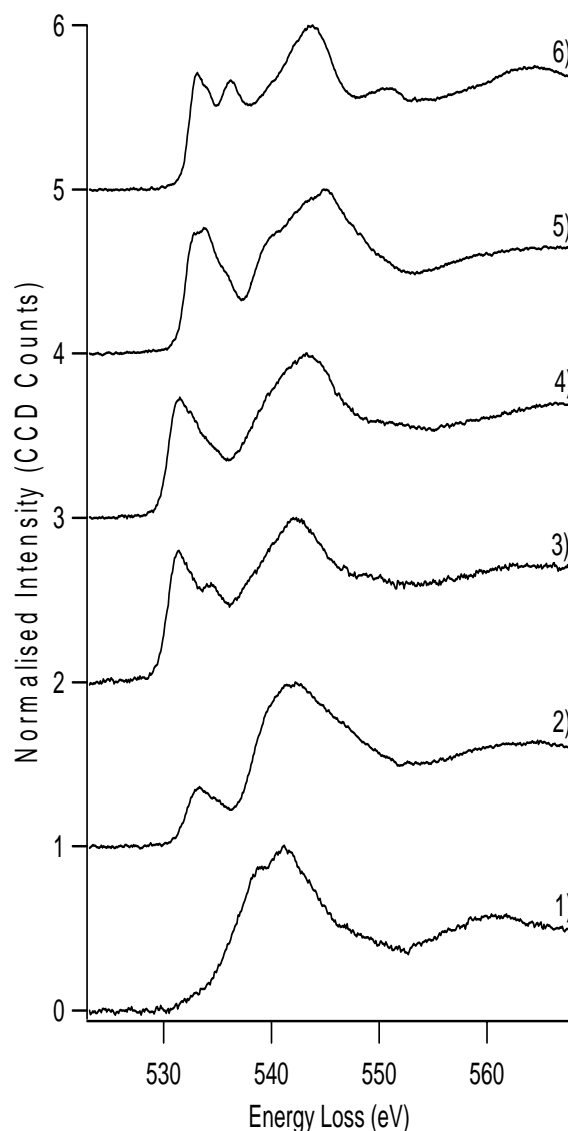


Figure 2 O K-edges

octahedral co-ordination with oxygen, $O\ sp^2$ - $Mn\ 3d$ bonds will form with the vacant e_g orbitals as they point at the ligands. It has been shown [7 & 8] shown that the degree of $O\ sp^2$ -TM $3d$ hybridisation (covalency of the Metal-O bond) is reduced as the number of $3d$ -electrons in the transition metal increases. Thus, Mn^{3+} minerals would be expected to show a strong feature as compared with Mn^{2+}

minerals, as is seen in the current study. The splitting of the pre-peak is thought to result from the t_{2g} - e_g crystal field splitting of the O sp^2 -Mn $3d$ hybridised bonds. The observed splitting of ~ 6 eV in hausmannite the pre-peak is also observed in the Mn $L_{2,3}$ -edge. The series of broad peaks in the O K-edges are attributed to O $2p$ -states hybridised with the transition metal $4s$ and $4p$ -states [7].

3.4 Interpretation of the Mn $L_{2,3}$ -edges

The Mn $L_{2,3}$ -edges obtained in this study show a characteristic fine structure and energy-loss with changing Mn valence state and match with published data [3, 4 & 5]. The unknown Mn-silicate has been assigned a valence of Mn^{2+} based on comparison with data in the literature [5]. With the exception of poldervaartite Mn is in octahedral co-ordination with O. This gives octahedral Mn^{2+} the electronic configuration of $(t_{2g})^3 (e_g)^2$ and octahedral Mn^{3+} the electronic configuration of $(t_{2g})^3 (e_g)^1$ and the likelihood of Jahn Teller distortion of the octahedra. This would suggest that for Mn^{2+} the first empty states would be the spin down t_{2g} and for Mn^{3+} , ignoring Jahn Teller distortion, the first empty states would be in the e_g orbitals. Unfortunately, this electronic configuration is very difficult to relate to the ELNES observed or to interpret in terms of crystal field theory and as such it suggests that for the TM $L_{2,3}$ -edges crystal field theory breaks down as a good description. Interpretation in terms of atomic multiplet theory [9] may be more applicable to this system.

4. Conclusions

This preliminary EELS study has shown that many of the nominally single valence rare minerals in this deposit are in fact mixed valence. Pyrochroite in particular shows evidence of oxidation, first to a composition approaching that of hausmannite and finally to an almost pure Mn^{3+} composition. Further detailed investigation and quantification of the various Mn-valences, will be used to track oxidation changes within these geochemical significant deposits.

5. Acknowledgements

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References

- [1] Gutzmer, J and Beukes N. J. (1996) *Ore Geology Reviews*, **11**, 405-428.
- [2] Kirschvink, J. L., Gaidos, E. J., Bertani, L. E., Beukes, N. J., Gutzmer, J., Maepa, L. N. and Steinberger, R. E. (2000) *Proceedings of the National Academy of Sciences of the United States of America*, **97**(4), 1400-1405.
- [3] Paterson, J. H. and Kirvanek, O. J. (1990) *Ultramicroscopy*, **32**, 319-325.
- [4] Kurata, H. and Colliex, C. (1993) *Physical Review B*, **48**(4), 2102-2108.
- [5] Garvie, L. A. J. and Craven, A. J. (1994) *Physics and Chemistry of Minerals*, **21**, 191-206.
- [6] Calvert C. C., Brown, A and Brydson, R. (2005) *Journal of Electron Spectroscopy and related Phenomenon*, **143**, 173-187.
- [7] de Groot, F. M. F., Grioni, M., Fuggle, J. C., Ghijsen, J., Sawatzky, G. A. And Petersen, H. (1989) *Physical Review B*, **40**(8), 5715-5723.
- [8] Colliex, C., Manoubi, T. and Ortiz, C. (1991) *Physical Review B*, **44** (20), 11402-11411
- [9] van der Laan, G. and Kirkman, I. W. (1992). *Journal of Physics: Condensed Matter*, **4**, 4189-4204.