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Manganese oxides from the British Isles

RECENT lists of British minerals by Livingstone and Macpherson (1983), Bevins (1988) and Ryback *et al.* (1988) have added significantly to the original work of Greg and Lettsom (1858) and subsequent updates by Spencer (1898, 1931, 1958) and Embrey (1978). This note reports on the discovery of six manganese oxide minerals previously unrecorded in Britain, summarizes the difficulties involved in the accurate identification of this group of minerals and, in this context, discusses the reliability of the early identifications.

Manganese oxides are an often neglected and ill-defined group of minerals. They frequently occur as black, very fine-grained, often soft, coatings, cements and masses, and are commonly regarded as ubiquitous, amorphous weathering products of little mineralogical interest. However, while the bulk of the oxides may be (or appear to be) amorphous, close inspection under the binocular microscope can reveal crystalline grains which can be identified by X-ray diffraction (XRD). Studies of such occurrences, together with those on recognized manganese deposits, have confidently identified a total of sixteen manganese oxide minerals in Scotland alone (Nicholson, 1989). It is hoped that this work will encourage further studies on seemingly insignificant manganese oxide occurrences in Britain since, from the author's experience, it is likely that more manganese oxides await identification.

Early mineralogical works cite the presence of only four manganese oxides: manganite, psilomelane, pyrolusite and wad (Greg and Lettsom, 1858; Heddle, 1901). (Note that 'wad' is not now considered to be a valid species, and the term 'psilomelane' applied to a specific mineral has been replaced by 'romanechite'.) As a consequence of these entries, subsequent lists of British minerals have not included any new accounts or confirmation of these species. However, the early identifications are unreliable as they are based on the appearance of the mineral which, for the manganese oxides, is variable and not a dependable means of identification. In this respect, 'manganite' was applied to a grey-black crystalline mineral with a metallic lustre, while 'pyrolusite' referred to the blue-black equivalent. 'Psilomelane' described any hard, black, often botryoidal, mass with an earthy lustre, with 'wad' as the soft counterpart. As an example, minerals which Heddle (1901) described as pyrolusite, have been subsequently identified by the author as cryptomelane and hollandite. Mis-identifications such as these, and omissions in the oxide mineralogy from a locality, are understandable since it is difficult, usually impossible, to differentiate and identify different manganese oxides in hand-specimen. Identification by instrumental techniques and microscopy is not always a simple matter (Nicholson, 1989). Optimum results are obtained in XRD

studies by using a graphite filter or Mn-filtered Fe–$K\alpha$ radiation to reduce fluorescence and lower the background. Polished sections are best prepared by vacuum impregnation of the samples with resin prior to using the grinding procedure of Crosbie (1980).

Fourteen manganese oxide minerals have been previously recorded in Britain. Greg and Lettsom (1858) noted manganite, psilomelane, pyrolusite and wad, the need for confirmation of these species has been discussed above. Spencer (1898) added braunite and hausmannite although, according to Macpherson (1983), both minerals require confirmation. Hubnerite, jacobsite and pyrophanite were added by Spencer (1958), and Embrey (1978) included birnessite, coronodite, cryptomelane and lithiophorite in his list. Manganite, pyrolusite and romanechite were all identified by Chew (1978), confirming the occurrence of these minerals. Bevins (1988) confirmed the presence of braunite and hausmannite, and also added hollandite and pyrochroite. In addition to these species, a further six manganese oxides have now been identified in the British Isles and the occurrence of each of these will be briefly described.

Chalcophanite [$ZnMn_3O_7 \cdot 3H_2O$] occurs as a minor fine-grained, black constituent of a supergene manganiferous ironstone at the Lecht mine, near Tomintoul, Banffshire [NJ 238 159]. It is hosted by a hydrothermal eruption breccia and association with cryptomelane, lithiophorite, pyrolusite and woodruffite (Nicholson, 1987).

Groutite [α-MnOOH] was found as a black surface coating on hollandite from supergene veins deposited by groundwater in Dalradian Jura Quartzite, Islay, Argyllshire [NR 283 406] (Nicholson, 1988*a*).

Quenselite [$PbMnO_2(OH)$] occurs in black, soft grains up to 1 mm in diameter within an amorphous manganese oxide cement to a raised beach deposit, Luce Bay, Wigtownshire [NX 261 511]. It is associated with birnessite and lithiophorite (Nicholson, 1988*b*).

Ramsdellite [MnO_2] was found as a black surface coating on a goethite-cryptomelane sample from the supergene Lecht manganiferous ironstone, near Tomintoul, Banffshire [NJ 238 159] (Nicholson, 1987).

Todorokite [$(Na,Ca,K)(Mn,Mg)Mn_5O_{12} \cdot xH_2O$] occurs in fine-grained reddish-blue to black ferromanganese sediments of exhalative origin at Noblehouse, Peeblesshire [NT 186 501]. It is associated with birnessite, hematite and goethite (Nicholson, 1983).

Woodruffite [$(Zn,Mn)_2Mn_5O_{12} \cdot 4H_2O$] occurs as a black, fine-grained mineral in veinlets of manganese oxides within hydrothermal eruption breccias at the Lecht mine, near Tomintoul, Banffshire [NJ 238 159]. It is associated with chalcophanite, cryptomelane, lithiophorite and pyrolusite (Nicholson, 1987).

To summarise, a total of twenty manganese oxides have been recognised in the British Isles (birnessite, braunite, chalcophanite, coronodite, cryptomelane, groutite, hausmannite, hollandite, hubnerite, jacobsite, lithiophorite, manganite, pyrochroite, pyrolusite, pyrophanite, quenselite, ramsdellite, romanechite, todorokite, woodruffite); of these quenselite is a rare mineral and this represents only the fourth occurrence recorded worldwide.

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