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Pyrolusitic supergene manganese oxides: inductive properties, EM conductivity and magnetic susceptibility

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Introduction

Manganese is a significant industrial metal, after iron, aluminium, and copper, it is the most widely used – finding application in steel alloys, oxidising treatments, glassmaking, and dry cell batteries. It has an atomic weight (54.94) similar to iron (55.85) and some similarity of chemical behaviour, but it is more mobile and soluble than iron and less readily precipitated, so that deposits of Fe and Mn oxides are usually separated in oxidation zones.

The earth's crust contains about 1000 ppm Mn (compare Fe: 53 000 ppm) giving it 12th rank in element abundance. Dark manganese minerals are everywhere in nature. Manganese has five oxidation states +2, +3, +4, +6, +7 (compare Fe +2, +3) allowing it to form a large variety of oxides such as occur in rock dendrites where they crystallise in attractive branching patterns on bedding or fracture planes (Figure 1). The rock varnish seen in outback outcrops comprises a very thin coating of manganese oxides, iron oxides, and clay (Voynick, 2017, 2018). The impressive building sandstones of the Sydney Basin Triassic sequence, if sideritic, can be discoloured after quarrying and exposure of the blackened stone surfaces to the atmosphere (Franklin, 2000). Small amounts of manganese, centred in the siderite, are released into solution upon oxidation and crystallise on the surface as black manganese dioxide, thus blackening the stone.

Primary manganese minerals occur in sedimentary, hydrothermal, and metamorphic environments. The largest primary deposits are to be found in sedimentary beds; the major secondary deposits are residuals derived by oxidation of primary sediments (Bateman, 1959). The former include vast low-grade manganese carbonate (rhodocrosite) beds that, after diagenesis and weathering, generate the latter, sometimes in the form of high tonnage (100 Mt+), high grade (Mn 46%+) supergene deposits, in suitable cavities or on suitable surfaces in the zone of oxidation. Manganese oxides are quite dense. Manganese dioxide, pyrolusite, is often the major component of secondary deposits. Details of residual Mn deposits in Queensland, Northern Territory, New South Wales, and Western Australia may be found in McLeod (1966), McAndrew (1970), Knight (1975), Hughes (1990), and Phillips (2017).

Manganese ores are an important component of Australia's mineral production. Demonstrated reserves amount to ~200 Mt, i.e. 10% of the world's resources. When beneficiated, Mn ore is worth ~\$200 per tonne, similar in value to coal. The total tonnage mined is about twice the beneficiated tonnage owing to yields of 50% after treatment[1].

Dentith et al. (1994) note that magnetic anomalies may be associated with some Australian manganese mineralisation. For regional scale exploration, airborne EM can be used for conductive manganese ores. At prospect or local scale, gravity generally offers a cheaper alternative for the direct detection of manganese mineralisation.

Hashemi et al. (2005) carried out Sub-Audio Magnetic (SAM) surveys over known EM-responsive Mn deposits. They compare

Figure 1. *Manganese is a mobile element and manganese oxides are very widely distributed. They are quite commonly observed precipitated in bedding planes and flaws in host rocks where they occur in a dendritic i.e. branching pattern. A ferruginous claystone, from the Sydney Basin, has dendrites on a fracture plane. Galvanic microprobing indicates that the black oxides, which presumably here include pyrolusite, are slightly conductive, ~ 1 S/m. The fracture face view is 50 x 40 mm.*

[1]Approximate values, subject to grades and price fluctuations.

SAM results with high-resolution gravity, HoistEM, gradient-array induced polarization (GAIP), dipole-dipole induced polarization (DDIP), and ground time domain electromagnetic (TEM) surveying over five EM-responsive manganese deposits, which varied in size and burial depth. They conclude that the SAM technique detects conductive manganese occurrences at shallow depths (<40 m), adding that the use of multiple geophysical techniques is more reliable.

Murthy et al. (2009) give examples of geophysical exploration for manganese deposits from the Keonjhar district, Orissa (India). In terms of magnetic properties the pyrolusite and psilomelane varieties showed paramagnetic (antiferromagnetic) responses comparable to that of hematite. Within a background of phyllite, shale, conglomerate or quartzites the manganese ores can be expected to show detectable magnetic responses. They emphasise the need for gravity and magnetic surveys supplemented by physical property studies of host rocks and ores.

Harvey (2018) identifies pyrolusite (along with pyrite and graphite) as a mineral of significance in electrical geophysics.

This article gives the results of preliminary experimental work on the mesoscale physical properties of some secondary Mn ores containing two common black/dark grey supergene Mn oxides, pyrolusite, mainly, and cryptomelane. The crystalline hardness of these oxides is comparable to that of haematite i.e. H ~6 on Moh's scale.

Mineralogy

Pyrolusite (β MnO2, 63% Mn), a paramagnetic semiconductor, is one of the most common Mn oxides to occur in oxidation zones where, in supergene concentrations, it can form all or part of economic Mn deposits. Geophysically, pyrolusite is of particular interest owing to its conductivity, a property most, if not all, other Mn minerals lack. Cryptomelane (KMn_8O_{16}, 60% Mn) is another common supergene Mn mineral, which frequently occurs intergrown with pyrolusite in microcrystalline or cryptocrystalline aggregates of high tensile strength, i.e. very tough. Some details of these two important secondary Mn oxide minerals are given in the notes to Table 1.

Thirty secondary manganese oxide samples were tested from a variety of locations in Australia and overseas (Table 1). The sample constituents are mainly pyrolusite and cryptomelane. Minor or trace amounts of other manganese oxides, such as braunite, may be present along with silica and iron oxides such as goethite. Summaries of Mn minerals may be found in Read (1970) and Klein and Hurlbut (1993). Extensive detail is provided by Frenzel (1980) who documents the variety and complexity of many Mn oxides. If the American Geosciences Institute is to be followed (Neuendorf et al., 2011), the sample test suite would be broadly classified as psilomelane: 'a general term for mixtures of manganese oxide minerals'. However, psilomelane is also the name applied for many years to hydrated manganese oxide containing varying amounts of barium and potassium oxides, so it is not used here.

The physical properties of semiconducting pyrolusite and the alkali bearing Mn oxide cryptomelane are not very clear, even regarding density. Both have porosity at lattice scale (tunnel structures), microscale, and mesoscale. Both can be hydrated with chemisorbed water. Common pyrolusite is β MnO_2 with a theoretical density of 5.23 g/cc, but field densities are usually taken as ~4.8 g/cc owing to the submicroscopic porosity[2].

Pyrolusite's magnetic susceptibility is low ($\sim 125 \times 10^{-5}$ SI), as would be expected for a paramagnetic mineral. Kropáček and Krs (1975) report a range of values. Subordinate amounts of iron oxides can affect the magnetic properties of manganese oxides. Gutzmer and Beukes (1995) describe a magnetic form of hausmannite (Mn_3O_4) from the giant Kalahari deposit in South Africa which is hydrothermally altered and strongly magnetic. These workers found up to 11% ferric oxide in their more magnetic samples. Non-magnetic hausmannite containes less than 3% ferric oxide.

Shuey (1975) cites electrical conductivity measurements from 0.1 to over 100 S/m for natural pyrolusite; Olhoeft (1981) gives 1 S/m; Bertin and Loeb (1976) 0.2–50 S/m; Keller (1982) 0.03–143 S/m, and Harvey (1928) up to 1000 S/m. Quite a range.

Not much is known about the physical properties of cryptomelane. Its density is ~4.3 g/cc, but its magnetic susceptibility and conductivity appear not to have been investigated. Cryptomelane's chemical formula can vary considerably depending on its formative environment (Frenzel, 1980). We were not able to locate test specimens of pure cryptomelane.

To try to clarify the physical properties of pyrolusite, four collector grade samples from Morocco, USA, and the Philippines; of coarsely crystalline (#1, 2, 29), and finely crystalline (#30) materials were tested. The pyrolusite crystals are acicular (needle shape) and aggregated haphazardly or obliquely in fibrous bundles imparting an open texture. The hard, though brittle, crystalline material contains pockets and seams of softer, sooty pyrolusite.

Samples #3–28 from Queensland, Western Australia, and Northern Territory are quite different. They comprise

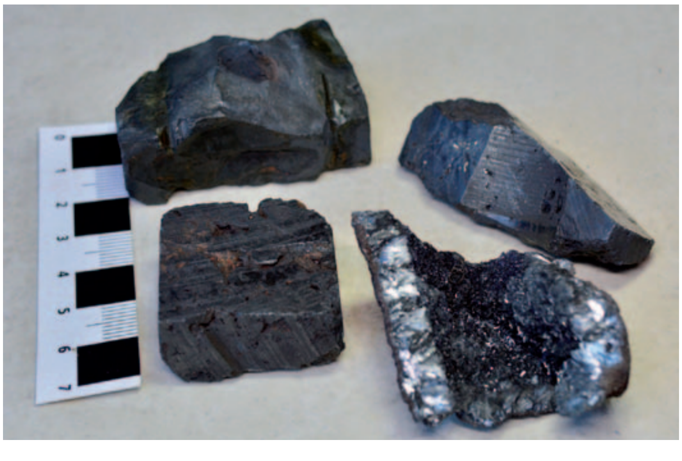

Figure 2. *Three offcuts from the very finely crystalline, supergene Mn oxides tested (cm/mm scale shown): tight (low porosity 1%), relatively conductive 68 S/m material from Qld, sample 3 in Table 1, top left; porous (8%) low conductivity, 19 S/m, material from NT, sample 4, top right; vughy quite porous (14%) marginally conductive, 2 S/m, ferruginous material from WA, sample 12 bottom left; also included is an offcut of coarse grained crystalline, very porous (37%), pure pyrolusite with sooty pyrolusite coatings and pockets, low conductivity, 11 S/m, material from Morocco, sample 1, bottom right.*

[2] The battery active manganese oxide is nsutite, γ MnO2 (hydrated), sometimes called ramsdellite. Nsutite is extremely hard, H = 8½, with a density ~4.6 g/cc; it is not thought to be present in the sample suite.

heterogeneous, microcrystalline to cryptocrystalline mixes of Mn oxides, dominantly pyrolusite and cryptomelane. Tough textures are imparted by tight intergrowths of extremely fine grains.

Some samples are shown in Figure 2.

Measurements

This study focussed on the inductive properties of magnetic susceptibility (k) and conductivity (σ) as they are quickly and conveniently measured. Following Yang and Emerson (1997), the responses of cored subsamples were measured over a frequency range in induction coils to give k and σ (Figure 3). Remanence measurements were also carried out at CSIRO North Ryde using a 2G Enterprises 755R three-axis cryogenic magnetometer. As an aid to interpretation mass properties were determined following Emerson (1990). Galvanic measurements, carried out at microprobe and core scales, corroborated the EM conductivities, allowing for differences caused by texture. The samples were measured in the 'as received' air dried condition with residual pore water as this was thought to approximate oxidised zones in the field. Vacuum saturation with fresh water was applied in the mass property measurements.

Figure 3. *An induction coil of the type used in the conductivity measurements. The wire winding is 70 mm long × 30 mm internal diameter. A conductive core inserted in the coil causes a change in its resistance, ΔR, which is measured on an impedance bridge. If the core is magnetic it also causes a change in the coil inductance, ΔL. From these quantities electromagnetic conductivity and magnetic susceptibility are derived (Yang and Emerson, 1997). The measurements are usually run in the kHz to MHz range (below the onset of skin effect). An air gap correction would be necessary if this method is used for a mag k measurement. The 54 mm long, 25 mm diameter Mn oxide test core shown is sample 9 with an 8 S/m EM conductivity and 114 × 10^{-5} SI mag k. The core is porous and siliceous.*

Results

The data set for the mass and inductive physical properties measured is given in Table 1.

The bulk density, BD, is the preferred reference parameter for viewing the results. This is regarded as the field density near surface or shallow depth materials above any water table – as would be the case in many supergene Mn oxide deposits. The density, BD, includes residual pore moisture, as quantified by Sw in Table 1; it is not the dry bulk density, DBD, which is 105°C oven dried density (Sw→0) also given in Table 1.

A perspective of the mass properties is provided in Figure 4 where porosities are plotted against dry bulk density. Substantial porosities are evident. The overtly crystalline samples #1, 2, 30 have an apparent grain density of ~4.8 g/cc and clearly plot in the pyrolusite field. Sample #29 has quartz grains interstitial to the acicular pyrolusite crystals and plots to the left of the pyrolusite field. Samples #3 to 28 are massive cryptocrystalline, hard, tough, heterogeneous aggregates of Mn oxides (mainly pyrolusite and cryptomelane) together with quartz, clay, and iron oxides in various, usually minor, proportions. This results in a spread of densities with respect to the reference mineralogy. The average porosity of the four coarser crystalline pyrolusites is very high, 31%. The range of microcrystalline pyrolusite/cryptomelane porosity is 1–19%, average 7.5%, for the 26 samples.

Magnetic susceptibility is plotted against bulk density in Figure 5. This has three interpreted features. An envelope of 21 relatively low susceptibility samples manifesting a low angle trend and regarded as representing mixtures of pyrolusite, cryptomelane, and other mineralogies. Above this are two groups thought to contain Fe oxides. Kropacek and Krs (1975) note that mineral aggregates of natural Mn-oxides, generated under the influence of atmospheric agents, bind Fe-oxides. So many natural aggregates of Mn-oxides display weak ferromagnetism.

The conductivity results are conveniently viewed in Figure 6 where EM conductivity is plotted against bulk density, both quantities are for the air dried state.

The interpreted plot has four features:

1. The crystalline pyrolusites show an increasing conductivity with density #1→2, #29→30, up to a maximum of ~10 S/m, which seems a reasonable limit given the unfavourable crystallinity (needles), the poor crystal to crystal suturing, the very high porosities, and the sooty pyrolusite vughs and lenses. Galvanic microprobing suggests that the sooty pyrolusite is about three times less conductive than the crystalline material, which, as mentioned, in aggregate is not very conductive. It is emphasised that these comments obtain for secondary, sooty and acicular pyrolusites. Hydrothermal pyrolusite and rare large prismatic pyrolusite crystals have not been investigated. Polianite is an uncommon variety of pyrolusite with well formed tetragonal crystals. Suitable samples of such material could not be obtained for testing.
2. Most of the micro/cryptocrystalline, low to moderate porosity, samples plot in a broad belt of conductivity increasing with density. The variability within the envelope is a consequence of the main Mn and minor Fe oxide mineralogy, texture, and the occurrence of silica and clay impurities. The NT samples have more silica and clay and plot on the left side of the envelope.
3. Sample #10 is very siliceous; samples #7, 9 are quite clayey/siliceous. These three samples plot in a lower density trend to the left.
4. An increase in density is regarded as reflecting an increase in pyrolusite content so the broad trend for the tough, extremely

Table 1. Manganese oxides: mass and inductive physical properties

#	Code	BD	DBD	P_A	WBD	GDA	S_W	magk	Q	EM cond.
		g/cc	g/cc	%	g/cc	g/cc	%	SI x 10^{-5}		S/m
Morocco										
1	▲	3.25	3.20	34.4	3.54	4.88	15	98	<0.01	11
2		3.09	3.06	37.1	3.43	4.86	9	100	<0.01	9
Queensland										
3	■	4.44	4.43	1.0	4.44	4.45	56	177	<0.01	68
Northern Territory										
4		3.90	3.87	7.9	3.94	4.20	43	160	0.18	19
5		3.89	3.87	6.0	3.93	4.12	33	138	0.01	12
6		4.08	4.07	10.3	4.18	4.54	9	140	0.06	57
7	■	3.75	3.74	2.5	3.76	3.84	50	143	0.05	27
8		3.53	3.50	8.3	3.58	3.82	38	137	0.15	4
9		3.59	3.57	3.5	3.61	3.70	50	114	0.04	8
10		2.95	2.93	11.1	3.04	3.30	18	68	0.03	4
Western Australia										
11		3.87	3.85	2.5	3.88	3.95	67	128	1.00	10
12		3.61	3.57	14.1	3.71	4.16	29	496	3.60	2
13	●	4.12	4.10	3.0	4.13	4.23	67	277	1.80	49
14		3.88	3.84	7.8	3.92	4.16	50	426	0.37	17
15		4.32	4.29	4.8	4.34	4.51	60	333	<0.01	18
Western Australia										
16		4.17	4.15	7.1	4.22	4.47	29	460	<0.01	10
17		4.15	4.12	7.6	4.19	4.46	43	181	0.01	20
18		4.60	4.57	5.6	4.62	4.84	60	185	0.01	35
19		3.91	3.90	19.3	4.09	4.83	5	127	<0.01	31
20		4.30	4.27	4.6	4.32	4.48	60	453	<0.01	28
21		4.16	4.10	8.4	4.18	4.48	75	138	0.02	67
22	●	3.82	3.81	3.3	3.84	3.94	30	94	0.01	7
23		3.42	3.40	6.5	3.46	3.64	33	97	0.03	2
24		3.67	3.60	8.4	3.74	3.99	50	133	0.05	4
25		3.80	3.76	10.8	3.87	4.26	37	297	1.06	17
26		4.10	4.08	9.9	4.18	4.53	20	148	<0.01	33
27		3.64	3.61	7.3	3.69	3.89	38	201	0.39	5
28		3.46	3.41	13.4	3.54	3.94	37	151	0.07	4
Arizona, USA										
29	●	3.08	3.06	26.6	3.33	4.20	7	93	<0.01	3
Philippines										
30	■	3.71	3.53	25.7	3.79	4.75	69	198	0.40	8

Notes:

- BD – bulk density air dried, as collected; DBD – dry bulk density, 105°C dried; WBD – freshwater saturated density; P_A – apparent (water accessible) porosity; GDA – inferred grain density; S_W – residual water saturation level in pores in air dried state; measurements made @ 20°C temperature.
- Magnetic susceptibility, magk, various methods including induction coil 460 Hz; Q Koenigsberger ratio modulus of J_{NRM}/J_{IND}, J magnetization intensity, NRM remanence, IND induction J = kF, F earth's field.
- EM conductivity, EMσ, induction coil 2.5 MHz, air dried state.
- Cited values rounded off.
- MnOx is a collective term for mix of manganese oxides not specifically determined; These supergene test samples are mainly mixtures of pyrolusite and cryptomelane – two of the most common oxidiation zone Mn oxides.
- pyrolusite β MnO_2, either crystalline, dark grey-black, silvery, metallic lustre, Moh's hardness >6; or soft, sooty fine grained, dull black, Moh's hardness ~2; blackish grey streak; theoretical density 5.23 g/cc, field density 4.8–5.0 g/cc (quite high).
- cryptomelane $K(Mn^{4+} > Mn^{2+})_8O_{16}$ steel-grey, submetallic lustre, Moh's hardness ~6, black streak; in addition to K, this mineral can have other metal ions substituting in its lattice (e.g. Ba) and its formula can be quite complex; density 4.3 g/cc (lower than pyrolusite)
- braunite, $3Mn_2O_3.MnSiO_3$ (10% by weight silica) may be present in some of the WA samples #11–28, but was not positively identified at mesoscale, it is thought that braunite's mag k exceeds that of pyrolusite, however in the absence of suitable reference samples this could not be substantiated
- pyrolusite, cryptomelane, braunite are paramagnetics and crystallise in the tetragonal system
- samples 1, 2 from Imini mine Morocco are coarsely crystalline pyrolusites with sooty pockets and minor/trace quartz; sample 29 from Pima mine Arizona has coarsely crystalline acicular (needle) pyrolusite, sooty pyrolusite, and quartz; sample #30 from Larena, Siquijior Island, Philippines, fine grained crystalline pyrolusite and sooty pyrolusite bands
- the Australian samples #3–28, generally hard, tough, extremely fine grained, and variably porous, are from various locations in Queensland, Northern Territory and Western Australia.
- the crystalline pyrolusites are highly porous and comprise often haphazardly stacked, fibrous splays or bundles of acicular (needle) pyrolusite crystals a few microns in diameter and tens of microns in length; the open 'loose' textures in #1, 2, 29, 30 are in complete contrast to those in #3–28.
- pyrolusite: nominally BD 5.0 g/cc, 100 S/m cond; 125 × 10^{-5} SI mag k, reported values for pyrolusite show considerable variation especially in conductivity; sooty soft pyrolusite's conductivity is less than that of crystalline pyrolusite; cryptomelane: nominally 4.3 g/cc but mag k and conductivity not reported
- samples #3–28 are heterogeneous in composition, they contain minor amounts of silica, clays, iron oxides, and MnOx other than pyrolusite and cryptomelane.

fine grained interlocked oxides, #3–28, suggest that 100 S/m would be a reasonable notional value to ascribe to a material comprising 100% pyrolusite of this nature.

A plot of conductivity against inferred grain density (porosity removed) is given in Figure 7 where the features are similar to those in Figure 6.

Conductivity does not appear to depend on Sw, the residual water saturation (crossplots for Sw not shown here), this is to be expected because the preferable mode of conduction would be through the pyrolusite content, either massive or networked, and not through relatively resistive residual pore moisture.

For the tough heterogeneous cryptocrystalline Mn oxide samples (#3–28) there are no clear correlations or features when conductivity is plotted against porosity (not shown here) so the relatively low porosities, average 7.5%, are not regarded as having a predictable influence when the group is

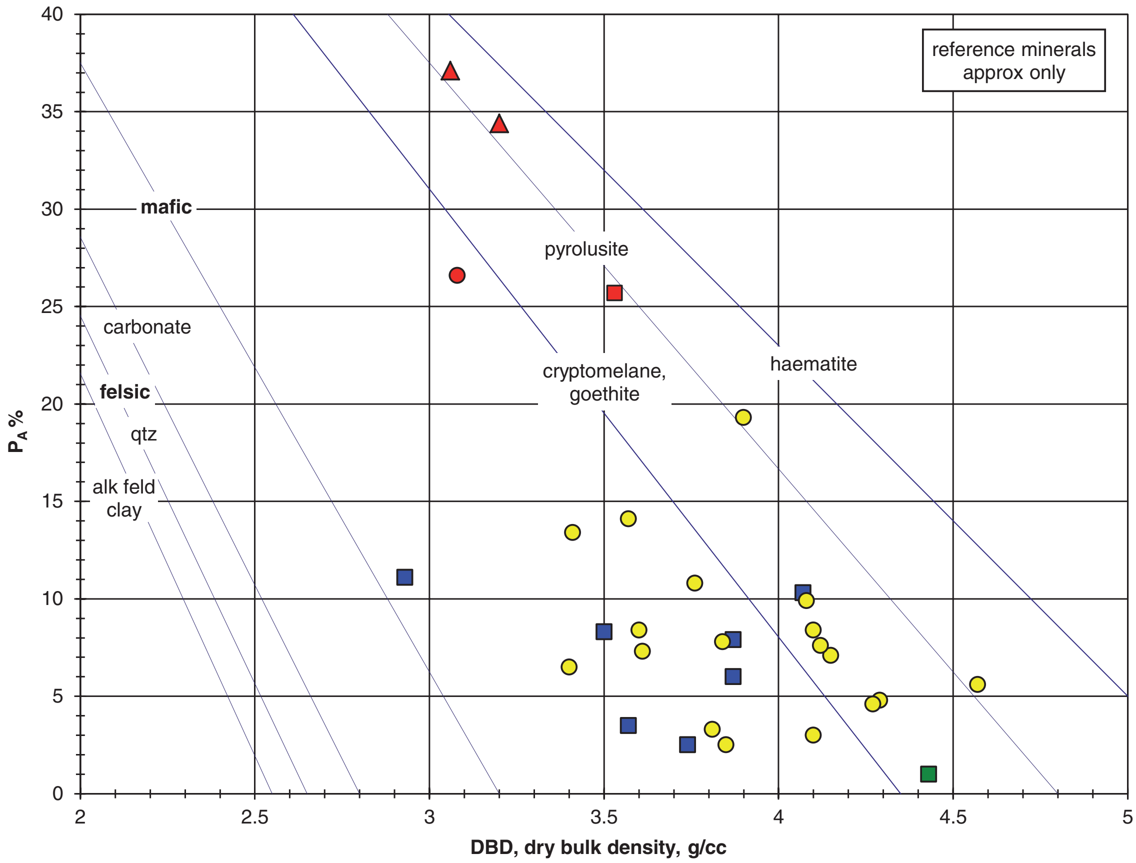

Figure 4. *Porosity plotted against dry bulk density with reference mineralogy trends shown. The reference 'text book' mineral densities are approximate only, variations can occur. See Table 1 for plot point colour code.*

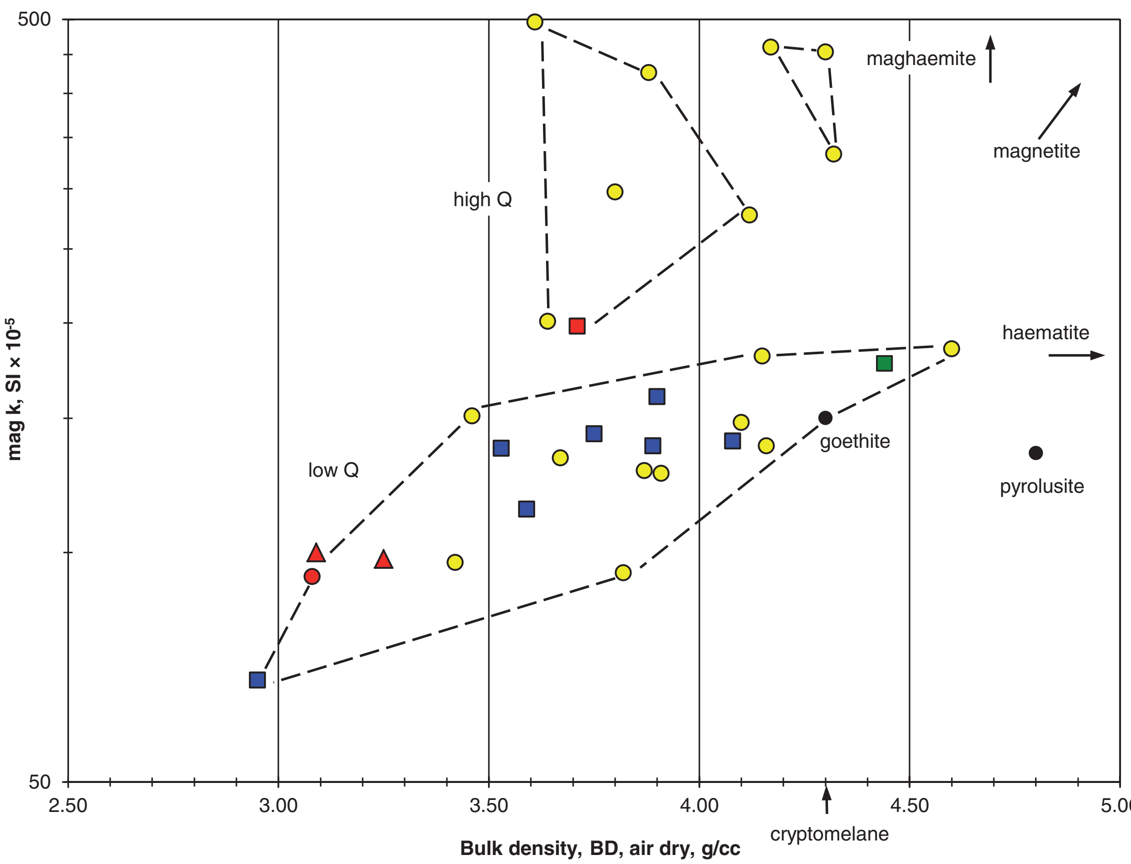

Figure 5. *Magnetic volume susceptibility plotted against bulk density (for the air dried state) showing three features interpreted from the data. Reference mineral values are approximate only, they can vary considerably.*

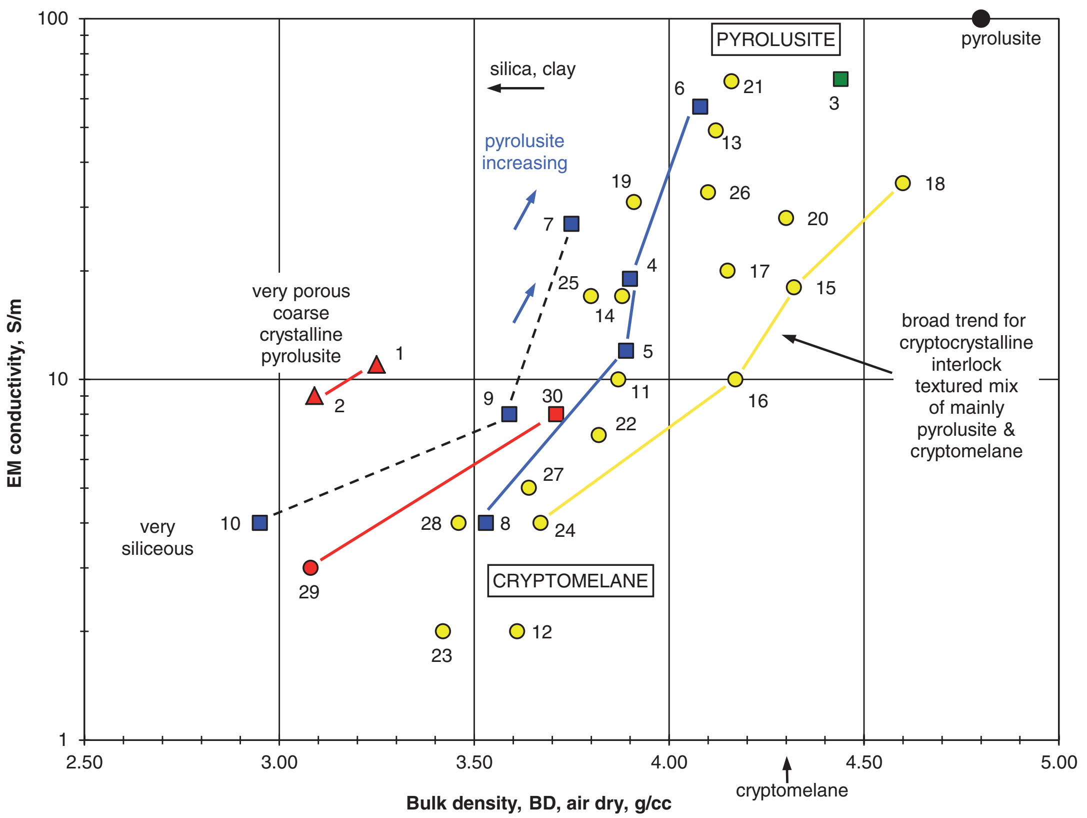

Figure 6. *Induced (EM) conductivity plotted against bulk density (air-dry state) with features interpreted from the data. The reference value for pyrolusite is nominal. For the variably ferruginous cryptocrystalline materials, samples at the top of the plot are rich in pyrolusite, e.g. #3; those at the bottom are pyrolusite poor and have more cryptomelane, e.g. #28. Conductivity rises with increasing pyrolusite content, and also with improvement in pyrolusite networking. The coarser crystalline pyrolusites #1, 2, 29, 30 have quite different textures and exhibit a separate behaviour.*

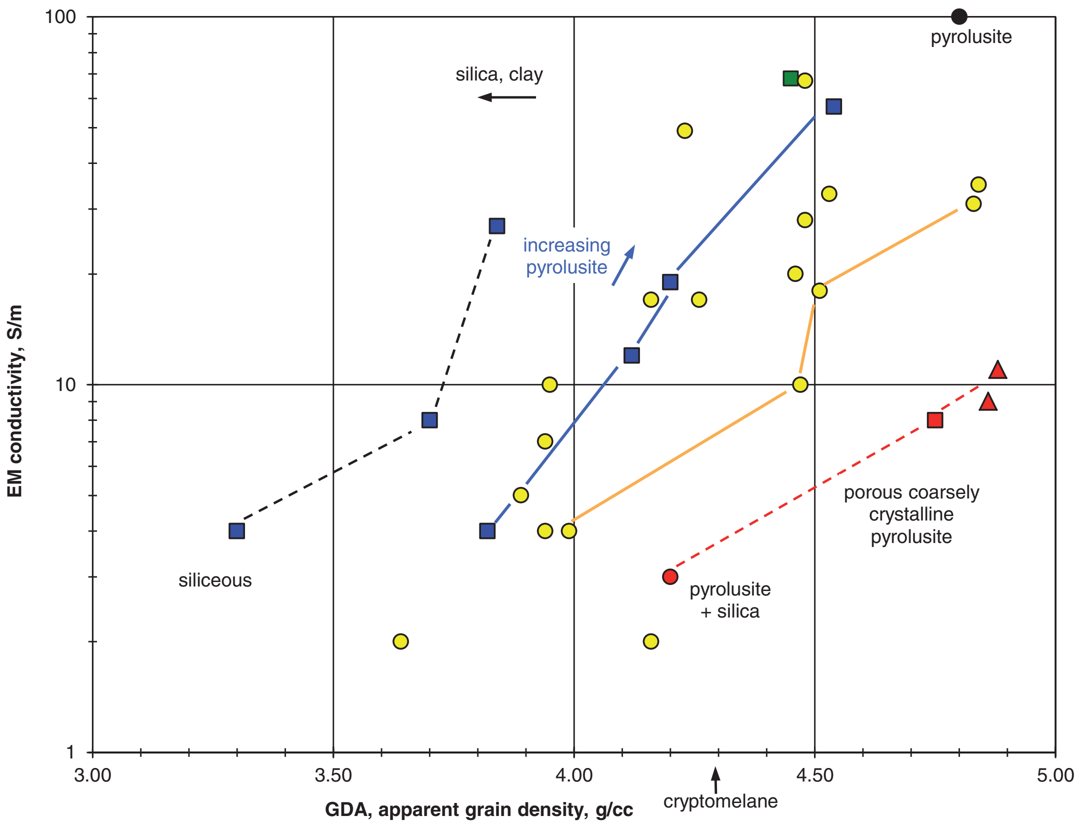

Figure 7. *An adjustment of Figure 6 showing induced (EM) conductivity plotted against inferred grain density (i.e. porosity removed). See Table 1 for plot point colour.*

considered as a whole. However, it would be expected that the conductivity of an individual sample would be boosted if the void space was occupied by semiconducting pyrolusite. So the crystalline pyrolusites (#1, 2, 29, 30) with large void spaces could show a significant increase in conductivity if filled with pyrolusite. However, even if conductivity doubled, to say around 20 S/m, it would not render these materials very conductive; their textures are simply not favourable for good electrical continuity.

Concluding remarks

The results of the sample tests suggest that surficial or near surface, secondary, residual, porous Mn deposits comprising mainly pyrolusite and cryptomelane in massive, tough, cryptocrystalline form, have low to moderate conductivities, ~1 S/m up to ~70 S/m, and moderate to high densities, ~3.5–4.5 g/cc. The conductivities increase with pyrolusite content. Overtly crystalline, fibrously textured, very porous, quartz-free pyrolusite has a conductivity of ~10 S/m. About a third of the volume of these overtly crystalline samples is void space, and it is considered that this, the needle grain shape, and poor grain boundary suturing, account for the lower conductivity of the coarsely crystalline pyrolusite.

Frenzel (1980) states that manganese oxides are, as a rule, electrically non-conducting. Pyrolusite is the exception to this rule. It is not known whether cryptomelane is a conductor. We were not able to access literature values or obtain good samples of cryptomelane for testing. Tentatively, on the basic of galvanic microprobing of samples and the results presented here, a conductivity of ~5 S/m is ascribed to a compact microcrystalline Mn oxide mix comprising mainly cryptomelane with subordinate pyrolusite content (e.g. #27, 28), but it is likely that sparsely networked pyrolusite imparts the conductivity.

The air dried state conductivities of the tough microcrystalline Mn oxide assemblages are low to moderate and largely dependent on the pyrolusite content. The conductivities are not directly diagnostic of Mn grade as insulating or only slightly conductive Mn minerals other than pyrolusite, e.g. cryptomelane, can be present in high concentration. High grade secondary pyrolusite ore comprising by volume 60% pyrolusite, 20% cryptomelane, 10% felsics, and 10% porosity (Sw = 0) would have an Mn content of ~58% by weight, a density of ~4 g/cc, and an expected conductivity ~55 S/m based on the analysis of the 26 samples in Table 1. If the ore is 10% pyrolusite, 70% cryptomelane, 10% felsics, and 10% porosity (Sw = 0) then it would contain 56% Mn, its density would be ~3.8 g/cc, and its expected conductivity ~5 S/m. Similar Mn contents do not mean similar physical properties.

The lower than expected conductivities for the four overtly crystalline pyrolusites are surprising. The inductive data were checked with galvanic microprobing and four electrode core scale DC galvanic resistivity tests. All this data shows without doubt, that such pyrolusites, or at least the four tested, are not very conductive. This, for want of a better explanation, is ascribed to porosity, crystal shape and grain boundary effects, and to the frequent occurrence of pockets of sooty pyrolusite with conductivity below that of the crystalline material.

The results of this work are not definitive but they are indicative for the types of mineralisation documented here. The accuracy of the physical property measurements is better than 1%. If samples #3 to #28 can be regarded as reasonably representative elementary volumes of oxidation zone Mn oxide deposits comprising a mixed, very fine grained pyrolusite – cryptomelane mineralogy, then such deposits are indicated by this study as likely having EM conductivities in the 1 to 100 S/m range and magnetic susceptibilities in the 100 to 500 × 10^{-5} SI range. The conductivities are dependent on the pyrolusite content and sensitive to the effects of texture and to the presence of other minerals such as silica. The susceptibilities depend on all the Mn oxides present, as all Mn oxides are paramagnetic and manifest low to moderate susceptibilities. Iron oxides, if present, would contribute to susceptibility. If magnetic effects derive from Mn oxides of the type documented here, it is probable that they will be low order (k ≈ 100 × 10^{-5} SI) and of limited, if any, use in exploration, especially in the magnetic noise of ferruginous weathered zones.

Mn oxide rock assemblages have other interesting properties: temperature effects, where pyrolusite shows behaviour typical of many semiconductors (Shuey, 1975) in that conductivity increases with temperature (about three-fold from room temperature to 100°C); saturated state resistivities (very dependent on saturant salinity); and IP effects (for saturated state pyrolusite typically ~100 mr phase lag @ 0.1 Hz). These aspects are not dealt with here, but some data on compressional (P) wave velocities are given in Appendix 1.

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The source of the image used in the title is 'Manganese dendrites on a limestone bedding plane from Solnhofen, Germany. Scale in mm.'. Public domain; https://commons.wikimedia.org/wiki/File:Dendrites01.jpg.

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Appendix 1. Compressional (P) wave velocity and porosity

Compressional (P) wave velocities were measured on ten air-dried samples (Table A1). Ultrasonic (200 kHz) transit times were recorded under 10 kN uniaxial load. Although the velocities are not indicative of conductivities (the rationale for the measurements) the results are included here as there appear to be little or no published velocity data for Mn oxides.

Velocities are seen to decrease as porosity increases (Figure A1), a behaviour commonly observed in all rock types, and on which an extensive literature exists (Mavko et al., 1998). The data do suggest that at zero porosity a velocity of about 7500 m/s may obtain, i.e. a high velocity similar to the other metal oxides such as haematite. However, here seven of the materials are not monomineralic, but rather very fine grained heterogeneous mixtures of pyrolusite, cryptomelane and a minor miscellany of other Mn oxides, with or without some silica and clay. The two pure coarse grained Moroccan pyrolusites have low velocities on account of their texture and very high porosities. The Pwave velocity depends on the elastic moduli and density of the whole mass of rock, on which porosity exerts a strong influence; the conductivity depends on the amount, distribution and networking of pyrolusite, and porosity, unless very high, exerts only a second order minor influence. The calculated acoustic impedances [Zac = Vp x BD] in Table A1 suggest the compact, tight (low porosity), high velocity microcrystalline Mn oxides (e.g. #3, 7) could present strong reflectivity contrasts to sedimentary host rocks.

Table A1. Compressional (P) wave velocities were measured on 10 air-dried samples. Refer to Table 1

#	BD	V_p	Z_{ac}	P_A	EM cond
	g/cc	m/s	ktm^{-2} s^{-1}	%	S/m
1	3.25	1924	6.3	34.4	11
2	3.09	1902	5.9	37.1	9
3	4.44	7129	31.7	1.0	68
5	3.89	5129	20.0	6.0	12
6	4.08	4255	17.4	10.3	57
7	3.75	6864	25.7	2.5	27
8	3.53	5704	20.1	8.3	4
19	3.91	2918	11.4	19.3	31
27	3.64	6100	22.2	7.3	5
28	3.44	5233	18.0	13.4	4

A rough rule of thumb for an empirical relationship between P wave velocity (Vp) and unconfined compressive strength (UCS) is: UCS ≈ (Vp^3), here UCS is in MPa and Vp is km/s. So for sample #3 UCS ≈ 362 MPa (very strong material), and for sample #1 it is much lower, UCS ≈ 7 MPa (quite weak, mechanically). These features were noted in core cutting: the tight cryptocrystalline samples, e.g. #3 were extremely difficult to drill, whereas the coarse, porous samples, e.g. #1 were easy to cut.

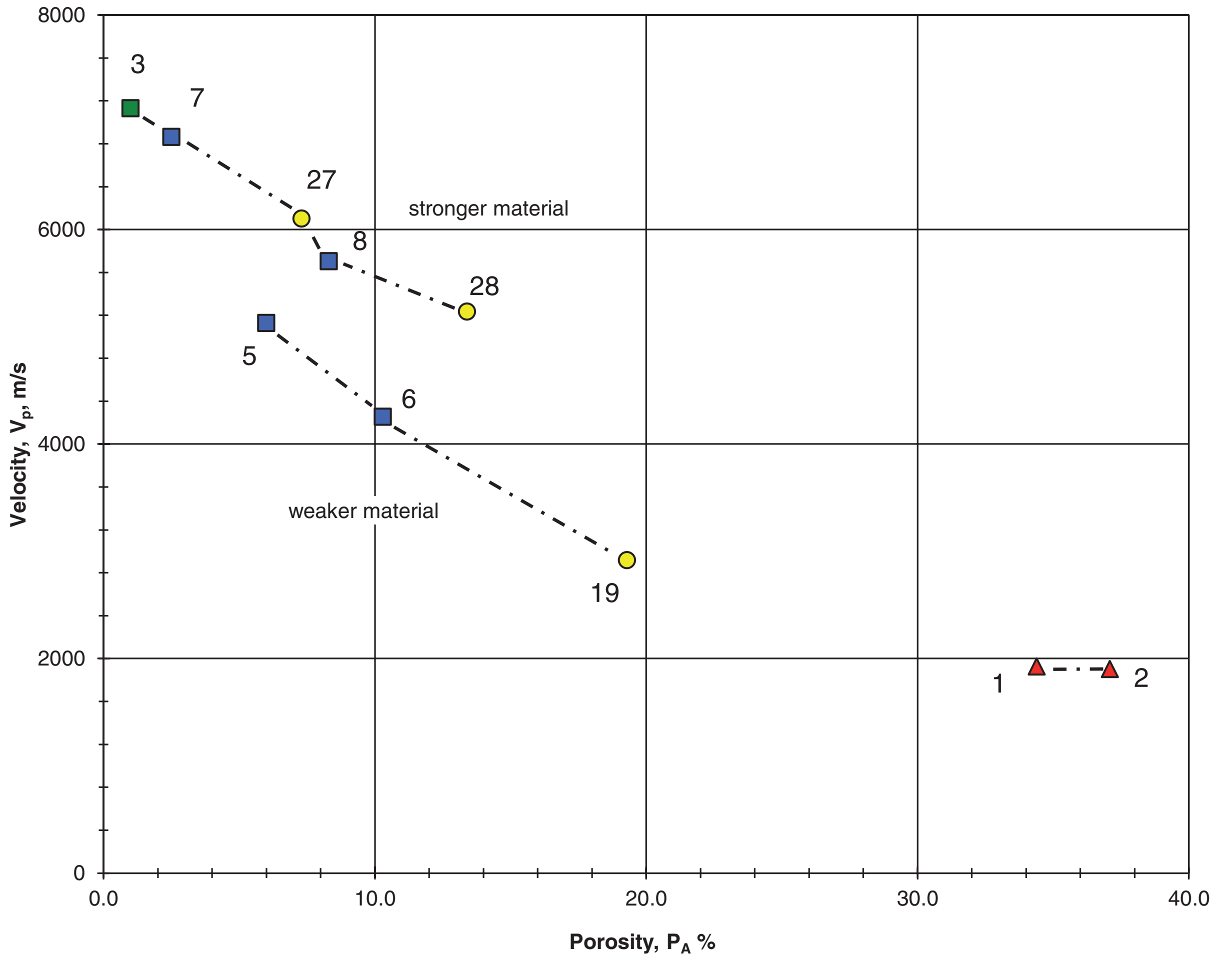

Figure A1. *Ultrasonic compressional (P) wave velocity plotted against porosity shows a pronounced decrease in velocity as porosity increases in the very fine grained heterogeneous Mn oxides, a diminution in velocity is associated with fracturing in three of these (#5, 6, 19); the coarsely crystalline very highly porous pyrolusites (#1, 2) have quite low velocities.*