Significance of a lithiophorite interface between cryptomelane and florencite

K. M. Scott

CSIRO Division of Mineral Physics and Mineralogy, P.O. Box 136, North Ryde, NSW 2113, Australia

Abstract

The presence of a lithiophorite interface between cryptomelane and florencite, kaolinite, and goethite in coatings on weathered siltstone at Lake Moondarra in northwest Queensland (Australia) is explained as the result of redistribution of ions originally adsorbed onto amorphous Mn oxides. Large cations (radius ~1.3 Å) were accommodated in cryptomelane, with smaller cations and anions moving outward until the nucleation of lithiophorite stabilized the 0.7-Å-radius cations and some Al. Rare-earth elements and other cations of ~1.0-Å radius were then stabilized as florencite, which formed with kaolinite and goethite in an outer thin band.

Introduction

Lithiophorite $(Al,Li)MnO_2(OH)_2$ occurs in many places in Australia, ranging from ore deposits to isolated occurrences in manganese wads (e.g., Ostwald, 1984). It is also well developed in nodules in Australian soils, where its presence is important because of its high trace-element content (Taylor et al., 1964; Taylor, 1968). Near the upper reaches of Lake Moondarra in northwest Queensland, it occurs as black colloform and botryoidal surface coatings on weathered siltstone. This note presents data on the compositions of lithiophorite and the surrounding minerals and discusses the reasons for their association.

Occurrence

In the Mount Isa region of northwest Queensland, weathering of Proterozoic dolomitic siltstones may result in the formation of a variety of colloform surface coatings of manganese oxides. They are generally members of the cryptomelane-hollandite-coronadite solid-solution series $[(K,Ba,Pb)_{1-2}Mn_8O_{16}·xH_2O]$ and become increasingly rich in Pb with proximity to the Mount Isa lode. However, near the upper reaches of Lake Moondarra, 7 km northeast of Mount Isa, lithiophorite occurs as a thin band in a coating from a fault zone (Scott, 1986).

The host rock to the lithiophorite is fawn-colored, weathered and brecciated Moondarra Siltstone cut by a 15-mm red band of hematite containing quartz breccia fragments. Black colloform and botryoidal manganese oxides coat the surfaces of fractures. X-ray diffraction study revealed that these manganese oxides were cryptomelane and lithiophorite.

Composition

These Mn minerals, and florencite that occurs with them, are capable of considerable compositional variation (e.g., Milton and Bastron, 1971; Frenzel, 1980); therefore, their exact compositions were determined by electron-microprobe analysis. Such investigations revealed that the approximately 200-μm-thick colloform coating is composed of several distinct zones. The innermost zone consists of 100 μm of colloform goethite followed by 40 μm of cryptomelane $[K_{1-2}Mn_8O_{16}·xH_2O]$, 20–40 μm of lithiophorite, and an outer 10-μm-thick coating of florencite $[CeAl_3(PO_4)_2(OH)_6]$ admixed with kaolinite and goethite (Fig. 1).

As shown in Figure 2 and Table 1, these mineralogical changes reflect substantial chemical changes. Residual goethite, upon which the colloform material is formed, contains only minor Si, Al, Zn, and P. Colloform goethite generally has higher Si, Al, Mn, and S than residual goethite. The Cu and Zn contents are also high, especially in the innermost bands within the colloform goethite. In the cryptomelane zone, Si, Al, Fe, S, and P contents decrease, whereas K, Ba, Co, Ca, and Zn all increase with the dramatic rise in Mn content. The lithiophorite zone shows the highest Co, Cu, Ni, and Zn contents, but Mn content is lower and Al higher than in cryptomelane. The outer band is particularly rich in Si, Al, Ca, Sr, REE, S, and P, with Fe and K contents also significant. Mn and base metal contents are low.

Discussion

The outward sequence from residual goethite to colloform goethite, followed by cryptomelane, lithiophorite, and florencite + kaolinite + goethite is one of decreasing Fe and increasing Si, Al, S, P, and REE contents. Mn, K, and base-metal contents are highest between the iron oxide–rich and florencite-rich zones. Cryptomelane is relatively free from Al, whereas Al-rich lithiophorite has little K and is enriched in Ni, Co, and Zn relative to cryptomelane, despite their proximity. These features are consistent with the proposal of Wagner et al. (1979) that Al^{3+} substitution for Mn^{4+} promotes Co^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} uptake. In lithiophorite these divalent cations may sub-
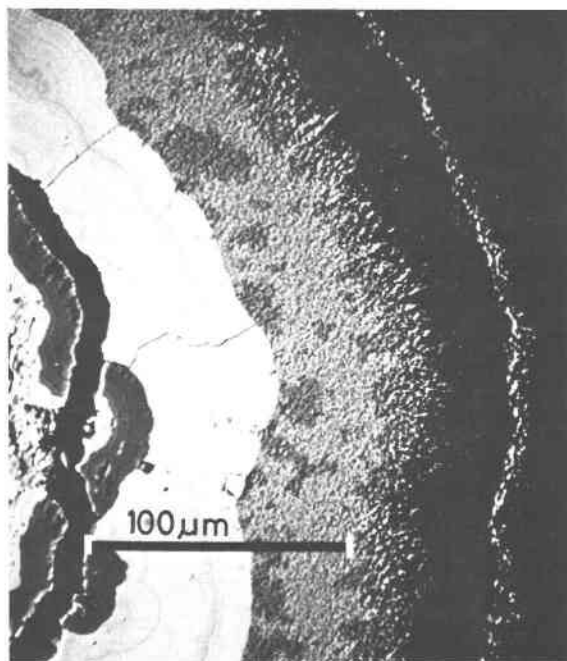
Fig. 1. Back-scattered-electron image of a colloform band from a fault near Lake Moondarra, showing the outward progression from goethite (100-μm-thick light and dark bands showing fine colloform texture), to cryptomelane (40-μm-thick speckled area), to lithiophorite (20–40-μm dark area) and florencite, kaolinite, and goethite (10-μm light band). The dark area to the right and the crack within the goethite are plastic-filled.
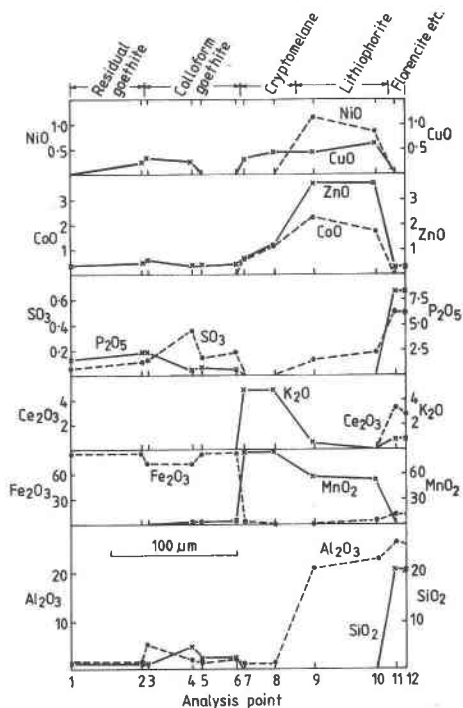

Fig. 2. Selected elemental variations for the sequence from residual goethite through the colloform band to florencite, kaolinite, and goethite (wt%). Complete analyses are given in Table 1.

stitute completely for similarly sized Li^+ (Mitchell and Meintzer, 1967). Thus the high base-metal and Al contents in the lithiophorite at Lake Moondarra may imply that its Li content is low.

Lithiophorite, with its intermediate position, structure, and composition between Mn-rich (cryptomelane) and Al-rich (florencite and kaolinite) neighbors, appears to be genetically related to them. It is also found between Al-rich materials (clays or gibbsite) and manganese oxide (pyrolusite) at Nye County, Nevada (Hewett et al., 1968), and at Groote Eylandt (Ostwald, 1980). A REE-bearing florencite is also associated with manganese oxides (lithiophorite and todorokite) at Sausalito, California, where the REE are considered to have been adsorbed onto colloidal manganese oxides and redistributed during crystallization (Milton and Bastron, 1971). At Lake Moondarra this process can be expanded to include the whole crystallization sequence from cryptomelane to florencite. All the cations (K, Al, base metals, REE) are considered to have been adsorbed originally onto presumably amorphous manganese oxides. When crystallization occurred, large ions like K and Ba were able to fit into the cavities in the MnO_2 framework and to stabilize it as cryptomelane. Smaller ions migrated outward, and when lithiophorite with its alternating layers of MnO_2 and $(Al,Li)(OH)_3$ formed, cations with a radius of ~0.7 Å and most of the Al^{3+} were incorporated. Larger cations—Sr, Ca, and REE

with a radius of ~1.0 Å—and the anions SO_4^{2-} and PO_4^{3-} finally nucleated as florencite in the intergrown florencite, kaolinite, and goethite mixture on the outer edge of the colloform coating. The epitaxial relationship commonly developed between lithiophorite and kaolinite (Bricker et al., 1976) suggests that, in the present case, the kaolinite may have formed by using the lithiophorite structural framework as a template.

The alternative possibility of formation from a solution of changing composition must also be considered, especially as it appears to be the mechanism for colloform goethite formation (see below). However, the broad banding (tens of micrometers) in the manganese oxides relative to the fine (micrometer) banding in colloform goethite and the concentration of metals in specific minerals (cf. Burns and Burns, 1978) imply that recrystallization of the manganese oxides occurred at Lake Moondarra.

The fine banding of the colloform goethite (Fig. 1) indicates that it was deposited intermittently from solution (cf. Segnit, 1984). The fact that analysis 4 (representing the dark band in the goethite in Fig. 1) is more siliceous than the other colloform goethites implies that extensive homogenization did not take place after deposition. As the goethites become progressively more Mn-rich and Cu-poor (Table 1, Fig. 2), the compositions of the solutions from which the goethite precipitated appear to have changed with time. The hypothesis that elemental redistribution occurs in the material represented by the cryp-

TABLE 1. Compositions (wt%) along traverse from residual goethite through colloform band

Mineral: Analysis point:	Residual goethite		Colloform goethite				Cryptomelane		Lithiophorite		Florencite + kaolinite + goethite	
	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	1.76	1.41	1.15	4.88	2.55	2.68	0.24	0.26	0.15	0.32	20.6	20.2
Al_2O_3	1.56	1.60	5.26	2.10	1.84	2.36	0.97	1.43	20.5	22.6	26.1	25.3
Fe_2O_3	86.9	85.3	73.3	73.8	85.3	85.0	1.88	0.18	0.38	1.47	9.75	9.42
MnO_2	0.12	0.14	0.26	0.86	1.07	1.96	86.5	86.3	56.7	53.1	0.42	0.34
CaO	<0.1	0.11	<0.1	0.11	<0.1	0.11	0.10	<0.1	<0.1	<0.1	0.79	0.70
Na_2O	<0.1	<0.1	<0.1	0.27	<0.1	<0.1	<0.1	1.14	0.26	<0.1	—	—
K_2O	<0.1	<0.1	<0.1	0.11	<0.1	<0.1	4.81	4.83	0.51	<0.1	0.79	0.89
BaO	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	0.39	0.44	<0.25	<0.25	—	—
SrO	—	—	—	—	—	—	—	—	—	—	0.85	0.55
CuO	0.15	0.27	0.38	0.28	0.17	0.12	0.31	0.46	0.46	0.62	0.22	<0.12
CoO	<0.20	0.20	0.25	<0.20	<0.20	0.22	0.68	1.12	2.26	1.75	—	—
NiO	<0.12	<0.12	<0.12	0.13	<0.12	<0.12	<0.12	<0.12	1.13	0.83	—	—
ZnO	0.41	0.46	0.58	0.38	0.40	0.43	0.66	1.15	3.66	3.67	0.29	0.29
La_2O_3	—	—	—	—	—	—	—	—	—	—	2.06	1.61
Ce_2O_3	—	—	—	—	—	—	—	—	—	—	3.23	2.73
Nd_2O_3	—	—	—	—	—	—	—	—	—	—	0.77	0.46
Pr_2O_3	—	—	—	—	—	—	—	—	—	—	0.67	<0.2
SO_3	<0.1	0.11	0.12	0.35	0.14	0.18	<0.1	<0.1	0.11	0.17	0.50	0.51
P_2O_5	1.62	2.40	2.40	0.55	0.86	0.51	<0.1	0.10	<0.1	<0.1	8.18	8.27

Note: Compositions determined on Cambridge Microscan V microprobe with Link energy-dispersive system (Pb and S determined using wavelength spectrometers). Pb $\leq$ 0.12.

tomelane to florencite bands but not in the goethite suggests that the Mn-rich material was deposited subsequent to the goethite, i.e., depositing solutions changed from Fe-rich to Mn-rich.

Source of cations

The Fe, Mn, base metal, and REE in the colloform band can all be derived by weathering of the dolomitic Moondarra Siltstone. Dolomite from this region is quite ferroan and manganoan, e.g., dolomite from the nearby and similar Urquhart Shale has a composition $Ca_{50}Mg_{43}Fe_{6.4}Mn_{0.4}Sr_{0.03}(CO_3)_{100}$ when unmineralized (van den Heuvel, 1969). Thus the dolomite readily explains the Fe, Mn, and Sr contents in outcrop.

Base metals in the Fe and Mn oxides are derived from minor sulfides within the Moondarra Siltstone. Although no fresh sulfides were analyzed, casts after pyrite contained goethite with up to 150 ppm Co, 2100 ppm Cu, 200 ppm Ni, 600 ppm Pb, and 4400 ppm Zn (Scott, unpub. report, 1978). The low Pb contents in the colloform band reflect the low solubility of Pb relative to the other base metals. The Ba and K, which were originally associated in K-feldspar in the dolomitic siltstone (Scott, unpub. report, 1978), maintain their association in the secondary cryptomelane.

The percentage levels of REE found in florencite can be derived by weathering of shales with no need to appeal to any enriched source (Milton and Bastron, 1971). Thus, as fresh siltstones in this area contain ~80 ppm La (Smith and Walker, 1971), i.e., similar to the levels at Sausalito, the Moondarra Siltstone is the most likely source of REE at Lake Moondarra.

The presence of the fault aids penetration of groundwater to greater depth and hence provides a greater vol-

ume of material from which to derive cations than in nonfaulted areas. Therefore, the Mn- and REE-rich assemblages are best developed in the fault zone.

CONCLUSIONS

Weathering of the dolomite, K-feldspar, and minor sulfides in the Moondarra Siltstone freed the elements that have been incorporated into a colloform coating in the cavities within a fault ironstone. Within this coating, the iron oxides with their fine banding and lack of homogenization appear to have been formed prior to the precipitation of the manganese oxides. The originally amorphous manganese oxides contained adsorbed phosphate, sulfate, K, base metals, REE, and some Fe, Al and Si. When crystallization occurred, K was able to fit into the MnO_2 structure to form cryptomelane. Smaller cations and the anions, unable to fit into that structure, migrated outward. With the nucleation of a mixed MnO_2-$Al(OH)_3$ structure (i.e., lithiophorite), the base metals and some Al were accommodated. The remaining Al, Si, Fe, Ca, Sr, PO_4, and REE were then incorporated into $Al(OH)_3$- and $Fe(OH)_3$-based structures in a complex florencite, kaolinite, and goethite mixture.

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