

CHARACTERIZATION OF FIBROUS CRYPTOMELANE FROM THE TODOROKITE-CRYPTOMELANE MINERAL ASSEMBLAGE AT THE SEBILLO MINE, NORTHERN CAPE PROVINCE, SOUTH AFRICA

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ABSTRACT

A 30-cm hand sample was obtained from the lowermost manganese ore bed, directly below the Kalahari unconformity within the supergene zone, at the Sebillo manganese mine in the Kalahari Manganese Field, Northern Cape Province, South Africa. The sample comprises an intergrowth of rare supergene fibrous cryptomelane and todorokite, as well as traces of pre-supergene manganese oxides. A chemical analysis of hausmannite concretions within remnant diagenetic manganese ore fragments in the supergene mineral assemblage shows leaching of pre-existing carbonate and silicate compounds from the primary diagenetic ore (Kleyenstüber 1984, 1985, Chetty 2008, Vafeas 2016) *via* descending meteoric fluids along the Kalahari unconformity. This resulted in the initial development of todorokite, forming the bulk of the matrix, and the coeval development of early-stage calcite within the todorokite pores. Subsequent to this, late-stage calcite precipitated from descending Ca-bearing supergene fluids and is seen to superimpose the todorokite matrix. Growth of the supergene mineral assemblage ended with the formation of rare medium- and coarse-grained acicular cryptomelane crystals that are orientated perpendicular to the host fracture surface.

Keywords: Cryptomelane, manjiroite, todorokite, Kalahari, manganese, Sebillo, Mamatwan, Wessels, supergene.

INTRODUCTION

Sebillo Resources (Pty) Ltd. (Fig. 1A) operates a relatively new open-cast manganese mine ("Sebillo") that is currently mining the lowermost of three sedimentary manganese ore beds of the Hotazel Formation. The recent mining activity has made available new mineralogical information in an area that until now has remained buried beneath the arid sediments of the Kalahari Formation. Below the Kalahari Formation in the southern portion of the Kalahari Manganese Field (KMF), the Hotazel Formation is unconformably transected by the Kalahari unconformity, below which supergene alteration is

thought to have begun at approximately 42 Ma (Gutzmer *et al.* 2012), resulting in the development of several supergene manganese phases (Du Plooy 2002, Gutzmer & Beukes 2000).

The lower manganese ore bed at Sebillo is in direct contact with the overlying Kalahari unconformity and is therefore subject to supergene alteration through descending meteoric fluids (Fig. 1B). As such, the upper portion of this ore bed is host to a number of supergene manganese minerals. These include rare occurrences of fibrous Mn⁴⁺-oxy-hydroxides such as romanechite, manjiroite, pyrolusite, todorokite, and cryptomelane, the latter two of which are the focus of this study. The supergene manganese phases were first

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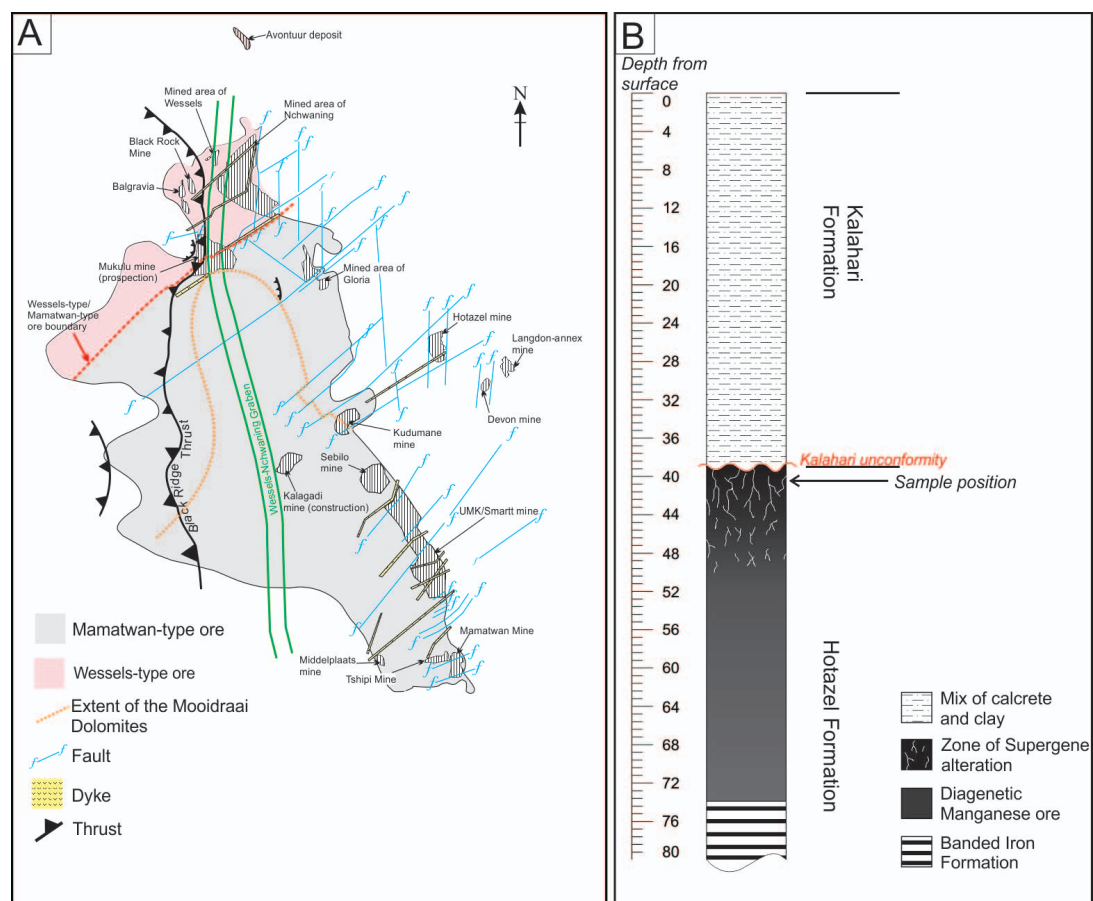


FIG. 1. (A) Structural map of the Kalahari Manganese Field illustrating the distribution of manganese mines currently mining the Hotazel Formation as well as the major structural features in the area (after Kleyenstüber 1984, Cairncross & Beukes 2013, Vafeas 2016). (B) The general stratigraphy exhibited at the Seblo mine, illustrating the lower manganese ore bed of the Hotazel Formation unconformably overlain by the arid sediments of the Kalahari Formation. The relative position of the cryptomelane-todorokite hand sample is indicated to be directly below the Kalahari unconformity, within the zone of supergene alteration.

described by Frankel (1958), who identified a fibrous, dull-black mineral assemblage as a fine intergrowth of cryptomelane and montmorillonite. It was only in 1970 that this mineral assemblage was determined by Van Biljon (in De Villiers 1970) to contain todorokite and not montmorillonite as previously thought. Further investigation into the supergene mineral assemblage by Gutzmer & Beukes (2000) identified the minerals from the Smartt mine, directly south of the Seblo mine (Fig. 1A), as a microscopic intergrowth of “asbestiform” manjiroite and todorokite with an $\text{Ar}^{39}\text{-Ar}^{40}$ age of approximately 37 Ma.

Todorokite is a hydrated Na-, Ca-, K-, Mg-bearing manganese oxide mineral with a general formula of

$(\text{Na}, \text{Ca}, \text{K}, \text{Ba}, \text{Sr})_{0.3-0.7}(\text{Mn}, \text{Mg}, \text{Al})_6\text{O}_{12} \cdot 3.2-4.5\text{H}_2\text{O}$ (Yoshimura 1934, Ostwald 1986) and a formula for the specimen found at the Smartt mine of $(\text{Na}_{0.36}\text{Ca}_{0.2}\text{K}_{0.05})(\text{Mg}_{0.4}\text{Mn}^{2+}_{0.06}\text{Fe}^{3+}_{0.05}\text{Al}_{0.04})(\text{Mn}^{2+}_{1.0}\text{Mn}^{4+}_{5.0})\text{O}_{12}$ (Gutzmer & Beukes 2000). Cryptomelane, however, is a rarely occurring, K-rich endmember of the hollandite-group of minerals (Biagioni *et al.* 2012) with an ideal endmember formula of $\text{A}^{+}_{1-1.5}[\text{M}^{4+}_7\text{M}^{3+}]_6\text{O}_{16}$ when the dominant tunnel cation has a charge of 1+ (Biagioni *et al.* 2012), with K and Na occupying A^{+} , Mn and Ti occupying M^{4+} , and Fe and Al occupying M^{2+} (Biagioni *et al.* 2012). Both todorokite and cryptomelane have been noted in multiple publications to occur in the



FIG. 2. Approximately 30-cm long, 6-cm thick hand sample comprising a cryptomelane-todorokite mineral assemblage exhibiting distinct acicular crystals. The crystal growth occurred perpendicular to the fracture plane in which it formed. The contact between the bi-directional crystal growth is clearly distinguishable in the center of the sample.

supergene environment of manganese ore deposits (Nicholson 1992, Nicholson *et al.* 1997, Gutzmer & Beukes 2000, Chang *et al.* 1996).

Due to the relatively limited published chemical information on cryptomelane in the Kalahari Manganese Field, very little is known about this supergene mineral phase. It is the purpose of this study to further enhance the current information on cryptomelane of the Kalahari Manganese Field and its textural relationships with related phases, specifically at the Sebillo mine. In addition, a comparison is made between the Sebillo cryptomelane and examples from the Langdon-annex mine in the Kalahari Manganese Field (Fig. 1A), as well as the neighboring Postmasburg Manganese Field, a discontinuous manganese deposit situated roughly 80 km south of the Kalahari Manganese Field (Gutzmer & Beukes 1997b). It can be noted that while the manganese ore from the Sebillo and Langdon-annex mines share a common depositional origin within the Kalahari Manganese Field, the manganese ore from the Postmasburg Manganese Field is sourced from residually enriched dolomite.

The occurrence of hausmannite has been well documented in several KMF-related studies (Kleyenstüber 1985, 1993, Beukes *et al.* 1995, Gutzmer 1993, 1996, Gutzmer & Beukes, 1995, 1996, 1997a, 1998); however, until now the occurrence of hausmannite concretions or “ovoids” included within supergene mineral assemblages and related ore directly below the Kalahari unconformity has not been analyzed in detail. In addition to enhancing the limited information on the KMF supergene mineral phases, cryptomelane and todorokite in particular, it is

hoped that by analyzing hausmannite ovoids included within the cryptomelane-todorokite assemblage this study will provide important information on how this typically diagenetic oxide of the low-grade manganese ore was affected by descending meteoric fluids. Based on textural relationships, we report the sequence of formation of cryptomelane and todorokite within the supergene environment at the Sebillo mine in the southern KMF, South Africa.

GEOLOGICAL SETTING

The Sebillo mine is one of several open cast manganese mines currently exploiting the lower manganese ore bed of the Paleoproterozoic Hotazel Formation of the Transvaal Supergroup in the Northern Cape province, South Africa (Fig. 1A), a chemosedimentary sequence of three manganese ore beds intercalated with a banded iron formation (Nel *et al.* 1986). The majority of the approximately 20–40 m thick lower ore bed at Sebillo is transected by the Kalahari unconformity, placing a large portion of the exploited ore within the so-called “zone of supergene alteration” (Fig. 1B). This zone is an approximately 2–8 m thick zone of brecciated, supergene-altered manganese ore that is void of any significant diagenetic carbonate minerals and with little to no diagenetic manganese oxide compounds (Nel *et al.* 1986, Du Plooy 2002). The ore is cemented by pink to white calcrete with abundant bedding-parallel fractures filled with calcite and/or chalcedony crystals and Mn-oxyhydroxide aggregates. With depth, the calcrete, calcite, and oxyhydroxides dissipate and the ore reverts into typical low-grade carbonated ore, the bulk product of the mine (Fig. 1B). Locally, the ore bed exhibits undulations and an overall dip of around 6–9° to the west. There are two major types of manganese ore currently mined in the KMF (Fig. 1A), the northern hydrothermally enriched, high-grade Wessels type, and the southern low-grade diagenetic Mamatwan-type manganese ores (Kleyenstüber 1984, Gutzmer & Beukes 1995, Fig. 1A), the latter of which is being mined at Sebillo (Fig. 1B).

PETROGRAPHY AND CRYSTAL MORPHOLOGY

From the zone of supergene alteration directly below the Kalahari unconformity, an approximately 30-cm long, 6-cm thick visually altered hand sample was selected (Fig. 2). Macroscopically, the hand sample comprises an inhomogeneous mixture of closely compacted acicular cryptomelane and todorokite crystals (Fig. 2) that developed approximately perpendicular to the ore-fracture plane. The cryptomelane exhibits a metallic silvery-black luster which alternates with dull, matte-black todorokite. During

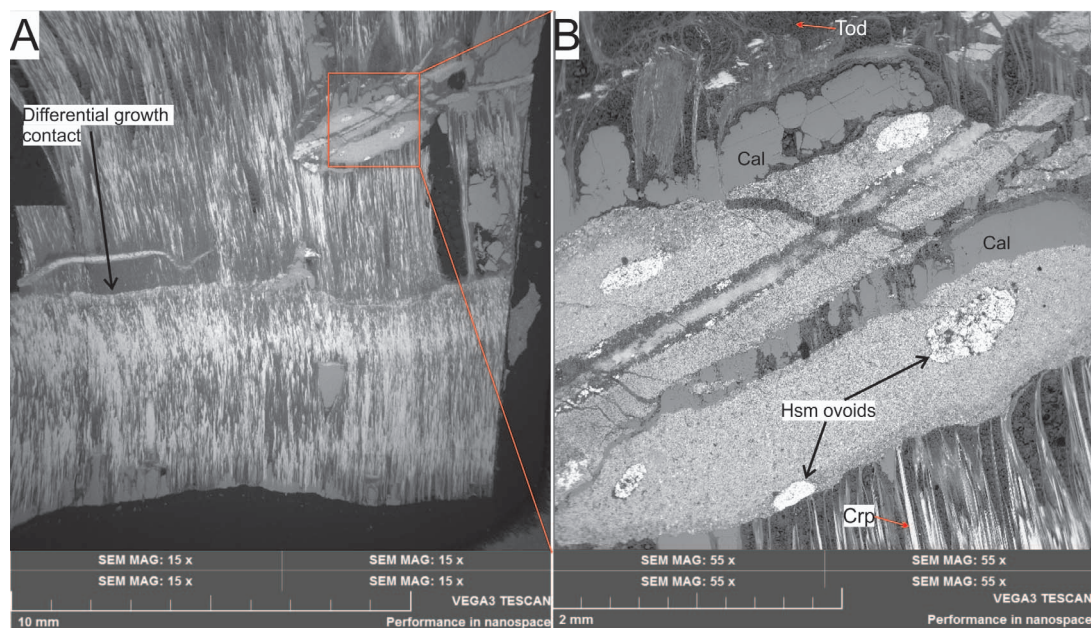


FIG. 3. (A) BSE image showing the compaction contact resulting from the bi-directional growth pattern of the bright white cryptomelane (Crp) and the dull-grey matrix-forming todorokite (tod). (B) A higher magnification BSE image of the remnant diagenetic manganese ore fragment, indicated with a red box in (A), illustrates the preserved hausmannite (hsm) ovoids that developed. Coarse, supergene-related calcite (Cal) developed along the boundaries of the remnant ore fragments.

polishing, the minerals' respective hardness becomes apparent, with todorokite being particularly soft; while cryptomelane polishes to a glossy, smooth surface, todorokite is unable to attain the same finish. Abundant roughly 1-cm cubic calcite crystals that precipitate from gradually alkalizing, descending meteoric fluids occur along the exterior surface and within fractures in the hand sample.

The observable growth pattern of cryptomelane-todorokite within the hand sample occurs in two directions, namely from the base-substrate upwards and from the overhanging-substrate downwards (Fig. 2). Upon converging in the center of the fracture, these bi-directional growth patterns effectively "collide", creating a clear compaction boundary in the fracture (Fig. 3A). There are a number of preserved, earlier-formed, remnant diagenetic manganese ore fragments that appear as though "suspended" in the cryptomelane-todorokite mineral assemblage. These ore fragments comprise a mixture of iron and manganese oxides, predominantly hematite and hausmannite, and contain a number of pre-supergene alteration, diagenetically formed ovoids (Fig. 3B; Gutzmer & Beukes 1996). These ovoids consist almost entirely of hausmannite, a common replacement manganese oxide

mineral that develops through diagenetic and hydrothermal processes (Gutzmer 1996, Gutzmer & Beukes 1997a, Chetty 2008, Vafeas 2016), exhibiting only a few remnant inclusions of the original diagenetic carbonate (Gutzmer 1996). Using backscattered electron (BSE) imagery, the outer margins of the ore fragments were seen in places to exhibit a slightly duller color than the interior. This is likely attributed to the continued replacement of the ore to accommodate the formation of higher-order manganese phases.

The cryptomelane in the present study occurs in two forms: large, single needle-like crystals measuring up to 120 μm in diameter (Fig. 4A) and masses of fine, tightly packed, parallel crystals with each individual crystal measuring approximately 0.5 to 2 μm in diameter (Fig. 4B). Both these cryptomelane occurrences measure up to several centimeters in length, with the finer-grained (~ 0.5 μm) cryptomelane syntactically overgrowing the coarser-grained (120 μm) variant. The thin (~ 0.5 μm) crystals are generally aggregated into thick 200 μm bunches, while the thick crystals are visible as individual crystals.

Todorokite below the Kalahari unconformity within the supergene alteration zone has a fibrous, dendritic texture and exhibits a high porosity, within which

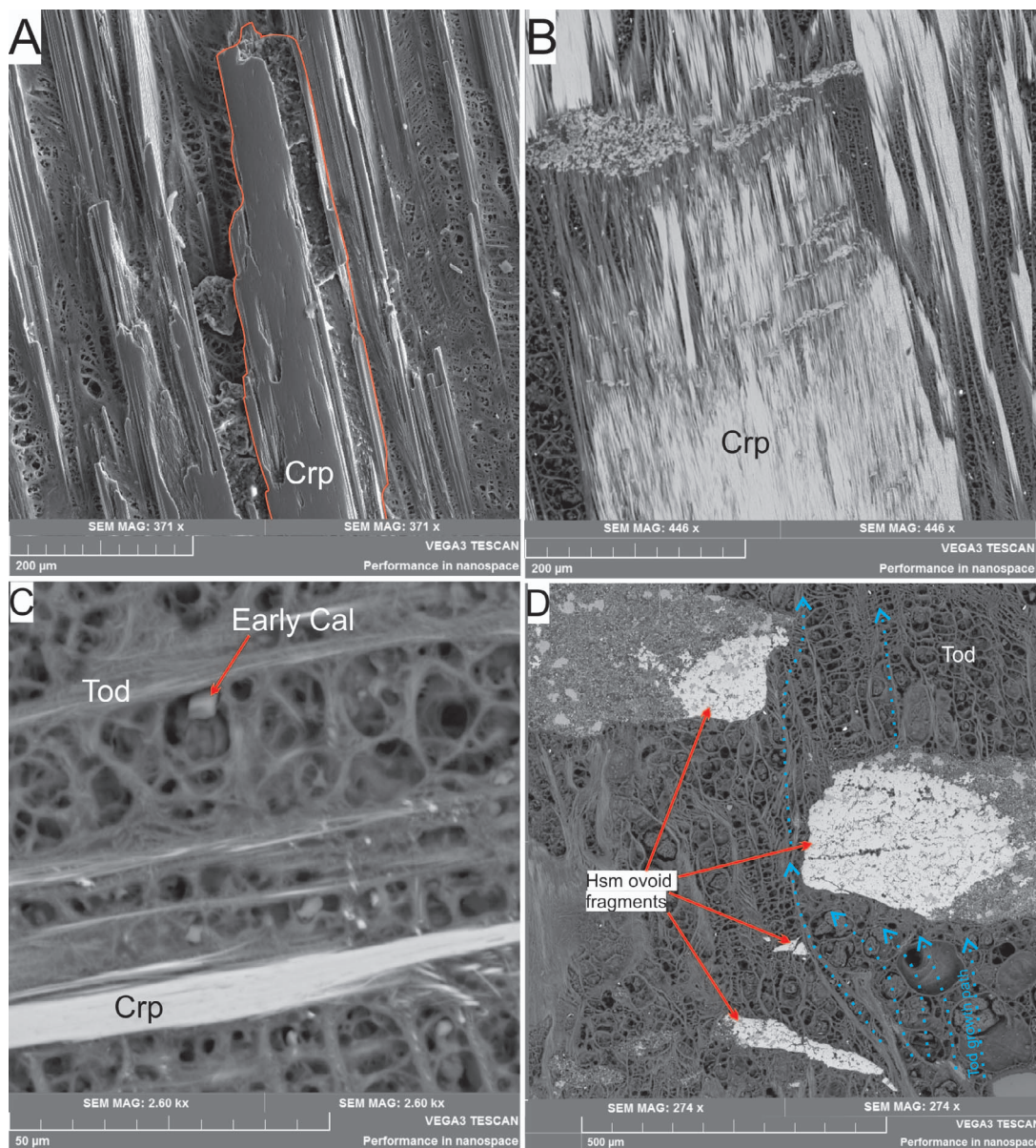


FIG. 4. (A) Secondary electron (SE) image of a single, large cryptomelane (Crp) crystal measuring approximately 120 μm in cross section. (B) A BSE image of a single mass of thin, bundled cryptomelane crystals, each measuring approximately 0.5 to 2 μm in cross section. (C) High-magnification image of the dull-grey todorokite (tod) matrix exhibiting abundant porosity with early calcite developed within the pores. (D) BSE image showing the unidirectional growth pattern of the todorokite between the ovoidal fragments. The blue arrows illustrate the average growth direction of the todorokite.

numerous, small, supergene-related calcite crystals are observed (Fig. 4C). It is interesting to note that, unlike other todorokite-bearing examples from the Smartt mine (Gutzmer & Beukes 2000), pyrolusite was not detected in the Sebilu mineral assemblage.

Microscopically, todorokite growth occurs unidirectionally away from the sourced substrate in an overall upward direction (Fig. 4D). The growth of todorokite between hausmannite-replaced ovoidal fragments has effectively sutured the ovoidal fragments

together in a manner that corresponds to the growth direction of the todorokite (Fig. 4D). The apparent growth direction of the todorokite crystals is seen to redirect around pre-existing ore fragments (Fig. 4D), possibly resulting in slightly denser fiber growth trajectory. The deviated growth trajectory is indicated by the blue arrows in Figure 4D.

The sample appears to contain two generations of calcite: early formed small calcite crystals enclosed within todorokite pores (early calcite; Fig. 4C) and coarser-grained calcite that appears to be restricted to growth along fractures and boundaries of the remnant diagenetic manganese ore fragments (late calcite; Fig. 5A and B). South of Sebilo at the Smartt mine (Fig. 1A), the formation of todorokite was described to post-date manjiroite and coincide with the growth of calcite and chalcodony (Gutzmer & Beukes 2000). Unlike the relationship between todorokite and manjiroite from the Smartt mine, in the present study the textural relationships suggest that the todorokite formed initially at the expense of the original diagenetic manganese ore prior to the development of cryptomelane and late calcite (Fig. 5A and B).

As Gutzmer & Beukes (2000) suggested, development of todorokite coincided with the formation of early calcite, which developed within pores in the todorokite assemblages. This was followed by development of late calcite along the margins of remnant diagenetic manganese ore fragments, which visually superimposes the todorokite matrix (Fig. 5B and C). The sequence of supergene mineral formation within the supergene-altered zone concluded with the development of cryptomelane, which superimposes on todorokite and deflects around the margins of the remnant diagenetic manganese ore fragments (Fig. 5A) and the late calcite crystals (Fig. 5B).

ANALYTICAL METHODS

An X-ray diffraction (XRD) analysis was undertaken on a small, visually representative piece of the studied hand sample (Fig. 2). Due to the soft character of the hand sample and associated supergene phases, the sample was crushed and hand-ground into a fine (approximately 10–15 μm) powder using an agate mortar and pestle. The sample powder was loaded in a steel (nickel-finish) sample holder using back-loading techniques.

X-ray diffraction analysis was conducted on the hand sample using a Phillips X'Pert PRO diffractometer in the Central Analytical Facility (SPECTRUM) in the Faculty of Science at the University of Johannesburg, in order to confirm the petrographically identified phases. Due to the high iron content, an incident beam monochromator was used to reduce the

scan background. The analysis was conducted using a step size of 0.02° with a scan step time of 196 s between a 2θ angle of 4 and 90° . Measurements were taken using a fixed divergence slit at an ambient temperature of 25°C using a copper (Cu) anode material with generator settings of 40 mA and 40 kV. Upon completion of the XRD scans, interpretation was conducted using PANalytical's Highscore Plus software (Version 4.1). The spectrum background was adjusted manually prior to mineral identification by setting granularity to 22, searching for peaks individually, and stripping the spectrum of second order $K\alpha_2$ peaks.

In addition to mineral identification, a CAMECA SX100 electron microprobe (EMP) in the SPECTRUM facility was utilized to analyze the chemical abundances of six major and one trace element (Table 1) within the hausmannite-rich ovoids. Each spot was analyzed using a spot size of 15 μm , an absorbed current of 10 nA, and an accelerating voltage of 20 kV. Interpretation was done using Peak Sight V. 4.0 software. Analyses were conducted on hausmannite ovoids obtained from two different stratigraphic locations at Sebilo: (1) below the supergene alteration zone using a second collected sample of unaltered, low-grade diagenetic manganese ore, at a depth where supergene phases are no longer present (Loc1); and (2) within the cryptomelane-todorokite-bearing hand sample (Fig. 2) obtained directly below the Kalahari unconformity within the zone of supergene alteration (Loc2; Fig. 1A). The results are tabulated in Table 1.

The EMP analysis conducted on cryptomelane crystals in the Sebilo hand sample utilized identical analytical parameters to those selected for the hausmannite EMP analysis. Table 2 shows the major elemental data obtained from 11 cryptomelane crystals as well as calculated abundances of Mn^{3+} and Mn^{4+} oxides. All minerals and elements present were first confirmed using electron dispersive spectroscopy (EDS) methods prior to the EMP analysis.

RESULTS

X-ray diffractometry

In confirmation of the petrographic findings exhibited in Figures 4 and 5, the analyzed sample was found to be predominantly comprised of a mix of todorokite and cryptomelane with lesser amounts of calcite (Fig. 6). The three greatest-intensity peaks, positioned at 2θ angles of 12.64° , 18.00° , and 28.66° , are due to cryptomelane (Fig. 6). The fourth highest-intensity peak is given by todorokite and is positioned at a 2θ angle of 9.23° (Fig. 6).

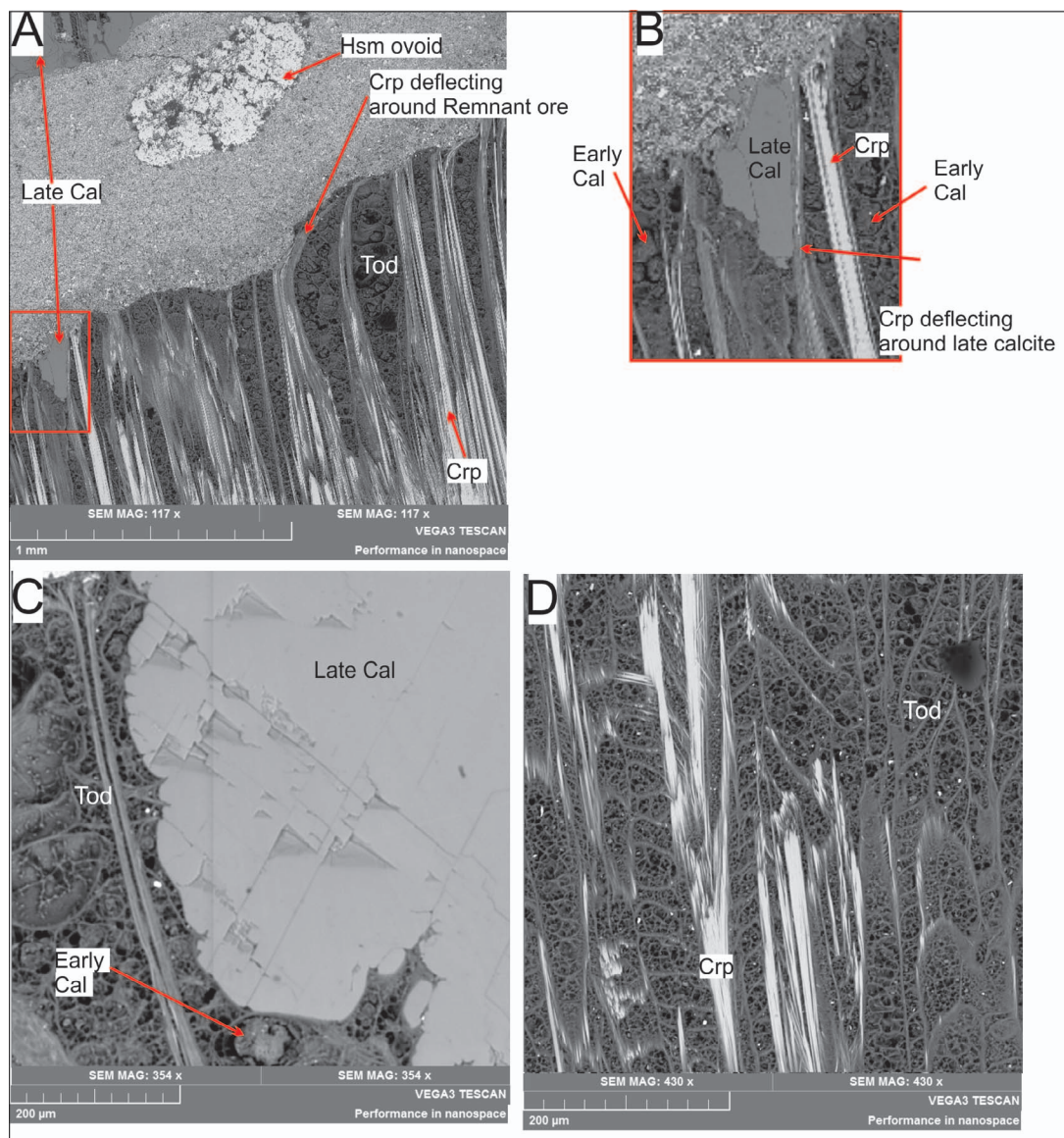


FIG. 5. BSE images depicting the textural relationship between the various mineral phases in the sample. (A) The remnant manganese ore fragment within the sample. The margin of this fragment exhibits a subtle difference in BSE grey scale relative to the rest of the fragment, indicative of marginal alteration of the ore to higher-order Mn phases. A hausmannite (hsm)-replaced ovoid is present within the fragment. Note how the growth of cryptomelane (Crp) deviates around the ore fragments as well as the late calcite fragment. (B) Enlarged image of the late calcite fragment. (C) Development and emplacement of late calcite on top of todorokite (tod). (D) Development of cryptomelane on top of earlier-formed todorokite.

Mineral chemistry

Ovoidal hausmannite from Loc2, sampled from within the supergene altered zone, exhibits an enrichment in Mn_2O_3 and Al_2O_3 and a depletion in

SiO_2 , Fe_2O_3 , CaO , and MgO relative to that from Loc1, from a stratigraphically lower depth (Table 1). CoO appears to remain relatively similar in both locations. Manganese ore in contact with the Kalahari unconformity is typically ferruginized by descending

TABLE 1. ELECTRON MICROPROBE ANALYSIS (wt.%) ILLUSTRATING THE CHEMICAL CHANGE FROM UNALTERED OVOIDAL HAUSMANNITE OCCURRING BELOW THE SUPERGENE ALTERED ZONE IN THE LOW GRADE ORE (Loc1) TO SUPERGENE ALTERED OVOIDAL HAUSMANNITE WITHIN CRYPTOMELANE-TODOROKITE ASSEMBLAGE WITHIN THE SUPERGENE ALTERED ZONE (Loc2) AT THE SEBILO MINE

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Mn ₂ O ₃	MgO	CaO	CoO	Total
Det. Limit (wt.%)	0.02	0.05	0.04	0.03	0.03	0.04	0.03	
Loc1 Hsm1	0.83	0.06	28.09	68.69	0.60	1.71	0.03	99.09
Loc1 Hsm2	0.98	0.05	22.38	74.01	0.31	2.46	0.04	100.27
Loc1 Hsm3	2.42	0.06	36.01	63.88	0.61	0.47	0.05	101.54
Loc1 Hsm4	2.05	0.18	31.20	57.96	0.57	0.62	0.04	98.91
Loc1 Hsm5	0.73	0.05	29.53	67.27	0.33	0.81	0.03	98.76
Loc2 Sup Hsm1	0.01	0.15	3.00	94.98	0.03	0.06	0.03	98.28
Loc2 Sup Hsm2	0.04	0.15	2.91	95.05	0.04	0.07	0.04	98.32
Loc2 Sup Hsm3	0.03	0.23	3.05	95.41	0.00	0.01	0.01	98.74
Loc2 Sup Hsm4	0.02	0.18	2.62	95.93	0.02	0.04	0.00	98.84

Note: A CAMECA SX100 electron microprobe was used for microanalysis. Standards used included diopside (Si), wollastonite (Ca), rhodonite (Mn), almandine (Al), hematite (Fe), olivine (Mg), jadeite (Na), orthoclase (K), and cobalt metal (Co).

fluids, but data in Table 1 indicate a depletion in Fe₂O₃ within the supergene hausmannite (Loc2). The enrichment of iron in the Loc1 hausmannite is likely the result of a closer proximity to the underlying iron formation of the Hotazel Formation compared to Loc2, suggesting that the ore at Loc1 was inherently richer in iron compared to the ore at Loc2. With that stated, however, manganese within the supergene hausmannite (Loc2) is further residually enriched through the leaching of carbonate and silicate compounds. The

inherent lack of significant abundances of Al₂O₃ in the Kalahari manganese ore (Kleyenstüber 1984, Chetty 2008, Gutzmer 1993, 1996, Vafeas 2016), coupled with the relative enrichment of Al₂O₃ in Loc2 compared to Loc1, indicates that the addition of Al₂O₃ into the system is likely the result of clastic material accumulation along the unconformity.

An EMP analysis of cryptomelane from Sebilu exhibits K₂O concentrations several orders of magnitude higher than that of Na₂O, a finding that

TABLE 2. COMPOSITION OF MAJOR ELEMENTS (wt.%) IN THE CRYPTOMELANE SAMPLES FROM THE SEBILO MINE (Seb-1 to Seb-11) COMPARED TO THAT FROM THE POSTMASBURG MANGANESE FIELD (Crp1) AND LANGDON-ANNEX MINE (Crp2)

Sample	Na ₂ O	MgO	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃	Al ₂ O ₃	Mn ₂ O ₃ [*]	Total	Mn ₂ O ₃ ^a	MnO ₂ ^b
Seb-1	1.15	0.04	0.08	4.85	0.39	0.02	0.04	83.70	90.27	12.31	78.62
Seb-2	1.04	0.18	0.09	4.87	0.40	0.00	0.03	83.99	90.60	12.64	78.58
Seb-3	1.15	0.11	0.06	4.95	0.40	0.02	0.04	83.73	90.46	12.78	78.14
Seb-4	1.39	0.06	0.08	5.22	0.30	0.09	0.05	84.27	91.46	13.37	78.09
Seb-5	1.39	0.06	0.09	5.22	0.31	0.07	0.04	83.80	90.98	13.40	77.54
Seb-6	0.93	0.03	0.13	5.80	0.25	0.00	0.05	82.81	90.00	12.91	76.98
Seb-7	0.77	0.02	0.11	6.04	0.20	0.00	0.04	84.13	91.31	12.73	78.64
Seb-8	0.98	0.09	0.10	5.79	0.62	0.00	0.05	83.43	91.06	14.30	76.14
Seb-9	1.06	0.12	0.13	5.75	0.60	0.00	0.03	83.17	90.86	14.50	75.63
Seb-10	1.12	0.10	0.09	5.15	0.31	0.00	0.04	84.25	91.06	12.75	78.75
Seb-11	1.13	0.41	0.09	4.39	0.67	0.00	0.03	82.72	89.44	13.73	75.98
Crp1	0.45	0.27	0.52	5.42	0.17	0.00	1.33	76.21	84.37		
Crp2	0.13	0.26	0.1	6.96	0.23	2.63	0.4	75.89	86.9		

Note: Crp1 and Crp2 comprise data obtained for cryptomelane from the Postmasburg area (Gutzmer & Beukes 1997b) and Langdon-annex mine in the Kalahari Manganese Field (Kleyenstüber 1985) respectively. Mn₂O₃^{*} = total manganese expressed as Mn₂O₃. Mn₂O₃^a and MnO₂^b are the split results of Mn(III) and Mn(IV) respectively. Analytical standards and instrument parameters remained the same as described in Table 1.

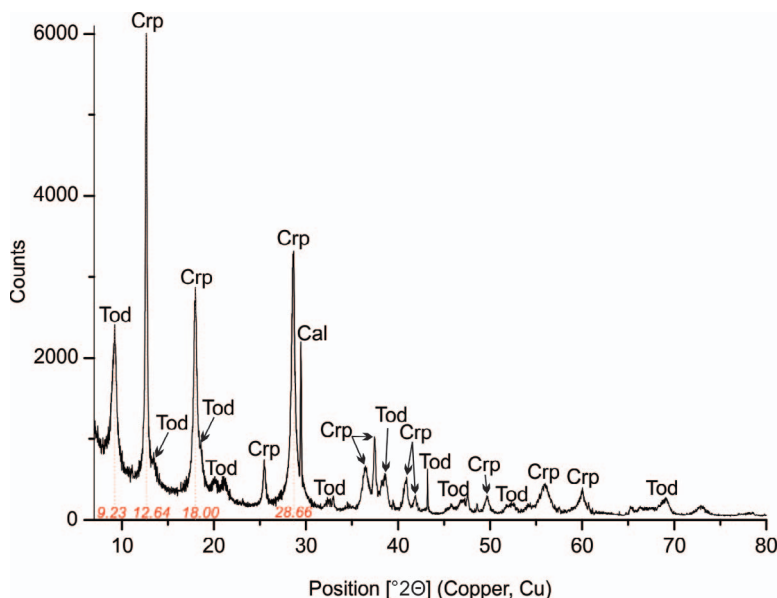
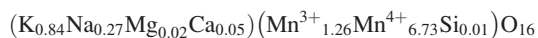


FIG. 6. X-ray diffraction spectrum of todorokite and cryptomelane from the hand sample obtained from the Sebilu mine. Peak positions for the four largest peaks are indicated in red.

corresponds to cryptomelane examples from the neighboring Postmasburg Manganese Field (Gutzmer & Beukes 1997b) and Langdon-annex mine (Kleyenstüber 1985; Table 2). Similarly, concentrations of Mn_2O_3 from the Sebilu cryptomelane correlate with those from the Postmasburg Manganese Field and Langdon-Annex mine, ranging between approximately 84 and 91 wt.% (Table 2, Fig. 7). In general, concentrations of Fe_2O_3 are low to non-existent in cryptomelane from Sebilu, corresponding to Fe_2O_3 concentrations from the Postmasburg Manganese Field. In contrast to this, cryptomelane from the Langdon-annex mine exhibits significantly higher Fe_2O_3 abundances (Fig. 7). The residual nature of the Postmasburg Manganese Field accounts for the relatively high abundances of SiO_2 in the Postmasburg Manganese Field Cryptomelane (Gutzmer & Beukes 1997b). In addition, cryptomelane from Sebilu exhibits distinctly lower abundances of MgO , SiO_2 , and Al_2O_3 relative to examples from both the Postmasburg Manganese Field and the Langdon-annex mine (Fig. 7).

Based on the ideal endmember formula of $\text{A}^{+}_{1-1.5}[\text{M}^{4+}_7\text{M}^{3+}] \text{O}_{16}$ (Biagioni *et al.* 2012), Mg and Ca were grouped with the A^{+} tunnel cations, *i.e.*, K and Na. Similarly, Mn^{3+} and Mn^{4+} occupy the M^{4+} valency. Si^{4+} has been grouped with Mn^{3+} and Mn^{4+} in the M^{4+} valency. Fe^{3+} and Al^{3+} would generally occupy the M^{3+} valency, but the observed concentra-

tions of Fe_2O_3 and Al_2O_3 are negligible (Table 2) and thus are not included in the empirical formula. Lastly, cryptomelane is typically an anhydrous variant of the hollandite group, with water having no crucial role within the tunnels (Frenzel 1980, Kleyenstüber 1985, Biagioni *et al.* 2012); therefore, water is omitted from the general formula. As the formula suggests, the manganese within cryptomelane exists in two valence states, trivalent and tetravalent. Based on the assumption that the averaged sum of Mn^{3+} and Mn^{4+} oxides equate to the total averaged manganese content within the analyzed cryptomelane (Table 2), coupled with an M:O ratio of 8:16 as stated by the general formula for cryptomelane, Mn^{3+} and Mn^{4+} were split on the assumption of 32 positive charges. The mineral formula is thus approximately as follows:



CONCLUSION

The descent of meteoric water through the manganese ore directly below the Kalahari unconformity within the supergene altered zone resulted in the leaching of Ca, Mg, and Si from the original manganese ore. This led to a significant residual increase in the manganese grade of the ore, a finding consistent with previous studies in the area (Du Plooy 2002, Kleyenstüber 1993). The mobile elements that

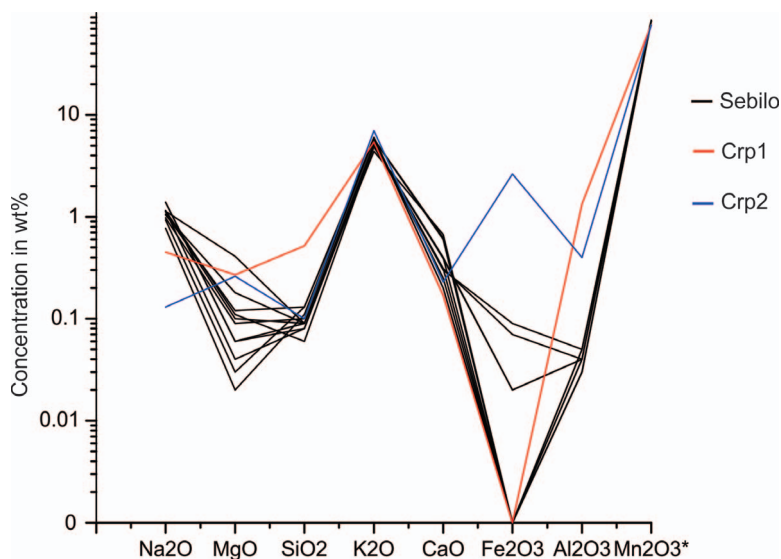


FIG. 7. EMP data for the 11 cryptomelane crystals obtained from a hand sample within the supergene alteration zone at the Sebilo mine compared to examples of cryptomelane from the Postmasburg Manganese Field (Crp1) and the Langdon-annex mine (Crp2).

were leached by the descending meteoric fluids, including Na^+ , K^+ , Ca^{2+} , and Mg^{2+} (Gutzmer & Beukes 2000) formed important constituents in the development of rare Mn-oxyhydroxide supergene minerals, including todorokite and uniquely coarse acicular cryptomelane.

Similar to that previously described by Gutzmer & Beukes (2000) for the formation of todorokite and manjiroite at the Smartt mine, south of Sebilo, alkali fluids, bearing dissolved K and Na, infiltrated bedding-parallel fractures in the original Mamatwan-type manganese ore at Sebilo. The manganese ore acted

as a reservoir for Ca, Mg, Fe, CO_2 , Mn^{3+} , and Mn^{2+} (Stage 1 in Fig. 8).

The alkali fluids leached the above elements and compounds from the primary manganese ore. This is confirmed through an EMP analysis of the pre-supergene altered hausmannite ovoids within the cryptomelane-todorokite assemblage that indicates the removal of carbonates and silicates from the primary manganese ore. These leached elements contributed to the overall abundance of Ca and Mg within the alkali fluids, aiding in the development of todorokite and early calcite (Stage 2 in Fig. 8). The calcite seen represents two relatively close genera-

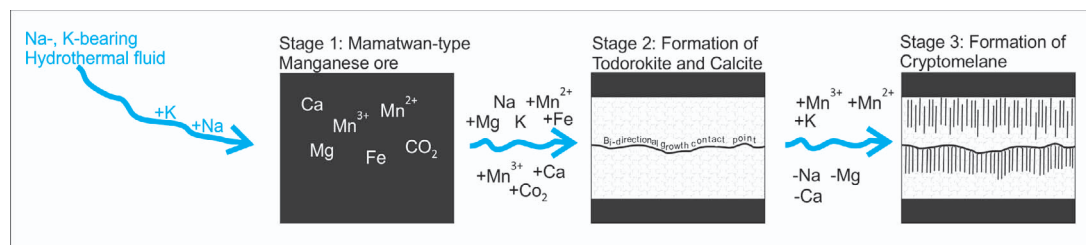


FIG. 8. Flow chart illustrating the mechanism and sequence for cryptomelane-todorokite mineral assemblage development in the supergene-altered zone below the Kalahari unconformity in the Kalahari Manganese Field. Stage 1: Alkali fluids infiltrate bedding-parallel fractures in the original manganese ore (Gutzmer & Beukes 2000). Stage 2: Elements and compounds leached from Stage 1 contribute to the formation of todorokite and calcite. Stage 3: As a result of the formation of these phases, Na, Ca, and Mg are gradually depleted in abundance, leading to a residual enrichment of K and the formation of cryptomelane.

tions, late and early calcite. Early calcite formed simultaneously with todorokite and is represented by small crystals hosted within the many pores in the todorokite assemblages. Late calcite developed subsequent to the formation of the todorokite and only along the boundaries of remnant, pre-supergene, diagenetic manganese ore fragments within the supergene mineral assemblage. This is evident by the emplacement of the late calcite on top of the todorokite (Fig. 5C).

With the depletion of Na, Mg, and Ca during the formation of todorokite, the fluids became residually enriched in K, Mn^{3+} , and Mn^{2+} , leading to the formation of cryptomelane (Stage 3 of Fig. 8) that postdates the development of the late calcite. Extended periods of supergene alteration resulted in multiple generations of cryptomelane within the supergene-altered zone below the Kalahari unconformity, exhibiting younger, finer crystals syntaxially superimposing older, coarser ones. Unlike findings from previous studies (Kleyenstüber 1985, Du Plooy 2002) in which cryptomelane is found as tiny 1 to 3 μm diameter crystals in the Kalahari Manganese Field, cryptomelane crystals at Sebilu measure up to 120 μm across, significantly larger than previously described, a finding that is so far unique to the area. Continued chemical characterization of cryptomelane from other locations, both locally and globally, would greatly benefit our understanding of this mineral's formation and assist in defining area-specific chemical signatures.

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