WEATHERING SEQUENCE AND ALTERATION PRODUCTS IN THE GENESIS OF THE GRASKOP MANGANESE RESIDUA, REPUBLIC OF SOUTH AFRICA

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Abstract—Although numerous, small, manganese oxide deposits associated with dolomite in the Eastern Transvaal escarpment, Republic of South Africa, have been known for many years, their mineralogical make-up is somewhat controversial. Chemical, mineralogical, and morphological properties of the weathering products of dolomite and the coexisting manganese oxide material in the Graskop area were therefore determined. Mn and Fe occur only in minor accessory minerals in the original rock; however, in the weathering residue, these elements are concentrated and occur as separate mineral phases, chiefly birnessite, nsutite, and goethite. Thin veins of pure muscovite and quartz traverse the residua. Rare, pure calcite and maghemite nodules were noted throughout the residual manganese material. The properties of this weathering sequence suggest that the manganese wad deposits were formed in situ as a result of the congruent dissolution of dolomite, leaving a porous, sponge-like structure, highly enriched in Mn and Fe oxides.

Key Words—Birnessite, Dolomite, Infrared spectroscopy, Manganese, Nsutite, Petrography, Wad, Weathering, X-ray powder diffraction.

INTRODUCTION

The existence of numerous, mainly small, manganese oxide deposits associated with dolomite (so-called “manganese wads”) in the Eastern Transvaal escarpment has been known for many years. The largest and probably best-known of these occurs in the Graskop area (lat. 24°56'S; long. 30°50'E), which has a mean annual rainfall of 1800 mm. On the basis of X-ray powder diffraction (XRD) analysis alone, De Waal and Hiemstra (1966) stated that the main constituent of this deposit is cryptomelane. In the present work, preliminary selective dissolution studies showed that the potassium was linked to aluminum silicate minerals and not to the manganese and that the manganese was present almost entirely in a dioxide form (evolution of Cl with warm HCl; a near violent reaction with 30% H2O2). A small particle size and structural disorder are characteristic of many manganese oxides and oxyhydroxides, making them difficult to identify by XRD alone. In the present paper, the morphology, chemistry, and mineralogy of the weathering and alteration products of the parent dolomite rock are described to explain more fully their very high Mn content in relation to the small amount of Mn in the original rock. An attempt is also made to clarify the Mn mineral identification of the Graskop manganese wads. The mineralogy of transecting veins and nodule accumulations is also reported.

SITE AND SAMPLES

The Graskop manganese deposit is located in a steep-sided valley; about 2 m of weathered material has been exposed in a quarry (Figure 1). The heterogeneity of gravels and stones in the solum clearly reflects the colluvial nature of the overlying soils, as is expected in a steep-sided valley. These colluvially transported soils do not contribute directly to the genesis of the underlying deposits and were not examined in any detail. The manganese residua are black (N 1,5/0), lightweight, and friable, even in the moist state. Parts of the deposits are dense due to compression by overburden, which is shown in some samples by the presence of slickensides. Three samples of the manganese wads from positions progressively farther away from the weathering dolomite rock were analyzed. These positions, 1, 2, and 3, are shown diagrammatically in Figure 1. White veins, differing in hardness and morphology, transect the deposits. Sparse nodules of soft, white material are scattered throughout the deposit. Black, magnetic nodules were also found in the deposit. Samples of the gray, unweathered dolomite rock, the brown, weathering-front material (distinct transition between the rock and the manganese wad, ~1 cm thick), and the black, residual manganese wad were analyzed. Minerals in the veins and nodules, the residue of HCl-treated samples, and the magnetic products of an ignited wad sample were also identified.

EXPERIMENTAL

The samples were examined petrographically. Three samples of the residual manganese material were prepared in water for transmission electron microscopy (TEM). The materials were homogenized in a Sieb mill for 30 s. Carbonates were removed by treating the samples with 1.0 M acetic acid prior to the extractions. Samples were extracted with sodium citrate-bicarbonate-dithionite (CBD) (Mehra and Jackson, 1960) in preparation for infrared analysis. Organically bound
RESULTS AND DISCUSSION

Micromorphology

Figure 2b is a photomicrograph of a thin section of the dolomite rock and the morphologically and texturally different material above it; the transition is indicated by the arrows. The residual manganese material is shown in Figure 2a. Figures 2c, 2d, and 2e are higher magnification micrographs of the residual manganese material, the transitional material (weathering front), and the dolomite, respectively. The weathering front (Figures 2b and 2d), which constitutes a distinct transition between the dolomite and residual manganese material, has a skeletal framework of dolomite which contains dark material inclusions. The high birefringence of the dolomite can be seen under cross-polars, particularly in weathered zones adjacent to areas of dark Fe-Mn oxides. In Figures 2a and 2c, the dolomite rock appears to be completely altered, and only a porous, spongy microstructure of fine-grained, optically isotropic, manganiferous material is left. The original dolomite has apparently been “replaced” by a skeletal framework with a large amount of pore space. No downward migration or reprecipitation of migrating manganese was observed. A few quartz grains are scattered throughout the fabric.

Some of the most important factors contributing to the weathering patterns of minerals are their crystallographic properties (e.g., cleavage) and chemical composition. The dolomite rock (Figures 2b and 2e) contains fine, intergranular, contact microcracks, fractures, and cleavage planes, which probably were the first conduits for the weathering solution into the rock. During weathering, water presumably flowed into these microcracks and reacted with the dolomite. Weathering proceeded along these planes of weakness by dissolution and removal of dolomite, creating new porosity. The end result seems to be a porous mass of Fe and Mn oxides (Figures 2a and 2e), hence, the very low bulk density of the residual material. No clay minerals were apparently formed from the dolomite.

Chemical composition and mineralogical identification

Table 1 gives the bulk oxide composition of the weathering sequence samples. Mn and Fe occur only in minor amounts in the original rock. The relative decrease in bulk density, established in preliminary analyses, from unweathered rock (2.97 g/cm³) to the manganese oxide residua (average 0.13 g/cm³) is 22.8:1 and is similar to the relative increase in total Mn content of 1:21.5. The removal by leaching of the Ca and Mg carbonates (totaling 80% in the dolomite rock) would give a relative Mn increase of 1:21.5, which is also in close agreement. Figure 3 shows the bulk composition of this sequence plotted on the compositional diagrams CaO-Mgo-MnO and CaO-MnO-Fe₂O₃. The solution of dolomite during weathering leads to the almost complete removal of Mg and Ca and the relative accumulation of Mn and Fe (Table 1, Figure 3). The manganese residua do not appear to be chemically homogeneous, and the Mn (and Fe) concentration varies from one sample to another. The trends, however, are...
very much the same. Interestingly, apart from residue 3, the MnO/Fe$_2$O$_3$ ratio is of similar order (~2.6) (Table 1; Figure 3, straight line), which suggests that the original Mn and Fe in dolomite rock were responsible for the skeletal framework of the manganese wads.

The Al and K contents of the manganese wads suggest the presence of variable amounts of clay minerals. The XRD data of the residue after HCl treatment indicate that the dominant clay mineral is muscovite.

The brittle, white veins consist of almost pure muscovite (10% K$_2$O ≈ 100% muscovite) (Table 1, XRD). The hard, white veins consist of almost pure quartz (99.9% SiO$_2$ ≈ 100% quartz) (Table 1, XRD). The white nodules consist of calcite (46.1% Ca ≈ 100% calcite) (Table 1, XRD), and the magnetic nodules consist of maghemite (80–90%), together with some hematite (XRD). The maghemite and hematite may have formed by slow oxidation and simultaneous dehydra-
Table 1. Total chemical analysis (%) expressed on an air-dried basis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>CaO</th>
<th>K₂O</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>LOI</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite rock</td>
<td>0.65</td>
<td>1.72</td>
<td>29.2</td>
<td>&lt;0.01</td>
<td>0.90</td>
<td>0.14</td>
<td>20.9</td>
<td>46.1</td>
<td>99.6</td>
</tr>
<tr>
<td>Weathering front</td>
<td>1.14</td>
<td>2.75</td>
<td>28.8</td>
<td>&lt;0.01</td>
<td>0.83</td>
<td>0.34</td>
<td>20.5</td>
<td>45.2</td>
<td>99.7</td>
</tr>
<tr>
<td>Manganese residue (1)</td>
<td>10.2</td>
<td>26.5</td>
<td>10.9</td>
<td>&lt;0.01</td>
<td>1.80</td>
<td>10.1</td>
<td>5.62</td>
<td>7.1</td>
<td>98.9</td>
</tr>
<tr>
<td>Manganese residue (2)</td>
<td>10.96</td>
<td>31.58</td>
<td>0.64</td>
<td>1.66</td>
<td>15.6</td>
<td>5.13</td>
<td>0.59</td>
<td>31.4</td>
<td>97.7</td>
</tr>
<tr>
<td>Manganese residue (3)</td>
<td>19.36</td>
<td>37.01</td>
<td>0.06</td>
<td>3.40</td>
<td>15.3</td>
<td>8.43</td>
<td>0.53</td>
<td>12.2</td>
<td>97.0</td>
</tr>
<tr>
<td>Muscovite vein</td>
<td>1.71</td>
<td>0.19</td>
<td>0.04</td>
<td>9.89</td>
<td>48.8</td>
<td>30.0</td>
<td>2.2</td>
<td>5.0</td>
<td>99.0</td>
</tr>
<tr>
<td>Quartz vein</td>
<td>0.09</td>
<td>0.06</td>
<td>0.03</td>
<td>0.02</td>
<td>99.9</td>
<td>0.12</td>
<td>&lt;0.01</td>
<td>0.1</td>
<td>100.3</td>
</tr>
<tr>
<td>Calcite nodules</td>
<td>0.53</td>
<td>0.35</td>
<td>46.1</td>
<td>0.01</td>
<td>4.0</td>
<td>0.45</td>
<td>0.54</td>
<td>43.0</td>
<td>95.3</td>
</tr>
</tbody>
</table>

1 Including minor amounts of P₂O₅, TiO₂, Na₂O, SO₃.

ignition of goethite (Taylor and Schwertmann, 1974). On ignition of the manganese wad material at 1000°C overnight, some separate, Fe- and Mn-rich, magnetic minerals were formed, namely magnetite and partridgeite (Figure 4d). Goethite and maghemite normally convert to hematite on heating >600°–800°C, the conversion temperature being related to the Fe²⁺ content, i.e., higher for more ferrous compositions (Brown, 1980). This may explain the formation of magnetite on ignition instead of hematite; however, the Fe²⁺ content of these samples was not determined. Moreover, the influence of possible Mn substitution in Fe minerals or vice versa can also not be excluded.

XRD lines of the residual manganese minerals in samples 1–3 are broad and relatively indistinct (Figure 4). Samples 1 (Figure 4a) and 2 (Figure 4b) contain different amounts of birnessite (~7.2, 2.46, 2.33 Å) and todorokite (9.69, 4.8 Å), whereas sample 3 (Figure 4c) is essentially nstite (2.44, 2.15, 1.66 Å). Some poorly crystalline goethite is also present (4.18 Å).

In Figure 5, numbers A, B, and C represent IR data for samples 1, 2, and 3, respectively, whereas spectrum a in each case is the difference spectrum of the unextracted sample (spectrum b) and that of the CBD extracted sample (spectrum c, corrected intensity). Potter and Rossman (1979a, 1979b) were the chief source references for the IR band allocations. [The IR spectra were compared with calibrated IR spectra of well-crystallized materials, published by Potter and Rossman (1979a).] The IR bands of the wads are broad and not clearly resolved, indicating disorder. The two intense, poorly resolved bands near 500 cm⁻¹ are characteristic of birnessite and are said to distinguish it from all other manganese oxides, although other bands of birnessite may easily be confused with those of highly disordered todorokite (Potter and Rossman, 1979a). A broad band near 580 cm⁻¹ and weak bands at wavenumbers slightly less than 400 cm⁻¹ indicate nstite (Figure 5C). The spectrum of sample 1 is similar to that of birnessite, but the greater intensity of the major absorption bands, together with XRD evidence, suggests that sample 1 probably consists of a highly disordered todorokite (Figures 4a and 5A). The positions of the weak shoulders at higher wavenumbers (673 cm⁻¹, Figure 5A; 700 cm⁻¹, Figure 5B) also suggest the presence of some birnessite in samples 1 and 2. The distinction between the two minerals by IR analysis is more difficult if the bands are broad and not clearly resolved. The present observations could support Potter and Rossman’s (1979a) suggestion that a continuum exists between the
two minerals. Recent studies of todorokite samples using high-resolution transmission electron microscopy (HRTEM) by Turner and Buseck (1981) and Turner et al. (1982) suggest families of manganese oxide minerals with different end-members. The IR data also preclude cryptomelane identification, for which absorption bands occur at 300 cm$^{-1}$. In all samples, Fe was found to be a major constituent; thus, Fe could have prevented the formation of pure, crystalline Mn structures. Fe-substitution in the structures could have caused the shifted and broad bands of the IR spectra.

Sample 1 (collected immediately above the weathering front) also contains a large amount of dolomite which dilutes the manganese minerals and thus hinders their positive identification. Sample 2 (taken higher in the profile) contains birnessite and a lesser amount of todorokite, whereas sample 3 (taken still further from the weathering front) is essentially nsutite.

Crystal morphology using transmission electron microscopy

Manganese sample 2 consists of chains of small (670 Å), rounded structures which with the help of a hand lens, seems to be made up of concentric rings of particles (arrowed) (Figures 6a and 6b). TEMs of sample 3 (Figures 6c and 6d) show an abundance of muscovite among groups of irregularly shaped particles (nsutite),
Figure 5. Infrared spectra of: (A) manganese oxide sample 1, (B) manganese oxide sample 2, (C) manganese oxide sample 3. a = difference spectrum of b and c (corrected intensity); b = unextracted sample; c = citrate-bicarbonate-dithionite-extracted sample.

Figure 6. Transmission electron micrographs of (a, b) sample 2 (birnessite and todorokite), showing the rounded structures exhibiting a concentric arrangement (arrowed) of minute particles; (c, d) sample 3 (nsutite). Muscovite platelets are indicated by arrows.
which seem more condensed than the spherical particles of birnessite or todorokite (Figures 6c and 6d).

SUMMARY AND CONCLUSIONS
The main factors controlling the distribution and reorganization of Mn in the residual oxide material appear to have been properties of the parent material and the amount of moisture in the soil. Processes of weathering have tended toward an in situ accumulation of soft and porous material. The dolomite seems to have altered by congruent dissolution, thereby diminishing the cores of the original material. Eventually only voids were left, leaving a porous, "sponge-like" structure highly enriched in Mn and Fe.

Under these well-drained, oxidizing conditions, Mn and Fe appear to have been relatively immobile during the stages of weathering. MnO$_2$ concentrations and oxide structures vary with depth and from site to site. From the XRD and IR data, and the fact that only traces of HCl-extractable cations other than Mn were found, these manganese wads appear to be a continuous series of compositions of manganese oxides. Mn and Fe essentially crystallized into separate mineral phases—Mn into a series of manganese oxide compositions within which there were several stable and metastable mineral forms (i.e., nsutite, birnessite, and poorly ordered todorokite) and Fe essentially into goethite. Natural manganese oxides, however concentrated, are difficult to distinguish from each other, even by the most sophisticated techniques. The explanation of the natural accumulation and concentration of Fe in the form of magnetic nodules (maghemite and hematite) has not been attempted.

The accessory minerals, i.e., veins of quartz and muscovite, do not seem to have any direct bearing on the manganese residua development. They were probably formed during another cycle of rock weathering, sediment transportation, and deposition.

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REFERENCES

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