

Rancieite associated with a karstic bauxite deposit

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Abstract

A black deposit formed at the contact between bauxite and underlying limestone near Itéa, Greece, contains nearly pure rancieite. After allowance for small amounts of impurities, the composition is shown to be $(\text{Ca}_{0.65}\text{Mn}_{0.22}^{2+}\text{Mg}_{0.04})\text{O} \cdot 4\text{MnO}_2 \cdot 3.66\text{H}_2\text{O}$. The X-ray powder diagram is indexed with hexagonal parameters, $a = 2.83(4)$, $c = 7.55\text{Å}$. A similar structural unit found in other hydrous manganese oxide minerals suggests that rancieite contains Mn–O octahedral sheets interlayered by Ca, Mn^{2+} ions and water molecules. The rapid weight loss from 25° to 300°C corresponds to the loss of molecular water, and X-ray data show collapse of the (001) spacing from 7.55 to about 5.3Å. The high-temperature phases include Mn_3O_4 and CaMn_2O_4 , but other non-identified phases also occur; consequently the loss of oxygen in these reactions cannot be calculated precisely, but an estimated value agrees reasonably with the thermogravimetric analysis.

Introduction

Petrographic and mineralogic studies of karstic bauxites in the Parnassós area of Greece (Bardossy and Mack, 1967) have noted the occurrence of manganese minerals, mainly lithiophorite sometimes accompanied by todorokite, at contacts between the bauxite and the underlying limestone. Cryptomelane and groutite occurred rarely and psilomelane and pyrolusite were not found.

The present study is concerned with a less well-known mineral, rancieite, in a bauxite mine about 4 km NW of Itéa in the same area of Greece. The field relations are illustrated in Figure 1. A light-gray stratified Titonian limestone rests on a red bauxite (the so-called Middle Bauxite horizon) which in turn rests on a massive white Kimmeridgian limestone with a karstified surface. A 10–20 cm thick dark-gray to black crust covers the limestone surface, with a fairly quick transition into pink bauxite. The main bauxite body is dark red and has a boehmite-hematite composition with smaller amounts of diaspore, kaolinite, anatase, and rutile. Calcite-filled fissures a few mm wide occur in the lower part of the bauxite.

It appears that the dark-colored Mn-rich crusts were formed by precipitation when downward-moving acid solutions containing manganese dissolved from the bauxite encountered the underlying limestone. Rancieite, which contains CaO as a component, is formed during precipitation in the presence of Ca ions. The occurrence of nearly pure rancieite provides an opportunity for further study of this mineral.

Mineral analysis of Mn-crust materials

Four samples of dark-colored Mn-crust materials have been examined with the following results:

Dark-gray, almost black crust: This material, taken from a depression in the karstified surface, consists dominantly of rancieite, as shown by chemical and X-ray data given later. Material with a peculiar glossy, almost metallic silvery appearance is nearly pure rancieite. A trace of lithiophorite may be present; it is indicated by its strongest X-ray reflections, which match those where lithiophorite is present in larger amounts, and by a trace of Li_2O in the chemical analysis.

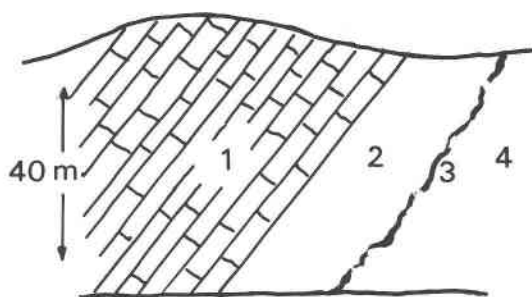


Fig. 1. Sketch of bauxite mine, near Itéa, Greece; (1) light-gray stratified limestone; (2) red bauxite; (3) black manganese-rich crust; (4) massive white limestone.

Brownish-gray crust: Rancieite and lithiophorite are the main components together with some gibbsite, goethite, and calcite.

Brownish-gray crust, transition into bauxite: Boehmite is dominant in a complex mixture containing lithiophorite, kaolinite, gibbsite, and other components.

Dark brownish-gray crust, with small nests of gibbsite: Gibbsite is dominant, with important amounts of rancieite and lithiophorite; calcite and other components also occur. Along with rancieite, lithiophorite, gibbsite, goethite, and calcite are of secondary origin.

Rancieite

Chemical analysis

Table 1 summarizes the chemical analysis of a rancieite-rich sample. The analysis was made by conventional wet-analytical methods. For each measurement 1 g of powdered material was used. The MnO_2 content was determined by the well-known iodometric method in the presence of KF. Each determination was repeated and averages taken. The ignition loss of the material from normal temperature to $1030^\circ C$, not shown in Table 1, was measured as 21.72 and 21.3 percent (G.B.) and 20.4 percent (G.W.B., estimated from the thermogravimetric curve shown in Fig. 2). The weight percent H_2O of the sample is derived from the ignition loss of 21.72 percent with allowance for loss of oxygen, $MnO_2 \rightarrow Mn_3O_4$ (weight loss 7.95 percent), gain of oxygen, $MnO \rightarrow Mn_3O_4$ (weight gain 0.22 percent), and CO_2 loss (0.3 percent). The weight percent H_2O is then $21.72 - 7.95 + 0.22 - 0.30 = 13.69$ percent.

The 0.7 percent SiO_2 , together with 0.60 percent Al_2O_3 and 0.21 percent H_2O , is attributed to 1.50 percent kaolinite. The remaining Al_2O_3 and the Fe_2O_3

Table 1. Total chemical analysis* of rancieite sample and derivation of rancieite composition

| | | | | Relative moles | |
|-----------|-------|-----------|-------|----------------|------|
| MnO_2 | 64.8% | MnO_2 | 64.8% | MnO_2 | 4.00 |
| SiO_2 | 0.7 | MnO | 3.0 | MnO | 0.22 |
| Al_2O_3 | 5.6 | CaO | 5.7 | CaO | 0.55 |
| Fe_2O_3 | 2.9 | MgO | 0.32 | MgO | 0.04 |
| CaO | 6.1 | H_2O | 12.3 | H_2O | 3.66 |
| MnO | 3.0 | boehmite | 5.9 | | |
| MgO | 0.32 | goethite | 3.2 | | |
| H_2O | 13.69 | kaolinite | 1.5 | | |
| TiO_2 | 0.01 | calcite | 0.7 | | |
| CO_2 | 0.3 | K_2O | 0.12 | | |
| K_2O | 0.12 | Na_2O | 0.11 | | |
| Na_2O | 0.11 | TiO_2 | 0.01 | | |
| SrO | trace | | | | |
| Total | 97.65 | Total | 97.66 | | |

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are attributed to the respective monohydrates, and require 1.21 percent H_2O . The weight percent H_2O attributed to rancieite is $13.69 - 1.21 - 0.21 = 12.27$ percent. The 0.3 percent CO_2 is attributed to 0.7 percent calcite. No specific allocation is made of the K_2O and Na_2O , both of which are small items.

With the results as set out in Table 1, the composition of the rancieite is $(Ca_{0.55}Mn_{0.22}^{2+}Mg_{0.04})O \cdot 4MnO_2 \cdot 3.66H_2O$. The total RO is 0.81. This composition comes close to that of rancieite from Cuba given by Richmond *et al.* (1969): $(Ca_{0.73}Mn_{0.21})O \cdot 4MnO_2 \cdot 3.25H_2O$, with total RO = 0.93.

Thermal analysis

The results of thermal analysis by thermogravimetric (TG) measurements and by differential thermal

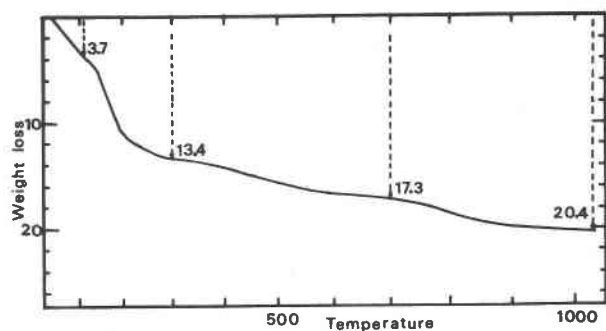


Fig. 2. Thermogravimetric curve of rancieite, $5^\circ C/min$. Weight loss as percentage of weight at $25^\circ C$, temperature $^\circ C$.

analysis (DTA) and differential thermogravimetric analysis (DTG) are shown in Figures 2 and 3. The total weight loss, 20.4 percent, shown in Figure 2 is close to that listed in the chemical analysis, 21.7 percent. The difference is attributed to different humidity conditions and/or different particle sizes of the material in these wholly independent determinations.

The differential curves in Figure 3 indicate five main reactions at or near 100°, 270°, 420°, 620–650°, and 1030°C. The two higher-temperature reactions are probably due to loss of oxygen (see later) and are shown more clearly by the DTG than the DTA curve. The three lower-temperature reactions are due to loss of water. The DTG curve below 200°C showed large fluctuations associated with the rapid loss of weight (water) in the 100–200°C range, which are off the scale of Figure 3.

The weight loss shown in Figure 2 can be divided into four stages as follows:

| | |
|------------------------------|---------|
| 20–110°C, weight loss 3.7% | } 13.4% |
| 110–300°C, weight loss 9.7% | |
| 300–700°C, weight loss 3.9% | } 7.0% |
| 700–1050°C, weight loss 3.1% | |

The combined loss from 20–300°C correlates well with the 13.7 percent of H₂O in the rancieite and associated impurities. The combined weight loss from 300–1050°C, 7.0 percent, is close to the calculated net loss of oxygen, 7.7 percent. A discrepancy between the temperature ranges in which water is lost in the thermogravimetric recording and the lower-temperature peaks in the DTG and DTA curves can be related partly to a slower heating rate, 5°C/min, for the TG curve is compared with 10°C/min for the differential curves, and possibly other experimental factors.

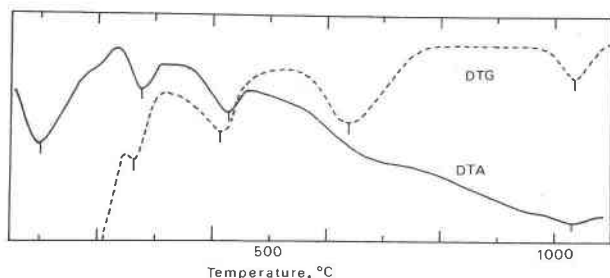


Fig. 3. DTA curve of rancieite recorded at 10°C/min. Peak temperatures marked on the curve are 104°, 272°, 428°, and 1030°C; a broad peak occurs near 680°C. DTG curve recorded at 10°C/min. Peak temperatures at 264°, 416°, 640°, and 1030°C.

These results for rancieite are broadly consistent with results for other manganese minerals. Pyrolusite (β -MnO₂) gives endothermic DTA peaks at 650–700°C and 950–1050°C, the latter a smaller peak, which are associated respectively with the formation of Mn₂O₃ and Mn₃O₄ (Kulp and Perfetti, 1950). X-ray data for rancieite given later show similar high-temperature reactions. The DTA and DTG data of Figure 3 indicate that water is lost in several stages and the peak near 400°C probably arises from a dehydroxylation reaction. Manganite, γ -MnO(OH), shows an endotherm near 400°C (Kulp and Perfetti, 1950) and groutite, α -MnO(OH), transforms to pyrolusite at 300°C under static heating (Lima-de-Faria and Lopes-Vieira, 1964).

X-ray powder diffraction analysis

Table 2 records X-ray powder diffraction data taken with Ni-filtered CuK α radiation, recorded at 1°(2 θ)/min. Only two reflections stand out prominently with $d = 7.56$ and 3.77Å. Other reflections are broad and cannot be located with higher accuracy than about ± 0.01 Å. The results agree generally with those of Richmond *et al.* (1969), particularly their data for rancieite from Cuba. When rancieite is dispersed in water by ultrasonic vibration and allowed to dry on a glass slide, the 7.56 and 3.77Å reflections are greatly enhanced but higher orders are still not observed. The powder pattern for rancieite has not been indexed previously, but by comparison with data for other hydrated manganese oxides is readily indexed with hexagonal parameters $a = 2.83(4)$ and c

Table 2. X-ray powder data for rancieite

| Observed (1) present data d, Å | I | Calculated (2) d, Å | hkl | Observed (3) Richmond, et al., (1969) d, Å | I |
|--------------------------------------|-----|------------------------|-----|---|----|
| 9.4 L | 10 | — | — | — | — |
| 7.56 | 100 | 7.55 | 001 | 7.57 | s |
| 4.75 vb, L | 7 | — | — | — | — |
| 3.77 | 20 | 3.775 | 002 | 3.77 | m |
| 2.46 b | 12 | 2.454 | 100 | 2.46 | mw |
| 2.35 vb | 10 | 2.334 | 101 | 2.34 | m |
| 2.06 vb | 10 | 2.058 | 102 | 2.06 | m |
| 1.76 vb | 8 | 1.757 | 103 | 1.76 | m |
| — | — | 1.496 | 104 | — | — |
| 1.42 vb | 7 | 1.417 | 110 | 1.423 | m |
| 1.40 vb | 5 | 1.393 | 111 | — | — |

(1) Sample from Itéa, Greece

(2) Hexagonal parameters, $a = 2.834$, $c = 7.55$ Å.

(3) Sample from Oriente Prov., Cuba.

L = lithiophorite reflections

v = very, b = broad, s = strong, m = medium, w = weak

= 7.55Å. The calculated spacings and *hkl* indices are given in Table 2. The strong 001 and 002 reflections which are enhanced by preferential orientation and the poorly-defined other reflections are consistent with a layer structure with poorly-ordered stacking of the layers.

The results suggest that rancieite belongs to a group of layer-type structures formed by Mn–O or Mn–O,(OH) octahedral sheets with various cations and water molecules between the sheets which Giovanoli (1969) referred to as "the birnessite family." Burns and Burns (1977) have summarized available data under the heading "The birnessite problem." A common feature is a hexagonal or pseudo-hexagonal unit with $a \approx 2.85\text{Å}$, which corresponds to a close-packed sheet of Mn–O octahedra. The *c* spacing, around 6.9–7.6Å, corresponds to the spacing of these sheets with various cations and water molecules between them.

Thermal tests on rancieite gave interesting results. After an overnight treatment at 140°C, the strong (001) basal reflection was greatly reduced and with subsequent heatings to 300°C was eliminated completely. During this process a reflection at about 5.3Å appeared, very broad after 200° heating, becoming stronger and sharper up to about 370°, and then diminishing and finally disappearing at about 700°C. Other reflections were not improved by the heat treatment. The collapse of *d*(001) from 7.56 to about 5.3Å by heating to 370°C clearly corresponds to a loss of water in this range of temperature. The spacing change from 7.56 to 5.3Å is less than corresponds to a similar loss of water from smectites, but interlayer cations also may be involved.

The X-ray pattern of rancieite heated at 700° is consistent with a loss of oxygen, showing the reflections of hausmannite, Mn₃O₄, and possibly of marokite, CaMn₂O₄, both of which are seen more clearly after heating the sample to 1000°C. Other reflections, not so far identified, are also seen in the diffraction patterns of material heated to 1000°C

Scanning electron micrographs

Figures 4a, b, c show scanning electron micrographs of rancieite at progressively higher magnifications. The platy character is clearly evident, the surfaces of the plates being (001) planes. The individual particles appear to be mainly of about 1μm or smaller, but larger plates and aggregates also occur. In several places, small rod-shaped crystals are seen on the surfaces of the aggregates and are probably

boehmite crystals. Figure 4d shows a particularly clear group of these particles.

Discussion

A major difficulty in describing minerals such as rancieite and most naturally-occurring birnessites lies in the very poor quality of their X-ray diagrams. The only well-defined reflections are 001 and 002, which probably correspond to a layer separation determined by interlayer cations, water molecules, and perhaps hydroxyl ions. Burns and Burns (1977) summarize X-ray powder data by different investigators for several natural birnessites from different localities and of these, five give only four diffractions and one gives only three diffractions with spacings 7.24–7.37, 3.55–3.69, 2.40–2.46, and 1.41–1.42Å. These values correspond with the 001, 002, 100, and 110 reflections recorded here for rancieite. Evidently rancieite has a *c* parameter larger than the values for birnessites.

Chemically, rancieite has Ca²⁺ as the main cation other than Mn⁴⁺. Birnessite from the type locality (Jones and Milne, 1956) contains Na_{0.40}Ca_{0.17} on the basis of 4MnO₂. Takanelite, discussed by Nambu and Tanida (1971), gives the same diffraction pattern as rancieite with a strong 7.57Å reflection and contains the cations (Mn_{0.89}Ca_{0.23}Mg_{0.03}) relative to 4MnO₂.

From these considerations, the question arises whether a single mineral name can be used for all these materials, prefixed appropriately to indicate the cations other than Mn⁴⁺. The situation may be analogous to Na–montmorillonite, Ca–montmorillonite, *etc.* The name rancieite then deserves careful consideration as the group name, for although rancieite has received less publicity in recent years than birnessite, it is a much older mineral name. It appears to have originated with Leymerie (1859) in his "Cours de Minéralogie", II, p. 329, and was discussed by Lacroix (1910) in his "Minéralogie de la France", vol. 4, pp. 24–26. Fleischer and Richmond (1943) gave chemical and X-ray data and considered rancieite "to be an independent species," and subsequently Richmond *et al.* (1969) amplified the data. Hendricks and Laird (1943) and Sorem and Gunn (1967) recognized rancieite as an important and common secondary mineral manganese. Perseil (1967) studied rancieite from the type locality, Rancié, France. Over a period of a century the name has been spelled in slightly different ways, but the only recent variation is the use of é, or e without accent. The type locality and the pronunciation are indicated more clearly by é, but e without accent is simpler to use. Further study of

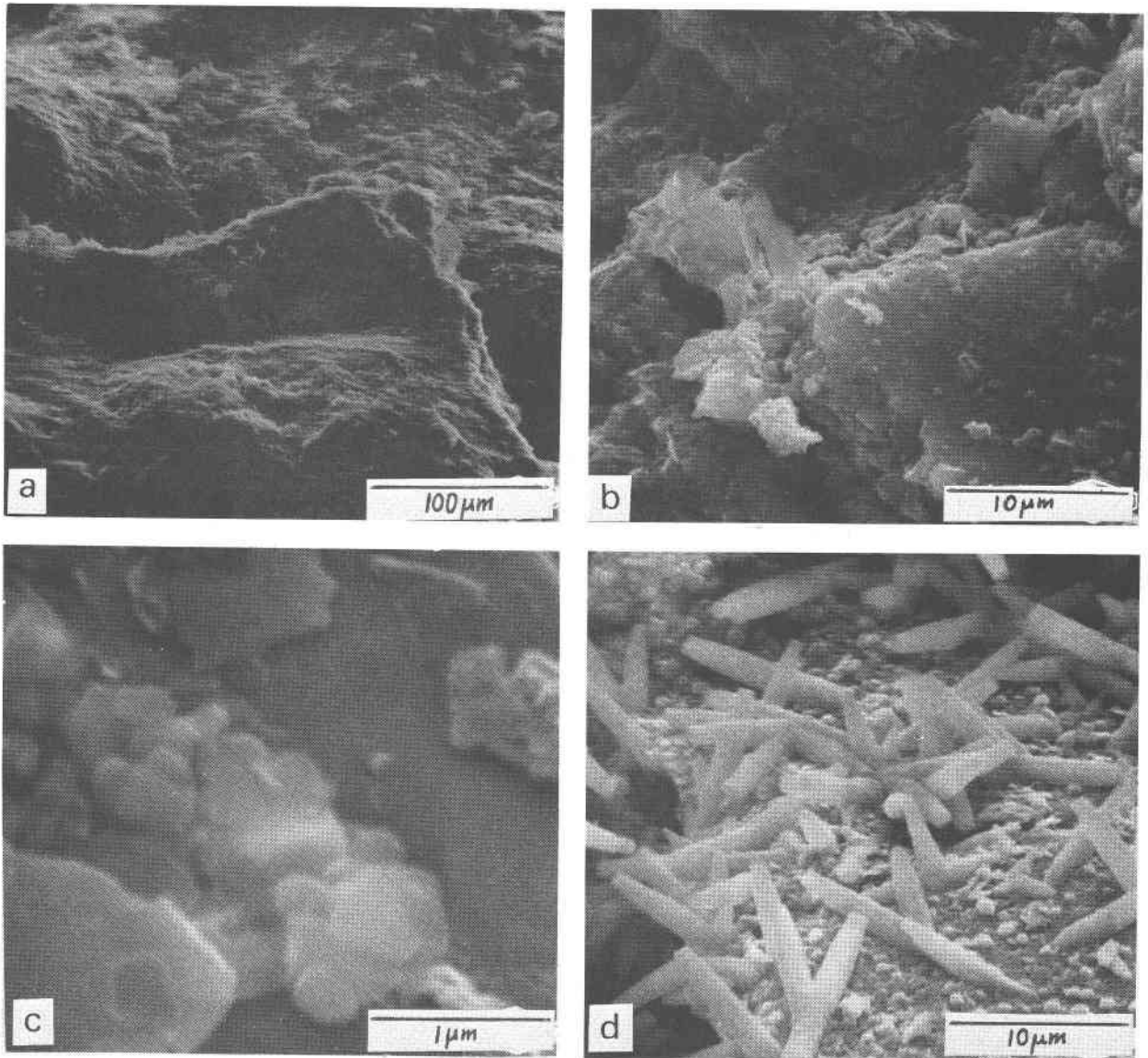


Fig. 4. Scanning electron micrographs of rancieite, (a), (b), (c), and of associated boehmite, (d).

these manganese minerals is necessary before changes of nomenclature can be recommended.

Acknowledgments

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