

Ranciéite from Mazzano Romano (Latium, Italy)

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ABSTRACT. Ranciéite occurs as stalactites coated with 10 Å halloysite in an open fissure crossing the Mazzano Romano Mn-impregnated tuffs. Chemical analysis (by EMPA) gave: MnO₂ 71.9, CaO 6.11, BaO 2.85, MgO 1.53, K₂O 0.86, Na₂O 0.53 plus minor oxides, total 85.07% (average of sixteen spots). Thermal analysis gave a total loss of ~20 wt% of which 13.9% can be attributed to bonded water. The resulting formula contains 4H₂O rather than 3H₂O, as in most published references. The loss of water leads to the formation of hausmannite plus unidentified phases, after a complex sequence of reactions. Dehydration is directly followed by an X-ray amorphous stage. The X-ray pattern and IR spectrum indicate a poor structural order, in agreement with the likely formation conditions of the Mazzano ranciéite at atmospheric pressure and very low temperatures (less than 50 °C), from cold water percolating through the main Mn deposit.

KEYWORDS: ranciéite, thermal analysis, Mazzano Romano, Italy.

THE present knowledge on manganese(IV) hydroxides is still unsatisfactory in a number of ways, despite their widespread occurrence in marine and terrestrial environments. This is due to two main reasons: (a) they are too poorly crystalline to be precisely characterized by conventional X-ray diffraction methods; (b) they are usually intimately intergrown with other fine-grained and/or amorphous phases, so that their chemical composition is also rather uncertain.

We discovered a vast amount of almost pure ranciéite at Mazzano Romano while studying this Mn deposit in the tuffs of Latium (Barbieri *et al.*, unpubl. data). This discovery led us to reinvestigate the phase using a variety of techniques, in order to clarify this poorly known species from the crystal-chemical and mineral-systematic viewpoints.

Previous investigations. The name 'ranciéite' dates back to Leymerie (1859), who classified as a new species the soft dark material with reddish-brown powder that he had found filling the cavities of massive hematite and limonite deposits occurring in Devonian limestones of the French Pyrenees.

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Although the name was also used by Lacroix (1910) for chemically analysed material from other localities in the Pyrenees having similar appearance, ranciéite was actually considered a synonym of psilomelane until Perseil (1967) reviewed material from the type-locality and Richmond *et al.* (1969) made a systematic study on a variety of occurrences from USA, Cuba, France, and Bulgaria. Later studies by Burns and Burns (1977), Bardossy and Brindley (1978), and Potter and Rossman (1979) showed that ranciéite is a phyllo-manganate of the 'birnessite family' (Giovanoli, 1969), the structure of which consists of disorderly stacked hexagonal layers of MnO₆ or Mn(OH)₆ octahedra, with Ca as the main cation sited among these layers. Therefore the accepted formula of ranciéite is (Ca,Mn²⁺)Mn₄⁴⁺O₉·3H₂O, in contrast with birnessite that contains Na dominant over Ca (Bardossy and Brindley, 1978), and the ill-defined takanelite (Nambu and Tanida, 1971) that contains Mn²⁺ in excess of Ca in the interlayers.

Ranciéite, as with all the other members of the birnessite family, differs from the chemically analogous members of the todorokite group in having a prominent X-ray diffraction line about 7 Å ('7 Å manganite'; Buser, 1959) instead of 10 Å. These two varieties of manganite s.l. occur frequently in association: indeed this is the case also at Rancié (Perseil and Giovanoli, 1979).

Ranciéite has been described from a variety of environments (see compilations and reviews by Frenzel, 1980; Burns and Burns, 1979; etc.). In particular, we note the presence of ranciéite nodules in the thick sequence of tuffs of basaltic to dacitic composition in the Oriente province, Cuba (Fleischer and Richmond, 1943; Richmond *et al.*, 1969), and its formation from percolated cold waters genetically connected with travertines and limestones as in North Dakota, USA (Hewett and Fleischer, 1960; Hendricks and Laird, 1943) and Itéa, Greece (Bardossy and Brindley, 1978).

Occurrence and association. The Monte Gelato deposits, on the right bank of River Treia in the area of Mazzano Romano, north of Rome, Italy (latitude 42° 11' 10" N; longitude 12° 23' 33" E.

Greenwich) is one of numerous Mn occurrences that have been explored, worked and abandoned, throughout the Quaternary potassic volcanic province of Latium. The deposit is located in a sequence of tuffaceous layers, 5 to 120 cm thick, subhorizontal or very gently dipping to the south, derived from the activity of the Sabatini volcanoes ('tufi varicolori della Storta', Mattias and Ventriglia, 1970). Normally, these tuffs were deposited in a subaerial environment, but at Mazzano they were deposited in a lake. The fresh water circulated through them and produced an upward migration of Mn to precipitate as an impregnation at the tuff/water interface. After a break, due to a second cycle of volcanic activity that deposited a second tuff sequence, the Mn leaching and impregnation process continued, so that the Mazzano deposit now consists of two major horizons (0.5 m) separated by 0.5 m of Mn-depleted tuffs (Barbieri *et al.*, in press). The stratified sequence lies on top of massive 'tufo rosso a scorie nere' that in turn overlies massive 'tufo grigio a scorie nere' (also known as 'piperno di Mazzano') both related to the activity of the Vico volcano (Locardi, 1965; Mattias and Ventriglia, 1970). A brief description of the deposit is given by Fornaseri (1950), who also made three bulk analyses and classified the Mn-mineral as psilomelane.

The examined ranciéite is located in a swarm of minor faults and fractures, a few metres long and a few centimetres thick, that crosses the 'tufo rosso a scorie nere' and fades out in the overlying stratified sequence. In particular, one of these fractures opens up into a large subvertical cavity, 5 m high and at least 40 cm wide, entirely encrusted with shiny

black stalactites, 2–3 cm long, in turn formed by aggregation of small pisolitic grains. The cavity is covered by debris at the bottom, so the actual vertical extent cannot be seen, and it enters the rock-wall for 2–3 m before closing up into a narrow fracture.

Experimental methods. Microprobe analyses were performed on a Jeol JXA 50 A instrument fitted with a LINK energy-dispersive analytical system. Spectrum deconvolution was by a multiple least-squares fitting, and standard matrix correction procedures were used. Standards included pure metals, synthetic and natural minerals, all of international availability.

For scanning electron microscopy, a Cambridge Stereoscan 250 was used. The thermal behaviour was studied on a Stanton-780 instrument that simultaneously records DTA, DTG and TG; and the IR spectrum was run on a Perkin Elmer model 983 photometer.

X-ray crystallography. The X-ray powder diffraction pattern recorded at $1^\circ 2\theta \text{ min}^{-1}$ with Mn-filtered Fe- $K\alpha$ radiation for the Mazzano ranciéite is given in fig. 1. Only two peaks, at 7.44 (100) and 3.69 (37) Å, stand out clearly, while a third peak, at 2.46 (22) Å, can be barely seen. The pattern was obtained from ranciéite dispersed in acetone and allowed to dry on a glass slide. Compressed ranciéite gave a similar pattern, but with a higher background. The pattern obtained with Ni-filtered Cu-radiation was also similar. The pattern confirms the relationship of ranciéite to the 'birnessite family' (Giovanoli, 1969) or '7 Å manganite group' (Buser, 1959); however it is too poor to allow calculation of

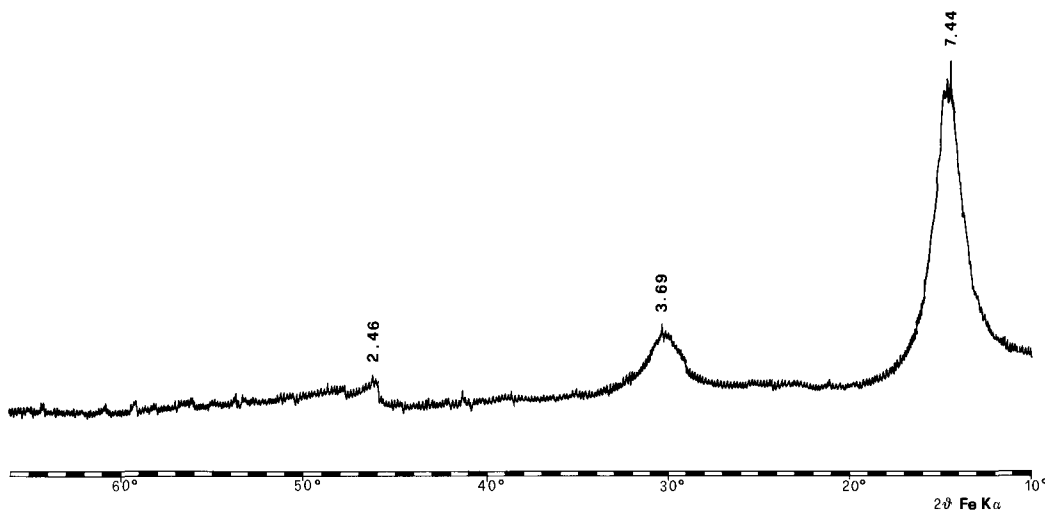


FIG. 1. Diffractometer pattern of ranciéite with Fe- $K\alpha$ radiation 40 kV, 20 mA.

the unit-cell parameters. When compared with the pattern of the Greek ranciéite, it is clear that only the 'basal' 001, 002, and 100 reflections, enhanced by preferred orientation, are present, but even these indicate, by their shape and broadness, that the Mazzano sample is very poorly ordered.

Chemical composition. The averages of sixteen spot analyses and the related standard deviations are reported in Table I. The major element present beside Mn is Ca, as expected in ranciéite, but our mineral is unusual in that it contains significant Mg and Ba, while being free of Fe. To our knowledge, Ba has never been found in ranciéite before, although it is a significant component of other Mn oxides such as hollandite and psilomelane (romanéchte). Since all the ranciéite analyses reported in the literature were by wet chemical methods, we assume that Ba was overlooked and precipitated with Ca.

The maximum amounts of the minor elements in individual analyses were 0.57 As_2O_3 , 0.45 TiO_2 , 0.35 Al_2O_3 , 0.27 P_2O_5 , and 0.20 wt. % Cl.

Furthermore the microprobe analysis shows chemical differences between the dark and light layers of the ranciéite colloform texture (fig. 2). The dark layers and nuclei are richer in Mn, Ba, and Si and poorer in Ca, Mg, K, Na than the light layers. These differences are, however, comparable with the standard deviations (Table I).

The average formula of the Mazzano ranciéite was calculated to 5 metal atoms per formula unit. The Mn sums close to four so that it can be assumed to be entirely Mn^{4+} . All the other elements detected are sited between the MnO_6 or $\text{Mn}(\text{OH})_6$ layers.

On a closer examination (Table I), the dark layers and nuclei have Mn in excess of 4.00, so that part of it can be reduced to divalent and allocated to interlayer cations, as in most published ranciéites and particularly in takanelite (Nambu and Tanida, 1971). The light layers are deficient in Mn^{4+}

TABLE I.

Microprobe analysis of the ranciéite of Mazzano Romano

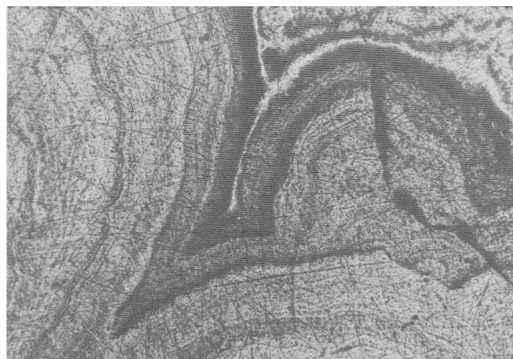
	dark nuclei n = 8	light layers n = 8	average n = 16	esd
MnO_2	72.8	71.4	71.9	1.42
CaO	5.70	6.32	6.11	0.66
BaO	2.97	2.83	2.85	0.32
MgO	1.35	1.72	1.53	0.39
K_2O	0.77	0.87	0.86	0.18
Na_2O	0.40	0.63	0.53	0.22
SiO_2	0.46	0.38	0.41	0.10
Al_2O_3	0.12	0.16	0.14	0.10
As_2O_5	0.16	0.18	0.18	0.18
P_2O_5	0.17	0.17	0.17	0.06
TiO_2	0.20	0.21	0.21	0.12
Cl	0.11	0.12	0.12	0.04
FeO	0.03	0.07	0.06	0.09
	85.24	85.06	85.07	

atoms p.f.u. on a total metal content = 5

Mn	4.069	3.948	3.997
Ca	0.494	0.542	0.527
Ba	0.094	0.089	0.090
Mg	0.163	0.205	0.183
K	0.079	0.089	0.088
Na	0.063	0.098	0.082
Si	0.037	0.030	0.033

* water: see text.

without showing another metal ion to substitute for it. Since halloysite is present overgrown on ranciéite, we initially assumed that light layers could be contaminated with it. However, the light layers are depleted in SiO_2 and have Al_2O_3 just as random as the dark layers, so that this contamination can be discounted.

Fig. 2. Dark layers and white layers of the ranciéite colloform texture, reflected light, $\times 500$.

The problem of contamination is a major one in analysing such fine-grained material. In our case it is minimized by the microprobe, but this cannot be said for the few ranciéite analyses reported in the literature, all carried out by wet chemistry on gram-size aliquots (cf. Bardossy and Brindley, 1978). For this reason, we refrain from comparing the Mazzano ranciéite with those of other localities: we simply note that the Mazzano ranciéite is free from the base metals (Pb, Co, Ni, Fe, etc.) frequently found in marine manganese nodules and concretions, including those of Quaternary age dredged from the Tyrrhenian sea (Morten *et al.*, 1980). On the other hand, the Mazzano ranciéite contains geochemically incompatible light elements typically related to fumarolic or late-volcanic activity (As, Cl, P). Another interesting point is that the light layers contain Na in excess of K, and the dark ones the reverse, despite the great availability of K in all the rocks of the potassic Roman province.

Water content and thermal behaviour. Analyses in Table I have low totals because they do not include H₂O or a elements lighter than Z = 11. Consequently, the formulae were computed on the anhydrous basis of 5 metals, this being in our opinion the most reasonable way of computing instrumental analyses (like EMPA) where no determination of light elements is possible.

However, water is an essential constituent of the ranciéite formula, and the way in which volatiles are released is an important criterion for discriminating between '10-Å manganites'. Thus, importance was attached to this determination, bearing in mind that significant discrepancies have been noted in the relevant literature (Radonova *et al.*, 1967; Chukhrov and Bonshtedt-Kupletskaya, 1967; Richmond *et al.*, 1969; Bardossy and Brindley, 1978).

The weight loss of the Mazzano ranciéite was determined by TG analyses carried out under different experimental conditions. The results are homogeneous, with small differences related to different sample sizes and heating rates. Typical DTA-DTG-TG curves are given in fig. 3.

A major weight loss (approx. 13.9%) occurs before 325 °C, mainly via two intense reactions at 120 and 198 °C, releasing ~ 6% and ~ 7% H₂O respectively. The further weight losses occur up to over 1000 °C, again stepwise, but much more gradually than before, with main reactions at 375, 535, and 640 °C involving losses of 1.2, 1.8, and 2% respectively.

The weight loss curve of fig. 3 is similar to the one observed by Bardossy and Brindley (1978) on the Greek ranciéite, though better defined in the details: therefore we agree with their interpretation. The weight lost up to 325 °C is clearly related to the

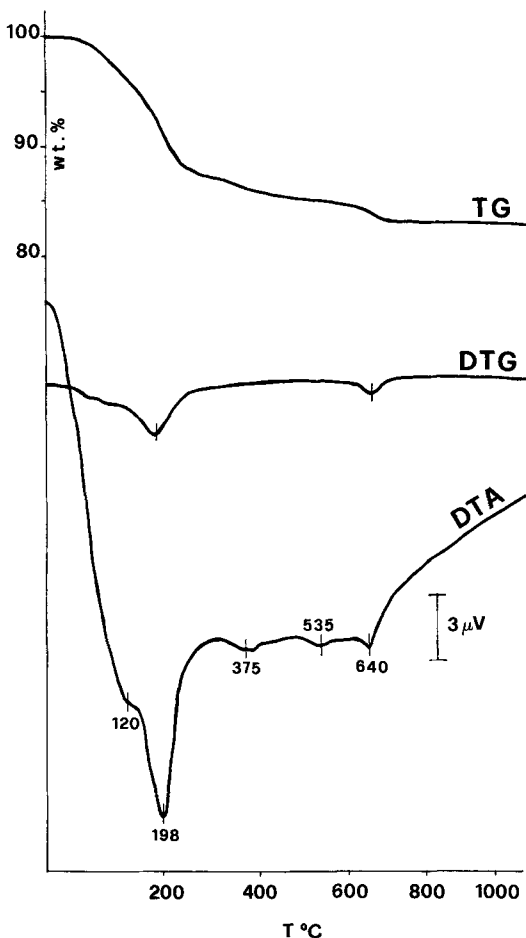


FIG. 3. TG, DTG and DTA curves of ranciéite: Stanton mod. 780 instrument, sample weight 9.90 mg, heating rate 15 °C/min; N atmosphere.

dehydration of ranciéite, occurring in two steps due to the different banding energies of two types of water present. The higher-temperature weight losses are related to reduction and structural rearrangements of the ranciéite decomposition products involving losses of oxygen, with the exception of the reaction at 375 °C which could be related to OH-release from manganite (Frenzel, 1980), an intermediate product of ranciéite dehydration, and formation of a pyrolusite-like phase MnO₂.

The reactions at 535 and 640 °C are typical of the reduction of MnO₂ to Mn₂O₃ while at c.930 °C the reduction of Mn₂O₃ produces Mn₃O₄ (hausmanite), the high-temperature stable product.

Both a water content of 13.9 wt. % (lost below 325 °C), or of 15.1, if the OH trapped in the

manganite intermediate products is considered as typical of the ranciéite precursor, fit well the EMPA chemical data (totals are 98.97 and 100.17% respectively). The corresponding numbers of water molecules in the formula of ranciéite are 3.728 and 4.050.

In contrast to the formula reported by Bardossy and Brindley (1978) and accepted by Fleischer (1983), our results support the H₂O value that can be deduced from Perseil's analysis (1967) on the Rancié material, although this has been later shown to contain todorokite (Perseil and Giovanoli, 1979). We therefore conclude that the water molecules in ranciéite are four and the correct formula is CaMn₄O₉ · 4H₂O.

In fact, even Bardossy and Brindley (1978) found 3.66 H₂O atoms per formula unit in their sample. They did not explain why they assumed 3H₂O as the preferred value, except that they considered it in agreement with the value 3.25H₂O given by Richmond *et al.* (1969).

TABLE II.
Thermal experiments on the Mazzano ranciéite
at atmospheric pressure

T (°C)	t (h)	Result
150	12	R (7.17, 3.60, 2.45, 2.33 Å)
150	24	R (7.08, vb peak 3.55, 2.44 Å)
150	72	R (6.98, 2.44 Å)
150	120	R (6.75, 2.44 Å)
150	180	R (6.55, 2.436 Å)
150	220	R (←6.3, 2.436 Å)
150	260	flat pattern, vb peak 2.44 Å
350	24	flat pattern, vb peak 2.43 Å
600	24	flat pattern, vb peaks 4.77, 3.08, 2.41 (H?)
600	60	H (4 broad weak peaks)
600	80	H (9 W peaks) + 2 peaks at 5.27 and 4.97 Å
600	720	H (11 sharp peaks)
1000	72	H (11 sharp peaks) + 11 peaks of unidentified phase/s

Note. R = ranciéite (starting material has 7.27 Å (100) main peak), H = hausmannite

When heated statically in air and examined by X-ray powder diffraction, ranciéite shows an unusual behaviour. At 150 °C, i.e. at a temperature above one of thermal effects shown in the DTA curve (fig. 3), the main peak at 7 Å shifts toward lower *d* values and decreases in intensity with increasing heating time (Table II) so that after 220 hours the pattern is almost flat while a very weak peak at 2.43 Å, typical of all the Mn oxides, is always present. We interpret the result (fig. 4) with a continuous release first of the weakly bonded OH, then of the more strongly bonded water, producing structural disorder. At 350 °C a similar behaviour is observed, but within 24 hours (Table II).

At 600 °C disordering occurs, but it is rapidly followed by the formation of hausmannite, that increases slowly in crystallinity so that the product appears to have recrystallized completely only after 1 month. On the contrary, three days at 1000 °C produce an excellent hausmannite pattern, plus extra peaks that we could not refer to marokite, as observed by Bardossy and Brindley (1978). During the thermal cycles even hausmannite changes in crystallinity and/or in composition, e.g. at 600 °C two peaks, at 5.27 and 4.97 Å, when first shown, progressively migrate with heating time to merge eventually in the single peak at 4.92 typical of pure hausmannite.

Infrared spectroscopy. The IR spectrum of ranciéite is reported in fig. 5. As with the thermal spectra of fig. 3, the spectrum was obtained with a random mixture of light and dark layers and therefore is an average. However, it compares well with the ranciéite spectra recently published by Potter and Rossman (1979), particularly with that of the Oriente, Cuba, ranciéite.

Although our spectrum was obtained in transmission, and therefore it cannot be quantitatively compared with the absorbance spectra published by Potter and Rossman (1979), the positions and intensities of most bands compare well. In particular the water stretching band with threshold at 3404 cm⁻¹ has a width of more than 600 cm⁻¹ implying the presence of multiple vibrations (at least three according to Potter and Rossman, 1979, Fig. 17). It also implies great structural disorder, as already shown by the X-ray diffraction spectrum. Such a superimposition of multiple vibrations can also be inferred from examination of the region of water bending, where the single band identified by Potter and Rossman (1979, Fig. 17 no. 5) can actually be split into at least two—a band at 1617 cm⁻¹ and a shoulder at 1710 cm⁻¹.

Weak bands at 1400, 1111, 1028, and 912 cm⁻¹ in our ranciéite were not labelled by Potter and Rossman (1979) although they were present in some of their spectra (e.g. no. 64, from Rancié). Possibly they are related to vibrations of the Ca and Ba, or to other cations present in the ranciéite layer structure.

The lower energy portion of the spectrum is characterized by the very intense band that distinguishes ranciéite from other manganese oxides, according to Potter and Rossman, 1979. This band is far too large in width (~ 300 cm⁻¹) to be single: clearly it is due to the superimposition of several bands. Even the minimum threshold at 438 cm⁻¹ can in fact be split. The second minimum, occurring at 452 cm⁻¹, may be referred also to the slight difference in composition between dark and light shells present in our composite specimen. The three

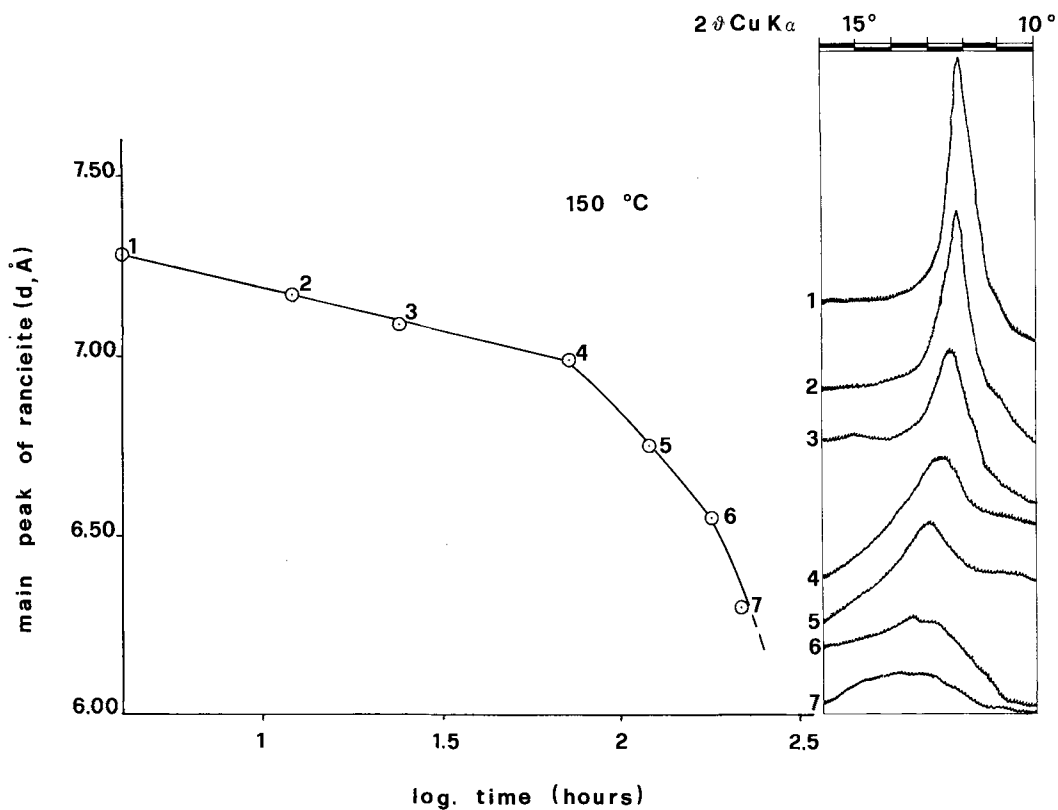


FIG. 4. Shift and broadening of 7 Å peak with increasing heating time at 150 °C.

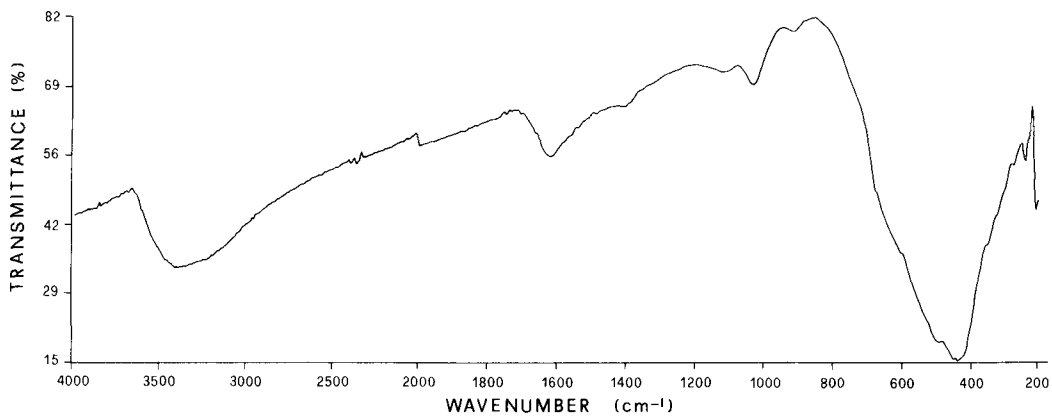


FIG. 5. Infra-red spectrum of ranciéite between 4000 and 200 cm⁻¹ (wavenumber); Perkin Elmer mod. 983 instrument; sample 2 mg in 200 mg KBr, scan time 15 minutes.

shoulders at 500, 602, and 674 cm^{-1} correspond to bands 2, 3, and 4 of Potter and Rossman (1979). The latter is particularly significant because it distinguishes ranciéite from birnessite and todorokite, even if structural disorder is present (Potter and Rossman, 1979).

The position and intensity of band 1 (at 438 cm^{-1}) is consistent with the inferred layer structure of ranciéite, and with the conclusion of Potter and Rossman (1979) that there is a structural continuity between birnessite and ranciéite, in the sense that they are both built by similar structural units varying in their ordering relationships.

Associated minerals and genetic conclusions. One mineral only has been detected associated with ranciéite in the open fissure. It appears in the form of a translucent, oil-yellow jelly film coating the ranciéite stalactites, and sometimes interleaved within the ranciéite pisolitic shells. It gives a poor X-ray pattern of highly disordered halloysite-10 Å, that is confirmed by the IR spectrum and by a qualitative chemical analysis performed by SEM-EDAX.

Halloysite-10 Å, also known as endellite or hydrated halloysite, is a common constituent of clays and exogenous deposits and particularly of weathered volcanic glass (Sudo and Yotsumoto, 1977; for Latium, see Lombardi and Mattias, 1979; and Lenzi and Mattias, 1978). It is also a rather good thermal indicator of supergene conditions, since it forms at a near neutral pH; after a short heating at $\sim 35\text{--}40^\circ\text{C}$ in a dry environment, or at $\sim 60\text{--}80^\circ\text{C}$ in a fully hydrous atmosphere (Azzaro *et al.*, 1976), it converts irreversibly into 7-Å halloysite, also known as metahalloysite.

The presence of 10 Å-halloysite coatings on ranciéite therefore brackets the formation of the latter mineral within the conditions of a climate close to the present climate of the Roman region, while at the same time the presence of a manganese mineral containing only Mn^{4+} is a good indicator of oxidizing conditions. The age of the formation of the ranciéite postdates the formation of the joints, that in turn is related to the N.-S. neotectonics of the Tyrrhenian borderline and displaces the 'tuffi varicolori della Storta', the radiometric age of which has been determined to be 0.225 ± 0.06 m.y. (Ambrosetti *et al.*, 1969).

In conclusion, the Mazzano ranciéite is a very recent product of the supergene minerogenesis in the Latian area: it probably formed by deposition 'per descensum' from cold waters leaching the manganese deposits of the olocenic Mazzano Lake. In turn this manganese derived from leaching of the Sabatinian tuffs (and possibly of the underlying Vico tuffs) by a process of circulation of the lake water throughout their porous substrate.

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