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HALLOYSITE AND OTHER HYDROTHERMAL MINERALS NEAR CAPALBIO, GROSSETO (TUSCANY, CENTRAL ITALY)

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Abstract: A widespread Quaternary hydrothermal event in Central Italy was responsible for large metalliferous mineralizations which include manganese oxides, pyrite, other sulphide phases and several clay minerals. The deposits occur in Carboniferous–Permian metasedimentary rocks of the Verrucano Formation near Capalbio, Grosseto Province, Tuscany. Among the clay minerals, the presence of halloysite with 10 Å and 7 Å terms is particularly important along with that of smectite and mixed-layer minerals of the I/MO.
All the aspects of the process can be pointed out by following the muscovite alteration phases: muscovite and/or sericite –> illite–> illite/smectite –> smectite–> 10 Å-halloysite–> 7 Å-halloysite.

Key words: Tuscany, Capalbio, hydrothermalism, clay minerals, 10 Å-halloysite.

Introduction

The Mount Monteti area near Capalbio, Grosseto Province, Tuscany is known for its hydrothermal metal mineralization.

The interaction between hydrothermal fluids and the parent rock, phyllites and shales, produced clay minerals such as halloysite, illite and smectite, as well as other hydrothermal minerals. In particular the halloysitic phases, sometimes characterized by very high purity, are mentioned in the Atlas of Clay Minerals Infrared Spectrometry, by Van der Marel & Beutelspacher (1976).

In this paper the effects of hydrothermal alteration with particular regard to the halloysitic phases are reported.

Geological setting

The hydrothermal zone crops out near the "Pozzo Picciolente" area, NNW of Mt. Monteti (425 m), 3 km from the town of Capalbio (Sheet no.135 of the Italian Geologic Map (Orbetello), Quadrant II–NW (Capalbio) (Fig. 1).

The area is characterized by large outcrops of the Verrucano Formation (Carboniferous–Permian) that includes shales, sericite-bearing slate, phyllites and interbedded sandstones grading into quartzites (Signorini 1954). It constitutes a topographical high (Mt. Monteti) and is the source of the argillic alteration products. According to Azzaro et al. (1975a,b, 1976) and Di Sabatino et al. (1977, 1978) long before the alteration this series was affected by low to very low grade metamorphism. If fresh, its phases appear dark-grey; alteration produces a yellowish to whitish color.

The phases present are muscovite and/or sericite, biotite, and quartz. Andreatta (1948) also reported the presence of K-feldspar and plagioclase, chlorite, kaolinite, rutile, zircon and apatite.

Hydrothermal alteration occurred mainly along fault zones. However the intrinsic properties of the material (i.e. fissility and slaty cleavage) made it easily permeable to the action of Quaternary thermal solutions (Signorini 1954).

The overlying "Calcare Cavernoso" formation (Upper Triassic), crops out E and S of Mt. Monteti. It is constituted by limestones, dolomitic limestones and dolostones, often with beds of gypsum and empty spaces measuring up to a few centimeters across. This formation was also affected by hydrothermal processes, as is indicated by patches of finely powdered dolostone found during the present survey. Some dolostone samples contain bituminous material that gives them a greyish appearance.

Overlying the "Calcare Cavernoso" is the "Galestri and Palombini" formation (Cretaceous), constituted by interbedded shales ("Galestri") and greyish, very fine-grained and compact limestone ("Palombini"); small outcrops of this formation occur N and W of Mt. Monteti.

The "Galestri and Palombini" is followed by the "Arenarie e argille laminate" formation, containing fresh-

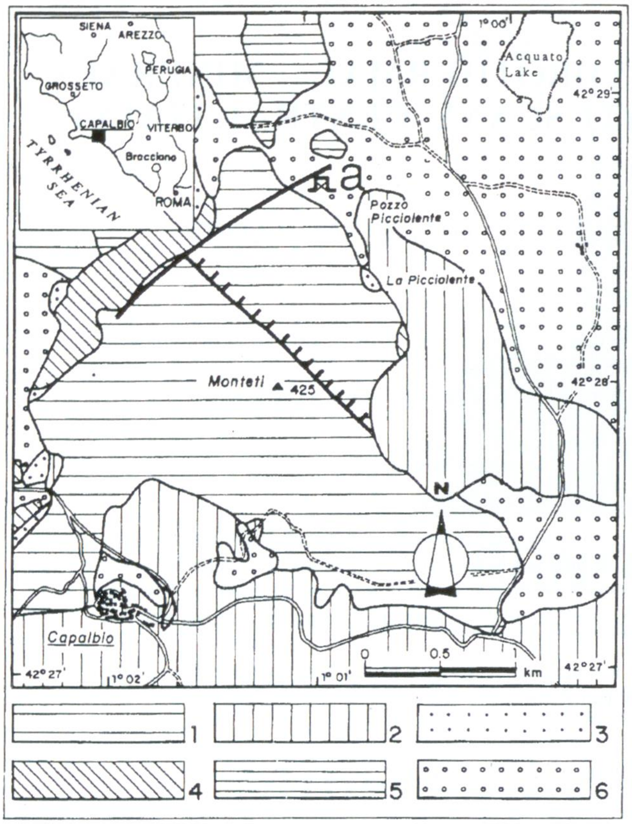


Fig. 1. Schematic geological map of the Capalbio area (Grosseto). 1. Phyllites with sandstones interbedded belonging to the Verrucano Formation (Carboniferous Permian); 2. Hollow limestones belonging to the "Calcare Cavernoso" Formation (Upper–Trias); 3. Argillaceous shales and grayish limestones interbedded belonging to the "Galestri and Palombini" Formation (Cretaceous); 4. Sandstones, argillaceous and fossiliferous shales (Upper and Middle Miocene); 5. Heterogeneous clastic elements made up with sandstones "Palombini" limestones and chert (Neogene); 6. Recent, present detritic deposits (Continental Quaternary deposits); a. Alteration area.

Fig. 2. Northern side of Mt. Monteti (425 m). In the foreground are shown the dumps of an abandoned iron and manganese mine. The rations stages of hydrothermal alteration, involving the development of halloysitic terms, can be observed in the dump materials.

Fig. 3. Main entrance to the mine on the Northern side of Mt. Monteti. Digging the tunnel allowed observation of all the stages of alteration involving the phyllites and / or shales of the Verrucano Formation.

water bivalves and ostracodes (Middle–Upper Miocene); widespread outcrops of it can be observed N and W of Mt. Monteti.

The "Conglomerati eterogenei" formation (Neogene) is constituted by clastic elements which include sandstones, limestones, chert, and jasper. Sometimes these are followed by Miocene–Pliocene sandstones and clays. The area is characterized by intense faulting which is responsible for the sharp contact between the Verrucano Formation and the "Arenarie e argille laminate".

The mineralized area is evidenced by the whitish, argillaceous rocks that crop out along a NE–SW striking fault, near the Pozzo Picciolente area (Figs. 2–3). In the past, a 160 m tunnel was dug along with a 40 m pit for exploration and mining of iron–manganese ore.

Amati (1945) reported for the first time the occurrence of halloysite among the alteration products; later Andreatta (1947–48; 1948; 1949a,b) focussed his attention on minerals with a mica type structure ("illite-hydromica"), suggesting the occurrence of halloysite, "metahalloysite", kaolinite and montmorillonite.

Signorini (1954) pointed out that the alteration process of Mt. Monteti had involved mainly the Verrucano Formation and suggested its hydrothermal origin on the basis, among other things, of the presence of numerous veins of hydrothermal quartz.

Pellizzer & Guidetti (1959a,b), studied some neoformation products and found phases which are transitional from micaceous unaltered minerals to altered ones.

Materials and methods

The samples were mostly collected on the ground near the main entrance to an abandoned mine on the northern side of the Mt. Monteti. All samples collected were systematically studied by XRD and the most representative ones by chemical analyses following XRF methods. However

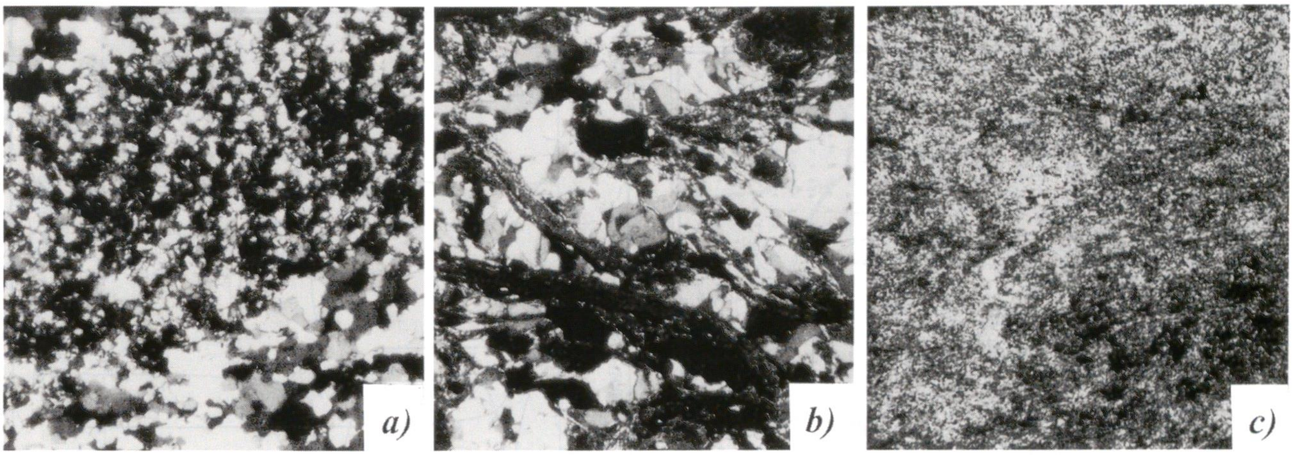


Fig. 4. a) Thin section of unaltered phyllites. Quartz clasts of varying size set in a very fine-grained micaceous matrix (30 x, crossed polars). b) Phyllitic mineral assemblages showing the effect of hydrothermal fluids. Metallic minerals and newly formed hydrothermal phases in veins with dominant halloysitic terms (45 x, crossed polars). c) Thin section of halloysitic alteration products. Larger crystals show cores with higher birifrangence than do smaller crystals. Opaque minerals are often present (80 x, crossed polars).

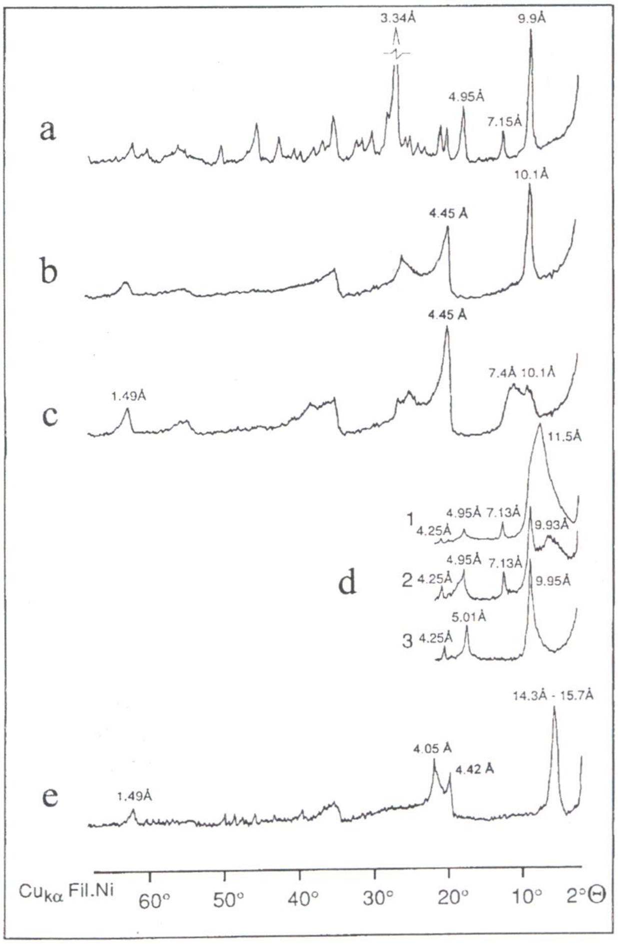


Fig. 5. X-ray diagrams of samples belonging to the Capalbio area: a) Unaltered parent rock—Verrucano Formation. b) 10 Å-halloysite. c) 10 Å-halloysite associated with the 7 Å phase. d) 1. Illite including mixed-layers of I/MO type (natural); 2. Treated with EG; 3. Heated to 550 ˚C. e) Smectite with CT-opal (a-cristobalite).

pure phases of halloysite were submitted to IR, DTA, TG, and DTG methods, and to SEM and TEM investigation. The parent unaltered rocks were studied by optical methods in thin sections. The chemical analyses were carried out using XRF methods, with typical and recommended standard.

Halloysite and other neoformation minerals

Optical observations disclosed all the features connected with the transition from unaltered to completely altered rock and confirmed that the fluids responsible for the alteration acted along cleavage or fracture surfaces (Fig. 4a–c).

Table 1 shows the chemical analyses of some unaltered raw rock cropping out near Pozzo Picciolente. Fig. 5 shows the diffraction pattern of an unaltered phyllite.

A) Clay minerals

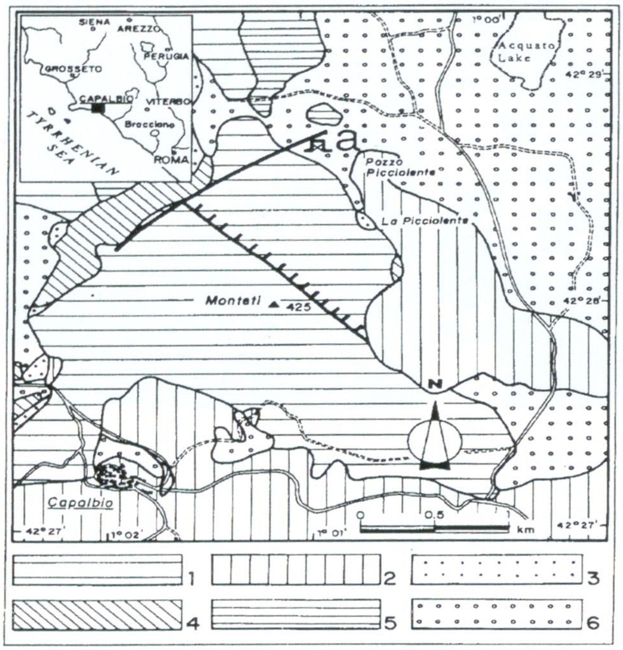
—10 Å and 7 Å halloysite

These are the most widespread phases in the out crops, consisting of whitish, porcellaneous masses, 20–30 cm in diameter, with conchoidal fracture. Sometimes they show an ochreous, yellowish colour due to iron hydroxides (limonite).

XRD allowed the transition from 10 Å to 7 Å phases to be observed. These phases always appear pure, with no other crystalline phases (Fig. 5b–c). Fig. 6 shows the DTA, TG and DTG curves for these materials.

In particular the first endothermic peak of the DTA, at about 135 ˚C, is related to a 7% loss of H_2O. The next peak, again endothermic is at about 555 ˚C and is produced by

Table 1: Chemical analyses of Capalbio.



[1] = Unaltered phyllite.
[2],[3] = Sericite–muscovite bearing slates.
[4] = 10 Å-halloysite.
[5] = "Mixed clay with prevailing alloysite and kaolinite"(Andreatta 1948).
[6] = "Mixed quarzose–halloysitic clay"(Andreatta 1948).
[7] = "Montmorillonitic clay"(Andreatta 1948).

the destruction of the phyllosilicate with an approx. 13.34% loss of OH. Finally, the last exothermic peak, at about 965 ˚C, is produced by the formation of mullite and does not produce weight variations.

Fig. 7 (a and b) shows the IR spectra of the halloysite of the present work and, for comparative purposes, the IR pattern of similar materials, always from Capalbio, taken from the Atlas of Van der Marel & Beutelspacher (1976). In the two diagrams, the bands at 3695 and 3620 cm^{-1} related to OH-stretch are evident. The trend of these bands is characteristic of halloysitic terms. The other bands (1132, 910, 754 etc. cm^{-1}) are typical of halloysite.

SEM photomicrographs show the typical tubular appearance of the crystals along with occasional platy morphologies of micaceous minerals or kaolinite (Fig. 8a–f). At the highest magnifications, it is possible to note the central orifice typical of the tubular halloysite crystals.

TEM images (Fig. 9) also show the typical tubular morphology of halloysite, with well-defined assial channels due to spiral winding. The lengths of the tubular crystals are variable; the largest crystals reach up to 5–7 nm with a dimension ratio (length-to-diameter) of 20 : 1. These crystal outlines appear sharp and well-defined, indicating a high degree of crystallinity. Sometimes spheroidal clots appear, probably consisting of allophane.

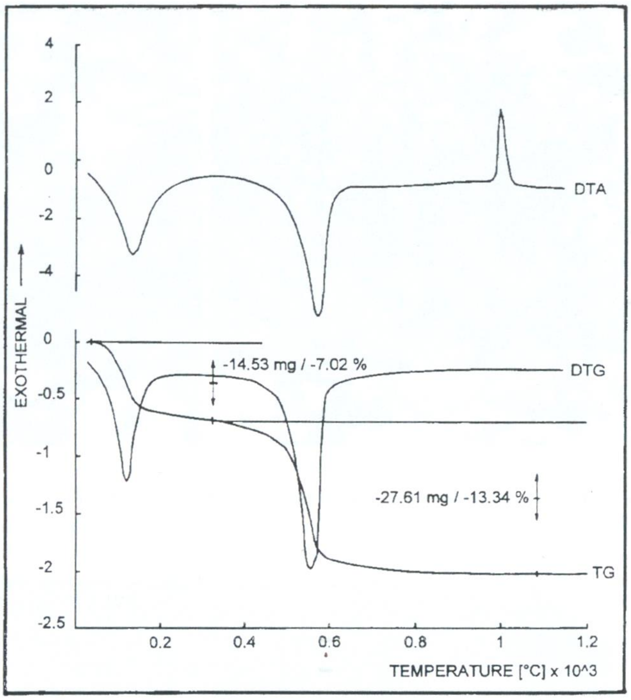


Fig. 6. The DTA, TG and DTG curves for 10 Å-halloysite are in agreement with those taken from the literature.

Table 1, column 4, shows the chemical analysis of a pure hydrous halloysite (10 Å), which includes some minor and trace elements. For comparison, the analyses of a "mixed clay with dominant halloysite and kaolinite" (column 5) and "mixed quartz-halloysite clay" from Capalbio (column 6) (Andreatta 1947–48) are shown in Table 1.

The geotechnical behaviour of the above material gave the following values for the Atterberg limits: WP = 38, WL = 49 and IP = 11. The IP value is in good agreement with that reported by Grim (1962) while the WL and WP values are lower.

—Illite

Illite is in close relationship with the phyllites involved in the hydrothermal process. By XRD all the transitions from muscovite-sericite to illite, reflecting an increase in the degree of alteration, were recognised. In particular, the thickness of the 10 Å peak increases as its angular value decreases. Illite is associated mainly with smectite and possibly trace amounts of residual kaolinite, quartz and feldspars.

—Mixed-layer minerals

In some diffraction patterns of mixed-layer clay minerals, a wide band ranging from 10.5 to 11.8–12 Å is present at low angles. Andreatta (1947–48, 1948, 1949a,b) and Pellizzer & Guidetti (1959b) reported some features.

Treatment in an ethylene-glycol atmosphere and heating caused clear modifications in diffraction patterns (Fig.

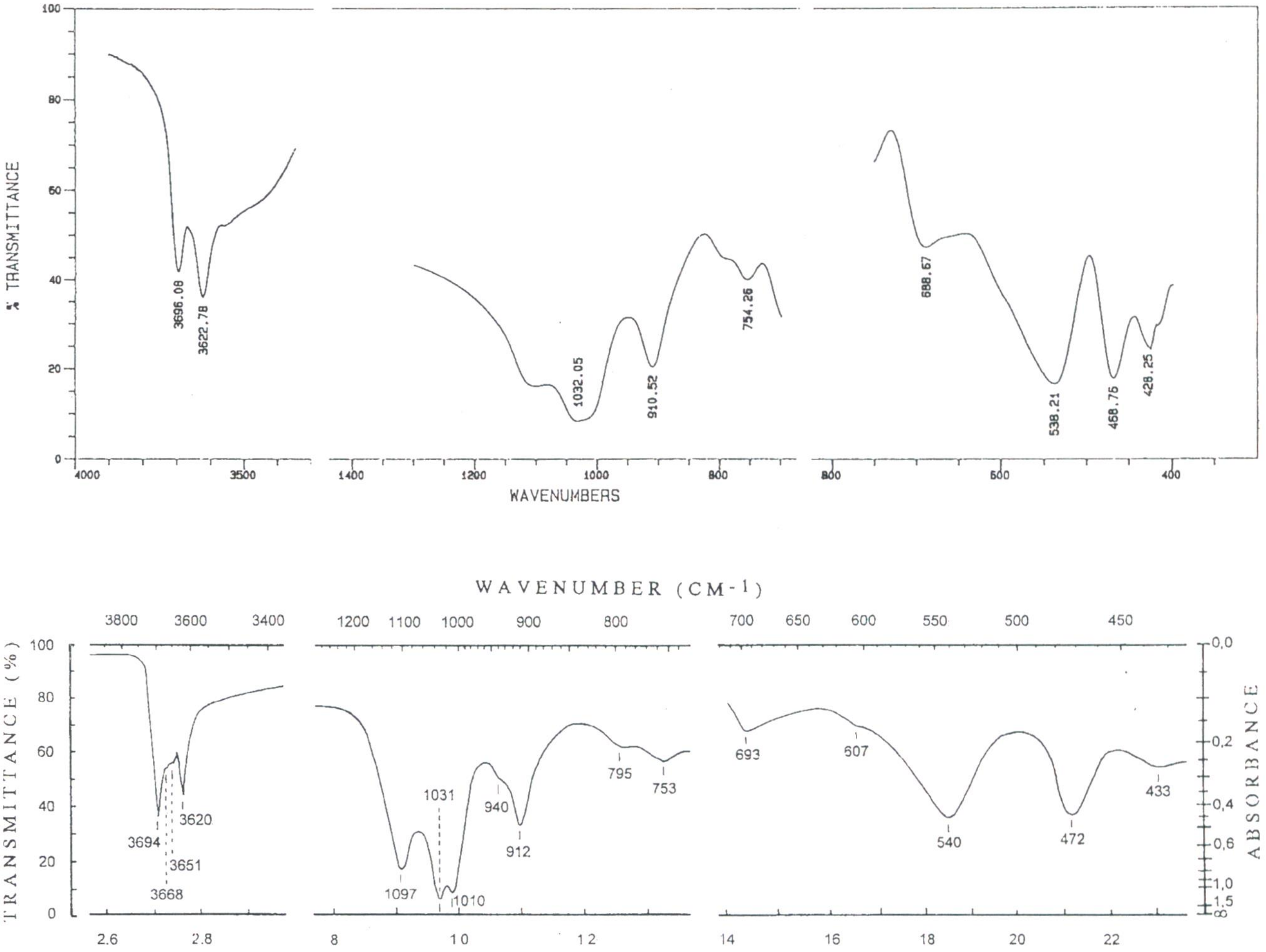


Fig. 7. a):I.R.diagram for samples studied in the present work and b):I.R.diagram for sample reported in the literature (Van der Marel & Beutelspacher 1976).

5d). In particular, thermal treatment caused the disappearance of the basal band and reinforcement of the 10 Å peak. These changes can be ascribed to sequences of mixed-layers of the illite-smectite (I/MO).

—Smectite

Smectite is rather rare on the surface and it is usually represented by whitish, pinkish, and greenish little masses.

XRD shows a d value between 14.3 Å and 15.7 Å, while the 060 reflection reveals its dioctahedral character (d = 1.49 Å). In ethylene-glycol atmosphere the basal reflection shifts towards 16.5–17.5 Å and collapses at 9.8 Å following thermal treatment at 550 °C for 2 h.

Smectite is always associated with other crystalline phases, especially to CT-opal, kaolinite and, less often, illite. Attemps by many Autors to isolate pure smectite by granulometric selections have not succeeded.

Andreatta (1948) analysed material defined as "montmorillonitic clay" (Table 1 — column 7); the high Al_2O_3 content (20.19%), along with the low MgO content (2.61%) confirmed its dioctahedral character.

B) Other neoformed minerals

—Quartz

Quartz is widespread in outcrops within the mineralized area as blocks measuring some 10–20 cm across. It is usually whitish, milky, yellowish and/or reddish with brownish veins. It is also present as amethyst. It forms veins and little dykes up to a few tens of centimeters thick. On some occasions, well-formed, isolated crystals, several centimeters long were found.

—CT-opal

Very often this is associated with smectite;the presence of its characteristic peak ranging between 4.04 and 4.07 Å suggests that the temperature of formation was rather low, between 25 °C and 115 °C (α-cristobalite of Jackson et al. 1977).

—Jarosite

In some X-ray diffraction patterns of illitic and/or smectitic terms, very faint peaks of jarosite are present, sometimes associated with low pyrite peaks.

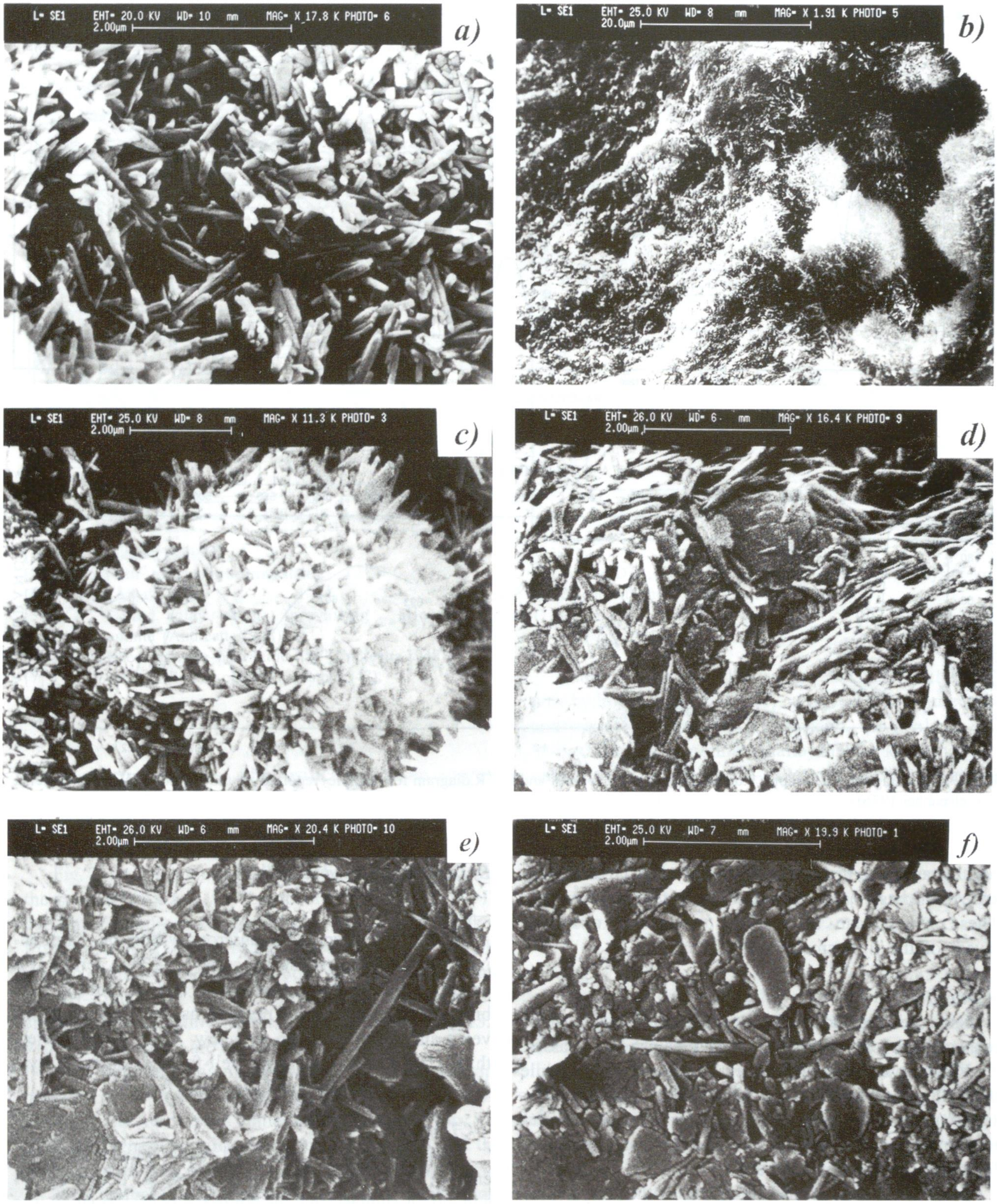


Fig. 8. SEM micrographs. Halloysite with characteristic tubular morphologies. Note the varying microporosity and the high degree of crystallinity of the halloysite (a). Different magnifications of halloysite materials (b, c) with laminae of kaolinite and illitic minerals (d, e, and f).

Andreatta (1948) also reported the presence of other sulphates such as gypsum and melanterite, consisting of well-formed and well developed crystals.

—Metalliferous minerals

In the past, during the 1940's and 1950's, mining exploration was carried out in the area under consideration for pyrite and manganese minerals. Early encouraging results led to the digging of a tunnel and a pit which made the recovery of small amounts of ore possible. However due to the limited extension of mineralization of acceptable grade, no production was started. Cinnabar and stibnite were reported in addition to other sulphides.

—Goethite–limonite

Very often blocks of yellowish to brownish spongy limonite, ranging from 30 to 40 cm in size, are found next to the main mineralized areas. Some small samples show cubes of pseudomorphosed pyrite.

Discussion and conclusions

The study of the alteration products of the Pozzo Picciolente area near Capalbio shows an extremely complex picture. The area is characterized by large out crops of Permian–Carboniferous phyllites and shales (Verrucano Formation) which have suffered intense tectonism evidenced by NW–SE and NE–SW oriented faults.

Hydrothermal fluids, the action of which was facilitated by the structure and texture of the phyllites and shales present, produced metallic minerals, clay minerals replacing silicatic rocks, and other hydrothermal phases.

The alteration processes were certainly influenced by the existence of specific microenvironments, due to the anisotropy of the original rocks. In particular, they must have been conditioned by the temperature, chemistry and duration of the interaction between the microenvironments present and the fluids. Undoubtedly the presence of micaceous phases favoured the formation of halloysite, illite, mixed-layers and smectitic terms. Leaching of K from the packets of the sericitic micas caused the formation of illite. During this process some packs may have attained a smectitic composition, yielding a more or less irregular mixed-layers structure of the illite-smectite type.

Such an environment was probably characterized by scarce drainage, an alkaline pH, and a concentration of K ions close to that typical for illite terms but low to very low for smectite terms, in which Na and/or Ca are dominant. On the other hand, halloysitic terms were produced in the presence of an acidic pH, a high Al concentration and intense drainage.

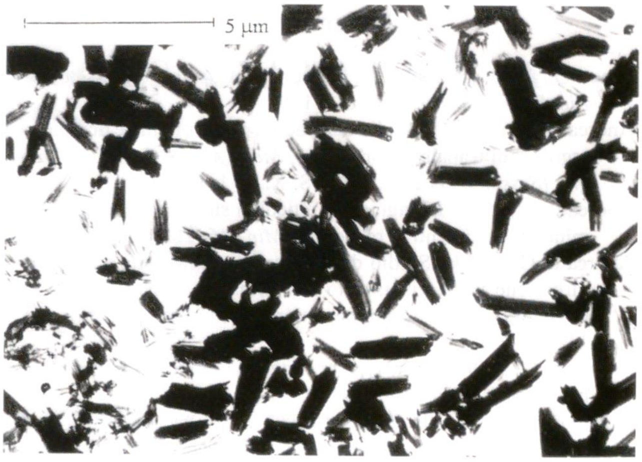


Fig. 9. TEM micrograph. Characteristic crystals of halloysite of varying size.

The purity of the material and the SEM and TEM images showing crystals of 5–7 nm indicate particularly favourable conditions of crystallisation. Conditions of abundant drainage along with an acidic pH are also confirmed by comparing the chemical analyses for major, minor, and trace elements of some unaltered rocks with those of the 10 Å-halloysite terms (Table 1).

The content of most oxides in halloysite is extremely low compared to that in the unaltered rock. The only exception that of by SiO_2, which maintains a fairly high concentration, and Al_2O_3, the concentration of which increases in the halloysite.

Of considerable interest is the comparison of the minor and trace element contents present in the unaltered rock and in the halloysitic terms. In particular, Rb, Y and Nb were completely leached out during the alteration, while La, Sr, Zr, Ba and Ce were considerably depleted. On the other hand, Cr and V remained fairly abundant in the newly formed phases. This is explained by the fact that large ionic radius elements are more easily leached out of siliceous rocks than are small ionic radius elements. SiO_2 was partly leached out, as is indicated by the occurrence, in as sociation with smectite, of opaline masses, large quartz crystals, and CT-opal (α-cristobalite) which indicates a rather low temperature of formation (Jackson et al. 1977).

This picture a fairly accurate characterization of the chemistry of the hydrothermal fluids during their action. Indeed, the solubility ratio between Al_2O_3 and SiO_2 as a function of pH, indicates an environment characterized by pH values of about 6, which could not allow the solubility of Al_2O_3.

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