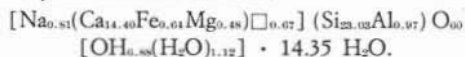


GYROLITE FROM ORTANO (ISLAND OF ELBA)

CARLO L. GARAVELLI, FILIPPO VURRO

Dipartimento Geomineralogico dell'Università, piazza Umberto I 1, 70121 Bari

ABSTRACT. — The results of diffractometrical, chemical and thermogravimetric studies on gyrolite from Ortano (Island of Elba, Tuscany) are given and discussed. Chemical analyses resulted in the crystal chemical formula:



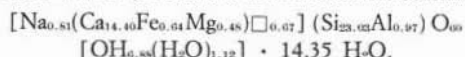
TGA and DTG curves show that dehydration takes place in two well distinct temperature intervals, corresponding to H_2O molecules in the « interlayer » in the first, and to hydroxyls + H_2O molecules within the layers in the second. In each main stage of dehydration, water loss occurs in different steps, and a structural interpretation of water losses in each step is given. The observed variations in c values, as a function of interlayer — dehydration degree, are also discussed.

Ortano gyrolite occurs associated with calcite, vesuvianite, prehnite and hydroxyapophyllite, the latter identified by means of microchemical tests and because its reticular parameters are slightly but significantly larger in comparison to fluorapophyllite.

The possible meaning of the observed assemblage is briefly discussed.

RIASSUNTO. — Vengono esposti e discussi i risultati di uno studio diffrattometrico, chimico e termogravimetrico della gyrolite rinvenuta a Ortano (Isola d'Elba).

Dalle analisi si ricava la formula cristallografica:



Le curve termogravimetriche e termogravimetriche differenziali mostrano che la disidratazione ha luogo in due intervalli di temperatura ben distinti, il primo corrispondente alle molecole H_2O nell'interstrato, ed il secondo agli ioni $\text{OH}^- + \text{H}_2\text{O}$ presenti entro gli strati. In ciascuno di questi stadi principali di disidratazione, la perdita di acqua avviene peraltro in gradini diversi: per ciascuno di essi è stato possibile dare un'interpretazione strutturale. Sono state anche discusse le variazioni osservate per la costante reticolare c in funzione del grado di idratazione concernente l'acqua di interstrato.

Ad Ortano, la gyrolite si trova associata con calcite in grandi cristalli, vesuvianite, prehnite e idrossiapofillite, identificata quest'ultima sia mediante saggi microchimici, sia per le costanti reticolari lievemente, ma significativamente, superiori rispetto alla fluoroapofillite. È stato infine brevemente discusso il possibile significato della paragenesi osservata.

Introduction

Some years ago, a few macrocrystals (up to 15 cm) of nearly water-clear calcite were collected, from the dumps of an underground prospect pit for iron ores, in the Ortano locality, some km south of the well known iron mine of Rio Marina, on the eastern coast of the Island of Elba (Tuscany, Italy). The brilliant surface of these crystals, evidently affected by corrosion and redissolution, appeared to be strewn with a large number of small (2-5 mm across), hemispherical aggregates of a white lamellar mineral, that subsequent studies showed to be gyrolite. Further details on the paragenesis of the mineral will be given below.

Gyrolite was discovered in Skye (Scotland) by ANDERSON (1851), who showed it to be a hydrated calcium silicate of approximate composition $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$. Subsequently, this mineral has been identified in a number of other localities, mostly in association with calcite, zeolites and different Ca hydrated silicates (e.g. okenite, tacharanite, tobermorite, xonotlite). As a rule, its mode of occurrence is in vugs and amygdules related to the latest crystallization stages of basaltic-type rocks. A slightly different occurrence, within andesitic tuffs, has been

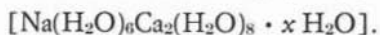
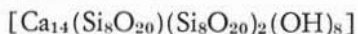
described by KOBAYASHI and KAWAI (1974). This mineral, associated with a number of zeolites and hydrated Ca silicates, was also found in drill cores from Yellowstone Park, U.S.A., within hydrothermally altered sediments, pyroclastites and rhyolitic flows (WHITE et al., 1975; BARGAR et al., 1981). Gyrolite may also occur (see below) as a very uncommon mineral in certain ore deposits.

Hence the elban occurrence of gyrolite appears rather uncommon and thus worthy of description; moreover new data obtained in this work may be of some interest in order to clarify the role of water in gyrolite, which represents the only still problematic detail in the crystal chemistry of this mineral.

The first investigation on gyrolite crystal chemistry was carried out by MACKAY and TAYLOR (1953); they established the formula $\text{Ca}_{16}\text{Si}_{24}\text{O}_{60}(\text{OH})_8 \cdot 12\text{H}_2\text{O}$ which, like the original one given by ANDERSON (1851), corresponds to an atomic ratio $\text{Ca} : \text{Si} = 0.67$. The same ratio was subsequently accepted by MAMEDOV and BELOV (1958), who proposed the quite similar composition $\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Chemical analyses of natural gyrolites, in close agreement with the above ratio, are quoted in a number of subsequent works (e.g. KUDRIASHOVA, 1958; SWEET et al., 1961; GOTTARDI and PAS-SAGLIA, 1967; see also MERLINO, 1984).

On the contrary, STRUNZ and MICHELSEN (1958) preferred the formula $\text{Ca}_{18}\text{Si}_{24}\text{O}_{60}(\text{OH})_{12} \cdot 12\text{H}_2\text{O}$ with a $\text{Ca} : \text{Si}$ ratio = 0.75, whereas MEYER and JAUNARAJ (1961), working on synthetic materials, proposed the chemical composition $\text{Ca}_2\text{Si}_4\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, corresponding to a 0.50 $\text{Ca} : \text{Si}$ atomic ratio. Quite recently, EBERHARD and HAMID RAHMAN (1982) accepted the formula $\text{Ca}_{13}(\text{Si}_8\text{O}_{20})_3(\text{OH})_2 \cdot 22\text{H}_2\text{O}$, and FLEISCHER (1983) quotes $\text{Ca}_2\text{Si}_3\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$.

The problem of both chemical composition and structure of gyrolite was definitively solved by MERLINO (1984). According to his results, gyrolite may be written as:



In this formula, the sum of positive charges (+129) appears not exactly balanced

by the negative ones (-128), but the charge equilibrium may be easily restored by a partial substitution of Si with Al, and of OH with H_2O , as well as by the presence of vacancies both in Ca and Na sites.

Structurally, the first part of MERLINO's formula refers to a « complex layer », with an ideal chemical composition $[\text{Ca}_{14}\text{Si}_{24}\text{O}_{60}(\text{OH})_8]^{-4}$, which alternates with an « interlayer sheet » containing two Ca and one Na octahedra. In this sheet, each Ca coordinates octahedrally 4 H_2O molecules, plus 2 oxygen each shared (at opposite sides of the « interlayer ») with a « complex layer ». On the contrary, the Na octahedron contains 6 H_2O molecules. A number x of additional H_2O molecules may also be contained in this « interlayer sheet »; according to many gyrolite analyses quoted by MERLINO (1984), x values may range from 0 to about 2, with some exceptions where the total number of H_2O molecules in the « interlayer » appears less than 14.

Gyrolite has a triclinic pseudo-hexagonal symmetry, with $a = b = 9.74 \text{ \AA}$; $c = 22.40 \text{ \AA}$; $\alpha = 95.7^\circ$; $\beta = 91.5^\circ$; $\gamma = 120.0^\circ$ (MERLINO, 1984). In previous works this mineral has generally been described as hexagonal: e.g. $a = 9.72$, $c = 132.8 (= 6 \times 22.13) \text{ \AA}$ after MACKAY and TAYLOR (1953); $a = 9.76$, $c = 22.26 \text{ \AA}$ after CANN (1965).

Physical and X-ray properties

The outward appearance of gyrolite from Ortano is quite different with respect to the well-known, often striking specimens from the famous pockets in the Deccan (India) basalts, especially from the so-called « Bombay quarry » (CURRIER, 1976). While in these localities gyrolite occurs as balls (or clusters of balls) up to 5 cm in diameter and mostly colored grayish, tan or pale green, Ortano gyrolite forms by far smaller hemispherical aggregates of flakes, pure white in color. The distinctive pearl luster in fracture surfaces of the balls is also lacking; the softness is another distinguishing feature of Ortano gyrolite, which can be very easily disaggregate.

Under the microscope, cleavage flakes exhibit a uniaxial, negative, optic figure. This agrees with the closely pseudo-hexagonal

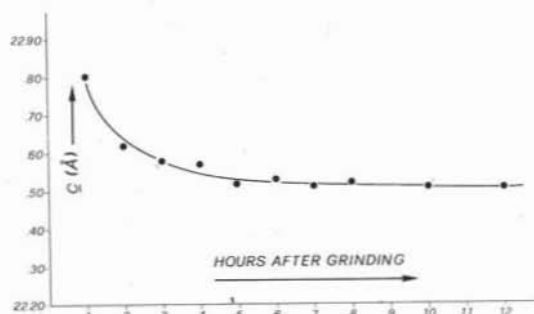


Fig. 1. — Variations in the reticular parameter c measured at various times after the preparation of the sample. Samples preserved in normal air.

symmetry of gyrolite, though in some cases a small 2V was observed (CANN, 1965). Indices of refraction resulted $\omega = 1.550 \pm 0.005$ and $\epsilon = 1.535 \pm 0.005$, well in agreement with previously published values: e.g. $\omega = 1.545$, $\epsilon = 1.535$ after MACKAY and TAYLOR (1953); $\alpha = 1.537$; $\beta = 1.547$ and $\gamma = 1.549$ after CANN (1965).

Ortano gyrolite single crystals are of too low a quality to attempt any interpretation of their diffraction patterns. Powder patterns of the mineral (diffractometric technique) showed, as strong and sharp peaks, only the 00 l reflections, all the others resulted in broad and very fuzzy maxima.

Thus, only a c diffractometrical evaluation was attempted, on the basis of the other unit-cell parameters determined by MERLINO (1984). Results obtained clearly show that a slight but appreciable variation in $d_{\{00l\}}$ spacings occurs, owing to the time interval between grinding the mineral and recording a 00 l reflection set.

For freshly powdered gyrolite, c values are about 22.80 ± 0.05 Å, while after 8-12 hours they drop to 22.50 ± 0.02 Å (fig. 1). Likely, this may be due to partial dehydration: no decrease occurs when powdered gyrolite is preserved in humid air (or even slight increases are observed), whereas c measured values are 22.38 ± 0.04 Å when kept in a dry atmosphere. These c values are to be compared with $c = 22.40 \pm 0.02$ Å, determined by MERLINO (1984) on gyrolite single crystal, having 13.68% total H₂O.

Specific gravity, measured by immersion

in bromoform + benzene, is 2.37. The calculated density value, derived from MERLINO's unit cell parameters and the actual chemical composition (see below), is 2.432 g/cm³. The calculated density drops to 2.389 g/cm³ if a c value of 22.8 Å is adopted.

Chemical analysis

A chemical analysis was performed on a gyrolite sample, well purified under the microscope. However a particular problem arose, concerning the hydration degree of the analyzed material: some preliminary observations showed that, in powdered gyrolite, the water content may change to a rather large extent according to the external humidity conditions, the observed H₂O wt.% ranging from 10.58 to 16.10.

A sample of freshly separated, unpowdered gyrolite was thus weighed and analyzed by chemical wet methods, avoiding any preliminary grinding. Under these conditions, the water content (Penfield's method) resulted 12.69%. The obtained values are given in table 1.

TABLE 1
Chemical analysis of gyrolite from Ortano

Oxydes	wt. %	Elements	wt. %	Atomic ratios
SiO ₂	51.55	Si	24.09	23.026
Al ₂ O ₃	1.85	Al	.98	.974
FeO	1.71	Fe	1.33	.639
CaO	30.09	Ca	21.51	14.401
MgO	.72	Mg	.43	.479
Na ₂ O	.94	Na	.70	.814
H ₂ O	12.69	O	37.82	63.447
	—	H ₂ O	12.69	18.907
Sum =	99.55			

Atomic ratios on the basis of (Si + Al) = 24.

The calculation of the crystal chemical formula, on the basis of 24 (Si + Al) and according to MERLINO's (1984) indications, leads to the following results:

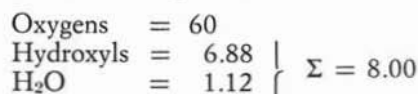
Tetrahedral cations:



Octahedral cations:

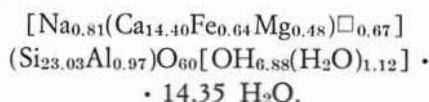


Anions in the « complex sheet »:



« Interlayer » H_2O molecules: 14.35.

Thus the following crystal chemical formula is obtained:



between 15.4 and 17.0 for octahedral cations; between 4.7 and 8.0 for hydroxyls; and between 11.6 and 18.8 for « interlayer » H_2O . Also Al and Na contents appear quite regular, whereas the amount of divalent Fe seems relevant: but this was to be expected owing the occurrence, within an iron mineralization, of the gyrolite studied in this work.

In the original description of gyrolite, ANDERSON (1851) first observed that a consistent amount of water may be lost even at moderate temperatures (loss at $100^\circ\text{C} = 4.42\%$). This behaviour was subsequently confirmed by MACKAY and TAYLOR (1953) who accomplished the first thorough study

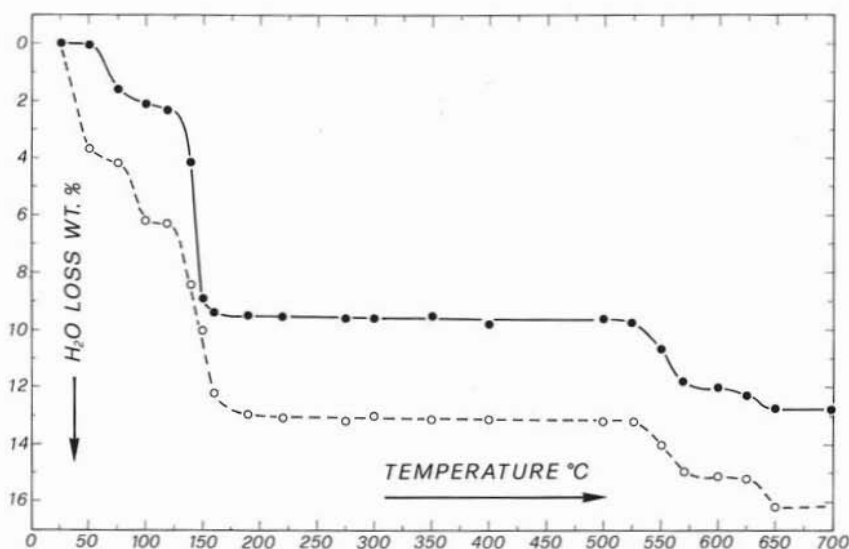


Fig. 2. — Examples of T.G. curves of Ortano gyrolites, obtained by heating to constant wt., step by step, in electric muffle with thermostat. See table 2 for numerical data. - ● = gyrolite with 12.7% H_2O ; ○ = gyrolite with 16.1% H_2O .

Since all microchemical tests for trivalent iron have failed, all the weighed Fe_2O_3 was calculated as FeO.

A spectrographic search for minor elements indicated the presence of very small quantities (about some hundreds ppm) of K and Mn, and minor traces of Cu and Zn.

No substantial difference arises from these results, when compared with the previously known gyrolite analyses (see a review in MERLINO, 1984). The listed values for gyrolites from various sources range

on gyrolite dehydration. They indicated that 4.15 wt. % of water is lost at 100°C ; but this loss continues up to 450°C . This first dehydration stage entails a loss of 9.0%; a second stage begins at about 500°C , is complete at 850°C and corresponds to 3.0% of the initial weight.

Subsequent works substantially agree with these observations: e.g. SWEET et al. (1961), who also stated that gyrolite regains water lost at 110°C on exposure to moist air. MERLINO (1984) concludes that his own

results are quite in keeping with those obtained by MACKAY and TAYLOR (1953), the two-stage loss of water corresponding to the loss of H_2O molecules and OH^- ions respectively.

In the present work, two different kinds of thermal dehydration experiments were performed. In the first one, a continuous heating technique was adopted, using a Perkin-Elmer apparatus at a rate of $2^\circ C/min$. in static atmosphere. In these runs, *TG* and *DTG* curves were recorded. A second series of measurements was carried out by heating the mineral step-by-step, at prefixed temperatures, in an open platinum crucible, until a constant weight was attained at any given temperature.

until all the water and hydroxyls are lost at about $680^\circ C$. Nevertheless, also in these dehydration diagrams, some discontinuities are evident, with regard to the slope of the curves at different temperatures (fig. 3).

In both types of curves, two well distinct main dehydration stages appear, corresponding to those observed by MACKAY and TAYLOR (1953). A striking result, however, is the evident splitting of each main stage in different dehydration steps.

As far as the second dehydration stage is concerned, occurring between 500 and $700^\circ C$, all thermogravimetric curves are almost identical, independently from the initial hydration degree of gyrolite. Two distinct weight-loss steps are shown: a major

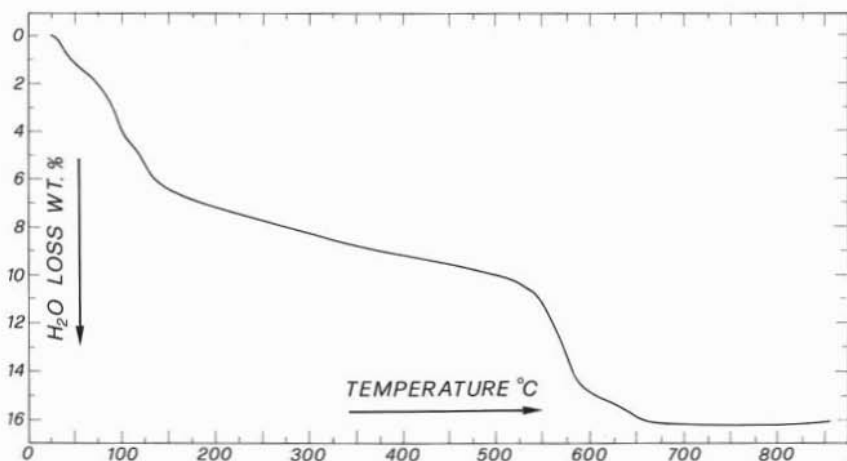


Fig. 3. — Example of *T.G.* curve, recorded by a Perkin-Elmer DTA mod. 1700 apparatus. Heating rate = $2^\circ C/min$; sample of fully hydrated gyrolite with 16.1 % H_2O .

As starting materials, different samples of Ortano gyrolite, at various hydration degrees, were used. Some heating runs have also been accomplished on samples of gyrolite from the « Bombay Quarry » (India), with results quite in keeping with the thermal behaviour of the Ortano mineral.

The obtained thermogravimetric curves appear quite different according to the heating technique employed. In the step-heating dehydration the weight losses occur within well-defined narrow temperature intervals (fig. 2). On the contrary, in the first type of heating runs the dehydration of gyrolite goes on in a continuous way,

step between 520 and $600^\circ C$, and a minor one between 600 and $680^\circ C$. In *DTG* curves, two separate peaks occur, with minima at 575 and $640^\circ C$ respectively (fig. 4).

On the contrary, the weight loss below $200^\circ C$ depends significantly upon the initial water content. Unpowdered, freshly separated natural gyrolite (12.69 % H_2O by Penfield's method; 12.75 % H_2O by dehydration curves; 14.35 molecules H_2O in the « inter-layer ») shows two steps in the first dehydration main stage: below $100^\circ C$, and between 100 and $180^\circ C$ respectively. When the mineral is fully hydrated ($H_2O = 16.0 \div$

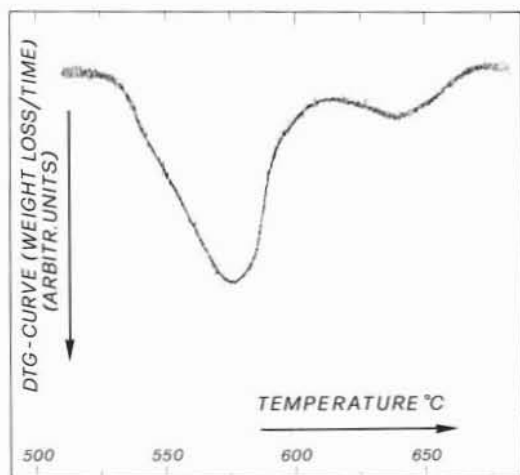


Fig. 4. — Example of DTG curve in the region between 500 and 700°C, recorded by a Perkin-Elmer TGS mod. 2 apparatus. Heating rate = 2°C/min. The amount of « interlayer » water does not affect the gyrolite DTG curves in this region.

16.1%) by long exposure to moist air, three steps occur: below 65°C, between 75 and 100°C, and between 100 and 200°C respectively.

Also in the section below 200°C a fair agreement exists between the dehydration steps and the peaks in DTG curves (fig. 5).

The major weight loss between 100 and 200°C corresponds to a forked DTG peak with minima at 90 and 115°C; weight losses below 100°C correspond to another, immediately foregoing, DTG peak: simple in the case of unpowdered gyrolite (minimum at 45°C) and forked for the fully hydrated mineral (minima at 35 and 50°C).

Weight losses observed in two step-by-step heating runs are listed in table 2, for the unpowdered and fully hydrated mineral respectively.

In table 3 a structural interpretation of the results from these step-heating TG curves is given, which is based on the gyrolite structure as solved by MERLINO (1984). The good quantitative correspondance between each observed and calculated weight loss gives experimental evidence to the proposed interpretation.

Moreover it is notable that, by dehydration at room temperature in a vacuum-sealed H₂SO₄ dessicator, the H₂O content becomes stable at a minimum value of 10.58%, which corresponds to 10.75 molecules H₂O in the « interlayer sheet ». Assuming that all the vacancies are located in the « interlayer », and from the above quoted analytical data, an agreeing value of 10.94 is calculated as the number of H₂O molecules coordinated by (0.81 Na + 1.52 Ca).

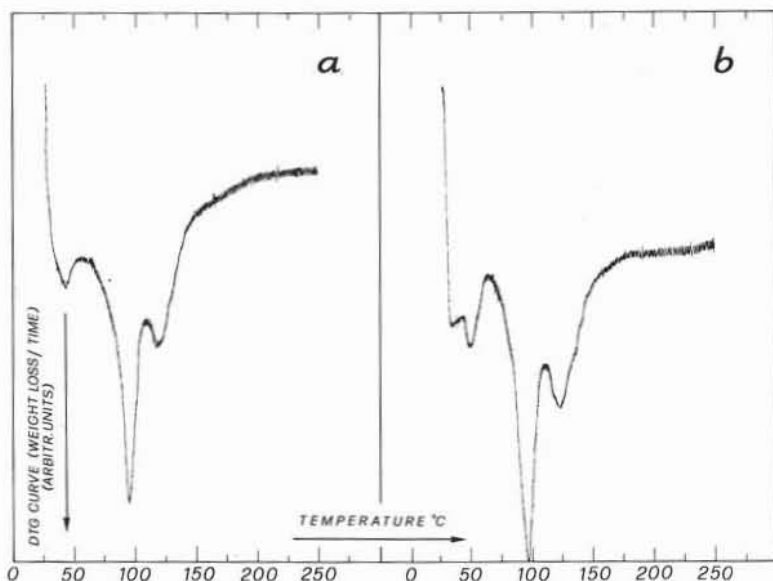


Fig. 5. — Examples of DTG curves in the region below 250°C, recorded in the same conditions as in fig. 4. - a) = Gyrolite with 12.7% H₂O; b) = Gyrolite with 16.1% H₂O: first minimum is forked.

TABLE 2
Water lost at various temperatures
in two step-heating runs

T (°C)	"Natural" gyrolite		"Fully hydrated" gyrolite	
	wt.%	molecules H ₂ O	wt.%	molecules H ₂ O
50	0.00	0.00	3.72	5.74
75	1.62	2.40	4.16	6.42
100	2.12	3.14	6.20	9.56
120	2.30	3.41	6.32	9.75
140	4.12	6.11	8.38	12.92
150	8.92	13.23	10.00	15.42
160	9.40	13.94	12.22	18.85
190	9.48	14.06	12.96	19.99
220	9.50	14.09	13.10	20.20
275	9.60	14.24	13.14	20.27
300	9.60	14.24	13.02	20.08
350	9.50	14.09	13.16	20.30
400	9.82	14.56	13.08	20.17
500	9.60	14.24	13.20	20.36
525	9.70	14.39	13.18	20.33
550	10.62	15.75	14.02	21.62
570	11.80	17.50	14.96	23.07
600	12.02	17.83	15.18	23.41
625	12.20	18.09	15.20	23.44
650	12.76	18.92	16.04	24.74
800	12.76	18.92	15.98	24.65

"Natural gyrolite": freshly separated sample, as employed for chemical analysis.

"Fully hydrated gyrolite": powdered sample, preserved some weeks in H₂O saturated atmosphere.

6.88 hydroxyls (=3.44 H₂O) in the formula unit correspond to 2.32 and 2.225 wt.% in the "natural" and "fully hydrated" gyrolite respectively.

Thus, the following conclusions may be reached.

a) The two main dehydration stages (below 200° C, and between 520 and 680° C) are not related to H₂O molecules and hydroxyls respectively. On the contrary, they are due to « interlayer » H₂O in the first, and to hydroxyls plus H₂O in the « complex layer » in the second.

b) H₂O molecules which substitute hydroxyls within the « complex layer », seem to be bonded in a slightly stronger way in comparison with hydroxyls themselves. But the experimental evidence supports this conclusion: however, its interpretation remains somewhat puzzling.

c) Also H₂O molecules in the « interlayer » are lost in distinct steps, owing to their different structural role. The less weak bond occurs for H₂O octahedrally coordinated by Ca and Na. Some evidence may arise from DTG curves (splitting of the 90-115° C peak) to suggest a possible distinction among these molecules.

d) As MERLINO (1984) states, « few further water molecules can be distributed with partial occupancies among various sites in the interlayer sheet ». They appear more weakly linked to the structure; it is likely that a portion of them (in the more hydrated gyrolites) is merely given by adsorbed water.

TABLE 3
A tentative interpretation of various dehydration steps in gyrolite

Temperature intervals °C	structural interpretation	"natural" gyrolite		"fully hydrated" gyrolite	
		calc. wt.%	obs. wt.%	calc. wt.%	obs. wt.%
< 75	"additional" (absorbed?) water	/	/		4.00
75 - 100	uncoordinated H ₂ O in "interlayer"	2.30	2.10	6.03	2.25
100 - 200	H ₂ O coord. by interlayer Ca and Na	7.38	7.50	7.07	6.85
500 - 600	hydroxyls in the "complex layer"	2.32	2.40	2.22	2.10
600 - 700	molecules H ₂ O in the "complex layer"	0.76	0.75	0.73	0.85
	Sum	12.76	12.75	16.05	16.05

Calculated wt.%: on the basis of analytical data (see above). For "fully hydrated" gyrolite an averaged value of 16.05 % H₂O is assumed.

Observed wt.% : averaged values for several step by step heating runs.

H₂O molecules acquired from moist air (about 6) differ from the remaining 3÷3.5 ones and are lost at a distinctively lower temperature. Likely, only these latter molecules, though uncoordinated, are to be considered as properly belonging to the structural framework.

e) Small variations observed and quoted above for 00*l* spacings of unheated gyrolite (*c* between 22.80 and 22.38 Å) are probably due to different amounts of H₂O in the «interlayer». Also by heating to about 300° C, only minor changes (to ~22.1 Å) are observed in *c* values. This relatively small shrinkage accounts for the statement by MEYER and JAUNARAJA (1961), that the gyrolite lattice is not contracted if the interlayer water is driven off. According to the structural determination by MERLINO (1984), the nature of the interlayer Ca coordination octahedra (sharing at opposite corners with apical oxygens of two successive «complex layers») easily explains this behaviour. After long exposure to the air, heat-treated (at 400° C) gyrolite regains a *c* value of about 22.4÷22.5 Å. Beyond 650-700° C, gyrolite structural building becomes irreversibly destroyed, and after protracted heating at 850° C some β-wollastonite peaks appear on diffractograms. No defined reflection ascribable to reyerite or to other hydrated Ca silicates appears in heat-treated gyrolite.

Paragenetic remarks

The iron sulphides ore deposit of Ortano has been described by GOTTARDI (1962). It belongs to an iron mineralized district which extends along the eastern coast of the Island of Elba, some km southward from Rio Marina. The main iron ores are oxides and sulphides, in some places (as at Ortano) associated to skarns chiefly given by hedenbergitic pyroxenes and ilvaite, with subordinate amphiboles (likely due to pyroxenes uralitization) and pistacite. In Elba deposits, apart from some supergene minerals such as Fe and Al sulphates, no low-temperature nonmetallic mineral has ever been observed other than chlorites, quartz, calcite and, far more scarcer, fluorite and dolomite. Calcite and quartz («prase» color-variety) from

these localities have sometimes provided conspicuous specimens of large and well-developed crystals. Some silicates (e.g. epidotes, vesuvianite, grossular, chlorites) may be present within thermometamorphic limestones near the contact with skarns.

Further details on the mineralogy of these deposits have been given by MANASSE (1912) (deposit of Capo d'Arco, a few km south), FEDERICO and FURNASERI (1953) (alteration of pyroxenes), and TANELLI (1977) (geology and mineralogy of the skarns).

Paragenetic sequences of ore and gangue minerals from eastern Elba iron deposits are still worthy of further work. However, it is very likely, at least in some cases, that we are not dealing with an ordered sequence of minerogenetic events, proceeding in a continuous way from higher (locally about 600° C) to lower temperatures. Also the composition of mineralizing agents appears rather variable from point to point, independently from temperature, and many different parageneses are chiefly related to differences in H₂O, oxygen and sulphur fugacities.

Thus, it is very difficult to insert the deposition of gyrolite at a definite point in a definite paragenetic sequence. Moreover, the gyrolite bearing specimens were not collected from their original position, but from waste dumps, so that it is impossible to locate them exactly within the Ortano mineralized body.

Gyrolite strewn calcite crystals were collected free of any matrix materials. Nevertheless, their implant surface is marked by a thin layer rich in microscopic crystals of a silicatic yellowish-green mineral, identified as vesuvianite. Thus it is very likely that calcite crystals were implanted not on skarn (as most frequent at Ortano), but on metamorphosed limestone.

Vesuvianite has been undoubtedly identified by X-ray diffraction: measured unit-cell parameters resulted $a = 15.614$; $c = 11.825$ Å.

Partly embedded in calcite crystals are present other minerals, namely prehnite and apophyllite, both up to now not observed within Elba iron mineralizations.

The first forms an hemispherical aggregate (1 cm across), as well as a number of smaller (1÷3 mm across) spherules entirely embed-

ded in calcite and located very near the implant surface of calcite. Its unit-cell parameters (powder diffraction) are: $a = 4.642$; $b = 5.484$; $c = 18.45 \text{ \AA}$.

More interesting is the presence of apophyllite. But in one Ortano specimen this mineral forms an euhedral crystal, pseudocubic in shape, of about 15 mm across, with some minor individuals in other specimens. The color is white with a light greenish tinge and a pearly luster. An accurate determination (powder diffractometry; step-scanning technique) of unit-cell parameters gave $a = 8.984 \pm 0.002$; $c = 15.848 \pm 0.006 \text{ \AA}$.

Recently (DUNN et al., 1978; DUNN and WILSON, 1978) two end-members have been recognized: fluorapophyllite and, up till now, the far scarcer hydroxyapophyllite. Very slight but yet significant differences exist in unit-cell parameters: $a = 8.965 \pm 0.002$; $c = 15.768 \pm 0.002 \text{ \AA}$ for fluorapophyllite (COLVILLE et al., 1971), and $a = 8.978 \pm 0.003$; $c = 15.83 \pm 0.01 \text{ \AA}$ for hydroxyapophyllite (DUNN et al., 1978).

Undoubtedly, measured unit-cell parameters of Ortano apophyllite agree well with hydroxyapophyllite ones (or are even slightly larger), and differ significantly with respect to fluorapophyllite. Moreover, a microchemical search of F showed this element to be absent or, at the most, present only in traces. Thus, Ortano mineral actually refers to hydroxyapophyllite.

As far as the described specimens are concerned, the paragenetic sequence appears as follows: vesuvianite (likely from the matrix) \rightarrow prehnite \rightarrow hydroxyapophyllite \rightarrow calcite \rightarrow gyrolite. A similar assemblage, though frequent in basaltic amigdules, is rather uncommon in ore deposits and till now unique for Elba iron mines.

Nevertheless, apophyllite and prehnite (sometimes associated) are known from a number of ore deposits. It may also be worthwhile to remember that some ore deposits are included among the very few ascertained occurrences of hydroxyapophyllite (DUNN and WILSON, 1978). Moreover, its type-locality is given by a metal deposit (Ore Knob Mine, N. Carolina, U.S.A.), where hydroxyapophyllite occurs as crystal druses on a pyrrhotite-chalcopyrite assemblage

(DUNN et al., 1978). Gyrolite itself was observed as crusts overlying apophyllite in New Almaden mercury mines (HINTZE, 1897); more recently STEPHENS and BRAY (1973) described a number of hydrated Ca silicates, including gyrolite, occurring in hydrothermally metamorphosed limestones at Bingham copper mine (Utah, U.S.A.).

The presence of these minerals in some ore deposits is generally attributed to hydrothermal actions at some time after main period of ore deposition, though at Bingham, according to STEPHENS and BRAY (1973), gyrolite occurs sometimes intergrown with sphalerite.

Although GOTTARDI (1962), in his detailed study of Ortano ores, did not observe traces of similar events, an intervention of hydrothermal actions has been considered by DE BENEDETTI (1951) for some eastern Elba localities.

Since the first work of FLINT et al. (1938), hydrothermal syntheses of gyrolite have been accomplished by a number of Authors. It is well established that gyrolite can be obtained in a wide range of pressures and at temperatures below 250°C (e.g. MAYER and JAUNARAJA, 1961), while different, less hydrated phases (such as reyerite) are formed at higher temperatures. According to WHITE et al. (1975), gyrolite found in drill cores from Yellowstone Park would have been deposited at about 125°C.

Genetical conditions of this type, though presumably infrequent in Elba iron deposits owing to the local rarity of the described assemblage, are quite compatible with a late stage in a sequence of metasomatic or contact-metamorphic mineralizing events.

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