

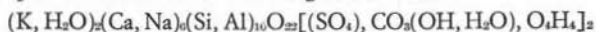
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CRYSTAL CHEMISTRY OF LATIUMITE

RIASSUNTO. — Sono stati presi in esame campioni di latiumite provenienti da tre località (Pitigliano, Campagnano e Baccano). Di questi vengono riportati i parametri ottici, le analisi chimiche, le costanti della cella elementare e lo spettro di polvere tipico dei tre campioni studiati, insieme ai dati di letteratura relativi a latiumite e tuscanite.

Sulla base delle analisi chimiche e di considerazioni strutturali viene estesa alla latiumite l'interpretazione cristallografica già proposta dagli autori per la tuscanite; in particolare, accanto alle vicarianze Ca-Na e Al-Si, vengono introdotte la sostituzione K-H₂O e la sostituzione dello ione SO₄⁼ con un anione carbonato (con l'ulteriore introduzione di uno ione OH⁻ o di una molecola H₂O a completare la geometria tetraedrica), ovvero con un raggruppamento tetraedrico (O₄H₄)⁴⁻.

Tutto questo può essere riassunto nella seguente formula:



formula che permette di razionalizzare la cristallografica dei diversi campioni di minerali dell'intero gruppo latiumite-tuscanite.

ABSTRACT. — Optical, crystallographic and chemical data for samples of latiumite from three localities are reported and compared with the known data for latiumite from Albano and for tuscanite.

All the chemical data can be rationalized on the basis of the following crystal chemical formula:



The extent of isomorphic substitutions is discussed and defined, on the basis of the analytical data and structural considerations.

Introduction

Latiumite is an aluminosilicate discovered by TILLEY and HENRY (1953) in the ejected blocks in the «peperino» tuff of the Albano hills. A second finding was made by BARBIERI and FORNASERI (1970) in Pitigliano (Tuscany, Italy). CANNILLO, DAL NEGRO and ROSSI (1973) determined the crystal structure of latiumite and classified it as a sheet silicate, characterized by the presence of double layers of (Al, Si) tetrahedra. Recently ORLANDI, LEONI, MELLINI and MERLINO (1977) found in Pitigliano a new mineral phase, tuscanite, closely related to latiumite.

The crystal structure analysis by MELLINI, MERLINO and ROSSI (1977) showed its main features to be double layers of aluminum and silicon tetrahedra, made up by single layers similar to those present in latiumite, but connected according to a different scheme. Unequivocal distinction between latiumite and tuscanite is possible only on the basis of single crystal X-ray diffraction spectra.

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Aim of this work is to give chemical, crystallographic and physical data on new findings of latiumite and to compare them with the earlier ones.

TABLE 1

X-ray diffraction pattern of Latiumite

d	indices	I/I ₀	d	indices	I/I ₀
11.44	100	71		221	
5.80	201	6	2.333	220	1
5.74	200	9		413	
5.20	002	1	2.318	014	1
4.58	011	6	2.302	122	4
	202			500	
4.51	201	12		402	
4.29	102	3	2.252	503	1
4.00	301	3		023	
3.835	211	16	2.054	223	1
	300			513	
3.710	112	1	2.000	215	4
	012			601	
3.634	103	3	1.994	215	5
	302			602	
3.468	003	3	1.907	420	6
3.396	202	6		502	
3.295	112	4		024	
	301		1.822	115	1
3.149	311	3		413	
3.067	310	47		604	
3.009	401	6		205	
2.961	312	16	1.794	324	5
2.900	402	7		601	
2.877	013	100		610	
	400			116	
2.829	212	9	1.693	215	1
2.772	311	2		611	
2.729	302	2		323	
2.655	203	2		016	
2.624	313	1	1.644	106	11
	403			224	
2.586	401	2		700	
2.553	020	7		025	
2.510	410	1	1.611	414	1
	120			116	
2.460	121	2	1.565	425	1
2.407	312	4		710	
2.376	502	1			
	214				

Occurrence and paragenesis

All the samples examined come from three localities, within a region (South Tuscany and Latium, Italy) which is geographically large, but petrographically homogeneous.

All samples were collected in ejected metamorphic calcareous blocks found in the « Sabatini » hills (latiumite from Campagnano and Baccano) and in the Pitigliano hills (latiumite from Pitigliano).

The most commonly associated minerals are vesuvianite, garnet (grossular and andradite), wollastonite, pyroxene.

Crystallographic properties

Identification was based on rotation and Weissenberg single crystal X-ray spectra. We also analyzed the powder diffraction pattern of our samples be-

cause, as quoted by ORLANDI et al. (1977) in their study on tuscanite, much misleading data are present in the literature. Our results are summarized in the pattern of table 1, which is typical of all the studied specimens. Our observations confirmed the finding of ORLANDI et al. (1977) about discrepancies in the pattern given by TILLEY and HENRY (1953). The lattice parameters, obtained by single crystal photographs and refined by least squares fitting of the powder data, are reported in table 2, together with the corresponding values for latiumite from Albano (TILLEY and HENRY, 1953) and tuscanite (ORLANDI et al., 1977).

TABLE 2

Unit cell parameters of Latiumites and Tuscanite

	Latiumite (Baccano)	Latiumite (Campagnano)	Latiumite (Pitigliano)	Latiumite (Albano) (Tilley and Henry, 1953)	Tuscanite (Pitigliano) (Orlandi et al., 1977)
a	12.064(2)	12.040(9)	12.036(4)	12.12	24.036(14)
b	5.107(2)	5.105(5)	5.106(3)	5.13	5.110(3)
c	10.882(3)	10.874(16)	10.925(9)	10.80	10.888(8)
β	107.08°(3)	106.98°(7)	107.08°(4)	108°	106.95°(3)

Optical properties

Optical examination showed monoclinic symmetry with elongation corresponding to the b axis, which is the γ axis of the indicatrix. The optical axial plane is thus perpendicular to (010).

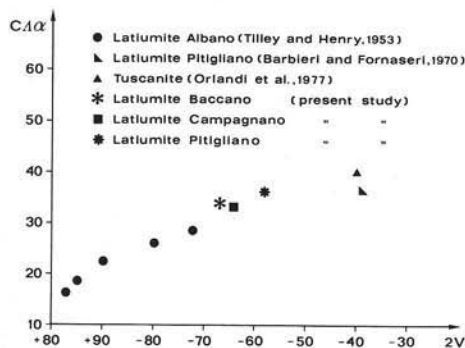


Fig. 1. — Optical axial angle and extinction angle relationship in latiumites and tuscanite.

TABLE 3
Optical properties of Latiumites and Tuscanite

	Latiumite (Baccano)	Latiumite (Campagnano)	Latiumite (Pitigliano)
α	1.589	1.586	1.582
β	1.596	1.594	1.587
γ	1.602	1.601	1.592
(γ α)	0.013	0.015	0.010

	Latiumite ^(a) (Pitigliano)	Latiumite ^(b) (Albano)	Tuscanite ^(c) (Pitigliano)
α	1.582	1.600	1.581
β	1.590	1.606	1.590
γ	1.591	1.614	1.591
(γ α)	0.009	0.014	0.010

- (a) BARBIERI e FORNASERI (1970);
 (b) TILLEY and HENRY (1953);
 (c) ORLANDI et al. (1977).

Carlo Erba elemental microanalyzer 1104 instrument, with gas-chromatographic separation of CO_2 and H_2O . SO_3 and Cl were determined by X-ray fluorescence spectrometry, using samples of latiumite added with known amounts of sulphur and chlorine as reference standard. On the basis of the known quantities of the other elements, K_2O , CaO , SiO_2 , Al_2O_3 and Fe_2O_3 were determined according to the X-ray fluorescence method developed by FRANZINI and LEONI (1972)

Latiumite is often twinned on (100), which is also a cleavage plane. The extinction angle $c \wedge a$ on (010) is variable and as suggested by TILLEY and HENRY (1953) is related to the $2V$ value; this relationship is described by fig. 1, which reports the data from TILLEY and HENRY (1953), BARBIERI and FORNASERI (1970), ORLANDI et al. (1977) together with our new data.

Refractive indices were determined by the double variation method utilizing bromoform and aniline as liquids. Results are reported in table 3 together with the literature data for latiumite and tuscanite.

The examination of fig. 1 and table 3 rises some doubts as to whether the latiumite from Pitigliano studied by BARBIERI and FORNASERI (1970) was really latiumite or rather tuscanite; however the question cannot be conclusively answered without a single crystal study.

Chemical composition

The chemical analysis was carried out by atomic absorption spectrophotometry for Na_2O , MgO and SrO . CO_2 and H_2O were determined by micro-determination of C and H by use of a

TABLE 4
Chemical analyses of Latiumites and Tuscanites

	Latiumite (Baccano)		Latiumite (Campagnano)		Latiumite (Tilley and Henry, 1953) (Albano)		Tuscanite (Orlandi et al., 1977) (Pitigliano)			
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)		
SiO ₂	30.48	5.72	31.25	5.80	28.33	4.93	26.99	4.93	34.64	6.34
Al ₂ O ₃	19.39	4.28	19.21	4.20	24.67	5.07	23.50	5.07	16.95	3.66
Na ₂ O	1.39	0.51	1.18	0.42	1.11	0.37	1.06	0.37	1.45	0.51
K ₂ O	5.58	1.33	4.85	1.15	7.20	1.60	6.86	1.60	3.79	0.88
CaO	27.68	5.56	28.21	5.61	29.41	5.49	28.02	5.49	26.76	5.25
MgO	0.49	0.14	0.46	0.12	0.76	0.20	0.72	0.20	0.40	0.11
MnO	n.d.	-	n.d.	-	0.02	0.01	0.02	0.01	-	-
SrO	n.d.	-	0.40	0.04	-	-	-	-	0.38	0.04
Fe ₂ O ₃	0.27	0.04	0.33	0.05	0.50	0.07	0.48	0.07	0.76	0.10
FeO	n.d.	-	n.d.	-	0.55	0.08	0.52	0.08	n.d.	-
Cl	0.08	0.03	0.08	0.03	0.14	0.04	0.13	0.04	0.02	-
SO ₃	7.54	1.06	9.32	1.30	5.42	0.71	5.16	0.71	10.04	1.38
CO ₂	5.03	1.29	1.65	0.42	1.60	0.38	2.67	0.67	2.20	0.55
H ₂ O	2.07	1.29	3.06	1.89	0.27	0.16	2.80	1.71	2.61	1.60
O		22.19		22.82		23.24		22.95		22.49
D _(obs.)		2.83		2.83		2.93		2.93		2.83
D _(calc.)		2.92		2.90		2.72		2.84		2.77

Total Fe content determined as Fe₂O₃; (a): Calculated on the basis of Si+Al=10 from the original data; (b): Calculated on the basis of Si+Al=10 from the original data modified by new analysis of CO₂ and H₂O. For explanation see section on chemical composition.

and modified by LEONI and SAITTA (1973), assuming that the sum of the weight percentages was 100. Table 4 reports the chemical and density data for latiumite. Unfortunately, among the four known findings of latiumite we can compare only three chemical analyses, since for latiumite from Pitigliano BARBIERI and FORNASERI (1970) did not yield analytical data because of the small quantity of material available. On the other hand we did have a sufficient amount of latiumite from Pitigliano to make a chemical analysis but we have serious doubts about the purity of the analysed material: in fact the powder pattern showed the presence of franzinite, a new mineral phase found in Pitigliano by MERLINO and ORLANDI (1977). Moreover its density, determined on relatively large fragments, appeared anomalously low ($d = 2.58 \text{ g cm}^{-3}$). Although we did not report the analytical data for latiumite from Pitigliano we give its optical properties (table 3) that were measured on a very little fragment, previously tested by X-ray single crystal diffraction techniques.

Table 4 gives the atomic ratios of latiumite from Campagnano, latiumite from Baccano and tuscanite from Pitigliano (ORLANDI et al., 1977), calculated on the basis of 10 (Si+Al) atoms, as indicated by the structure analysis of latiumite (CANNILLO et al., 1973) and tuscanite (MELLINI et al., 1977).

For tuscanite we report the content of half a cell. The atomic ratios of latiumite from Albano (TILLEY and HENRY, 1953) were recalculated on the basis of 10 (Si+Al) atoms (column a of table 4). Furthermore, on a sample of latiumite from Albano, provided by BARBIERI and FORNASERI, a new chemical analysis for CO₂ and

H₂O was made. The data reported in column *b* of table 4 are computed assuming our data as correct (2.67 wt% for CO₂ and 2.8 wt% for H₂O) and recalculating the other percentages, so that the sum of all the weight percentages is 100.

Crystal chemical considerations

TILLEY and HENRY (1953) supposed that latiumite was a solid solution series and CANNILLO et al. (1973) gave the limits for Si-Al substitutions on the basis of crystalchemical considerations. These authors pointed out that a complete substitution of Al by Si would unbalance the valence bond sum for some oxygen atoms; on the other hand an amount of Al greater than six atoms per unit cell would imply the replacement of Ca by some trivalent cation or of K by Ba. It should be observed that LOEWENSTEIN's rule (1954) (AlO₄ tetrahedra avoid being linked together) should indicate a still lower aluminum content. In fact both crystal structure determinations of latiumite and tuscanite indicate that two of the five independent tetrahedral sites in the silicon-aluminum layer, namely T(2) and T(5), are completely occupied by aluminum atoms; now if the Loewenstein's avoidance rule should be strictly observed T(1), T(3) and T(4) tetrahedra should be completely occupied by silicon atoms, as each of them shares vertices with T(2) or T(5) tetrahedra. As a consequence the aluminum content should correspond to four aluminum atoms for every ten cations in the silicon-aluminum layer. This corresponds fairly well with the chemical data for latiumite from Baccano and Campignano (4.28 and 4.20 aluminum atoms respectively) as well as for tuscanite (3.66 aluminum atoms). However chemical and structural data indicate that the Loewenstein's rule is not strictly observed in latiumite from Albano for which an aluminum content corresponding to five aluminum atoms (table 4) and an equal occupancy by silicon and aluminum atoms in the tetrahedral site T(3) (CANNILLO et al., 1973) were found.

The data given in table 4 show a strong correlation between aluminum and potassium contents, whereas sodium and calcium contents are most constant in tuscanite and latiumites from various sources, thus clearly indicating that the increasing substitution of silicon by aluminum is not balanced by calcium for sodium substitution, but by an increasing substitution of potassium cations for water molecules.

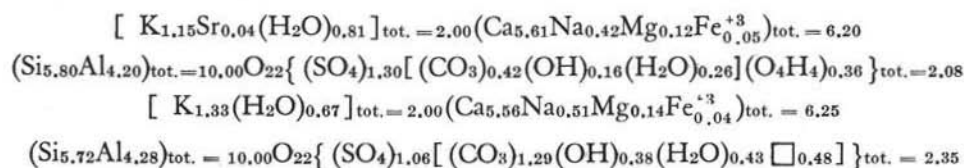
Table 4 indicates also that the water content is always larger than that corresponding to K-H₂O replacement; moreover the oxygen excess over 22.0 atoms in the unit cell (or in half a cell for tuscanite) suggests the presence of hydroxyl anions. With regard to the location of hydroxyl anions or water molecules it seems useful to recall the suggestions of ORLANDI et al. (1977) and MELLINI et al. (1977), who, in their studies on tuscanite, on the basis of chemical and structural data, proposed the following substitutions: *a*) in the CO₃-SO₄ replacement a planar carbonate group takes its place near the position corresponding to a face of the

tetrahedral sulphate group whereas an hydroxyl anion, or a water molecule, locates itself near the position corresponding to the fourth vertex of the sulphate tetrahedron; b) the tetrahedral grouping O_4H_4 of four hydroxyl anions may substitute for a sulphate group.

The results of our chemical analyses on latiumite from Baccano and Campagnano are fairly consistent with such suggestions so that the following general formula can be assumed:

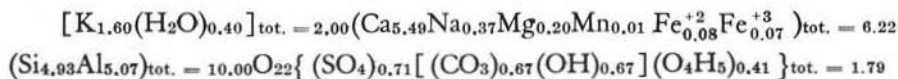


Therefore the crystalchemical formulas for latiumites from Campagnano and Baccano respectively may be written:

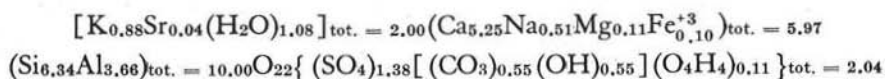


In the last formula the vacancies were introduced because the sum of the hydroxyl anions and water molecules is less than the number of carbonate groups and we would rather conform to the general formula given above. However, as the sum of carbonate groups and sulphate groups is well over 2.00, which is the upper limit imposed by structural considerations, the chemical formula for latiumite from Baccano indicates an excess of carbonate groups rather than a lack of hydroxyl anions or water molecules.

With regard to the latiumite from Albano the chemical data given by TILLEY and HENRY (1953) do not agree well with our crystalchemical formula. However, as we said previously, we made a new analysis for CO_2 and H_2O . The cell content recalculated by taking into account these new data corresponds to the following satisfactory formula:



where (O_4H_5) indicates a tetrahedral grouping of three hydroxyl anions and one water molecule. To complete the comparison we report the formula obtained for tuscanite (ORLANDI et al., 1977):



On the basis of the proposed substitutions and the corresponding crystalchemical formula, the chemical compositions of latiumites from various sources as well as of tuscanite can therefore be reasonably well accounted for.

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