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Tuscanite, a new mineral related to latiumite

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Abstract

Tuscanite is a new mineral from Pitigliano, Tuscany, Italy. It occurs as flattened, transparent crystals, up to about 1 cm × 1 cm × 0.2 cm in size, in ejected metamorphic calcareous blocks from a pumice deposit. The chemical formula

$$[K_{0.88}Sr_{0.04}(H_2O)_{1.08}](Ca_{5.25}Na_{0.51}Fe^{3+}_{0.10}Mg_{0.11})(Si_{6.34}Al_{3.66})O_{22}[(SO_4)_{1.38}(CO_3OH)_{0.55}(O_4H_4)_{0.11}]$$

monoclinic symmetry, space group $P2_1/a$ and lattice dimensions of a = 24.036(14), b = 5.110(3), c = 10.888(8) A, β = 106.95(3)° indicate that the new mineral is closely related to latiumite. Optical data are α = 1.581, β = 1.590, γ = 1.591, $2V_\alpha$ = 40°, $X\Lambda c$ = 40°. The density is 2.83 g cm^{-3}. Cleavage (100) distinct. The powder pattern of tuscanite is quite similar to that of latiumite, with strongest reflections at d = 11.51(100), 5.75(17), 3.832(24), 3.065(47), 2.962(24), 2.872(100). Additional features in the pattern of tuscanite are weak reflections at d = 3.573(1), 2.422(1), 2.017(1) and the splitting of some peaks which are single in latiumite.

Introduction

Within a program of a comprehensive study on chemical, optical, and crystallographic properties of latiumite from various localities, a sample was found which, although its powder pattern was very similar to that of latiumite, presented a clearly different single-crystal diffraction pattern; in fact while "normal" latiumite has space group $P2_1$, the anomalous sample showed $P2_1/a$ symmetry with a doubled a parameter. Subsequent work indicated clearly that the anomalous specimen deserved the status of a new mineral. The new mineral was named tuscanite, from the name of the Italian region, Tuscany, where it was found. The new mineral and its name were approved by the New Minerals and Mineral Names Commission of I.M.A.. Type material was kindly given us by the collector L. Liotti, to whom it was returned after our study was completed. The material is now deposited in the museums of the Istituto di Mineralogia e Petrografia dell'Università di Pisa and of the Istituto di Mineralogia dell'Università di Modena.

Paragenesis

The enviroment in which the new mineral was found has been described by Merlino and Orlandi (1977) in their paper on liottite. Both latiumite and tuscanite occur in "ejected blocks found in a pumice deposit, which is indicative of the explosive activity of a small volcanic center set up in the Pleistocene on the rims of the great Latera caldera. These blocks are the product of a syntexis between the carbonate rocks which make up the walls of the vent of the magmatic reservoir and a trachytic magma." The sample used in the present study comes from a block where a very large crystal (1.0 × 1.0 × 0.2 cm) was found together with other much smaller crystals. Vesuvianite, garnet (grossular and andradite), pyroxene and subordinately, wollastonite, anorthite, brandisite, and latiumite are the most common minerals associated with tuscanite in these blocks.

Crystallographic and physical properties

The crystals of tuscanite are transparent, colorless and platy on (100), with distinct (100) cleavage. As the only clearly observable faces are the cleavage planes, no morphological study was made. Normal twinning is frequent, with (100) as twin plane. The density, determined by the heavy liquids method, was 2.83 g cm^{-3}. The hardness was 5.5–6.

Weissenberg and precession photographs (Ni-filtered CuKα radiation) indicated Laue symmetry $2/m$. Systematic extinctions ($h0l$ reflections for $h = 2n + 1$ and $0k0$ for k = $2n + 1$) indicated space group $P2_1/a$. The X-ray powder data (Table 1) were ob-

tained by means of a Philips diffractometer, scanning speed 0.5° per min, Ni-filtered Cu$K\alpha$ radiation. The powder pattern was indexed using the single-crystal photographs as a guide. The cell parameters obtained in the single crystal study were refined by a least-squares method, using twenty lines whose indices were unambiguously determined; they are given in Table 2, together with the values given by Cannillo *et al.* (1973) for latiumite.

In Table 1 the powder pattern of tuscanite is com-

Table 1. X-ray powder diffraction data for tuscanite and latiumite

Tuscanite			Latiumite*		Tuscanite			Latiumite*	
d(Å)	hkl	I/I$_o$**	d(Å)	I	d(Å)	hkl	I/I$_o$**	d(Å)	I
11.51	200	100	–	–	–	–	–	2.33	m
–	–	–	7.2	vw	2.298	1000	5	2.31	m
5.78	$\bar{4}01$	8	–	–	2.250	$\bar{1}14$	1	2.25	w
5.75	400	17	–	–	2.160	$\bar{4}05$	1	2.15	vw
5.20	002	4	–	–	2.120	911 620	1	2.12	w
4.58	011 $\bar{4}02$	12	4.6	m	2.070	613	1	2.08 2.06	w
4.51	401	9	4.5	m	2.053	023 $\bar{4}23$ $\bar{7}21$ $\bar{10}13$	2	2.05	w
4.30	202	3	4.3	w					
3.995	$\bar{6}01$	4	4.0	w					
3.832	$\bar{4}11$ 600	24	3.83	m					
–	–	–	3.69	w	2.017	720 621	1	–	–
3.632	$\bar{2}03$ $\bar{6}02$	1	3.63	w	1.997	$\bar{1}23$ $\bar{12}02$	7	1.997	m
3.573	$\bar{3}12$	1	3.53	vw	1.992	$\bar{12}01$ $\bar{9}14$	7		
3.469	003	4	3.46	w					
3.398	402	8	3.38	m	1.959	$\bar{6}23$ $\bar{6}15$ 522 205	1	1.957	m
3.287	601	4	3.28	m					
3.149	$\bar{6}11$	2	3.14	w					
3.065	610	47	3.06	s					
3.004	$\bar{8}01$	13	3.01	w	–	–	–	1.943	w
2.962	$\bar{6}12$	24	2.96	s	1.909	820 1002	7	1.903	m
2.899	$\bar{8}02$	7	2.90	w					
2.872	013 800	100	2.86	s	1.866	622	1	–	–
2.830	412	16	2.82	m	1.861	$\bar{2}24$ $\bar{12}12$	1	1.858	w
2.771	611 113	4	2.77	w	–	–	–	1.846	vw
					1.832	$\bar{10}05$	1	1.831	vw
2.731	602 $\bar{7}12$	4	2.72	w	1.824	813 215 024	4	1.812	m
2.621	$\bar{8}03$ $\bar{6}13$	4	2.63	vw	1.793	12,01 12,10	4	1.792	w
2.582	801	4	2.58	vw					
2.554	020	15	2.54	s	1.712	$\bar{12}14$ $\bar{14}02$ $\bar{4}16$ 1020	1	1.715	vw
2.500	313 810 220	2							
2.480	$\bar{1}21$	1	2.49	vw	–	–	–	1.687	w
2.422	320	1	–	–	1.642	14,00 605 525	4	1.641	m
2.408	612	2	2.40	m					
2.402	$\bar{3}14$	2							
2.371	$\bar{1}14$ $\bar{4}14$	3	2.37	m	1.613	814 025	4	1.604	m

* From Tilley and Henry (1953)

** Integrated intensity

Table 2. Unit-cell parameters and optical properties of tuscanite and latiumite

	Tuscanite	Latiumite
Space group	$P2_1/a$	$P2_1$
a	24.036(14)Å	12.06(1)Å
b	5.110(3)	5.08(2)
c	10.888(8)	10.81(1)
β	106.96(3)°	106.0°
Refractive indices		
α	1.581	1.600
β	1.590	1.606
γ	1.591	1.614
x_{Ac}	40°	from 16° to 28°
$2V_\alpha$	40°	from +83° to -72°
	γ ∥ b	γ ∥ b

Crystallographic data for Latiumite from Cannillo et al. (1973); optical data from Tilley and Henry (1953)

pared with that of latiumite from Albano, reported by Tilley and Henry (1953). Such comparison deserves the following comments: the peaks at d values of 11.51, 5.78, 5.75, and 5.20 in the spectrum of tuscanite were also observed in all samples of latiumite; moreover no sample of latiumite showed the peak at d = 7.20 reported by Tilley and Henry (1953). These authors did not give the recording conditions; we can only speculate that they could not observe the peak at d = 11.51 because it lay at the boundary of the blind region, and the peak at d = 5.20 because of its low intensity. As regards the doublet at 5.78 and 5.75 we assume that it was not resolved in the spectrum of Tilley and Henry, and for the peak at 7.20 we hypothesize a transcription error by Tilley and Henry (2ϑ = 15.3 for d = 5.79 and 2ϑ = 12.3 for d = 7.20 for Cu$K\alpha$). In fact we would remark that a peak at d = 7.2 cannot be indexed on the basis of the cell parameters of latiumite (nor of tuscanite). A photographic powder pattern of latiumite from Albano was kindly given us by Professor Fornaseri and we ascertained that no peak at 7.2 was recorded, whereas peaks at 5.76 and 11.5 were clearly recorded. Three low-intensity reflections, absent in the pattern of latiumite, are present in the powder pattern of tuscanite, namely the reflections at d = 3.573 with indices $\bar{3}12$, at d = 2.412 with indices 320, and at d = 2.017 with indices 123, 621, 720. Furthermore, the three reflections at 2.49, 2.40, and 1.997 in the spectrum of latiumite correspond to the following doublets in that of tuscanite: 2.500 (indices 313, 810, 220) and 2.480 (indices $\bar{1}21$); 2.408 (indices 612) and 2.402 (indices $\bar{3}14$); 1.997 (indices $\bar{1}202$) and 1.992 (indices $\bar{1}201$, $\bar{9}14$).

The optical data of tuscanite are reported in Table 2 together with the corresponding values given by Tilley and Henry (1953) for latiumite from Albano. Refractive indices of tuscanite were determined by a double-variation method using bromoform as liquid. The data are referred to a wavelength of 5893 A; the standard deviation is less than ± 0.001.

Chemical composition

The chemical composition was obtained as follows: CaO, Na_2O, K_2O, MgO, and SrO were determined by atomic absorption spectrometry on a sample of 30 mg, using a Perkin Elmer 303 instrument; CO_2 and H_2O were determined by microdetermination of C and H, by the Carlo Erba elemental microanalyzer 1104 instrument, on 1 mg; Cl and SO_3 were determined by X-ray fluorescence spectrometry on 40 mg of material, using, as reference standard, samples of latiumite to which known amount of sulphur and chlorine were added. On the basis of the known quantities of the other elements, SiO_2, Al_2O_3, and Fe_2O_3 were determined by X-ray fluorescence spectrometry on the same material, according to the method of Franzini and Leoni (1972), modified by Leoni and Saitta (1973), introducing the appropriate correction factors for sulphur and chlorine and as-

Table 3. Chemical composition of tuscanite and latiumite.

	Tuscanite		Latiumite*	
	wt %	**	wt %	**
SiO_2	34.64	6.34	28.33	4.93
Al_2O_3	16.95	3.66	24.67	5.07
Fe_2O_3	0.76	0.10	0.50	0.07
FeO	n.d.	-	0.55	0.08
MgO	0.40	0.11	0.76	0.20
MnO	-	-	0.02	-
CaO	26.76	5.25	29.41	5.49
SrO	0.38	0.04	n.d	-
Na_2O	1.45	0.51	1.11	0.37
K_2O	3.79	0.88	7.20	1.61
H_2O	2.61	1.60	0.27	-
SO_3	10.04	1.38	5.42	0.71
CO_2	2.20	0.55	1.60	0.37
Cl	0.02	-	0.14	-
O		22.49		23.22

* *From Tilley and Henry (1953)*

**: *atoms based on Si + Al = 10*

suming that the sum of the weight percentages was 100. This assumption was based on the fact that we ascertained by a qualitative fluorescence analysis that no other elements were present, at least in appreciable quantities. Table 3 compares the results of the analysis with those given by Tilley and Henry for latiumite from Albano.

Relations between tuscanite and latiumite

The crystal structure of latiumite was solved by Cannillo *et al.* (1973), who gave the following crystal-chemical formula for latiumite

$$(K_{0.85}\square_{0.15})Ca_3(Si_{2.15}Al_{2.85})O_{11}(SO_4)_{0.7}(CO_3)_{0.3}$$

where $\square$ indicates vacancy. The low potassium content of tuscanite, together with its high water content, suggests that water molecules may partially occupate the site which in latiumite is nearly completely occupied by potassium cations. The oxygen excess over 22.0 suggests the presence of 0.98 OH^- (0.49 O + 0.49 H_2O) in tuscanite.

To guess the possible location of hydroxyls in the structure the following considerations seem useful: the substitution (CO_3F) and (CO_3OH) for PO_4 in carbonate apatites is frequently introduced to explain the chemistry of these minerals, since the first suggestion made by Borneman-Starinkevic and Belov (1953) that when a planar carbonate ion substitutes for a tetrahedral phosphate ion the vacant oxygen site is occupied by a fluorine ion, which would complete the coordination of the cations in the structure. Moreover the substitution H_4O_4 for SO_4 may be proposed; this kind of substitution is well established in phosphates such as apatite and in silicates such as hydrogrossular. On these bases the following formula, which assures a fair agreement of the chemical data with crystal chemistry, was obtained for tuscanite:

$$[K_{0.88}Sr_{0.04}(H_2O)_{1.08}](Ca_{5.25}Na_{0.51}Fe^{3+}_{0.10}Mg_{0.11})$$
$$(Si_{6.34}Al_{3.66})O_{22}[(SO_4)_{1.38}(CO_3OH)_{0.55}(O_4H_4)_{0.11}]$$

The formula gives a calculated density D(calc) = 2.77 which compares with the observed value D(obs) = 2.83 g cm^{-3}.

The most important difference between tuscanite and latiumite is the doubling of the a axis in tuscanite relative to latiumite. The structural study of tuscanite, reported in the following paper (Mellini *et al.* 1977), has shown the structural basis of such differences. It is well known that latiumite is characterized by the presence of double layers, parallel to the clevage (100), of (Si,Al) tetrahedra. The single layer is quite similar in latiumite and tuscanite, but while in the former mineral the double layer is obtained from the single one by the operation 2_1, in the latter mineral the double layer is obtained by the operation of the inversion center. As a consequence, while in latiumite all the tetrahedra of the five-membered rings, which by their connection give rise to the double layer, point upward, in tuscanite three tetrahedra of each ring point upward and two downward. The crystal-structure determination indicates also that a pseudo-translation of $a/2$ is present for all the heavy atoms and for most of the oxygen atoms of the tetrahedra layer; this results in a general weakening of the reflections with $h = 2n + 1$ and in a powder pattern hardly distinguishable from that of latiumite.

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