American Mineralogist, Volume 60, pages 471–474, 1975

Re-examination and Crystal Structure Analysis of Litidionite

JOSE M. MARTIN POZAS[1], GIUSEPPE ROSSI, AND VITTORIO TAZZOLI

C.N.R., Centro di Studio per la Cristallografia Strutturale,
Istituto di Mineralogia, via Bassi 16, 27100 Pavia, Italy

Abstract

Litidionite, $CuNaKSi_4O_{10}$, occurs with tridymite in lapilli strongly modified by fumarolic activity in the Vesuvius crater. It is triclinic, space group $P\bar{1}$; the lattice parameters are: a = 9.80(1) b = 8.01(1), c = 6.97(1) Å, α = 114.12(8)°, β = 99.52(6)°, γ = 105.59(8)°, Z = 2. Its crystal structure—determined by Patterson and Fourier methods, using single crystal diffractometer X-ray data, and refined to an R index of 0.032 for 1450 reflections with $F_o > \sigma F_o$—is the same as for fenaksite, $FeNaKSi_4O_{10}$. Tubular chains of silica tetrahedra, formed by the condensation of vlasovite-type chains, are interconnected by copper and sodium atoms which have a five-fold pyramidal coordination. Potassium atoms occur in the large cavities within the chains.

Introduction

The name litidionite was given by E. Scacchi in 1880 (Zambonini, 1935) to very tiny blue crystals associated with glass of the same color in lapilli found in the Vesuvius crater. Zambonini (1935) had difficulty measuring the interfacial angles of litidionite and could only conclude it to be triclinic or monoclinic sphenoidal. He also determined $2V_x$ = 56°, and indices α_D = 1.548, β_D = 1.574. The chemical analysis he carried out, which yielded the formula $(K, Na)_2Cu(Si_3O_7)_2$, is very doubtful owing to the difficulty in obtaining pure litidionite.

No further data or publication appeared on this mineral other than an unindexed powder pattern (JCPDS card No. 18-713). In the text books litidionite is considered as an inadequately characterized and doubtful species. Accordingly we have re-examined litidionite and determined its crystal structure. Material used in this study was provided by Professor Carobbi from specimens that had been previously studied by himself and Zambonini.

Occurrence

Litidionite occurs as tiny plates in lapilli strongly modified by the fumarolic activity subsequent to the Vesuvius eruption of 1873. The dimension of the lapilli range from a few millimeters up to 25-30 mm. The nuclei of the lapilli are small fragments of rock or well-formed augite crystals ejected by the volcano. The fumarolic action coated the nuclei with a layer of white microcrystalline tridymite (considered as opal by Zambonini) which is overlaid by a blue glassy crust whose cavities are coated by litidionite, tridymite, and minor wollastonite. Litidionite is the unique copper mineral occurring in these lapilli, although several other copper minerals (covellite, tenorite, chlorothionite, cyanochroite, chalcocyanite, and others) were produced by the fumarolic activity in the Vesuvius crater.

X-Ray Crystallography

The lattice parameters of litidionite (Table 1) were measured with a Philips PW 1100 computer-controlled diffractometer. Its X-ray powder pattern, obtained with a Philips PW 1050 diffractometer using Cu$K\alpha$ radiation and NaF as internal standard, is compared in Table 2 with the data on the JCPDS card No. 18-713. The three strong lines of the JCPDS data—d = 4.31, d = 4.10, and d = 3.82 Å—correspond to the three strongest lines of tridymite (JCPDS card No. 18-1170).

The powder pattern and the lattice parameters of litidionite are very close to those of fenaksite, $FeNaKSi_4O_{10}$ (Golovachev *et al*, 1971).

Chemical Formula

Carobbi (Zambonini, 1935) carried out one chemical analysis of litidionite and gave the tentative formula $Na_2K_2CuSi_2O_7$. Zambonini (1935) considers

---

[1] Present address: Depto. de Cristalografia y Mineralogia, Facultad de Ciencias, Universidad de Madrid, Spain.

TABLE 1. Unit Cell Data of Litidionite and Fenaksite

	litidionite	fenaksite
a	9.80(1) Å	10.00 Å
b	8.01 "	8.18
c	6.97 "	6.98
α	114.12°(8)	114.7°
β	99.52°(6)	100.7°
γ	105.59°(8)	105.0°
Chemical formula	$CuNaKSi_4O_{10}$	$FeNaKSi_4O_{10}$
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
$D_{obs.}$	2.75	
$D_{calc.}$	2.85	

The unit cell parameters given by Golovachev et al. did not correspond to the reduced cell and were transformed to those given in this Table through the following matrix $(0\ 1\ 1/\bar{1}\ \bar{1}\ 0/1\ 0\ 0)$.

the analysis as very doubtful owing to the difficulty in separating the mineral from associated tridymite and blue glass. In effect, if it is assumed, on the basis of the close resemblance of the crystallographic data, that litidionite and fenaksite are isostructural, the formula should be $CuNaKSi_4O_{10}$. A chemical formula very close to this can be obtained from Carobbi's analysis if we assume that the material analyzed contained about 40 percent tridymite.

The crystal structure analysis fully confirms that

TABLE 2. X-ray Powder Data of Litidionite

This paper*				JCPDS 18-713		
$d_{obs.}$	$d_{calc.}$	hkl	I	d	I	
6.75	6.76	$\bar{1}10$	35	6.73	50	
				6.08	10	
				5.16	10	
4.485	4.483	200	12			
				4.31	60	trid.
				4.10	60	trid.
4.046	4.048	$\bar{1}11$	15			
				3.82	40	trid.
3.652	3.664	$\bar{2}11$	18	3.66	10	
3.372	3.379	$\bar{2}20$	100	3.36	100	
3.223	3.226	210	75	3.22	60	
3.046	3.042	$1\bar{1}2$	10			
3.027	3.033 3.020	111 002	10	3.04	30	
2.976	2.977 2.976 2.973	$\bar{3}11$ $21\bar{2}$ $\bar{2}02$	13	2.96	60	
2.835	2.840	120	18	2.82	30	
2.675	2.672	$31\bar{1}$	37	2.65	30	
2.567	2.563	$\bar{3}02$	13			
2.460	2.457	$0\bar{3}2$	7			
2.409	2.413	$\bar{2}30$	85	2.40	80	
				2.23	10	
1.980	1.982	$\bar{1}22$	10			
1.924	1.920	$0\bar{4}2$	10			
1.916	1.919	510	10	1.91	10	
				1.84	10	
1.817	1.810	$3\bar{4}2$	5	1.80	10	
1.789	1.793	500	15			

*The unit cell parameters given in Table 1 were used for indexing

TABLE 3. Atomic Coordinates* and Equivalent Isotropic Temperature Factors**

Atom	x/a	y/b	z/c	$B_H(Å^2)$
Cu	0.4122(1)	0.1287(1)	0.1624(1)	0.74
Si(1)	0.8593(1)	0.1742(2)	0.8119(2)	0.65
Si(2)	0.7222(1)	0.3545(2)	0.5664(2)	0.66
Si(3)	0.2110(1)	0.2877(2)	0.9582(2)	0.59
Si(4)	0.7256(1)	0.3825(2)	0.1557(2)	0.68
O(1)	0.5682(3)	0.2072(4)	0.0323(4)	1.25
O(2)	0.2716(3)	0.1161(4)	0.9166(5)	1.04
O(3)	0.8535(3)	0.3320(4)	0.0452(5)	1.22
O(4)	0.0302(3)	0.1851(4)	0.8549(5)	1.64
O(5)	0.2521(3)	0.0432(4)	0.2803(5)	1.34
O(6)	0.7943(3)	0.4314(4)	0.4102(4)	1.20
O(7)	0.5561(3)	0.2017(4)	0.4459(5)	1.30
O(8)	0.2562(4)	0.4471(5)	0.2155(5)	1.76
O(9)	0.8331(3)	0.2535(4)	0.6323(5)	1.30
O(10)	0.2716(3)	0.4072(4)	0.8286(5)	1.61
K	0.0038(1)	0.2033(1)	0.3348(2)	1.58
Na	0.4090(2)	0.1295(3)	0.6633(4)	1.57

* *With standard deviations in parentheses.*
** *After Hamilton (1959).*

TABLE 4. Analysis of the Anisotropic Thermal Parameters in Litidionite*

Atom	r.m.s.	$U_i a$	$U_i b$	$U_i c$	Atom	r.m.s.	$U_i a$	$U_i b$	$U_i c$
Cu	0.084(1)	64	57	155	O(5)	0.103(6)	128	125	50
	0.089(1)	38	106	67		0.129(5)	111	54	60
	0.114(1)	64	145	100		0.154(5)	134	54	126
Si(1)	0.073(3)	160	92	63	O(6)	0.082(7)	90	63	171
	0.091(2)	71	127	29		0.112(6)	46	65	96
	0.105(2)	82	143	100		0.163(5)	137	38	84
Si(2)	0.067(3)	80	65	178	O(7)	0.098(6)	133	118	46
	0.090(3)	85	37	88		0.107(6)	64	99	44
	0.112(2)	169	65	91		0.169(5)	53	151	91
Si(3)	0.078(3)	123	62	53	O(8)	0.100(7)	81	95	149
	0.086(3)	97	29	143		0.134(6)	113	10	118
	0.095(2)	146	97	94		0.197(5)	155	98	77
Si(4)	0.064(3)	75	58	168	O(9)	0.087(7)	85	56	170
	0.093(3)	76	52	78		0.124(6)	35	134	99
	0.113(2)	170	54	92		0.162(5)	124	117	94
O(1)	0.093(7)	107	86	141	O(10)	0.084(7)	87	164	53
	0.109(6)	51	56	129		0.121(6)	44	106	132
	0.165(5)	136	34	90		0.199(5)	133	89	115
O(2)	0.085(7)	51	155	67	K	0.112(2)	95	147	87
	0.119(5)	103	85	29		0.149(2)	27	96	126
	0.134(5)	138	115	73		0.160(2)	117	58	144
O(3)	0.105(6)	99	123	112	Na	0.109(3)	55	78	155
	0.121(6)	40	78	138		0.135(3)	52	78	72
	0.144(5)	52	145	56		0.172(3)	57	162	73
O(4)	0.079(8)	163	74	96					
	0.118(6)	97	30	88					
	0.205(5)	75	65	174					

* Root mean square thermal vibrations along the ellipsoid axes (Å) and angles (°) between the crystallographic axes and the principal axes (U_i) of the vibration ellipsoid.

TABLE 5. Interatomic Distances and Principal Bond Angles in Litidionite*

Atoms	Distances	Atoms	Angles
Si(1) - O(3)	1.623 Å	O(3) - Si(1) - O(4)	106.0°
O(4)	1.623	O(5)	114.6
O(5)	1.572	O(9)	108.4
O(9)	1.633	O(4) - Si(1) - O(5)	110.6
		O(9)	105.4
Average	1.613	O(5) - Si(1) - O(9)	111.3
Si(2) - O(6)	1.622	O(6) - Si(2) - O(7)	113.4
O(7)	1.578	O(8)	105.0
O(8)	1.618	O(9)	102.9
O(9)	1.630	O(7) - Si(2) - O(8)	114.5
		O(9)	111.4
Average	1.612	O(8) - Si(2) - O(9)	109.0
Si(3) - O(2)	1.580	O(2) - Si(3) - O(4)	107.1
O(4)	1.626	O(8)	114.3
O(8)	1.614	O(10)	110.7
O(10)	1.632	O(4) - Si(3) - O(8)	109.2
		O(10)	107.9
Average	1.613	O(8) - Si(3) - O(10)	107.5
Si(4) - O(1)	1.582	O(1) - Si(4) - O(3)	112.8
O(3)	1.632	O(6)	112.7
O(6)	1.627	O(10)	115.3
O(10)	1.635	O(3) - Si(4) - O(6)	103.2
		O(10)	106.7
Average	1.619	O(6) - Si(4) - O(10)	105.1
Cu - O(2)	1.961	Si(1) - O(3) - Si(4)	137.2
O(5)	1.978	Si(1) - O(4) - Si(3)	157.0
O(7)	1.981	Si(1) - O(9) - Si(2)	135.5
O(1)	1.990	Si(2) - O(6) - Si(4)	131.8
O(1')	2.549	Si(3) - O(8) - Si(2)	160.1
		Si(3) - O(10) - Si(4)	133.2
Na - O(7)	2.386		
O(2)	2.409	O(1) - Cu - O(2)	85.8
O(1)	2.505	O(5)	177.9
O(5)	2.555	O(7)	94.7
O(7')	2.581	O(2) - Cu - O(5)	92.6
O(10)	2.850	O(7)	167.3
O(9)	2.932	O(5) - Cu - O(7)	87.2
		O(1') - Cu - O(1)	75.8
K - O(6)	2.667	O(2)	93.5
O(4)	2.734	O(5)	102.9
O(2)	2.822	O(7)	98.8
O(9)	2.844		
O(3)	2.973		
O(5)	3.049		
O(6)	3.069		
O(8)	3.168		

* *The estimated standard deviations are 0.003 Å and 0.2° respectively for bond distances and for bond angles.*

fenaksite and litidionite are isostructural and that the chemical formula of the latter is $CuNaKSi_4O_{10}$.[2]

X-Ray Data Collection

The intensities were collected from a crystal fragment (dimensions: 0.02 × 0.06 × 0.08 mm) using the single crystal automatic diffractometer and Mo$K\alpha$ radiation monochromatized by a flat graphite crystal. A unique set of data was collected out to $2\theta = 60°$ by the $\theta - 2\theta$ scan mode with a symmetric scan range of 1° in 2θ from the calculated scattering angle. The scan rate was 0.05°/sec. Processing of the data was carried out in the manner described by Davies and Gatehouse (1973) to yield values of F_o and σF_o.

The intensities of 2677 independent reflections were measured; of these 1450 have $F_o > \sigma F_o$ and were used in subsequent calculations. Three standard reflections, monitorized at three-hour intervals, showed no variation in intensity greater than 5 percent. No absorption nor extinction corrections were applied.

Crystal Structure Analysis

The crystal structure analysis was carried out by Patterson and Fourier methods and confirmed that litidionite and fenaksite are isostructural. The least squares isotropic refinement, carried out on the structure amplitudes with the program ORFLS (Busing, Martin, and Levy, 1962), reduced the conventional *R* index to 0.047. Three successive least squares cycles performed with anisotropic thermal parameters led to an *R* index of 0.032 for the 1450 observed reflections. At this stage the refinement was stopped as the shifts of the atomic parameters were less than one tenth the standard deviations.

The final atomic parameters are given in Tables 3 and 4; bond distances and angles are listed in Table 5. The observed and computed structure factors are compared in Table 6.[3]

Description and Discussion of the Structure

The crystal structure analysis confirmed that the structure of litidionite is similar to that of fenaksite (Golovachev *et al*, 1971) and showed no deviation from the adopted chemical formula $CuNaKSi_4O_{10}$. The basic structural feature of both minerals is a tubular silicate radical $Si_8O_{20}^{8-}$ (Figs. 1 and 2). This radical is made up by the condensation of two vlasovite type chains (Voronkov and Pyatenko, 1962) which are formed by rings of four tetrahedra. The tubular chains are parallel to *c* and are interconnected by Cu and Na atoms. Potassium occurs in the large cavities existing in the pipe-like tetrahedral chains with K-O distances ranging from 2.67 to 3.17 Å (Table 7).

The coordination polyhedron of copper is a fairly regular square pyramid whose base is formed by four oxygen atoms at distances ranging from 1.96 to 1.99 Å. An oxygen atom 2.55 Å from copper is the vertex

---

[2] P. H. Ribbe and T. D. Kurtz carried out a microprobe analysis of litidionite and found only small amounts (less than 0.5 wt percent) of Ca, Ti, and Fe, besides the elements given in the formula.

[3] To obtain a copy of Table 6, order Document AM-75-004 from The Mineralogical Society of America, Business Office, 1909 K St., N.W., Washington, D.C. 20006. Please remit in advance $1.00 for a copy of the microfiche.

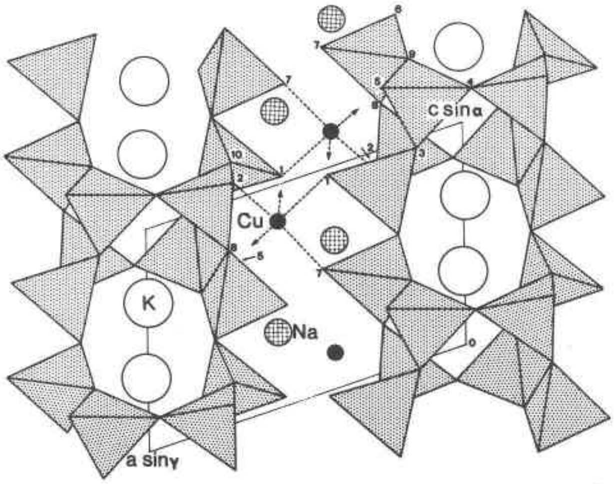

FIG. 1. The crystal structure of litidionite projected along [010]. The bonds terminated by an arrow refer to oxygen atoms O(1) and O(5) occurring in chains which are not shown in the figure.

of the pyramid. The distance to the next closest oxygen is 3.24 Å. In fenaksite the oxygen atoms of the base have Fe–O distances ranging from 1.98 to 2.16 Å while the apical oxygen is 2.37 Å from Fe.

The coordination polyhedron around sodium atoms is similar to that around copper but is more distorted. Besides the five bonds with oxygen atoms forming the distorted pyramid, sodium has two longer bonds with O(9) and O(10), respectively 2.85 and 2.93 Å.

Each coordination pyramid around copper is connected by edge sharing to another copper pyramid and to one sodium pyramid in such a way that pairs of pyramids around copper alternate with pairs of pyramids around sodium forming serrate chains parallel to *c*.

The Si–O bond lengths show a well marked difference between the distances of Si from bridging oxygen atoms and the distances of Si from non-bridging oxygens, as has been pointed out by Cruickshank (1961). In the former group the mean Si–O distance is 1.578 Å and in the latter it is 1.626 Å.

The balance of electrostatic charges computed with the method of Brown and Shannon (1973) is satisfactory. The sum of the electrostatic charges reaching each oxygen atom ranges from 1.84 to 2.20 v.u. It should be noted that the non-bridging oxygen atoms are underbonded (from 1.84 to 1.94 v.u.) while the bridging ones are overbonded (from 2.03 to 2.20 v.u.).

Acknowledgments

The authors are much indebted to Dr. P. H. Ribbe and Mr. T. D. Kurtz, Virginia Polytechnic Institute and State University, Blacksburg, who carried out the microprobe analysis of litidionite.

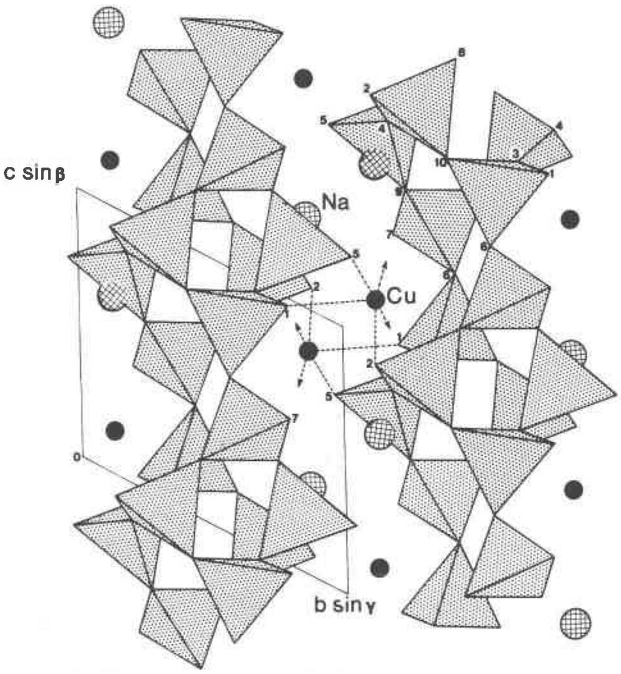

FIG. 2. The crystal structure of litidionite projected along [100]. The bonds terminated by an arrow refer to oxygen atoms O(1) and O(7) occurring in chains which are not shown in the figure. The potassium atoms have been omitted for clarity.

References

BROWN, I. D., AND R. D. SHANNON (1973) Empirical bond-strength-bond-length curves for oxides. *Acta Crystallogr.* **A29,** 266–282.

BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a Fortran crystallographic least-squares program. *U.S. Nat. Tech. Inform. Serv.* ORNL-TM-**305.**

CRUICKSHANK, D. W. J. (1961) The role of 3*d* orbitals in π bonds between (a) silicon, phosphorus, sulphur or chlorine and (b) oxygen or nitrogen. *J. Chem. Soc.*, p. 5486–5504.

DAVIES, J. E., AND B. M. GATEHOUSE (1973) The crystal and molecular structure of unsolvated μ-oxo-bis *N,N'*-ethylene-bis(salicyl-aldiminato) iron(III). *Acta Crystallogr.* **B29,** 1934–1942.

GOLOVACHEV, V. P., YU. N. DROZDOV, E. A. KUZ'MIN, AND N. V. BELOV (1971) The crystal structure of fenaksite. *Dokl. Akad. Nauk SSSR,* **15,** 902–904 (English trans.).

HAMILTON, W. C. (1959) On the isotropic temperature factor equivalent to a given anisotropic temperature factor. *Acta Crystallogr.* **12,** 609–610.

VORONKOV, A. A., AND YU. A. PYATENKO (1962) The crystal structure of vlasovite. *Sov. Phys.-Crystallogr.* **6,** 755–760.

ZAMBONINI, F. (1935) *Mineralogia Vesuviana,* S.I.E.M. Naples, p. 435–439.

Manuscript received, August 5, 1974; accepted for publication, December 31, 1974.