

Crystal Structure of Triclinic Lazurite

V. G. Evsyunin*, A. N. Sapozhnikov**,
A. A. Kashaev***, and R. K. Rastsvetaeva****

* *Institute of the Earth's Crust, Siberian Division, Russian Academy of Sciences,
ul. Lermontova 128, Irkutsk, 664033 Russia*

** *Vinogradov Institute of Geochemistry and Analytical Chemistry, Siberian Division,
Russian Academy of Sciences, ul. Favorskogo 1a, Irkutsk, 664033 Russia*

*** *Irkutsk Pedagogical Institute, Irkutsk, 664033 Russia*

**** *Shubnikov Institute of Crystallography, Russian Academy of Sciences,
Leninskii pr. 59, Moscow, 117333 Russia*

Received November 11, 1996

Abstract—The structure of triclinic lazurite from the Malaya-Bystraya deposit (Southern Baikal area) has been determined (sp. gr. $P1$, $R_{hkl} = 0.061$, 5724 reflections, 210 crystallographically nonequivalent atoms). The form of the incorporation of a sulfur atom into the structure and the character of the displacement and substitution modulations of all the structure atoms have also been determined.

INTRODUCTION

The mineral lazurite has been known in Europe since the late 13th century. Since then, it has attracted widespread attention, in particular, as a valuable ornamental color stone and as a source of high-quality blue pigment. Being related to the sodalite group, lazurite has been known for quite a long time as a cubic mineral. Optically anisotropic lazurite was first observed by Voskoboinikova [1]. Then, orthorhombic, monoclinic, and triclinic lazurites were also studied [2, 3].

Interest in the structural studies of lazurites is explained mainly by two reasons. (i) The chemical analysis of lazurites with the aim to check whether their chemical formula coincides with the typical formula of sodalite-like minerals yields an excessive number of anions, which, in terms of the electrostatic balance, are sulfide sulfur ions S^{2-} . Trying to interpret this fact, Hogarth and Griffin [4] assumed that S atoms substitute some O atoms in the framework. Belov [5] assumed more justly that the sodalite-like cuboctahedral cavities in lazurite are occupied by clusters of S atoms. (ii) It is well known that diffraction patterns of lazurites are characterized by additional superstructural reflections. Nevertheless, the structures of isotropic lazurites from the Sary-Sang deposit (Afghanistan) and from the Baffin Island deposit were studied in the space group $P43n$, ignoring the satellite reflections substantially complicating the corresponding diffraction patterns [6]. It was established [6] that the thermal parameters of Si and Al atoms substantially exceed those in sodalite structures. The oxygen atoms of the framework are statistically distributed over two $24(i)$ positions, whereas the Na and Ca atoms are distributed over three $8(e)$ positions. In the specimens from the Baffin island deposit, the

SO_4 -groups have two orientations that differ by a 90° -rotation about the fourfold axis. Thus, the form of the incorporation of S atoms into the structure and the interpretation of the specific features of this structure reflected in the presence of superstructural reflections on the diffraction patterns of lazurite stimulate the further structural study of this mineral.

The least symmetric lazurite variety from the Malaya Bystraya deposit (Southern Baikal area) was studied in our earlier work [7] in its monoclinic form within the space group $P2_1$ (because two angles of the unit cell were close to 90°). It was established that one of the reasons for the formation of superstructural reflections on the lazurite diffraction patterns is the displacement of Si and Al atoms from their "average" (sodalite) positions described by the sum of the cosine and rectangular waves with the same phases. Nevertheless, detailed study of the character of commensurate modulation in this mineral was hindered by the low accuracy of the structure determination (the reliability factor was as high as $R_{hkl} = 0.12$). The present study was aimed at the complete determination of the structure of the same lazurite specimen but within the triclinic symmetry.

CRYSTAL STRUCTURE DETERMINATION

An X-ray study was performed on a $0.25 \times 0.25 \times 0.15$ -mm-large lazurite single crystal. The amount of sulfide sulfur was determined by the methods of analytical chemistry. The microprobe analysis allows one to write the following formula for the specimen studied:

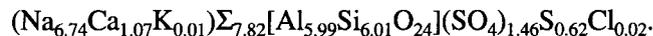


Table 1. Positional ($\times 10^4$) and equivalent thermal parameters B_{eq} ($\times 10, \text{\AA}^2$) of the framework atoms in triclinic lazurite

Atom	x/a	y/b	z/c	B_{eq}	Atom	x/a	y/b	z/c	B_{eq}
Si(1)	2438(1)	2484(1)	3738(1)	8(1)	O(10)	8357(15)	1955(10)	3268(5)	12(3)
Si(2)	7485(4)	2578(3)	3740(1)	7(1)	O(11)	3534(13)	2986(9)	1772(4)	5(3)
Si(3)	2764(6)	2581(4)	8766(2)	8(1)	O(12)	0389(15)	3488(11)	0049(5)	15(3)
Si(4)	5550(6)	3773(4)	6883(2)	8(1)	O(13)	1464(15)	1592(11)	3445(5)	16(3)
Si(5)	5042(6)	-1251(4)	9369(2)	9(1)	O(14)	1767(15)	3347(11)	9084(5)	16(3)
Si(6)	4853(6)	3742(4)	1873(2)	8(1)	O(15)	1877(15)	1855(11)	8328(5)	17(3)
Si(7)	9785(6)	-3751(4)	4402(2)	7(1)	O(16)	6272(15)	1529(10)	1023(5)	13(3)
Si(8)	0482(6)	1215(4)	6872(2)	7(1)	O(17)	9712(14)	8542(10)	7509(5)	9(3)
Si(9)	5436(6)	1211(4)	5633(2)	8(1)	O(18)	4559(13)	6434(9)	7500(5)	13(3)
Si(10)	0484(6)	-6229(4)	5604(2)	11(1)	O(19)	1254(13)	3506(10)	1051(5)	10(3)
Si(11)	2713(6)	-2500(4)	6254(2)	9(1)	O(20)	8721(14)	6526(10)	6065(5)	14(3)
Si(12)	4637(6)	-3792(4)	3127(2)	6(1)	O(21)	-0693(15)	0086(11)	1756(5)	14(3)
Si(13)	9708(6)	-1241(4)	3125(2)	6(1)	O(22)	-1570(13)	2030(9)	1764(5)	9(3)
Si(14)	9901(6)	6255(4)	9347(2)	8(1)	O(23)	9088(15)	1610(11)	6534(5)	15(3)
Si(15)	9890(6)	3744(4)	0657(2)	7(1)	O(24)	3414(15)	2012(11)	0766(5)	15(3)
Si(16)	7678(6)	7517(4)	6270(2)	9(1)	O(25)	6272(15)	3502(10)	1503(5)	14(3)
Si(17)	7790(4)	2471(3)	8781(1)	5(1)	O(26)	1896(15)	-6839(11)	5819(5)	19(3)
Si(18)	4826(6)	-1208(4)	4398(2)	7(1)	O(27)	3879(15)	3298(10)	8424(5)	12(3)
Si(19)	4853(6)	1269(4)	0660(2)	7(1)	O(28)	0094(13)	1501(9)	7479(5)	8(3)
Si(20)	5056(6)	6289(4)	8095(2)	8(1)	O(29)	6974(16)	3182(11)	6680(5)	19(3)
Si(21)	7086(6)	-2475(4)	1264(2)	8(1)	O(30)	6063(15)	-3302(10)	3398(5)	16(3)
Si(22)	0102(6)	8755(4)	8107(2)	9(1)	O(31)	0371(15)	1523(11)	2459(5)	13(3)
Si(23)	2094(6)	-2483(4)	1224(2)	8(1)	O(32)	3681(15)	-3478(10)	6462(5)	15(3)
Si(24)	-0184(6)	1309(4)	1869(2)	6(1)	O(33)	5148(16)	1480(11)	5052(5)	19(3)
Al(1)	4953(6)	1302(4)	4375(2)	8(1)	O(34)	4339(15)	0103(11)	0765(5)	15(3)
Al(2)	5460(6)	3828(4)	8151(2)	6(1)	O(35)	8441(15)	3029(11)	0761(5)	19(3)
Al(3)	0227(6)	3764(4)	9416(2)	9(1)	O(36)	6319(15)	-1682(11)	4180(5)	16(3)
Al(4)	-0068(6)	1272(4)	3106(2)	8(1)	O(37)	3309(14)	1905(9)	4188(5)	11(3)
Al(5)	7949(6)	2507(4)	6232(2)	8(1)	O(38)	0460(15)	9934(10)	8230(5)	14(3)
Al(6)	0114(6)	3757(5)	4361(2)	9(1)	O(39)	1127(16)	-1629(11)	1554(5)	17(3)
Al(7)	2988(6)	2468(4)	6261(2)	8(1)	O(40)	0725(15)	-5015(10)	5742(5)	15(3)
Al(8)	4971(6)	3730(4)	3110(2)	8(1)	O(41)	1525(15)	8076(11)	8255(5)	15(3)
Al(9)	5163(6)	1265(4)	9409(2)	9(1)	O(42)	6429(15)	7076(10)	8231(5)	12(3)
Al(10)	7341(6)	2539(4)	1266(2)	7(1)	O(43)	6866(15)	1861(10)	5785(5)	17(3)
Al(11)	0318(6)	1254(4)	8125(2)	6(1)	O(44)	4825(15)	-0007(10)	4227(5)	14(3)
Al(12)	2365(6)	2469(4)	1269(2)	7(1)	O(45)	6472(15)	1712(11)	4008(5)	17(3)
Al(13)	7204(6)	-2528(4)	3761(2)	8(1)	O(46)	6108(15)	-3281(11)	1590(5)	17(3)
Al(14)	7525(6)	7540(4)	8711(2)	9(1)	O(47)	3554(15)	6464(11)	8428(5)	17(3)
Al(15)	0235(6)	-1287(4)	6861(2)	7(1)	O(48)	1986(15)	1799(10)	6745(5)	16(3)
Al(16)	5202(6)	6276(4)	6858(2)	9(1)	O(49)	3710(15)	-1566(10)	6032(5)	11(3)
Al(17)	5204(6)	-1267(4)	5653(2)	9(1)	O(50)	1119(15)	-1645(10)	3414(5)	14(3)
Al(18)	0172(6)	-3717(4)	5657(2)	9(1)	O(51)	3035(13)	-3093(11)	1643(5)	16(3)
Al(19)	2528(6)	7449(4)	8737(2)	9(1)	O(52)	1706(15)	-2093(10)	6726(5)	13(3)
Al(20)	2214(6)	-2486(4)	3788(2)	7(1)	O(53)	9827(15)	-1502(10)	2526(5)	15(3)
Al(21)	9609(6)	6248(4)	0601(2)	10(1)	O(54)	1536(13)	3420(9)	3946(4)	10(3)
Al(22)	-0399(6)	-1192(4)	1865(2)	9(1)	O(55)	8657(13)	8500(9)	8424(5)	14(3)
Al(23)	4561(6)	-3774(4)	1863(2)	8(1)	O(56)	3923(16)	1538(11)	5946(6)	20(3)
Al(24)	4665(6)	-1211(5)	0630(2)	10(1)	O(57)	4702(15)	-1419(10)	5030(5)	18(3)
O(1)	5274(11)	3524(9)	7511(4)	8(3)	O(58)	8332(15)	-3269(11)	4130(5)	16(3)
O(2)	1278(15)	1506(10)	1498(5)	12(3)	O(59)	9350(15)	4937(11)	0737(6)	20(3)
O(3)	0383(13)	-6528(9)	5023(4)	12(3)	O(60)	5657(15)	5005(10)	6750(5)	12(3)
O(4)	9530(15)	-0013(10)	3240(5)	15(3)	O(61)	8751(15)	1676(10)	8445(5)	17(3)
O(5)	4315(15)	4917(11)	1745(5)	18(3)	O(62)	4018(13)	3364(9)	6611(4)	11(3)
O(6)	4421(14)	-4996(10)	3234(5)	10(3)	O(63)	6665(14)	7093(10)	6733(5)	13(3)
O(7)	5365(14)	3576(10)	2473(5)	10(3)	O(64)	8691(14)	8491(10)	6479(5)	12(3)
O(8)	3528(15)	2900(10)	3266(5)	14(3)	O(65)	6715(15)	7920(11)	5776(5)	15(3)
O(9)	6610(13)	3485(10)	3454(5)	12(3)	O(66)	1683(15)	-2905(10)	5779(5)	15(3)

Table 1. (Contd.)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{cq}	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{cq}
O(67)	6571(15)	-1732(10)	9180(5)	14(3)	O(82)	9553(16)	6552(11)	9936(5)	21(3)
O(68)	6661(16)	1748(11)	9074(5)	20(3)	O(83)	8502(16)	3050(11)	4173(5)	19(3)
O(69)	8941(15)	-6542(11)	5901(5)	17(3)	O(84)	5125(15)	-0029(10)	9233(5)	15(3)
O(70)	0690(14)	-0005(10)	6754(5)	13(3)	O(85)	3534(15)	1822(10)	9196(5)	14(3)
O(71)	3358(15)	-1676(10)	4123(5)	17(3)	O(86)	4808(17)	-1402(12)	9977(6)	26(3)
O(72)	6170(16)	-1619(11)	0956(6)	20(3)	O(87)	8534(15)	6570(10)	8985(5)	16(3)
O(73)	5652(14)	5140(10)	8229(5)	12(3)	O(88)	3624(16)	-1654(11)	9072(6)	24(3)
O(74)	8174(15)	-1750(11)	3318(5)	17(3)	O(89)	8007(15)	-1836(10)	1683(5)	14(3)
O(75)	3130(15)	-3264(11)	3323(5)	18(3)	O(90)	9853(15)	-4944(10)	4239(5)	18(3)
O(76)	5746(15)	-0014(11)	5747(5)	18(3)	O(91)	4692(15)	-3498(10)	2544(5)	16(3)
O(77)	0115(16)	5061(10)	9240(5)	17(3)	O(92)	8759(14)	3095(13)	9200(6)	26(4)
O(78)	8067(15)	-3081(11)	0839(5)	19(3)	O(93)	1406(15)	6895(10)	9175(4)	16(3)
O(79)	5339(17)	1504(12)	0068(5)	23(3)	O(94)	3045(14)	-1846(10)	0793(5)	15(3)
O(80)	7044(15)	3304(10)	8390(5)	16(3)	O(95)	9596(17)	-3476(12)	5019(6)	24(4)
O(81)	1252(16)	-3183(12)	4243(6)	24(3)	O(96)	1110(19)	-3295(13)	0923(6)	34(4)

The parameters of the triclinic unit cell refined on an automated Enraf-Nonius diffractometer are: $a = 9.067(3)$, $b = 12.896(3)$, $c = 25.708(6)$ Å, $\alpha = 89.98(2)$, $\beta = 90.08(2)$, $\gamma = 90.22(2)^\circ$, $V = 3006$ Å³, $Z = 4$. The parameters of the triclinic unit cell are related to the parameters of the cubic sodalite subcell by the relationships: $a = a_{\text{cub}}$, $b = \sqrt{2} a_{\text{cub}}$, $c = 2\sqrt{2} a_{\text{cub}}$. The diffraction experiment within the Ewald half-sphere ($\sin\theta/\lambda > 0.59$) consisted of 5861 nonzero reflections with $|F| > 3\sigma(F)$. Upon averaging symmetrically equivalent structure factors of a small number of reflections, the experimental set was reduced to 5724 reflections. All the crystallographic computations were performed using the AREN package of programs [8].

An attempt at determining the structure of triclinic lazurite in the centrosymmetric space group $P\bar{1}$ failed, similar to the earlier structure determination in the monoclinic system. The transition to the acentric group allowed us to localize all the framework atoms and most of the nonframework atoms and centrosymmetric fragments of the framework by the method of successive approximations. The positions of the remaining atoms were determined from difference electron-density syntheses. In particular, two pairs of electron-density peaks spaced about 2 Å apart were recorded in the regions with centers at $0\ 1/2\ 1/2$ and $1/2\ 1/2\ 1/2$. These peaks were identified with sulfide sulfur. The refinement showed that these positions are occupied only statistically.

Of all 32 positions of Ca and Na atoms, eight were characterized by the maximum electron-density. These positions can be divided into four pairs with the same y and z coordinates, whereas the x coordinates differ by

about 0.5. Assuming that each pair of these positions is statistically occupied by one Ca and one Na atom, we refined the corresponding positional parameters using the mixed f -curves. The final ratio of the Ca and Na atoms corresponded to the best R -factor (0.061) obtained in the approximation of the anisotropic atomic thermal vibrations with due regard for extinction ($E = -0.0000415$). The correction for absorption was introduced using the DIFABS program [10] for a specimen of an arbitrary shape. The coordinates and the equivalent atomic thermal parameters, the occupancies of the position of sulfide sulfur, and the Ca/Na ratios in the statistically filled positions are indicated in Tables 1 and 2; the interatomic distances are given in Tables 3 and 4.

STRUCTURE DESCRIPTION

I. Tetrahedral framework. As is well known, the structures of sodalite-like minerals consist of a framework built by Si and Al tetrahedra with the centers at the vertices of cuboctahedra. Neighboring tetrahedra share the vertices and form four- and six-membered rings of tetrahedra. In such structures, tetrahedra are characterized by average T -O distances ranging within 1.58–1.63 or 1.70–1.75 Å, which allows one to assume a high degree of Al and Si ordering over the framework positions.

According to [7], the framework of triclinic lazurite is divided into two equal blocks along the z -axis ($z = 0-0.5$ and $z = 0.5-1.0$) consisting of differently rotated tetrahedra (Fig. 1). Tetrahedra are synchronously rotated in the opposite directions about the z - and y -axes (for the first and the second block, respectively). In the sections $z = 0$ and $z = 0.5$ (at the unit-cell bound-

Table 2. Positional ($\times 10^4$) and equivalent thermal parameters B_{eq} ($\times 10$, \AA^2) of nonradical atoms in the triclinic lazurite structure

Atom	x/a	y/b	z/c	B_{eq}	Atom	x/a	y/b	z/c	B_{eq}
Na(1)	-1914(10)	3142(7)	2489(3)	21(2)	S(2)	0544(5)	4668(3)	7512(1)	13(1)
Na(2)	3073(11)	1821(8)	2498(4)	27(2)	S(3)	5306(6)	0333(4)	7621(2)	21(1)
Na(3)	1601(10)	5069(7)	1545(4)	25(2)	S(4)	9562(6)	-4643(4)	2509(2)	19(1)
Na(4)	1796(11)	4940(8)	3444(4)	33(2)	S(5)	0124(6)	9983(4)	9851(2)	15(1)
Na(5)	6979(10)	8239(7)	7478(3)	20(2)	S(6)	4732(6)	-0303(4)	2613(2)	21(1)
Na(6)	2254(10)	4928(7)	8619(4)	29(2)	S(7)	554(3)	-516(2)	-019(1)	266(4)
Na(7)	2139(10)	1878(7)	5063(3)	24(2)	S(8)	436(3)	-379(2)	022(1)	183(4)
Na(8)	2652(10)	-5079(6)	6358(3)	24(2)	S(9)	451(9)	-464(6)	486(3)	208(9)
Na(9)	8127(11)	1904(8)	0037(4)	26(2)	S(10)	440(5)	382(3)	482(2)	105(5)
Na(10)	2256(11)	2168(7)	9982(3)	28(2)	O(97)	058(2)	546(2)	7951(7)	327(4)
Na(11)	3442(10)	9959(7)	6583(3)	22(2)	O(98)	132(2)	-006(2)	4641(8)	52(5)
Na(12)	8034(12)	2178(8)	4976(4)	34(2)	O(99)	084(2)	523(1)	7041(6)	29(4)
Na(13)	1994(10)	-3106(7)	7487(3)	19(2)	O(100)	160(2)	391(2)	7612(7)	42(5)
Na(14)	6583(9)	0057(6)	1585(3)	21(2)	O(101)	582(4)	131(2)	7424(11)	100(6)
Na(15)	8438(9)	4969(6)	6568(3)	17(2)	O(102)	372(3)	047(2)	7807(13)	95(7)
Na(16)	8462(10)	0031(7)	5978(3)	21(2)	O(103)	955(2)	-538(1)	2946(7)	40(4)
Na(17)	1610(10)	0003(7)	0093(3)	24(2)	O(104)	915(2)	-517(1)	2052(6)	27(4)
Na(18)	7740(10)	-4873(7)	3600(3)	25(2)	O(105)	844(2)	-392(2)	2613(7)	42(4)
Na(19)	-2179(10)	8118(7)	0051(3)	22(2)	O(106)	467(5)	-125(2)	2404(12)	137(8)
Na(20)	-1702(9)	5094(7)	8424(3)	22(2)	O(107)	385(3)	013(2)	2989(10)	92(7)
Na(21)	1943(9)	-1862(7)	5047(3)	22(2)	O(108)	124(2)	983(2)	9461(8)	55(6)
Na(22)	1948(10)	7901(7)	9953(3)	24(2)	O(109)	-129(2)	017(1)	9601(6)	36(5)
Na(23)	7771(10)	7808(6)	4957(3)	26(2)	O(110)	-096(2)	419(1)	7501(6)	38(4)
Na(24)	7440(9)	5083(6)	1352(3)	22(2)	O(111)	099(2)	-419(1)	2485(7)	36(5)
M(1)	3110(6)	2432(4)	7534(1)	17(1)	O(112)	876(2)	011(2)	4451(7)	45(5)
M(2)	7016(7)	-2439(5)	2520(2)	19(1)	O(113)	958(2)	-090(1)	5179(7)	40(4)
M(3)	7575(7)	0052(4)	8767(2)	16(1)	O(114)	978(2)	092(1)	5202(7)	36(4)
M(4)	2267(7)	-2405(5)	2506(2)	19(1)	O(115)	522(2)	961(1)	7183(9)	56(5)
M(5)	7813(8)	2473(6)	7510(3)	19(1)	O(116)	522(2)	961(1)	7183(9)	56(5)
M(6)	7184(6)	0019(4)	3695(2)	15(1)	O(117)	043(2)	092(1)	0203(6)	36(4)
M(7)	2356(8)	-0008(5)	3773(3)	26(1)	O(118)	468(2)	051(1)	2214(6)	38(4)
M(8)	2816(7)	9992(6)	8691(3)	19(2)	O(119)	628(2)	995(2)	8008(8)	56(5)
S(1)	9854(6)	0023(4)	4850(2)	15(1)	O(120)	629(2)	954(2)	2837(10)	138(3)

Note: $M(1) = M(3) = \text{Ca}_{0.75}\text{Na}_{0.25}$, $M(5) = M(8) = \text{Na}_{0.75}\text{Ca}_{0.25}$, $M(6) = M(7) = \text{Na}_{0.5}\text{Ca}_{0.5}$, $M(2) = \text{Ca}_{0.55}\text{Na}_{0.45}$, $M(4) = \text{Na}_{0.55}\text{Ca}_{0.45}$, S(1–5) are sulfur atoms of the sulfate groups, S(7–10) are sulfur atoms of sulfate groups. The occupancies of S(7–10) positions are 0.89(3), 0.82(3), 0.48(3), and 0.30(2). The x - and y -coordinates for anions and the x -, y -, and z -coordinates for S(7–10) are multiplied by 10^3 .

aries and in its center), the tetrahedra are rotated as follows: three tetrahedra are rotated about the z -axis, whereas one tetrahedron is rotated about the y -axis; and *vice versa*, three tetrahedra are rotated about the y -axis and one tetrahedron is rotated about the z -axis. The above-described rotations are the consequence of displacements of tetrahedra from their average positions in the sodalite-like structure by the periodic law, with the character of the deviations being determined by the

directions of the crystallographic axes in the following way.

(1) The synchronous displacements of all the tetrahedra are observed only along the x -axis. Similar to the previous study [7], for each fixed y -value, the position of the modulation wave with respect to the origin is somewhat changed, but the phases and the amplitudes of vibrations are approximately the same (the ampli-

Table 3. Interatomic distances (Å) for framework atoms in triclinic lazurite

Cations	Range of T-O variation	Cations	Range of T-O variation
Si(1)	1.55–1.65	Al(1)	1.73–1.76
Si(2)	1.56–1.65	Al(2)	1.69–1.73
Si(3)	1.57–1.66	Al(3)	1.67–1.73
Si(4)	1.59–1.66	Al(4)	1.68–1.73
Si(5)	1.58–1.61	Al(5)	1.69–1.74
Si(6)	1.56–1.63	Al(6)	1.72–1.78
Si(7)	1.57–1.63	Al(7)	1.69–1.76
Si(8)	1.58–1.64	Al(8)	1.68–1.75
Si(9)	1.55–1.64	Al(9)	1.72–1.73
Si(10)	1.54–1.64	Al(10)	1.69–1.75
Si(11)	1.60–1.62	Al(11)	1.69–1.73
Si(12)	1.54–1.61	Al(12)	1.71–1.78
Si(13)	1.56–1.61	Al(13)	1.69–1.75
Si(14)	1.57–1.65	Al(14)	1.69–1.76
Si(15)	1.62–1.66	Al(15)	1.72–1.74
Si(16)	1.59–1.67	Al(16)	1.71–1.76
Si(17)	1.57–1.62	Al(17)	1.67–1.75
Si(18)	1.59–1.65	Al(18)	1.71–1.76
Si(19)	1.59–1.64	Al(19)	1.67–1.76
Si(20)	1.60–1.64	Al(20)	1.70–1.76
Si(21)	1.59–1.61	Al(21)	1.69–1.75
Si(22)	1.57–1.60	Al(22)	1.69–1.75
Si(23)	1.57–1.64	Al(23)	1.69–1.79
Si(24)	1.58–1.66	Al(24)	1.68–1.75

Note: The T–O distances are determined within an accuracy of 0.01 Å.

tude is about 0.3 Å). The character of the Δx displacement can be described by the superposition of the rectangular wave having an amplitude of 0.1 Å and the sinusoidal wave having an amplitude of 0.2 Å (Fig. 2a).

(2) The displacement wave along the y -axis is much weaker and its amplitude is about 0.06 Å, with synchronous vibrations in the pairs of chains of tetrahedra, Si(15)–Al(3), Al(21)–Si(14) ($y = 3/8$ and $5/8$) and Al(24)–Si(5) and Si(19)–Al(9) ($y = -1/8$ and $1/8$), whereas the pairs themselves are rotated in opposite directions (Fig. 2b).

(3) The displacement amplitude along the z -axis equals 0.08 Å. The chains are also divided into pairs but in a different way: one pair is composed by the Si(15)–Al(3) and Si(19)–Al(9) ($y = 3/8$ and $1/8$) tetrahedra and the other pair consists of the Al(21)–Si(14) and Al(24)–Si(5) tetrahedra ($y = 5/8$ and $-1/8$). The character of tetrahedron displacements in these chains is analogous to that described for the previous case (Fig. 2c). One can note that all three types of periodic displacement from

Table 4. Cation–anion distances (Å) and the coordination numbers for non-radical cations in the structure of triclinic lazurite

Cations	Distance	c.n.	Cations	Distance	c.n.
Na(1)	2.37–3.06	8	Na(22)	2.26–3.16	9
Na(2)	2.34–3.07	8	Na(23)	2.31–2.96	6
Na(3)	2.40–2.91	7	Na(24)	2.32–3.19	7
Na(4)	2.35–3.10	7	M(1)	2.35–2.98	9
Na(5)	2.43–3.02	7	M(2)	2.32–2.81	9
Na(6)	2.35–3.02	7	M(3)	2.28–2.96	8
Na(7)	2.48–2.82	7	M(4)	2.48–2.83	8
Na(8)	2.27–2.90	6	M(5)	2.34–2.98	8
Na(9)	2.37–3.08	8	M(6)	2.41–2.92	8
Na(10)	2.27–3.10	7	M(7)	2.37–2.90	8
Na(11)	2.27–2.99	6	M(8)	2.44–2.95	8
Na(12)	2.34–3.06	8	S(1)	1.43–1.48	4
Na(13)	2.36–3.09	8	S(2)	1.40–1.52	4
Na(14)	2.40–3.07	7	S(3)	1.42–1.52	4
Na(15)	2.40–2.96	7	S(4)	1.41–1.47	4
Na(16)	2.37–2.83	7	S(5)	1.44–1.54	4
Na(17)	2.35–3.11	8	S(6)	1.34–1.53	4
Na(18)	2.37–3.15	8			
Na(19)	2.45–2.99	7			
Na(20)	2.39–3.11	7	S(7)–S(8)	2.33	
Na(21)	2.32–3.02	8	S(9)–S(10)	2.00	

Note: The interatomic distances are determined within an accuracy of 0.01–0.02 Å; the distances for S(7–10) are determined within an accuracy of 0.03–0.04 Å.

the average have minimum values at about $z = 0$ and $z = 0.5$.

The modulation of the tetrahedral framework results in regular changes in the shape of the cuboctahedral cavities formed by oxygen atoms of the framework. In the yz section, these cavities have the shape of rhombuses with the diagonals parallel to the y and z -axes, respectively. At $y = 0$, the magnitudes of these diagonals change in such a way that the long diagonals of the rhombuses in the cuboctahedra neighboring along the z -axis are parallel either to the y - or to the z -axis and are equal to 8.98 and 9.13 Å (the average value 9.055 Å), 9.14 and 8.91 Å (9.025 Å), 8.99 and 9.09 Å (9.04 Å), and 9.17 and 8.98 Å (9.075 Å). The sections of cuboctahedra at $y = 0.5$ are “more isometric,” but their diagonals are different: 9.16 and 9.12 Å (the average value 9.14 Å), 9.01 and 9.02 Å (9.015 Å), 9.17 and 9.11 Å (9.14 Å), 9.09 and 9.01 Å (9.05 Å).

II. Distribution of sulfur atoms. Six of eight sodalite cavities are occupied by SO_4 -groups, whose

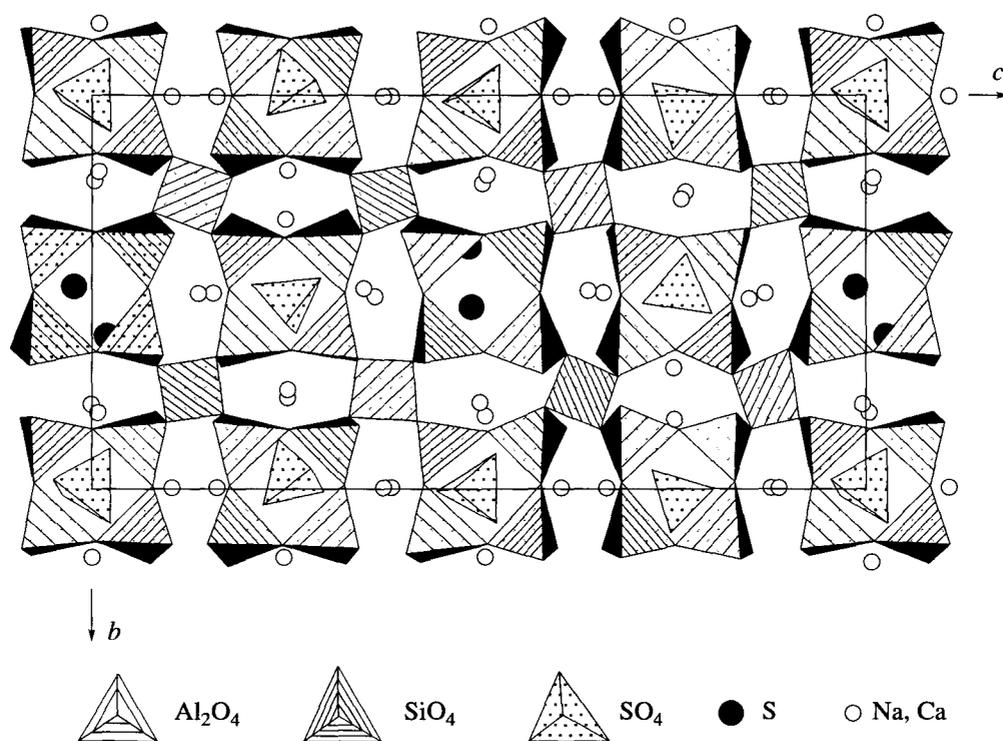


Fig. 1. Structure of triclinic lazurite projected onto the (100) plane.

positions and orientations differ from those of the analogous groups in nosean and häüyn [11–14] (where sulfur atoms are located in the centers of such cavities), whereas oxygen atoms lie on the body diagonals of the cubic unit cell. Each SO_4 -tetrahedron in this structure is rotated by about 90° about one of two diagonals of the sodalite subcell face coinciding with the y - and z -axes of the triclinic lazurite. The central S(1)–S(6) cations are displaced from the cavity centers (Fig. 1). Similar to Si and Al atoms, the modulations of these displacements in this case are the most pronounced along the x -axis. The positions of S atoms are also modulated along the y -axis. Two remaining cavities seem to be occupied by either S_2^- ions or by neutral H_2S_2 molecules. The first assumption is consistent with the greenish blue color of lazurite studied (according to the optical-absorption and luminescence spectra of lazurite, the green shade of this ornamental stone is caused by S_2^- ions [15]). The second assumption is confirmed by the fact that the S(7)–S(10) ions do not coordinate the Na atoms, because the shortest Na–S distance, Na(22)–S(8) = 3.16 Å, is larger than the sum of the ionic radii of S^{2-} (1.84 Å) and Na^{1+} (1.02 Å). It is also important that, in the latter case, the crystallochemical formula of lazurite, $(\text{Na}_7\text{Ca}_1)[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_{1.5}(\text{H}_2\text{S}_2)_{0.30}$, is electrostatically neutral.

III. Distribution of Na and Ca atoms. Large Na and Ca cations in the structure of triclinic lazurite are located in different positions. The first-type positions

(similar to those of Na atoms in sodalite [11]) are displaced from the centers of six-membered ditrigonal rings with an average $T\text{--}O\text{--}T$ angle of about 145° toward cuboctahedra and are filled with eight Na atoms (1, 2, 5, 11, 13, 14, 16, 17) forming valence bonds only with oxygen atoms of one SO_4 group. The second-type positions, occupied statistically by Ca and Na atoms (M -cations in Tables 2 and 4), are close to the plane of less distorted six-membered rings with an average $T\text{--}O\text{--}T$ angle of about 151° ; they are coordinated with six oxygen atoms from two SO_4 -groups from the adjacent cuboctahedral cavities. The degree of distortion of six-membered (ditrigonal) rings determines substantially different cation–anion distances for the atoms of the first and the second groups (Table 5). The remaining 16 third-type positions are located at the boundaries of the cavities containing sulfide sulfur and sulfate groups and are displaced closer to the latter groups. These positions are coordinated with the rings of an intermediate shape and are only occupied by Na atoms.

As a result, one can separate two $[\text{Na}_3\text{Ca}_1\text{SO}_4]^{3+}$ clusters with centers at S(3) and S(6) and four $[\text{Na}_{5.5}\text{Ca}_{0.5}\text{SO}_4]^{4.5+}$ clusters with centers at S(1), S(2), S(4), and S(5) in the unit cell of triclinic lazurite. In cubic nosean and häüyn [12], the oxygen atoms of the SO_4 groups coordinate the Na, Ca, and K atoms and form $[\text{Na}_4\text{SO}_4]^{2+}$ clusters in nosean and $[\text{Na}_3\text{Ca}_1\text{SO}_4]^{3+}$ and $[\text{K}_2\text{Ca}_1\text{SO}_4]^{3+}$ clusters in häüyn.

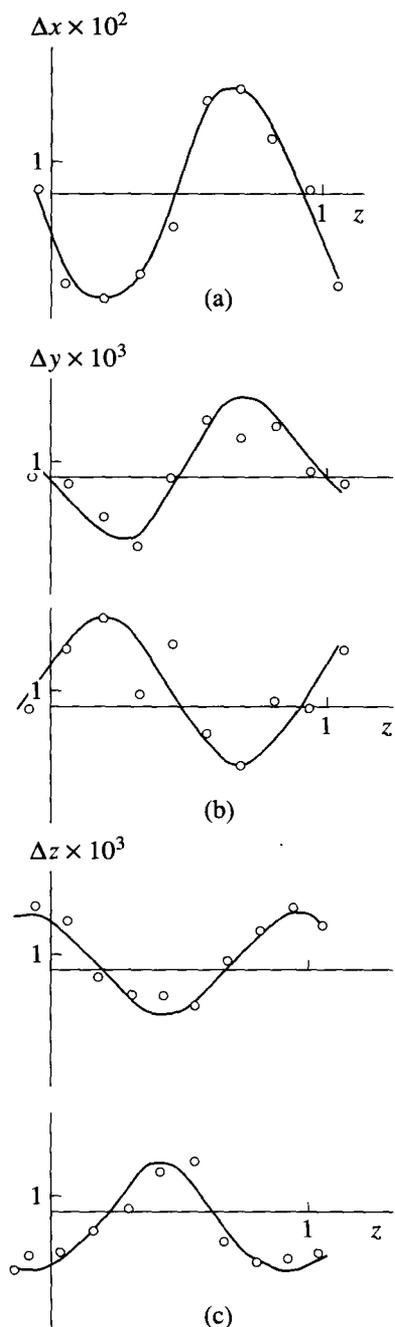


Fig. 2. Graphic representation of the displacements of Al and Si atoms from their average (sodalite) positions along the z -axis: (a) $\Delta x(z)$ in the chain of Al(24)–Si(5) tetrahedra; (b) $\Delta y(z)$ in the chain of Al(24)–Si(5) tetrahedra (the upper curve) and Al(21)–Si(14) tetrahedra (the lower curve); (c) $\Delta z(z)$ in the chain of Al(21)–Si(14) tetrahedra (the upper curve) and Si(19)–Al(9) tetrahedra (the lower curve).

DISCUSSION OF RESULTS

Thus, the positional ordering of Na and Ca cations results in modulations of displacements and substitutions. The six-membered rings with different angles of ditrigonal rotation coordinating these cations alternate

along the [010] and [001] directions. Since the angles of ditrigonal rotation determine the degree of “compression” of six-membered rings, one observes the periodic “compression” and “expansion” of the fragments of the sodalite framework along these directions, whereas, along the [100] direction, the corrugated bands of six-membered rings of one type are formed.

In a $\sim 9 \times 13 \times 26$ Å-large synthetic aluminate–sodalite crystal of the composition $\text{Ca}_8[\text{Al}_{12}\text{O}_{24}](\text{WO}_4)_2$ [16] (whose metrics is similar to that of triclinic lazurite), one also observes the positional ordering of Ca atoms giving rise to the rotation of WO_4 groups by 45° about the [100] direction and the wave-like distortion of the structure (displacement modulation). Nevertheless, in distinction from triclinic lazurite, in this case the symmetry becomes orthorhombic (*Aba2*).

The structure determination of lazurite also sheds light on the true symmetry of the haiyn structure, whose ideal formula, $\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_2$, can be described with the aid of the $[\text{Na}_3\text{Ca}, \text{SO}_4]^{3+}$ clusters revealed in the structure of triclinic lazurite. It is quite logical to assume that the symmetry of each individual unit cell of haiyn is lower than the symmetry of the diffraction pattern of lazurite and can be triclinic.

It is expedient to compare the structure of triclinic lazurite with the average structure of isotropic lazurite briefly described in the introduction. Its structure was studied [6] with no account of the satellite reflections. It was assumed that splitting of oxygen atoms of the framework between two close $24(i)$ positions is associated with different dimensions of the cavities containing S^{2-} and SO_4^{2-} groups and that the formation of the observed superstructural reflections is associated with the positional and isomorphous ordering of atoms. We believe that the positional ordering of the framework oxygen atoms can be interpreted in a different way—by the presence in the structure of two fragments with right- and left-hand rotation of the tetrahedra and similar to the fragments observed in triclinic lazurite. If one constructs the framework of isotropic lazurite using both split oxygen atoms, then the above-indicated fragments can be seen quite clearly and the anomalously large thermal vibrations observed for Al and Si atoms in the subcell [6] can be explained by the modulations of their displacements in the real structure. The distribution of the nonframework Na and Ca atoms over three close positions is quite consistent with the three types of positions of these atoms in the structure of triclinic lazurite: the Na(1) and Na(3) positions in the isotropic lazurite correspond to the first-type position in the triclinic lazurite, whereas the Na(2) position in the isotropic lazurite corresponds to the second- and third-type positions in the triclinic lazurite.

In conclusion, it should be emphasized once again that, although the crystal structure of lazurite was repeatedly studied, only the present study provides a complete description of its structure. The description of

Table 5. The average values of the $T-O-T$ angles (in deg) for six-membered rings in the structure of triclinic lazurite (Y and Z are the coordinates of ring centers)

Y	Z							
	0	0.125	0.250	0.375	0.500	0.625	0.750	0.875
0	–	146.8	–	149.8	–	147.2	–	150.6
	–	146.8	–	152.6	–	148.2	–	153.1
0.25	151.6	–	143.7	–	152.2	–	147.1	–
	152.1	–	144.3	–	151.0	–	150.2	–
0.50	–	148.7	–	147.7	–	147.0	–	152.7
	–	148.2	–	153.1	–	148.3	–	149.6
0.75	154.7	–	153.4	–	149.1	–	142.9	–
	152.8	–	154.1	–	148.5	–	143.5	–

Note: The range of $T-O-T$ angles is 138° – 165° ; $\langle T-O-T \rangle = 149.3^{\circ}$.

the lazurite superstructure in terms of commensurate modulations allowed us to explain an increase of its unit-cell parameters and the extreme lowering of its symmetry, from cubic (characteristic of sodalite) to triclinic. It should also be indicated that the determination and the refinement of 210 crystallographically independent positions of this structure would hardly be possible without AREN, a unique Russian package of crystallographic programs.

ACKNOWLEDGMENTS

The study was supported by the Swiss National Science Foundation (grant no. SUPJ 048718) and the Russian Foundation for Basic Research (project nos. 96-05-64633 and 96-05-64381).

REFERENCES

- Voskoboinikova, N.V., *Zap. Vses. Mineral. O-va*, 1938, vol. 67, no. 4, p. 501.
- Sapozhnikov, A.N., *Kristallografiya*, 1992, vol. 37, no. 4, p. 889.
- Ivanov, V.G. and Sapozhnikov, A.N., *Lazurity SSSR* (Lazurites of the USSR), Novosibirsk: Nauka, 1985.
- Hogarth, D.D. and Griffin, W.L., *Lithos.*, 1976, vol. 9, no. 1, p. 39.
- Belov, N.V., *Ocherki po strukturnoi mineralogii* (Reviews on Structural Mineralogy), Moscow: Nedra, 1976.
- Hassan, I., Peterson, R.G., and Grundy, H.D., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1985, vol. 41, p. 827.
- Kashaev, A.A., Sapozhnikov, A.N., Sokolova, G.V., Pobedinskaya, E.A., Dorokhova, G.I., and Drits, G.I., in *Metody difraktsionnykh issledovaniy kristallicheskikh materialov* (Methods of Diffraction Studies of Crystalline Materials), Novosibirsk: Nauka, 1989.
- Andrianov, V.I., *Kristallografiya*, 1987, vol. 32, no. 1, p. 228.
- Andrianov, V.I., *Kristallografiya*, 1989, vol. 34, no. 3, p. 592.
- Walker, N. and Stuart, D., *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1983, vol. 39, no. 1, p. 158.
- Hassan, I. and Grundy, H.D., *Acta Crystallogr., Sect. B: Struct. Sci.*, 1984, vol. 40, p. 6.
- Hassan, I. and Grundy, H.D., *Can. Mineral.*, 1989, vol. 27, p. 165.
- Evsyumin, V.G., Sapozhnikov, A.N., Rastsvetaeva, R.K., and Kashaev, A.A., *Kristallografiya*, 1996, vol. 41, no. 4, p. 659.
- Hassan, I. and Grundy, H.D., *Can. Mineral.*, 1991, vol. 29, p. 123.
- Platonov, A.N., *Priroda okraski mineralov* (Nature of Mineral Coloring), Kiev: Naukova Dumka, 1976.
- Depmeier, W., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, vol. 40, p. 226.

Translated by L. Man