Sodian stellerite from Capo Pula, Sardegna

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LITHOS

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The sodian stellerite (a zeolite) occurs as lustrous white or slightly pink, easily cleavable lamellae, filling cavities and fractures in an acid lava (andesite or rhyolite) in the cliff below S. Efisio Tower, near Capo Pula, Cagliari, Sardegna. Italy. The principal forms present are {010}, {011}, {111}. Single crystal photographs show an orthorhombic symmetry and *Amma* (or *Ammm*) space group. An indexed X-ray diffraction powder pattern is provided. Unit cell dimensions, chemical formula, density, optical properties and thermal behaviour are given.

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In a recent work Galli & Passaglia (1973) described a typical stellerite from Villanova Monteleone, Sardegna (Sardinia), and stressed the crystallographical and chemical differences between this mineral and stilbite. They emphasized particularly the chemical and physical features of stellerite: orthorhombic symmetry with space group F*mmm* (or F222 or F*mm*2), parallel extinction, absence of twinning, high Si content with small amounts of Na.

In this work we describe a mineral which has X-ray powder data similar to those of stilbite, but which is undoubtedly orthorhombic. Because of its morphological, structural and chemical properties it may be regarded as a particular kind of stellerite.

It should be mentioned here that a monoclinic Na-rich stilbite was discovered in Japan by Harada & Tomita (1967).

Occurrence and paragenesis

The sample was collected in an outcrop of volcanic rock near Capo Pula; more precisely, it was found in the cliff below S. Efisio Tower in the archaeological area of Nora (Cagliari).

The rock is weathered and its colour ranges from pink to brown. It is difficult to define petrologically because of the intense weathering, but it is undoubtedly one of the acid lavas (andesite, rhyolite) which are widespread in southern Sardegna.

The walls of large fractures and cavities are filled with lustrous white or slightly pink crystals on a thin crust of reddish heulandite.

Morphology

Most crystals occur as easily cleavable lamellae which may reach a size of 5×4×1 millimetres. The well-formed crystals have the morphology shown in Fig. 1. Goniometric measurements on single crystals indicate that the forms {010}, {011} and {111} are invariably present. {001} is also common but is always poorly developed. The best developed face is {010}. There is also a perfect cleavage in this plane.

X-ray data

In order to define the lattice symmetry, the following precession photographs (Ni-filtered,

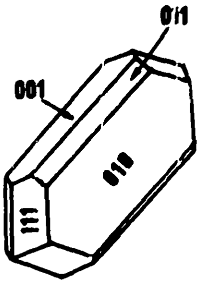

Fig. 1. Morphology of the sodian stellerite from Capo Pula, Sardegna.

Cu-radiation) were taken: (h0l), (h1l), (h2l), (hk0), (hk1) and (hk2). The (h0l) photograph allows us to observe $\beta = 90° \pm 10'$ and two mutually perpendicular mirror planes; in particular the intensities of (604) and ($60\bar{4}$) are the same, and according to Galli & Passaglia (1973), this pair of diffractions exhibit strong intensity differences in monoclinic structures. The mineral is therefore orthorhombic.

The above-mentioned photographs show strong reflections, compatible with space group F*mmm*, previously reported for stellerite, and weak reflections, compatible with space group A*mma*. Hence F*mmm* is the pseudogroup, the true group being A*mma* (or perhaps A*mmm*, as the analogy with the pseudogroup suggests). The absence or presence of diffractions (hk0) with $h \neq 2n$ is the factor which enables us to determine whether the true group is A*mma* or A*mmm*. These lines appear to be absent but as they would be weak diffractions, it is difficult to be certain in this case. X-ray powder data of the mineral are reported in Table 1. The $d_{obs.}$ values were obtained by means of a Philips diffractometer (Ni-filtered Cu-radiation) with $Pb(NO_3)_2$ as internal standard. The intensities were estimated visually. Inspection of the indexing of Table 1 led us to conclude that no line corresponding to indexes allowed in A*mma* but forbidden in F*mmm*, is detectable owing to their low intensities; in other words, a powder pattern is insufficient to distinguish a sodian stellerite A*mma* from a normal stellerite F*mmm*; single crystal photographs are necessary for this distinction, as shown by Galli & Passaglia (1973) for normal stellerite of Villanova Monteleone and by us in this research.

Cell dimensions were derived by a least squares computer programme using only the reflections marked by a star in Table 1. The other lines were discarded either because they were referable to more than one set of indices or because they were too far from the standard lines.

The values obtained are reported in Table 2 with the chemical formula and the calculated and observed densities. The observed density was determined by means of a torsion microbalance, using toluene as a liquid (Berman 1939).

Optical properties

The refractive indices were determined by the double variation method. The values obtained are reported in Table 3 with the calculated $2V_\alpha$, optical orientation and sign. The experimental determination of $2V_\alpha$ was not possible because of the thinness of the crystals; but the interference figures confirm a large negative axial angle. Few twinned crystals were observed, which implies that their structure is not exactly orthorhombic.

The values of the refractive indices are smaller than those reported in the literature for stilbites, stellerites and sodian stilbite. This suggests a correlation between refractive indices and Na-content, of the type already observed for chabazites by Passaglia (1970). Moreover, in comparison with stellerite, this mineral has a different optical orientation, β and γ being interchanged.

Chemical composition

SiO_2 was determined by a gravimetric method, Al_2O_3 by complexometric titration and Na, K, Mg, Ca, Sr, Ba, Fe^{III} and Mn by atomic absorption spectrometry using a Perkin-Elmer 303 instrument. H_2O was determined by TG using a thermal analyser manufactured by B.D.L. (Bureau de Laison, Paris). The chemical analysis is:

SiO_2	58.82	SrO	tr.
Al_2O_3	14.75	BaO	tr.
Fe_2O_3	0.04	Na_2O	5.97
MgO	0.24	K_2O	1.76
MnO	tr.	H_2O	16.40
CaO	1.66	Total	99.64

Table 1. X-ray diffraction powder data for sodian stellerite from Capo Pula.[a]

h	k	l[b]	I/I_0	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)
0	2	0	>100	9.10	9.10
0	0	2			8.92
2	0	0	4	6.83	6.821
1	3	1	6	5.301	5.294
1	1	3	5	5.227	5.223
2	2	2*	21	4.659	4.656
0	4	0*	6	4.552	4.550
0	0	4*	3	4.461	4.460
3	1	1*	12	4.285	4.283
1	3	3	100	4.054	4.055
0	4	2			4.053
(3	0	2)			4.052
0	2	4*	13	4.006	4.005
2	0	4*	12	3.732	3.733
(0	5	1)	1	3.566	3.566
3	3	1*			3.565
2	4	2*	12	3.483	3.484
4	0	0*	11	3.408	3.411
1	1	5*	11	3.393	3.392
4	2	0	16	3.189	3.194
4	0	2			3.186
0	4	4			3.185
3	3	3*	7	3.103	3.104
0	6	0	78	3.028	3.033
1	5	3			3.027
(3	4	2)			3.026
4	2	2	25	3.004	3.007
(3	2	4)			3.006
1	3	5			3.000
0	0	6*	4	2.974	2.974
2	4	4*	2	2.885	2.886
0	6	2*	3	2.871	2.872
0	2	6*	3	2.824	2.827
(2	5	3)			2.826
3	5	1*	3	2.805	2.806
(2	3	5)			2.804
3	1	5	22	2.773	2.774
2	6	0			2.772
4	4	0	3	2.727	2.729
2	0	6			2.726
4	0	4*	3	2.709	2.709
2	2	6	4	2.609	2.611
(3	4	4)			2.609
4	2	4			2.597
3	5	3*	6	2.563	2.564
(0	1	7)*	1	2.524	2.524
0	6	4	5	2.5070	2.5083
1	5	5			2.5049
0	4	6*	3	2.4874	2.4892
2	6	4*	3	2.3535	2.3542
(0	3	7)	3	2.3470	2.3499
1	7	3*			2.3468
6	0	0*	1	2.2741	2.2738
4	6	0*	1	2.2665	2.2666
0	0	8	3	2.2250	2.2302
3	5	5			2.2230
(2	3	7)			2.2218
3	1	7	2	2.2037	2.2070
6	2	0			2.2060
0	2	8	1B	2.1637	2.1661
5	1	5			2.1523
0	6	6*	4	2.1215	2.1235
2	0	8			2.1198
(1	6	6)	3	2.0965	2.0982
2	8	2*			2.0976
(0	5	7)	<1	2.0843	2.0879
3	3	7*			2.0876
1	7	5	1B	2.0752	2.0769
(5	4	4)			2.0722
2	2	8	3	2.0621	2.0646
1	5	7			2.0638
(4	5	5)	2	2.0395	2.0414
5	3	5*			2.0412
6	4	0*	3	2.0338	2.0340
2	6	6	3	2.0253	2.0275
0	8	4			2.0266
6	0	4			2.0258
4	6	4*	2	2.0180	2.0207
4	4	6*	<1	2.0124	2.0107
(5	0	6)			2.0105
(2	1	9)	3	1.8926	1.8934
4	8	0*			1.8926
5	7	1*	1	1.8702	1.8719
1	3	9	2	1.8640	1.8667
4	0	8			1.8666
5	5	5*	2	1.8595	1.8624
5	1	7	2	1.8545	1.8529
(3	8	4)			1.8511
6	4	4			1.8507
(5	4	6)	<1	1.8366	1.8390
3	9	1			1.8379
(6	5	3)			1.8345
(0	7	7)	17	1.8192	1.8201
0	10	0*			1.8200
3	1	9	4	1.8040	1.8083
0	8	6			1.8069

[a] Experimental settings for the Philips diffractometer: Ni-filtered Cu$K\alpha_1$ radiation ($\lambda = 1.54051$ Å); tube current 40 Kv, 20 mA; angular speed 1/4° per minute; 1 – 0.1 – 1 slits for $2\theta < 40°$ and 1 – 0.2 – 1 for $2\theta > 40°$; internal standard: $Pb(NO_3)_2$.

[b] Only the reflections marked with a star have been used for the refinement of the unit-cell dimensions.

When indexes are in brackets, the diffractions are possible in space group *Amma* and not in *Fmmm*, and therefore are very weak.

Table 2. Unit-cell data for sodian stellerite from Capo Pula.

a	13.643 ± 0.002 Å
b	18.200 ± 0.003 Å
c	17.842 ± 0.003 Å
cell volume	4430 ± 2 $(\text{Å})^3$
space group	*Amma* (or *Ammm*)
Chemical formula	$(Ca_{0.84}Mg_{0.17}Na_{5.45}K_{1.06})_{tot=7.52}$ $[(Al_{8.19}Fe^{III}_{0.01})_{tot=8.20}Si_{27.72}]O_{72}\cdot$ $25.78\ H_2O$
Z	2
$D_{calc.}$	$2.11 g.cm^{-3}$
$D_{meas.}$	$2.13 \pm 0.01\ g.cm^{-3}$

Table 3. Optical properties of sodian stellerite from Capo Pula.

α	1.4791 ± 0.0005
β	1.4851 ± 0.0005
γ	1.4891 ± 0.0005
$\gamma - \alpha$	0.0100
Sign	(–)
$2\ V_{\alpha}$ (calc.)	78° ± 8°
Orientation	$\alpha \rightarrow a$ $\beta \rightarrow b$ $\gamma \rightarrow c$

The chemical formula calculated on the basis of 72 oxygens (1/2 of unit cell) is:

$(Ca_{0.84}Mg_{0.17}Na_{5.45}K_{1.06})_{tot.=7.52}$
$[(Al_{8.19}Fe^{III}_{0.01})_{tot.=8.20}\ Si_{27.72}]O_{72}\cdot 25.78\ H_2O$.

From these values we can observe: (a) the SiO_2 content is almost equal to that of stellerite and higher than that of stilbite; (b) Na dominates among the exchangeable cations, while the Ca and K contents are almost equal.

Differential thermal analyses

DT curves were taken by a B.D.L. thermal analyser at a heating rate of 10°C/min for our mineral and the stellerite from Villanova Monteleone (Fig. 2).

The stellerite from Villanova Monteleone shows an endothermic doubled peak, the first is very broad at 91°C and the second very sharp at 201°C. Our mineral, on the contrary, shows a single and symmetric endothermic peak at 191°C. A study of the DT curves of stilbites (Koizumi 1953, Černý 1965, Harada & Tomita 1967) and of sodian stilbite (Harada & Tomita 1967) indicates that the shape of the endothermic peak is variable and does not follow recognizable rules.

Conclusions

The sample from Pula is a stellerite because its powder data are similar to those of stilbite and because it is orthorhombic. Its Si content is the same as that of stellerite. Since Na is predominant we can call it sodian stellerite. The sodian stilbite reported by Harada & Tomita (1967) is different from our mineral because it is monoclinic, its powder data are those of stilbite and not those of stellerite and its Si content is typical of stilbite. The new data reported here and the previously established data permit us to summarize the crystal chemical features of the two mineral species as follows:

(a) Stellerite: orthorhombic zeolite with a stilbite-like framework. The Si/(Si + Al + Fe) ratio (about 0.77) is greater than that of the stilbites. The Al content needs 8 Ca or about 16 Na in the unit cell. Among the exchangeable cations, Ca normally dominates and Na is present in small quantity; but the mineral described in this work is an example of stellerite with Na prevailing over Ca.

At this point it is necessary to emphasize that if a submicroscopically twinned stilbite with $\beta = 90°$ exists, it would be very difficult to distinguish from a truly orthorhombic stellerite. On the other hand a small change in the arrangement of the cations in the channels may be sufficient to cause the change from orthorhombic to monoclinic symmetry: in other words, the limits between stellerite and stilbite are probably not very sharp. That, in our opinion, would explain the presence of few twinned crystals in our sodian stellerite.

(b) Stilbite: monoclinic zeolite with a Si/(Si + Al + Fe) ≃ 0.72. Among the exchangeable cations Ca prevails, but the Na content is always considerable. The Al content needs a number of exchangeable cations ranging from 10 (8Ca + 2Na) to 14 (6Ca + 8Na) in the unit cell. The existence of the sodian stilbite (Harada & Tomita 1967) suggests the possibility of a continuous series between the Ca and Na end members. From present knowl-

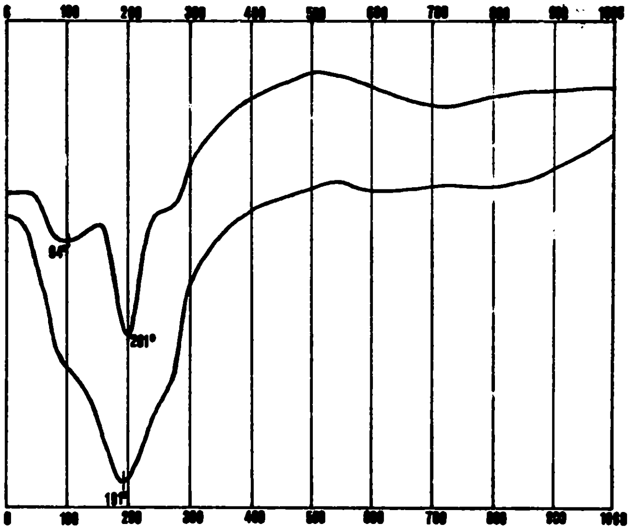

Fig. 2. DT curves of stellerite from Villanova Monteleone (Sardinia) (upper) and sodian stellerite from Capo Pula (lower).

edge, the four known types within the stilbite group are therefore:

(1) Stilbite: monoclinic with Ca > Na. This is the most widespread type.

(2) Sodian stilbite: monoclinic with Na > Ca. Sample from Onigajō (Harada & Tomita 1967).

(3) Stellerite: orthorhombic with Ca ≫ Na. Samples described by Galli & Passaglia (1973).

(4) Sodian stellerite: orthorhombic with Na > Ca. Sample described here.

Although a new name for type 4 would probably be justified we do not suggest one here as we are awaiting the proposals of an *ad hoc* committee of the IUPAC on the nomenclature of zeolites.

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