

COMPLETE Al–Si ORDER IN SCAPOLITE $Me_{37.5}$, IDEALLY $Ca_3Na_5[Al_8Si_{16}O_{48}]Cl(CO_3)$, AND IMPLICATIONS FOR ANTIPHASE DOMAIN BOUNDARIES (APBs)

SYTLE M. ANTAO[§]

Department of Geoscience, University of Calgary, Calgary, Alberta T2N 1N4, Canada

ISHMAEL HASSAN

Department of Chemistry, University of the West Indies, Mona, Kingston 7, Jamaica

ABSTRACT

The structure of an intermediate scapolite ($Me_{36.6}$) from Lake Clear, Ontario, was obtained using synchrotron high-resolution powder X-ray diffraction (HRPXRD) data and Rietveld structure refinement in space group $P4_2/n$. The chemical formula obtained by electron microprobe is $Na_{2.19}Ca_{1.35}K_{0.16}[Al_{3.95}Si_{8.05}O_{24}]Cl_{0.55}(CO_3)_{0.41}(SO_4)_{0.04}$, equivalent to $Me_{36.6}$. The unit-cell parameters are a 12.07899(1), c 7.583467(9) Å, and V 1106.443(2) Å³. The average distances are $\langle T1-O \rangle = 1.617(1)$ Å, $\langle T2-O \rangle = 1.744(1)$ Å, and $\langle T3-O \rangle = 1.601(1)$ Å. Therefore, the $T1$ and $T3$ sites contain only Si atoms, and the $T2$ site contains only Al atoms, so the Al and Si atoms are completely ordered. Complete Al–Si order was predicted for $Me_{37.5}$, ideally $Ca_3Na_5[Al_8Si_{16}O_{48}]Cl(CO_3)$, and is confirmed in this study. Antiphase domain boundaries (APBs) in scapolite cannot arise from Al–Si order because the average $\langle T-O \rangle$ distances indicate complete Al–Si order in $Me_{36.6}$. If APBs were to arise from Al–Si order, switching of the T sites across the APBs will occur, and complete Al–Si order cannot be observed. Therefore, Al–Si order, which is present to various extents across the scapolite series, can be ruled out as the cause for the APBs. Order involving Cl and CO_3 is the cause for the APBs in scapolite.

Keywords: scapolite, high-resolution powder X-ray diffraction (HRPXRD), crystal structure, complete Al–Si order, Cl– CO_3 order.

SOMMAIRE

Nous avons établi la structure d'une scapolite intermédiaire ($Me_{36.6}$) provenant du lac Clear, en Ontario, au moyen de la diffraction X sur poudre réalisée à résolution élevée avec un synchrotron (HRPXRD) et un affinement Rietveld dans le groupe spatial $P4_2/n$. La formule a été établie avec une microsonde électronique: $Na_{2.19}Ca_{1.35}K_{0.16}[Al_{3.95}Si_{8.05}O_{24}]Cl_{0.55}(CO_3)_{0.41}(SO_4)_{0.04}$, ce qui est équivalent à $Me_{36.6}$. Les paramètres réticulaires sont a 12.07899(1), c 7.583467(9) Å, et V 1106.443(2) Å³. Les distances moyennes sont $\langle T1-O \rangle = 1.617(1)$ Å, $\langle T2-O \rangle = 1.744(1)$ Å, et $\langle T3-O \rangle = 1.601(1)$ Å. Il en découle que les sites $T1$ et $T3$ ne contiennent que le Si, et que le site $T2$ ne contient que des atomes Al, de sorte que les atomes Al et Si sont ordonnés. Une mise en ordre complète de Al et Si avait été prédite pour $Me_{37.5}$, de formule idéale $Ca_3Na_5[Al_8Si_{16}O_{48}]Cl(CO_3)$, et elle est confirmée dans ce travail. Les interfaces antiphasées des domaines dans la scapolite ne pourraient être causés par le degré d'ordre de Al et Si parce que les distances moyennes $\langle T-O \rangle$ indiquent un degré d'ordre complet dans $Me_{36.6}$. Si ces interfaces antiphasées étaient attribuables au degré d'ordre, on verrait un interchangement des sites T sites en traversant l'interface, et une mise en ordre Al–Si complète ne serait pas possible. Il semble donc qu'un certain ordre impliquant Al et Si, présent à divers degrés dans la série des scapolites, ne pourrait rendre compte de ces interfaces antiphasées, qui seraient plutôt attribuables à une mise en ordre de Cl et CO_3 .

(Traduit ar la Rédaction)

Mots-clés: scapolite, diffraction X sur poudre à haute résolution (HRPXRD), structure cristalline, degré d'ordre Al–Si complet, ordre Cl– CO_3 .

[§] E-mail address: antao@ucalgary.ca

INTRODUCTION

Scapolite forms solid solutions between marialite, $\text{Na}_4[\text{Al}_3\text{Si}_9\text{O}_{24}]\text{Cl} = \text{Me}_0$, and meionite, $\text{Ca}_4[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{CO}_3 = \text{Me}_{100}$. There are two series that meet at Me_{75} , and the composition varies by the replacement of $[\text{Na}_4\bullet\text{Cl}]\text{Si}_2$ by $[\text{NaCa}_3\bullet\text{CO}_3]\text{Al}_2$ between Me_0 and Me_{75} , and by the replacement of $[\text{NaCa}_3\bullet\text{CO}_3]\text{Si}$ for $[\text{Ca}_4\bullet\text{CO}_3]\text{Al}$ between Me_{75} and Me_{100} (Evans *et al.* 1969, Hassan & Buseck 1988, Deer *et al.* 1992). In addition, chemical compositions of scapolite are represented by two straight lines that meet at Me_{75} , indicating two series (see Fig. 12 in Hassan & Buseck 1988, or Fig. 188 in Deer *et al.* 1992). The Ca–Na cations disorder on heating, but the Cl–CO₃ order remains to 900°C (Antao & Hassan 2002, 2008a, 2008b). The $\text{Me}_{37.5}$ composition (midway between Me_0 and Me_{75}), has ratio of clusters $[\text{Na}_4\bullet\text{Cl}]^{3+}:[\text{NaCa}_3\bullet\text{CO}_3]^{5+}$ equal to 1:1, where complete cluster order occurs and complete Al–Si order is also expected; this is where maximum intensities occur for the type-b ($h + k + l = \text{odd}$) reflections (Lin & Burley 1973c; see Fig. 2 in Hassan & Buseck 1988).

The ideal formula of $\text{Me}_{37.5}$ is $\text{Na}_5\text{Ca}_3[\text{Al}_8\text{Si}_{16}\text{O}_{48}]\text{Cl}(\text{CO}_3)$, such that each of the T1 and T2 sites are expected to contain eight Si atoms (= 16 Si atoms in total) and the T3 site contains eight Al atoms, such that we have the framework atoms $[\text{Al}_8\text{Si}_{16}\text{O}_{48}]$ and expect complete Al–Si order. The closest mineral to scapolite that has similar composition and contains large anions is sodalite, $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$, and the Al–Si order is complete with Al–O = 1.7435(2), and Si–O = 1.6100(2) Å (Hassan & Grundy 1983, Hassan *et al.* 2004, Antao *et al.* 2008). Similar $\langle T\text{--O} \rangle$ distances in scapolite will confirm complete Al–Si order. Such $\langle T\text{--O} \rangle$ distances may vary between narrow limits, depending on the interstitial atoms present (Antao *et al.* 2008).

One summary point from Sokolova & Hawthorne (2008) is: “In $P4_2/n$ scapolite, Al is strongly ordered at T(2), and Si is strongly ordered at T(3), but this order is never complete”. This is in disagreement with the prediction of complete Al–Si order in $\text{Me}_{37.5}$. To resolve this question, we carried out a Rietveld structure refinement on a $\text{Me}_{36.6}$ sample and found complete Al–Si order, as predicted by Lin (1975) and Hassan & Buseck (1988).

Type-b reflections [$h + k + l$ odd] are present in space group $P4_2/n$, and they give rise to antiphase domain boundaries (APBs). The interpretation of the APBs is either based on Al–Si order (Oterdoom & Wenk 1983, Seto *et al.* 2004), or Cl–CO₃ order (Phakey & Ghose 1972, Hassan & Buseck 1988). Complete Al–Si order has implications for the origin of APBs and provides an opportunity to further decide on one of the above reasons for its formation.

BACKGROUND INFORMATION

The structure of scapolite was determined by Pauling (1930) and Schiebold & Seumel (1932), and refined by several researchers in either space group $I4/m$ or $P4_2/n$ (Papike & Zoltai 1965, Papike & Stephenson 1966, Lin & Burley 1973a, 1973b, 1973c, 1974, Ulbrich 1973, Levien & Papike 1976, Peterson *et al.* 1979, Aitken *et al.* 1984, Comodi *et al.* 1990, Belokoneva *et al.* 1991, 1993, Teertstra *et al.* 1999, Sokolova & Hawthorne 2008). The space group $P4_2/n$ should be used for the average scapolite structure across the series that contains no phase transitions, but contain a discontinuity at Me_{75} (Antao & Hassan 2011). Additional data on scapolite were obtained using Rietveld refinement and MAS NMR spectroscopy (Sokolova *et al.* 1996, 2000, Sherriff *et al.* 1998, 2000), valence-matching principle (Hawthorne & Sokolova 2008), and electrostatic energy calculations (Chamberlain *et al.* 1985). A review of the scapolite series was given by Lin (1975).

TABLE 1. CHEMICAL COMPOSITION OF SCAPOLITE $\text{Me}_{36.6}$

Oxide	wt. %	Atom	apfu
SiO ₂	54.72	Si	8.050
Al ₂ O ₃	22.79	Al	3.950
FeO	0.08	ΣT	12.000
SrO	0.20		
MgO	0.00	Fe ²⁺	0.010
CaO	8.58	Sr	0.017
Na ₂ O	7.67	Mg	0.000
K ₂ O	0.84	Ca	1.352
Cl	2.21	Na	2.186
SO ₃	0.37	K	0.158
CO ₂	2.04	ΣM	3.724
– O = Cl	0.50		
Total	98.98	Cl	0.550
		(SO ₃)	0.040
		(CO ₃)	0.409
		ΣA	1.000
		Me%	36.6

$$\text{Me}\% = [\text{Ca}/(\text{Ca} + \text{Na} + \text{K})] \times 100.$$

EXPERIMENTAL

The scapolite sample used in this study is from Lake Clear, Ontario. The crystals are large (0.5 × 0.5 × 0.5 cm), white in color, and of high purity. Results of a chemical analysis obtained by electron microprobe are given in Table 1. The crystal is homogeneous, as judged by optical observations and microprobe data. The chemical composition for the Lake Clear sample is $\text{Na}_{2.19}\text{Ca}_{1.35}\text{K}_{0.16}[\text{Al}_{3.95}\text{Si}_{8.05}\text{O}_{24}]\text{Cl}_{0.55}(\text{CO}_3)_{0.41}(\text{SO}_4)_{0.04}$ and corresponds to $\text{Me}_{36.6}$, close to $\text{Me}_{37.5}$.

A crystal (about 0.2 × 0.2 × 0.2 mm) of scapolite was handpicked under a microscope, and finely crushed in an agate mortar and pestle for the synchrotron high-resolution powder X-ray diffraction (HRPXRD) experiment at room temperature that was performed at beamline 11-BM, Advanced Photon Source, Argonne National Laboratory. The sample was loaded into a

Kapton capillary (0.8 mm diameter) and rotated during the experiment at a rate of 90 rotations per second. The data were collected to a maximum 2θ of about 40° with a step size of 0.0005° and a step time of about 0.1 s/step. Additional details of the experimental set-up are given elsewhere (Antao *et al.* 2008, Lee *et al.* 2008, Wang *et al.* 2008).

RIETVELD REFINEMENT

The crystal structure of scapolite was modeled using the Rietveld method (Rietveld 1969) incorporated in the GSAS program (Larson & Von Dreele 2000) and using the EXPGUI interface of Toby (2001). Initial structural parameters were taken from Levien & Papike (1976). The structure refinement was carried out by varying parameters in the following sequence: scale factor, background (12 terms shifted Chebyshev), cell, zero shift, profile (type-3 function in GSAS), atom positions, and isotropic displacement parameters. Finally, all variables were refined simultaneously until convergence was achieved. The M cation and A anion site-occupancies were fixed to agree with the chemical composition. The $4/m$ (A) site is fully occupied by (Cl,C,S). The trigonal CO_3 group is disordered on the A

site, and the occupancy of OC7 site is also fixed to the chemical composition. Figure 1 displays the HRPXRD trace. Table 2 contains the Rietveld refinement statistics and unit-cell parameters. Table 3 contains the atom positions and isotropic displacement parameters, U . Table 4 contains selected bond-distances and angles.

RESULTS AND DISCUSSION

The unit-cell parameters are a 12.07899(1), c 7.583467(9) Å, V 1106.443(2) Å³ (Table 2). The $Me_{36.6}$ structure has $\langle T1-O \rangle = 1.617(1)$, $\langle T2-O \rangle = 1.744(1)$, and $\langle T3-O \rangle = 1.601(1)$ Å (Table 4). In sodalite, Al-O is 1.7435(2) Å and Si-O is 1.6100(2) Å; $\langle T-O \rangle$ distance varies within narrow limits depending on the interstitial

TABLE 2. REFINEMENT DATA FOR SCAPOLITE $Me_{36.6}$

Space group $P4_2/n$			
R_p^2	0.0688	a (Å)	12.07899(1)
N_{obs}	2959	c (Å)	7.583467(9)
2θ range ($^\circ$)	2.5 – 40	V (Å ³)	1106.443(2)
λ (Å)	0.40243(2)		

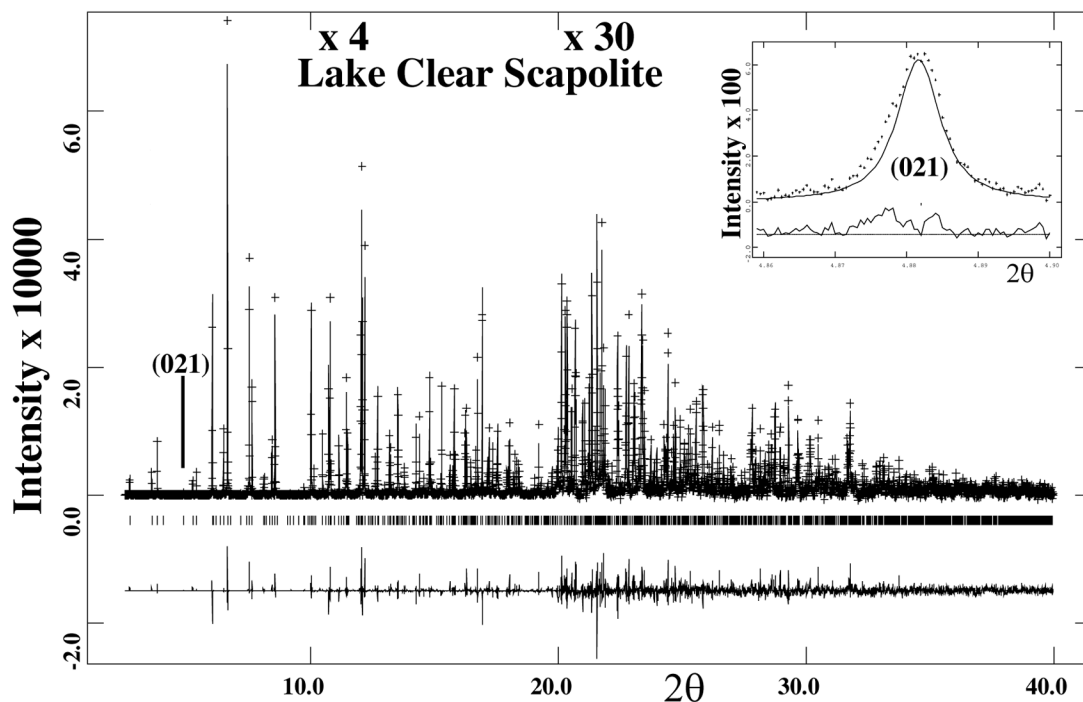


FIG. 1. HRPXRD trace for $Me_{36.6}$, at room T, together with the calculated (continuous line) and observed (crosses) profiles. The difference curve ($I_{obs} - I_{calc}$) is shown at the bottom. The short vertical lines indicate allowed positions of reflections. The (021) peak is indicated and shown in the inset. The trace beyond 10° and $20^\circ 2\theta$ is scaled by $4\times$ and $30\times$, respectively.

atoms (Antao *et al.* 2008). Therefore, the T1 and T3 sites contain only Si atoms, and the T2 site contains only Al atoms, so the Al–Si order is complete, as predicted by Lin (1975) and Hassan & Buseck (1988) for scapolite $Me_{37.5}$. The S10 sample (Me_{42}) from Sokolova & Hawthorne (2008) has $\langle T1-O \rangle = 1.614$, $\langle T2-O \rangle = 1.738$, and $\langle T3-O \rangle = 1.616$ Å; on that basis, they stated that Al–Si order is high, but not complete in the scapolite series.

The Cl atom is surrounded by four M cations in a square planar configuration, and the M–A distance is 3.0707(8) Å, which is longer than the Na–Cl distance in sodalite, where the Cl atom is in a tetrahedral coordination because of the repulsion between the M cations. The disordered CO₃ group has C–O = 1.328(4) Å, which is close the expected value (Table 4).

TABLE 3. ATOM POSITIONS AND VALUES OF U (Å²) FOR SCAPOLITE $Me_{36.6}$

	x	y	z	U
T1	0.58983(6)	0.65957(5)	0.2485(2)	0.0077(1)
T2	0.9101(1)	0.1659(1)	0.0494(1)	0.0089(1)
T3	0.66266(9)	0.0855(1)	0.9616(1)	0.0089(1)
O1	0.7085(1)	0.5997(1)	0.2516(3)	0.0178(4)
O2	0.9437(1)	0.1251(1)	0.2641(3)	0.0178(5)
O3	0.6013(2)	0.1901(2)	0.0431(3)	0.0221(7)
O4	0.7945(2)	0.0989(2)	0.9658(3)	0.0182(7)
O5	0.5202(2)	0.6174(2)	0.0785(3)	0.0209(8)
O6	0.6245(2)	0.9784(2)	0.0725(3)	0.0234(8)
† M	0.61414(6)	0.53529(7)	0.7632(2)	0.0201(2)
† A	0.75	0.75	0.75	0.0571(8)
O7C	0.8452(4)	0.7950(5)	0.8002(8)	0.0571(8)

† M = (Ca, Na, K); A = (Cl, C, S).

TABLE 4. BOND DISTANCES AND ANGLES FOR SCAPOLITE $Me_{36.6}$

T1 – O1	1.606(1)	M – O2	2.337(1)
T1 – O1'	1.598(1)	M – O3	2.519(2)
T1 – O5	1.621(2)	M – O4	2.492(2)
T1 – O6	1.644(2)	M – O5	2.826(2)
<T1 – O>	1.617(1)	M – O5'	2.735(2)
		M – O6	2.917(2)
T2 – O2	1.750(2)	M – O6'	2.982(2)
T2 – O3	1.746(2)	<M – O>[7]	2.687(1)
T2 – O4	1.734(2)		
T2 – O5	1.748(2)	M – O7C	2.126(6)
<T2 – O>	1.744(1)	M – O7C'	2.663(6)
		<M – O>[9]	2.622(1)
T3 – O2	1.604(2)		
T3 – O3	1.590(2)	M – A	3.0707(8)
T3 – O4	1.601(2)	C – O7C × 4	1.328(4)
T3 – O6	1.610(2)		
<T3 – O>	1.601(1)	T1 – O1 – T1	157.5(1)
<T2,3 – O>	1.673(1)	T2 – O2 – T3	137.60(8)
Mean T	1.654(1)	T2 – O3 – T3	147.0(2)
		T2 – O4 – T3	148.8(2)
		T1 – O5 – T2	137.0(2)
		T1 – O6 – T3	139.5(2)
		<T – O – T>	144.57(6)

Antiphase domain boundaries (APBs)

Type-b reflections [$h + k + l = \text{odd}$] are present in space group $P4_2/n$, and they give rise to APBs that are observed by transmission electron microscopy. The interpretation of the APBs is based on either Al–Si order (Oterdoom & Wenk 1983, Seto *et al.* 2004), or Cl–CO₃ order (Phakey & Ghose 1972, Hassan & Buseck 1988). There is direct evidence of Cl–CO₃ cluster order in HRTEM images obtained by Hassan & Buseck (1988). On heating, the Na–Ca order is destroyed, but Cl–CO₃ order remains, as inferred from the type-b reflections that are present to about 900°C (Antao & Hassan 2002, 2008a, 2008b). There is no evidence to show that the APBs in scapolite arise from Al–Si order. In this study, complete Al–Si order was observed. If Al–Si order were responsible for the APBs, complete Al–Si order could occur in $Me_{36.6}$. The T2 and T3 sites, in particular, and also the T1 site, would appear disordered to various extents if they give rise to APBs. Complete Al–Si order rules out Al–Si order in the formation of APBs, which must arise from Cl–CO₃ order, as was directly observed in HRTEM images and confirmed by image simulations (Hassan & Buseck 1988).

The $Me_{36.6}$ structure has $\langle T-O \rangle$ distances indicative of complete Al–Si order, and confirms the prediction of Lin (1975) and Hassan & Buseck (1988) for composition $Me_{37.5}$, ideally $Na_5Ca_3[Al_8Si_{16}O_{48}]Cl(CO_3)$. At this composition, there is maximum Cl–CO₃, Na–Ca, and Al–Si order, and the APBs are based on Cl–CO₃ order instead of Al–Si order. The c unit-cell parameter also has a maximum value at about $Me_{37.5}$ because of Al–Si order.

ACKNOWLEDGEMENTS

We thank R.C. Peterson for his constructive comments that helped to improve this paper. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. This work was supported by a Discovery grant from the National Science and Engineering Research Council of Canada, and an Alberta Ingenuity New Faculty Award.

REFERENCES

- AITKEN, B.G., EVANS, H.T., JR. & KONNERT, J.A. (1984): The crystal-structure of a synthetic meionite. *Neues Jahrb. Mineral., Abh.* **149**, 309-324.
- ANTAO, S.M. & HASSAN, I. (2002): Thermal behavior of scapolite $Me_{79.6}$ and $Me_{33.3}$. *Can. Mineral.* **40**, 1395-1401.
- ANTAO, S.M. & HASSAN, I. (2008a): Increase in Al–Si and Na–Ca disorder with temperature in scapolite $Me_{32.9}$. *Can. Mineral.* **46**, 1577-1591.

- ANTAO, S.M. & HASSAN, I. (2008b): Unusual Al–Si ordering in calcic scapolite, $Me_{79.6}$, with increasing temperature. *Am. Mineral.* **93**, 1470-1477.
- ANTAO, S.M. & HASSAN, I. (2011): The structures of marialite (Me_6) and meionite (Me_{93}) in space groups $P4_2/n$ and $I4/m$, and the absence of phase transitions in the scapolite series. *Powder Diffraction* **26** (in press).
- ANTAO, S.M., HASSAN, I., WANG, JUN, LEE, P.L. & TOBY, B.H. (2008): State-of-the-art high-resolution powder X-ray diffraction (HRPXRD) illustrated with Rietveld structure refinement of quartz, sodalite, tremolite, and meionite. *Can. Mineral.* **46**, 1501-1509.
- BELOKONEVA, E.L., SOKOLOVA, N.V. & DOROKHOVA, G.I. (1991): Crystal structure of natural Na, Ca-scapolite – an intermediate member of the marialite–meionite series. *Sov. Phys. Crystallogr.* **36**, 828-830.
- BELOKONEVA, E.L., SOKOLOVA, N.V. & URUSOV, V.S. (1993): Scapolites – crystalline-structures of marialite (Ma_{11}) and meionite (Me_{88}) – spatial group as a function of composition. *Kristallogr.* **38**, 52-57.
- CHAMBERLAIN, C.P., DOCKA, J.A., POST, J.E. & BURNHAM, C.W. (1985): Scapolite – alkali atom configurations, antiphase domains, and compositional variations. *Am. Mineral.* **70**, 134-140.
- COMODI, P., MELLINI, M. & ZANAZZI, P.F. (1990): Scapolites; variation of structure with pressure and possible role in the storage of fluids. *Eur. J. Mineral.* **2**, 195-202.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1992): *An Introduction to the Rock-Forming Minerals* (2nd ed.). John Wiley & Sons, New York, N.Y.
- EVANS, B.W., SHAW, D.M. & HAUGHTON, D.R. (1969): Scapolite stoichiometry. *Contrib. Mineral. Petrol.* **24**, 293-305.
- HASSAN, I., ANTAO, S.M. & PARISE, J.B. (2004): Sodalite: high temperature structures obtained from synchrotron radiation and Rietveld refinements. *Am. Mineral.* **89**, 359-364.
- HASSAN, I. & BUSECK, P.R. (1988): HRTEM characterization of scapolite solid solutions. *Am. Mineral.* **73**, 119-134.
- HASSAN, I. & GRUNDY, H.D. (1983): Structure of basic sodalite, $Na_8Al_6Si_6O_{24}(OH)_2 \cdot 2H_2O$. *Acta Crystallogr.* **C39**, 3-5.
- HAWTHORNE, F.C. & SOKOLOVA, E. (2008): The crystal chemistry of the scapolite-group minerals. II. The origin of the $I4/m = P4_2/n$ phase transition and the nonlinear variations in chemical composition. *Can. Mineral.* **46**, 1555-1575.
- LARSON, A.C. & VON DREELE, R.B. (2000): General structure analysis system (GSAS). *Los Alamos National Laboratory Rep. LAUR* **86-748**.
- LEE, P.L., SHU, D., RAMANATHAN, M., PREISSNER, C., WANG, J., BENO, M.A., VON DREELE, R.B., RIBAUD, L., KURTZ, C., ANTAO, S.M., JIAO, X. & TOBY, B.H. (2008): A twelve-analyzer detector system for high-resolution powder diffraction. *J. Synchr. Rad.* **15**, 427-432.
- LEVIEN, L. & PAPIKE, J.J. (1976): Scapolite crystal chemistry: aluminum–silicon distributions, carbonate group disorder, and thermal expansion. *Am. Mineral.* **61**, 864-877.
- LIN, S.B. (1975): Crystal chemistry and stoichiometry of the scapolite group. *Acta Geol. Taiwan* **18**, 36-48.
- LIN, S.B. & BURLEY, B.J. (1973a): Crystal structure of a sodium and chlorine-rich scapolite. *Acta Crystallogr.* **B29**, 1272-1278.
- LIN, S.B. & BURLEY, B.J. (1973b): The crystal structure of meionite. *Acta Crystallogr.* **B29**, 2024-2026.
- LIN, S.B. & BURLEY, B.J. (1973c): On the weak reflections violating body-centered symmetry in scapolites. *Tschermaks Mineral. Petrogr. Mitt.* **20**, 28-44.
- LIN, S.B. & BURLEY, B.J. (1974): The crystal-structure of an intermediate scapolite – wernerite. *Tschermaks Mineral. Petrogr. Mitt.* **21**, 196-215.
- OTERDOOM, W.H. & WENK, H.-R. (1983): Ordering and composition of scapolite – field observations and structural interpretations. *Contrib. Mineral. Petrol.* **83**, 330-341.
- PAPIKE, J.J. & STEPHENSON, N.C. (1966): The crystal structure of mizzonite, a calcium- and carbonate-rich scapolite. *Am. Mineral.* **51**, 1014-1027.
- PAPIKE, J.J. & ZOLTAI, T. (1965): The crystal structure of a marialite scapolite. *Am. Mineral.* **50**, 641-655.
- PAULING, L. (1930): The structure of some sodium and calcium alumino-silicates. *Proc. Nat. Acad. Sci.* **16**, 453-459.
- PETERSON, R.C., DONNAY, G. & LEPAGE, Y. (1979): Sulfate disorder in scapolite. *Can. Mineral.* **17**, 53-61.
- PHAKEY, P.P. & GHOSE, S. (1972): Scapolite: observation of anti-phase domain structure. *Nature Physical Science* **238**, 78-80.
- RIETVELD, H.M. (1969): A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* **2**, 65-71.
- SCHIEBOLD, E. & SEUMEL, G. (1932): Über die Kristallstruktur von Skapolith. *Z. Kristallogr.* **81**, 110-134.
- SETO, Y., SHIMOBAYASHI, N., MIYAKE, A. & KITAMURA, M. (2004): Composition and $I4/m - P4_2/n$ phase transition in scapolite solid solutions. *Am. Mineral.* **89**, 257-265.
- SHERRIFF, B.L., SOKOLOVA, E.V., KABALOV, Y.K., JENKINS, D.M., KUNATH-FANDREI, G., GOETZ, S., JÄGER, C. & SCHNEIDER, J. (2000): Meionite: Rietveld structure-refinement, ^{29}Si MAS and ^{27}Al SATRAS NMR spectroscopy, and comments on the marialite-meionite series. *Can. Mineral.* **38**, 1201-1213.

- SHERRIFF, B.L., SOKOLOVA, E.V., KABALOV, Y.K., TEERTSTRA, D.K., KUNATH-FANDREI, G., GOETZ, S. & JÄGER, C. (1998): Intermediate scapolite: ^{29}Si MAS and ^{27}Al SATRAS NMR spectroscopy and Rietveld structure-refinement. *Can. Mineral.* **36**, 1267-1283.
- SOKOLOVA, E.V., GOBECHIYA, E.R., ZOLOTAREV, A.A. & KABALOV, Y.K. (2000): Refinement of the crystal structures of two marialites from the Kukurt deposit of the east Pamirs. *Crystallogr. Rep.* **45**, 934-938.
- SOKOLOVA, E. & HAWTHORNE, F.C. (2008): The crystal chemistry of the scapolite-group minerals. I. Crystal structure and long-range order. *Can. Mineral.* **46**, 1527-1554.
- SOKOLOVA, E.V., KABALOV, Y.K., SHERRIFF, B.L., TEERTSTRA, D.K., JENKINS, D.M., KUNATH-FANDREI, G., GOETZ, S. & JÄGER, C. (1996): Marialite: Rietveld structure-refinement and ^{29}Si MAS and ^{27}Al satellite transition NMR spectroscopy. *Can. Mineral.* **34**, 1039-1050.
- TEERTSTRA, D.K., SCHINDLER, M., SHERRIFF, B.L. & HAWTHORNE, F.C. (1999): Silvialite, a new sulfate-dominant member of the scapolite group with an Al-Si composition near the $14/m-P4_2/n$ phase transition. *Mineral. Mag.* **63**, 321-329.
- TOBY, B.H. (2001): EXPGUI, a graphical user interface for GSAS. *J. Appl. Crystallogr.* **34**, 210-213.
- ULBRICH, H.H. (1973): Structural refinement of the Monte Somma scapolite, a 93% meionite. *Schweiz. Mineral. Petrogr. Mitt.* **53**, 385-393.
- WANG, JUN, TOBY, B.H., LEE, P.L., RIBAUD, L., ANTAO, S.M., KURTZ, C., RAMANATHAN, M., VON DREELE, R.B. & BENO, M.A. (2008): A dedicated powder diffraction beamline at the advanced photon source: commissioning and early operational results. *Rev. Sci. Instrum.* **79**, 085105.

Received February 28, 2010, revised manuscript accepted April 8, 2011.