Eur. J. Mineral.
2008, **20**, 993–998
Published online September 2008

**This paper is dedicated to
the memory of Werner Schreyer**

The crystal structure of sursassite from the Lienne Valley, Stavelot Massif, Belgium

FRÉDÉRIC HATERT[1, *], ANDRE-MATHIEU FRANSOLET[1], JOHAN WOUTERS[2] and HEINZ-JÜRGEN BERNHARDT[3]

[1]Laboratoire de Minéralogie, B18, Université de Liège, 4000 Liège, Belgium
*Corresponding author, e-mail: fhatert@ulg.ac.be
[2]Laboratoire de Chimie Biologique Structurale, Département de Chimie,
Facultés Universitaires Notre-Dame de la Paix (FUNDP), Rue de Bruxelles 61, 5000 Namur, Belgium
[3]Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, 44780 Bochum, Germany

Abstract: Sursassite occurs as orange-red needles associated with nsutite, hematite, apatite-(CaF), spessartine, manganoan clinochlore, and ardennite in quartz veinlets cross-cutting the red-purple schists of the Ottré Formation (Salm Group, Middle Ordovician) in the core of the Lienne syncline, Stavelot Massif, Belgium. The chemical composition of sursassite shows the presence of about 2 wt.% MgO and up to 4 wt.% CaO, while FeO does not exceed 1 wt.%. The crystal-chemical formula for sursassite, calculated on the basis 16 cations per unit cell, is $(Mn_{3.59}Ca_{0.44})_{\Sigma=4.00}(Al_{5.25}Mn^{3+}_{0.19}Mg_{0.44}Fe^{3+}_{0.12})_{\Sigma=6.00}(Si_{5.97}Al_{0.03})_{\Sigma=6.00}(O_{21.53}OH_{0.47})(OH)_{6.00}$. A single-crystal structure refinement has been performed to $R_1 = 0.0454$, in space group $P2_1/m$, with $a = 8.697(1)$, $b = 5.787(1)$, $c = 9.769(1)$ Å, and $\beta = 108.91(1)$°. The structure is based on chains of edge-sharing aluminium octahedra arranged along the *b* axis, connected together by sharing corners with the $Si(1)O_4$ tetrahedron and the $Si(2)Si(3)O_7$ group. Two independent manganese cations, Mn1 and Mn2, occur between the aluminium chains and are linked to seven and six oxygen atoms, respectively. The Mn1 site is occupied by Mn and minor amounts of Ca, while the Al1 sites contains aluminium and minor amounts of Mg, Mn^{3+}, and Fe^{3+}. The absence of Mg from the Mn1 and Mn2 positions is in accord with the low-pressure conditions in which sursassite crystallized in the Lienne Valley, conditions that have been estimated at 1–2 kbar.

Key-words: sursassite, Mn-Al-silicate, crystal structure, metamorphism, Stavelot Massif, Belgium.

Introduction

Among the manganese aluminium silicates, sursassite, $Mn_2Al_3(SiO_4)(Si_2O_7)(OH)_3$, is a rare mineral species known as a stable phase in Mn-rich environments up to 400–450 °C and over a broad pressure interval up to 10 kbar (Reinecke, 1986). Sursassite is isotypic with macfallite, $Ca_2(Mn,Al)_3(SiO_4)(Si_2O_7)(OH)_3$ (Moore *et al.*, 1979), is closely related to pumpellyite, $Ca_2Al_3(SiO_4)(Si_2O_7)(OH)_3$ (Mellini *et al.*, 1984), and shows a crystal structure based on chains of edge-sharing aluminium octahedra arranged along [010] and connected by SiO_4 and Si_2O_7 groups (Allmann, 1984; Mellini *et al.*, 1984; Gottschalk *et al.*, 2000).

The synthetic high-pressure phase $Mg_4(MgAl)Al_4[Si_6O_{21}(OH)_7]$, synthesized by Schreyer *et al.* (1986) at 5 GPa and 700 °C, was considered as a Mg-rich equivalent of pumpellyite on the basis of their similar X-ray powder diffraction patterns. This phase, called MgMgAl-pumpellyite by Schreyer *et al.* (1986, 1991), turned out later to be isotypic with sursassite rather than pumpellyite, and was therefore re-named Mg-sursassite (Gottschalk *et al.*, 2000). Due to its close chemical similarity to pyrope, $Mg_3Al_2Si_3O_{12}$, and to its high-pressure, low-temperature stability field (Fockenberg, 1998), Mg-sursassite was proposed to be an important water reservoir in cold subduction zones (Schreyer *et al.*, 1991; Fockenberg, 1998).

A sample of red shale containing orange-red acicular grains of sursassite was collected approximately 10 years ago by M. Blondieau, in the Lienne Valley, Belgian Ardennes. More recently, during a field trip to the eastern flank of the Lienne Valley at Moët-Fontaine, several loose blocks displaying quartz veinlets containing sursassite and Mn oxides were also collected, but no *in situ* outcrop of a sursassite-bearing veinlet has been found so far. In this area of the Stavelot Massif, the highest temperature reached has been estimated to be 300 °C by Theye *et al.* (1996). It is thus of interest to report here a new occurrence of sursassite in an environment of very low-grade metamorphism. The occurrence of sursassite in the manganiferous layers of Monte Alpe, Italy (Cortesogno *et al.*, 1979), is also known to be characteristic of the prehnite-pumpellyite facies, *i.e.*, of low-temperature metamorphic conditions.

This paper constitutes the first part of a detailed investigation of sursassite from the Lienne Valley. Due to the major petrogenetic significance of this mineral, it was necessary to refine its crystal structure in order to accurately establish the cationic distribution among its crystallographic sites. The role of Mg is of peculiar interest, since its presence and

0935-1221/08/0020-1890 $ 2.70
DOI: 10.1127/0935-1221/2008/0020-1890
© 2008 E. Schweizerbart'sche Verlagsbuchhandlung, D-70176 Stuttgart

location in the sursassite structure could be constrained by the pressure, as demonstrated by the synthesis of high-pressure Mg-sursassite (Schreyer *et al.*, 1986, 1991). The structural data reported in this study will consequently serve, in a forthcoming paper now in preparation, as a basis for establishing a thermodynamic model allowing an assessment of the *P–T* conditions which prevailed during the crystallization of sursassite in the Lienne Valley.

Geological setting

In the Belgian Ardennes, the Stavelot Massif essentially represents a large block of Cambro-Ordovician metasediments constituting the Caledonian basement of the Rhenohercynian orogenic belt. The Stavelot Massif is separated from the overlying Devonian and Carboniferous rocks by an angular unconformity. The age of major deformation and metamorphism in the Stavelot Massif has been shown to be Late Carboniferous (*e.g.*, Schreyer, 1975), although some deformation already took place in the Caledonian period. Metamorphism of the Stavelot Massif is of very low-grade type. For the rocks occurring in the southern part of the massif (zone of Vielsalm–Ottré), Kramm (1982) estimated *P–T* conditions of 1.5–2 kbar at 360–420 °C. These estimates are based on the assemblages with andalusite, Mn-chloritoid, and spessartine, as well as on the phengite contents of white micas, occurring in the Mn-rich metasediments of middle Ordovician age. In contrast, no *P–T*-diagnostic mineral assemblages are known from the Mn-poor sediments of the underlying lower Ordovician and Cambrian. Moreover, the Mn-rich metasediments are also of considerable current mineralogical interest. In this southern part of the Stavelot Massif, such rocks, as well as quartz veins which cross-cut them, exhibit spessartine, Mn-rich chloritoid, andalusite and sudoite. Very rare mineral species such as ottrélite, ardennite and davreuxite among the Mn-Al rich silicates were first described from the Stavelot Massif (Hatert *et al.*, 2002), and stavelotite (Bernhardt *et al.*, 2005). Virtually pure ottrélite (Theye & Fransolet, 1994) and kanonaite (Schreyer *et al.*, 2004) are known to occur as well.

Carpholite, with a chemical composition near the end-member $MnAl_2[Si_2O_6](OH)_4$, occurs only in the Mn-rich metasediments of the Lienne Valley, which is located in the western part of the Stavelot Massif. As in the southern part of the massif described above, the relevant mineral assemblages in the Lienne Valley occur only in red to purple schists of the Ottré Formation (Salm Group, middle Ordovician), except for the Mn-rich chloritoid found in thin green layers intercalated within the red material, which is decidedly rich in fine-grained hematite (Theye *et al.*, 1996). In the Lienne Valley area, the *P–T* conditions were estimated as ~ 300 °C, 1–2 kbar (Theye *et al.*, 1996).

The sursassite collected at Moët-Fontaine, Lienne Valley, occurs as orange to brownish needles reaching 5 mm in length. The needles are included in quartz veinlets and in the enclosing red schists, and are associated with nsutite, hematite, apatite-(CaF), spessartine, manganoan clinochlore, and ardennite.

Table 1. Representative electron-microprobe analyses of sursassite from the Lienne Valley, Belgium.

#	5 (25.01)	17 (25.01)	27 (26.01)	12 (25.01)	26 (26.01)
SiO_2	35.24	35.15	35.07	34.68	35.35
TiO_2	0.07	0.10	0.08	0.03	0.05
V_2O_5	0.02	0.05	0.02	0.00	0.00
Al_2O_3	26.99	26.21	25.51	25.71	27.22
Fe_2O_3	0.57	0.54	1.82	0.98	0.52
Mn_2O_3*	1.44	0.61	1.20	2.87	0.78
MnO*	26.54	22.33	24.29	25.23	26.35
$MnO_{tot.}$	27.83	22.88	25.37	27.80	27.05
MgO	1.46	2.13	1.97	1.36	1.77
ZnO	0.09	0.06	0.00	0.04	0.07
CaO	1.06	4.16	2.71	1.83	1.30
H_2O**	5.67	5.71	5.73	5.60	5.76
Total	99.14	97.05	98.40	98.32	99.18
Si^{4+}	5.967	6.008	5.975	5.947	5.963
Al^{3+}	0.033	0.000	0.025	0.053	0.037
Σ	6.000	6.008	6.000	6.000	6.000
Al^{3+}	5.353	5.280	5.098	5.143	5.374
V^{5+}	0.002	0.006	0.002	0.000	0.000
Ti^{4+}	0.009	0.013	0.010	0.004	0.006
Fe^{3+}	0.072	0.070	0.234	0.126	0.066
Mn^{3+}	0.185	0.080	0.156	0.374	0.100
Mg^{2+}	0.368	0.543	0.500	0.348	0.445
Zn^{2+}	0.011	0.008	0.000	0.005	0.009
Σ	6.000	6.000	6.000	6.000	6.000
Mn^{2+}	3.806	3.232	3.505	3.664	3.765
Ca^{2+}	0.192	0.762	0.495	0.336	0.235
Σ	3.998	3.994	4.000	4.000	4.000
$(OH)^-$	6.403	6.510	6.512	6.405	6.481
O^{2-}	21.597	21.490	21.488	21.595	21.519
Σ	28.000	28.000	28.000	28.000	28.000

Analyst: H.-J. Bernhardt. Cation numbers calculated on the basis of 16 cations per unit cell. *: The MnO and Mn_2O_3 value was calculated considering all Mn in the Al octahedra as Mn^{3+}. **: The $(OH)^-$ content was calculated to maintain charge balance.

The chemical composition of sursassite

Electron-microprobe analyses of sursassite were performed at the Ruhr-Universität Bochum, Germany, using the same instrument and identical conditions as reported by Schreyer *et al.* (2001). Selected chemical analyses reported in Table 1 show that the mineral is rather inhomogeneous, with significant variations of Fe_2O_3 (0.52 to 1.82 wt.%), Mn_2O_3 (0.61 to 2.87 wt.%), MnO (22.33 to 26.54 wt.%), MgO (1.36 to 2.13 wt.%), and CaO (1.06 to 4.16 wt.%). Systematic point analyses also show that additional inhomogeneities are caused by microscopic intergrowths of sursassite with ardennite.

According to the crystal structure determination of sursassite performed by Mellini *et al.* (1984), the cations occur on the following sites:

- *Mn1*: Mn and Ca
- *Mn2*: Mn and Ca
- *Al1*, *Al2*, and *Al3*: Al, Mg, Mn, Fe, and possibly Ti.

Consequently, Reinecke (1986) and Martin & Lombardo (1995) calculated analytical data on the basis of 16 cations per unit cell. Reinecke (1986) considered that the six tetrahedral sites are filled by Si exclusively. Al + Fe^{3+} + $Mn^{3+,2+}$ + Mg + Cu^{2+} + Ti^{4+} are assigned to the six octahedral sites Al1, Al2, and Al3. The four Mn1 and Mn2 sites contain the remaining Mn as Mn^{2+} and total Ca. Reinecke (1986) pointed out the dominant role of the substitution $Mn^{3+}Al_{-1}$. Consequently, for the interpretation of the chemical analyses of the Lienne Valley sursassite, all the manganese occurring in the aluminum octahedra was considered to be Mn^{3+}.

Starting from the analytical data collected on the material from the Lienne Valley (average of the 5 analyses reported in Table 1), a crystal-chemical formula for sursassite calculated on the basis of 16 cations per unit cell can be proposed as follows: $(Mn_{3.59}Ca_{0.44})_{\Sigma=4.00}(Al_{5.25}Mn^{3+}_{0.19}Mg_{0.44}Fe^{3+}_{0.12})_{\Sigma=6.00}(Si_{5.97}Al_{0.03})_{\Sigma=6.00}(O_{21.53}OH_{0.47})\ (OH)_{6.00}$.

X-ray structural results

The X-ray powder diffraction pattern of sursassite was recorded with a Panalytical PW-3710 powder diffractometer using Fe*K*α radiation (λ = 1.9373 Å). On the basis of the *d*-spacings calibrated with an internal standard of $Pb(NO_3)_2$, the least-squares refinement program LCLSQ 8.4 (Burnham, 1991) served to refine the unit-cell parameters of sursassite, which are $a = 8.685(4)$, $b = 5.790(2)$, $c = 9.756(4)$ Å, $\beta = 109.00(4)°$.

The X-ray structural study was carried out on an Oxford Diffraction Gemini PX Ultra diffractometer equipped with a Ruby CCD-area detector (FUNDP, Namur, Belgium) with a crystal fragment measuring 0.05 × 0.20 × 0.45 mm. 264 frames with a spatial resolution of 1° were collected by the φ/ω scan technique, with a counting time of 5 s per frame, in the range $7.02° < 2\theta < 55.38°$. 2383 reflections were extracted from these frames, corresponding to 1024 unique reflections. The unit-cell parameters refined from these reflections, $a = 8.697(1)$, $b = 5.787(1)$, $c = 9.769(1)$ Å, and $\beta = 108.91(1)°$, are in very good agreement with those refined from the X-ray powder data (see above). Data were corrected for Lorenz polarisation and absorption effects, the latter with an empirical method using the SCALE3 ABSPACK scaling algorithm included in the CrysAlisRED package (Oxford Diffraction, 2007).

Table 2. Experimental details for the single-crystal X-ray diffraction study of sursassite from the Lienne Valley, Belgium.

Dimensions of the crystal (mm)	*ca*. 0.05 × 0.20 × 0.45
a (Å)	8.697(1)
b (Å)	5.787(1)
c (Å)	9.769(1)
β (°)	108.91(1)
Space group	$P2_1/m$
Z	2
Calculated density	3.519
Diffractometer	Oxford Diffraction Gemini PX Ultra with Ruby CCD-area detector
Operating conditions	50 kV, 40 mA
Radiation	Mo*K*α (λ = 0.71073 Å)
Scan mode	φ/ω scans
$2\theta_{min}$, $2\theta_{max}$	7.02°, 55.38°
Range of indices	$-7 \le h \le 11$, $-7 \le k \le 7$, $-12 \le l \le 12$
Measured intensities	2383
Unique reflections	1024
Independent non-zero [$I > 2\sigma(I)$] reflections	644
Absorption correction	Empirical (SCALE3 ABSPACK scaling algorithm)
μ (mm^{-1})	3.105
Structure solution program	SHELXS-97 (Sheldrick, 1997)
l.s. refinement program	SHELXL-97 (Sheldrick, 1997)
Refined parameters	129
R_1 (on $F_0 > 2\sigma(F_0)$)	0.0454
R_1 (all)	0.0724
wR_2 (all)	0.1364
S (goodness of fit)	1.188
Max peak and hole in the final ΔF map (e/Å^3)	+1.55 and −1.01

The crystal structure was refined in space group $P2_1/m$, which was confirmed from systematic absences. The starting atomic coordinates were those of sursassite from Monte Alpe, Italy (Mellini *et al*., 1984), and scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from the *International Tables for X-ray Crystallography, Vol. C* (Wilson, 1992). Cation occupancies were refined to obtain a better agreement with the chemical composition of sursassite (Table 1). For the sake of simplicity, Ti, V, and Zn, which occur in very low amounts, were not taken into account in the crystal structure refinement. Finally, the relative occupancies of Mn and Ca on the Mn1 site, and of Al and Mn on the Al1 site, were refined. The occupancies of the Mn2, Al2, Al3, Si1, Si2, and Si3 sites were close to the ideal values and were therefore constrained to 1.0. The refinement was completed using anisotropic displacement parameters for all atoms. The final conventional R_1 factor ($F_0 > 2\sigma\ (F_0)$) is 0.0454. Further details on the intensity data collection and structure refinement are given in Table 2. Final positional and isotropic thermal parameters are given in Table 3, and selected bond distances are given in Table 4. Anisotropic thermal parameters are available from the authors. They have also been deposited and are freely accessible as supplementary material on the GSW website of the journal (http://www.eurjmin.geoscienceworls.org).

The basic structural features of sursassite from the Lienne Valley are identical to those of sursassite from Monte Alpe (Mellini *et al*., 1984) and from Andros, Cyclades Islands, Greece (Allmann, 1984). The structure is based on chains of edge-sharing aluminium octahedra arranged along the *b* axis (Fig. 1), and connected together by sharing corners with the $Si(1)O_4$ tetrahedron and the $Si(2)Si(3)O_7$ group. Two independent manganese cations, Mn1 and Mn2, occur between the aluminium chains (Fig. 1) and are linked to seven and six oxygen atoms, respectively. The coordination

Table 3. Final fractional coordinates (*x*, *y*, *z*), occupancy factors (*N*), and equivalent isotropic displacement parameters (U_{eq}) for sursassite from the Lienne Valley, Belgium.

Site	*x*	*y*	*z*	U_{eq}
Mn1*	0.1675(2)	0.25	0.3137(2)	0.0147(6)
Mn2	0.2675(2)	0.25	0.6750(2)	0.0187(6)
Al1**	0.5	0	0.5	0.0116(9)
Al2	0.5	0	0	0.0098(7)
Al3	0	0.5	0	0.0084(7)
Si1	0.3074(3)	0.75	0.1925(3)	0.0088(7)
Si2	0.2067(3)	0.75	0.8076(3)	0.0091(7)
Si3	0.1557(3)	0.75	0.4937(3)	0.0114(7)
O1	0.2646(5)	0.5134(8)	0.5019(4)	0.0145(12)
O2	0.1912(5)	0.5237(8)	0.1643(4)	0.0106(11)
O3	0.3139(5)	0.5168(8)	0.8333(5)	0.0128(12)
O4	0.4149(7)	0.75	0.0821(6)	0.0092(16)
O5	0.4491(8)	0.75	0.3538(7)	0.0117(16)
O6	0.0843(7)	0.25	0.9292(7)	0.0113(16)
O7	0.4385(7)	0.25	0.3672(7)	0.0125(17)
O8	0.0712(7)	0.75	0.8939(7)	0.0102(16)
O9	0.0919(7)	0.75	0.6372(7)	0.0104(16)
O10	−0.0085(8)	0.75	0.3568(7)	0.0170(18)
O11	0.4108(8)	0.25	0.0742(7)	0.0121(16)

*: 0.79(2) Mn + 0.21(2) Ca. **: 0.89(1) Al + 0.11(1) Mn.

Table 4. Selected bond distances (Å) in sursassite from the Lienne Valley, Belgium.

Mn1–O2	2.211(5) x 2	Mn2–O3	2.134(5) x 2
Mn1–O7	2.243(6)	Mn2–O10	2.172(7)
Mn1–O1	2.330(5) x 2	Mn2–O1	2.275(5) x 2
Mn1–O8	2.390(6)	Mn2–O5	2.570(5)
Mn1–O9	2.453(7)	Average	2.260
Average	2.310		
Al1–O7	1.904(4) x 2	Al2–O3	1.894(4) x 2
Al1–O5	1.983(4) x 2	Al2–O11	1.895(4) x 2
Al1–O1	2.055(4) x 2	Al2–O4	1.918(4) x 2
Average	1.981	Average	1.902
Al3–O6	1.856(4) x 2	Si1–O2	1.624(5) x 2
Al3–O2	1.909(4) x 2	Si1–O4	1.641(7)
Al3–O8	1.994(5) x 2	Si1–O5	1.660(7)
Average	1.920	Average	1.637
Si2–O3	1.614(5) x 2	Si3–O10	1.612(6)
Si2–O9	1.644(7)	Si3–O1	1.653(5) x 2
Si2–O8	1.657(7)	Si3–O9	1.670(7)
Average	1.632	Average	1.647

polyhedon of Mn1 shows a complex topology, which can be described as a distorted octahedron with one supplementary O9 oxygen. As shown on Fig. 2a, this polyhedron can also be described as a distorted trigonal prism, with one supplementary O7 position occurring above one square face of the prism. The Mn1 atom is displaced out of the O1–O2 plane, in the direction of O8 and O9, and is consequently located close to the geometrical centre of the trigonal prism (Fig. 2a). The topology of the Mn2 polyhedron corresponds to a fairly regular octahedron (Fig. 2b), with a coordination of (5+1) due to the significantly longer Mn2–O5 distance (Table 4).

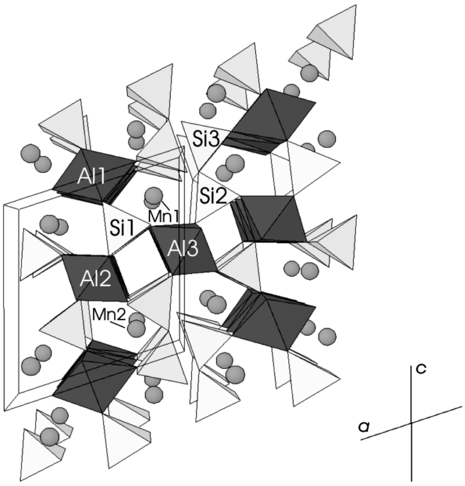

Fig. 1. Crystal structure of sursassite from the Lienne Valley, Belgium, projected along the *b* axis. The grey octahedra are occupied by aluminum, and the white tetrahedra by silicon. The light grey circles represent Mn atoms.

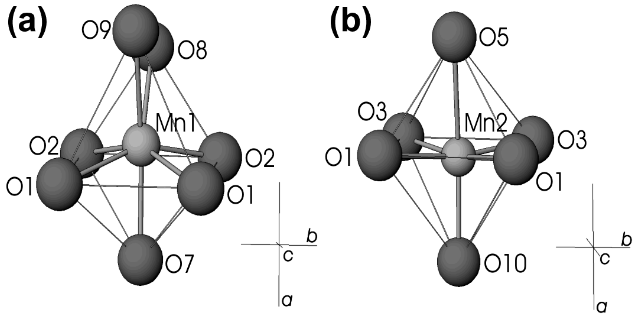

Fig. 2. Topologies of the $Mn(1)O_7$ and $Mn(2)O_6$ coordination polyhedra, in the crystal structure of sursassite from the Lienne Valley.

A detailed cationic distribution has also been established, in order to match as closely as possible the average chemical composition of sursassite reported in Table 1. The results given in Table 5 indicate that the refined site populations (RSP), obtained from the single-crystal structure refinement, are in good agreement with the assigned site populations (ASP), deduced from the chemical data. Moreover, the refined site scattering values (RSS) and the mean bond lengths (MBL) obtained from the structural data are very close to the calculated site scattering values (CSS) and the calculated bond lengths (CBL), respectively (Table 5). This agreement confirms the reliability of the assigned site populations.

The bond-valence table for sursassite is given in Table 6, where the bond-valence sums were calculated as $s = \exp[(R_0 - R)/0.37]$, by using R_0 values of Brese & O'Keeffe (1991). The bond valences for oxygen O1–O5, O8, and O9 are close to the theoretical value 2.00, and a good correspondence is observed between the theoretical and the calculated valence values for the cationic sites (Table 6). O6 and O11,

Table 5. Refined site populations (RSP, *apfu*), refined site-scattering values (RSS, *epfu*), mean bond-lengths (MBL, Å), assigned site populations (ASP, *apfu*), calculated site-scattering values (CSS, *epfu*), and calculated bond lengths (CBL, Å, calculated with effective ionic radii from Shannon, 1976) for sursassite from the Lienne Valley, Belgium.

Site	Results of the structure determination			Results of the chemical analysis		
	RSP	RSS	MBL	ASP	CSS	CBL
Mn1	0.79 Mn + 0.21 Ca	24.0	2.310	0.800 Mn^{2+} + 0.200 Ca^{2+}	24.0	2.348
Mn2	1.000 Mn	25.0	2.260	1.000 Mn^{2+}	25.0	2.170
Al1	0.89 Al + 0.11 Mn	14.3	1.981	0.635 Al^{3+} + 0.220 Mg^{2+} + 0.090 Mn^{3+} + 0.055 Fe^{3+}	14.6	2.012
Al2	1.000 Al	13.0	1.902	1.000 Al^{3+}	13.0	1.955
Al3	1.000 Al	13.0	1.920	1.000 Al^{3+}	13.0	1.955
Si1	1.000 Si	14.0	1.637	1.000 Si^{4+}	14.0	1.640
Si2	1.000 Si	14.0	1.632	1.000 Si^{4+}	14.0	1.640
Si3	1.000 Si	14.0	1.647	1.000 Si^{4+}	14.0	1.640

Table 6. Bond-valence table (*vu*) for sursassite from the Lienne Valley, Belgium.

	Mn1	Mn2	Al1	Al2	Al3	Si1	Si2	Si3	Σ
O1	0.256 x 2 ↓	0.270 x 2 ↓	0.359 x 2 ↓					0.925 x 2 ↓	1.81
O2	0.353 x 2 ↓				0.498 x 2 ↓	1.000 x 2 ↓			1.85
O3		0.395 x 2 ↓		0.519 x 2 ↓			1.027 x 2 ↓		1.94
O4				0.486 x 2 ↓→		0.955			1.93
O5		0.121	0.436 x 2 ↓→			0.907			1.90
O6					0.575 x 2 ↓→				1.15
O7	0.323		0.540 x 2 ↓→						1.40
O8	0.217				0.396 x 2 ↓→		0.915		1.92
O9	0.183						0.947	0.883	2.01
O10		0.356						1.033	1.39
O11				0.519 x 2 ↓→					1.04
$S_{calc.}$	1.94	1.81	2.67	3.05	2.94	3.86	3.92	3.77	
$S_{theor.}$	2.00	2.00	2.78	3.00	3.00	4.00	4.00	4.00	

The bond valences were calculated from the bond lengths given in Table 4, and from the assigned site populations of Table 5, with the parameters of Brese & O'Keeffe (1991).

however, show a bond valence sum of 1.15 and 1.04, thus indicating that they correspond to the OH groups of the sursassite structure. O7 and O10 show bond valence sums of 1.40 and 1.39, indicating that these oxygen have a mixed donor-acceptor role. This conclusion is in very good agreement with the bond valance calculations performed by Mellini *et al.* (1984), who showed that the O7 and O10 sites host hydroxyl and oxygen anions with equal occupancies.

Discussion

The occurrence of sursassite in the Lienne Valley, Stavelot Massif, Belgium, was a unique opportunity to investigate again the crystal structure of this rare mineral species. The reliable electron-microprobe chemical data, coupled with X-ray single-crystal data collected with a new diffractometer equipped with a CCD detector, allowed the establishment of a good structural model with an accurate cationic distribution, a model which converged to an R_1 value of 0.0454, lower than the R_1 value 0.0650 obtained by Mellini *et al.* (1984).

The cationic distributions established in the present study (Table 5) are in good agreement with those obtained by Mellini *et al.* (1984) and by Allmann (1984), with the Mn1 site occupied by Mn and minor amounts of Ca, and with the Al1 site containing aluminum and minor amounts of Mg, Mn, Fe, and Ti. It is noteworthy that the Al3 site of sursassite from the Lienne Valley is occupied by Al only, while this site contains 0.10 Mn in sursassite from Monte Alpe (Mellini *et al.*, 1984), and 0.12 Fe + 0.03 Mn in sursassite from Andros (Allmann, 1984).

Trivalent manganese occurs only in the Al1 site of the sample investigated here, together with Al, Mg, and Fe^{3+}. Although Mn^{3+} is not really essential for the stability of the structure (Reinecke, 1986), the presence of up to 0.4 Mn^{3+} per formula unit in the Lienne sursassite could indicate that some sedimentary horizons of middle Ordovician age are highly oxidized, thus allowing the presence of Mn^{3+} within hematite-rich schists.

The role of Mg in the sursassite structure is of particular importance, due to its potential petrogenetic significance. In the high-pressure synthetic sursassite-type phase $Mg_4(MgAl)Al_4[Si_6O_{21}(OH)_7]$, Mg occurs both in the M(1) (= Mn1) and M(2) (= Mn2) sites, while it shares the M(3) (= Al1) position with Al (Gottschalk *et al.*, 2000). In the natural sample from the Lienne Valley, Mg occurs only in the Al1 position. The absence of Mg from the Mn1 and Mn2 positions could therefore be interpreted as a confirmation of the low-pressure conditions under which sursassite crystallized in the Lienne Valley, conditions that were estimated by Theye *et al.* (1996) as 1–2 kbar. However, some caution must be used in this interpretation, because the existence of significant solid solution from the natural composition towards synthetic Mg-sursassite has not yet been confirmed.

Acknowledgements: The authors acknowledge the help of Michel Blondieau who provided the first sample of sursassite from the Lienne Valley, M. Pasero and T. Armbruster who accepted to review the manuscript, and W. Maresch who edited it. F.H. and J.W. are grateful to the FNRS (Belgium) for a position of "Chercheur qualifié" and for grant 2.4511.07.

References

Allmann, R. (1984): Die Struktur des Sursassits und ihre Beziehung zur Pumpellyit- und Ardennitstruktur. *Fortschr. Mineral., Beiheft 1*, **62**, 3-4.

Bernhardt, H.-J., Armbruster, T., Fransolet, A.-M., Schreyer, W. (2005): Stavelotite-(La), a new lanthanum-manganese-sorosilicate mineral from the Stavelot Massif, Belgium. *Eur. J. Mineral.*, **17**, 703-714.

Brese, N.E. & O'Keeffe, M. (1991): Bond-valence parameters for solids. *Acta Cryst.*, **B47**, 192-197.

Burnham, C.W. (1991): LCLSQ version 8.4, last-squares refinement of crystallographic lattice parameters. Dept. of Earth & Planetary Sciences, Harvard University, 24 p.

Cortesogno, L., Lucchetti, G., Penco, A.-M. (1979): Le mineralizzazioni a manganese nei diaspri delle ofioliti Liguri: mineralogia e genesi. *Rend. Soc. Ital. Mineral. Petrol.*, **35**, 151-197.

Fockenberg, T. (1998): An experimental study of the pressure-temperature stability of MgMgAl-pumpellyite in the system $MgO–Al_2O_3–SiO_2–H_2O$. *Am. Mineral.*, **83**, 220-227.

Gottschalk, M., Fockenberg, Th., Grevel, K.-D., Wunder, B., Wirth, R., Schreyer, W., Maresch, W.V. (2000): Crystal structure of the high-pressure phase $Mg_4(MgAl)Al_4[Si_6O_{21}/(OH)_7]$: an analogue of sursassite. *Eur. J. Mineral.*, **12**, 935-945.

Hatert, F., Deliens, M., Fransolet, A.-M., Van Der Meersche, E. (2002): Les Minéraux de Belgique, Deuxième édition. Imprimerie Bietlot, Gilly, 304 p.

Kramm, U. (1982): Die Metamorphose des Venn-Stavelot-Massivs, nordwestliches Rheinisches Schiefergebirge: Grad, Alter und Ursache. *Decheniana (Bonn)*, **135**, 121-178.

Martin, S. & Lombardo, B. (1995): Sursassite, spessartine, piemontite in Fe–Mn metacherts from Lago Bleu, upper Val Varaita (western Alps). *Bollettino Museo Regionale di Scienze Naturali, supplemento*, **13**, 2, 103-130.

Mellini, M., Merlino, S., Pasero, M. (1984): X-ray and HRTEM study of sursassite: crystal structure, stacking disorder, and sursassite-pumpellyite intergrowth. *Phys. Chem. Minerals*, **10**, 99-105.

Moore, P.B., Ito, J., Steele, I.M. (1979): Macfallite and orientate: calcium manganese (III) silicates from upper Michigan. *Mineral. Mag.*, **43**, 325-331.

Oxford Diffraction (2007): CrysAlis CCD and CrysAlis RED. Version 1.71. Oxford Diffraction, Oxford, England.

Reinecke, Th. (1986): Phase relationships of sursassite and other Mn-silicates in highly oxidized low-grade, high pressure metamorphic rocks from Evvia and Andros Islands, Greece. *Contrib. Mineral. Petrol.*, **94**, 110-126.

Schreyer, W. (1975): New petrologic evidence for Hercynian metamorphism in the Venn-Stavelot Massif, Belgium. *Geol. Rundschau*, **64**, 819-830.

Schreyer, W., Maresch, W.V., Medenbach, O., Baller, T. (1986): Calcium-free pumpellyite, a new synthetic hydrous Mg–Al silicate formed at high pressures. *Nature*, **321**, 510-511.

Schreyer, W., Maresch, W.V., Baller, T. (1991): A new hydrous, high-pressure phase with a pumpellyite structure in the system $MgO–Al_2O_3–SiO_2–H_2O$. *in* "Progress in metamorphic and magmatic petrology", L.L. Perchuk, ed. Cambridge University Press, UK, 47-64.

Schreyer, W., Fransolet, A.-M., Bernhardt, H.-J. (2001): Hollandite-strontiomelane solid solutions coexisting with kanonaite and braunite in late quartz veins of the Stavelot Massif, Ardennes, Belgium. *Contrib. Mineral. Petrol.*, **141**, 560-571.

Schreyer, W., Bernhardt, H.-J., Fransolet, A.-M., Armbruster, Th. (2004): End-member ferrian kanonaite: an andalusite phase with one Al fully replaced by $(Mn,Fe)^{3+}$ in a quartz vein from the Ardennes mountains, Belgium, and its origin. *Contrib. Mineral. Petrol.*, **147**, 276-287.

Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, **A32**, 751-767.

Sheldrick, G.M. (1997): SHELXS97 and SHELXL97. University of Göttingen, Germany.

Theye, Th. & Fransolet, A.-M. (1994): Virtually pure ottrelite from the region of Ottré, Belgium. *Eur. J. Mineral.*, **6**, 547-555.

Theye, Th., Schreyer, W., Fransolet, A.-M. (1996): Low-temperature, low-pressure metamorphism of Mn-rich rocks in the Lienne syncline, Venn-Stavelot Massif (Belgian Ardennes), and the role of carpholite. *J. Petrol.*, **37**, 767-783.

Wilson, A.J.C. (1992): International Tables for X-ray Crystallography, vol. C. Kluwer Academic Press, London, 883 p.

Received 21 June 2008
Modified version received 7 August 2008
Accepted 12 August 2008