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Forêtite, a new secondary arsenate mineral from the Cap Garonne mine, France

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ABSTRACT

Forêtite, ideally $Cu_2Al_2(AsO_4)(OH,O,H_2O)_6$, is a new secondary arsenate mineral from the Cap Garonne mine, Var, France (IMA2011-100). It has also been identified at the Salsigne gold mine, Languedoc-Roussillon, France. Although it was identified as a potentially new mineral in 1993, a formal description has only been possible as a result of a new find in a chamber called Annex S located near the entrance of the Cap Garonne mine. Forêtite occurs as pale sky blue to aqua aggregates, up to ~0.1 mm across, made up of minute plates no more than 20 μm in length. It has a very pale blue streak. Individual crystals have a vitreous lustre and are transparent, whereas clusters appear translucent. The calculated density is 3.286 g cm^{-3}. The crystals are brittle, with an irregular fracture and have a hardness of ~3–4 on Moh's scale. Forêtite is found in direct association with bariopharmacoalumite, cyanotrichite, parnauite, chalcophyllite and mansfieldite in an Al-rich assemblage which is presumed to have formed under acidic conditions. It is biaxial; the average refractive index measured in white light on aggregates of forêtite crystals is 1.620(5). The empirical formula (based on 10 oxygen atoms per formula unit) is $Cu_{1.94}(Al_{1.96}Fe_{0.04})_{\Sigma 2.00}(As_{0.84}S_{0.09}Si_{0.04})_{\Sigma 0.97}O_{10}H_{5.19}$. Raman spectroscopy confirms the presence of OH and H_2O in the structure. Forêtite is triclinic, space group $P\bar{1}$, with a = 6.969(9), b = 7.676(9), c = 8.591(11) Å, α = 82.01(9), β = 71.68(8), γ = 102.68(8)°, V = 415(1) $Å^3$ and Z = 2. The five strongest lines in the X-ray powder diffraction pattern [d in Å, (I), (hkl)] are as follows: 7.307, (100), (010, $0\bar{1}0$); 3.141, (24), (200, $\bar{2}00$); 2.818, (24), ($2\bar{2}0$, $\bar{2}20$); 4.519, (23), (111); 2.343, (22), ($1\bar{3}1$). The mineral is named in honour of Dr Jean-Paul Forêt, who co-founded the project that turned the Cap Garonne mine into a protected site and museum.

Keywords: Forêtite, new mineral, Cap Garonne mine, France, arsenate, secondary mineral.

Introduction

The first specimens of forêtite were collected at the Cap Garonne mine in the late 1980s. At that time, the mineral was considered to be wroewolfeite, probably due to its pale blue colour. One of the authors (GF) and E. Legrand, who are members of the Association des Amis de la mine de Cap Garonne (AAMCG), collected the first samples and provided several of them to PJC for analysis during his PhD on natural copper arsenates. Chiappero (1993) obtained powder X-ray diffraction (XRD) patterns of the mineral on Gandolfi and Debye–Scherrer cameras. However, the two cameras gave slightly different d spacings, and he was unable to resolve the

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discrepancy and index the patterns on any one cell. A preliminary study of the mineral was performed, including microprobe analyses and a description of the occurrence (Chiappero, 1993). The mineral was described as "Phase X2". Subsequent XRD analyses were made (e.g. the unpublished data by Uwe Kolitsch, which is currently available at www.mindat.org), but a full description of the mineral was not completed. New specimens of better quality were collected in 2011 during a scientific study of Cap Garonne minerals by the AAMCG in cooperation with the mine museum. This new material has enabled us to resume the study of the mineral, which has been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA–CNMNC) almost 25 years after the first specimens were discovered.

The mineral is named in honour of Dr Jean-Paul Forêt (b. 1943), a retired engineer of the French Ministry of Equipment, who worked as geologist-in-charge of major risks and the environment. He was a co-founder of the project which turned the Cap Garonne mine into a nationally protected site and museum in 1994 (Musée de la Mine de Cap Garonne), and has acted as a scientific advisor to the museum from then until now. The mineral and name have been approved by the IMA–CNMNC (IMA2011-100). Seven cotype specimens of forêtite have been deposited. Five of these are in the collection of the Natural History Museum of Los Angeles County, catalogue numbers 63573, 63574, 63575, 63576 and 63577 (all from Annex S), one is in the collection of Museum Victoria, Melbourne, Australia, registration number M51746 (from Annex S), and one is in the collection of the Muséum National d'Histoire Naturelle, Paris, France, catalogue number 211.58 (from pillar 44b).

Occurrence and paragenesis

Forêtite was found on specimens from the Cap Garonne mine, Var, Provence-Alpes-Côte d'Azur, France (43º6′23″N, 6º1′26″E), which is the type locality for 13 other minerals (e.g. Sarp *et al*., 1997; Mari and Sarp, 2006; Mills *et al*., 2011). More specifically, cotype specimens of forêtite were collected in the south mine, in a chamber located near the entrance, called Annex S, and also at pillar 44b in the north mine [for a more detailed explanation of the workings see Mills *et al*. (2011)]. As the majority of the analyses used to characterize the mineral were performed on specimens from the south mine and these analyses contributed most significantly to the study, we suggest that the Annex S in the south mine is designated as the type locality. Forêtite is therefore the second new mineral found in the south mine, after deloryite (Sarp and Chiappero, 1992). Cotype specimens of the new species bariopharmacoalumite were also found in the south mine (Mills *et al*., 2011). The first forêtite specimens were collected from pillar 44b in the north mine (Chiappero, 1993), which is also the type locality for bariopharmacoalumite (Mills *et al*., 2011).

The new material was discovered by GF in the floor of Annex S, where a horizontal bed of hard conglomerate containing red barite is exposed. The conglomerate is cut by numerous fractures which contain olivenite and minor zeunerite. A suite of secondary Al-bearing minerals was found in direct association with forêtite including bariopharmacoalumite, cyanotrichite, parnauite and chalcophyllite. The chalcophyllite was heavily altered to fragile white mansfieldite on some specimens.

Physical and optical properties

Forêtite occurs as pale sky blue to aqua aggregates, up to about 0.1 mm across (Figs 1 and 2), which consist of minute plates, each no more than 20 μm in length. The forêtite plates are typically <10 μm in any direction (Fig. 3). No forms could be measured due to the size of the crystals, but it is possible that the crystals are

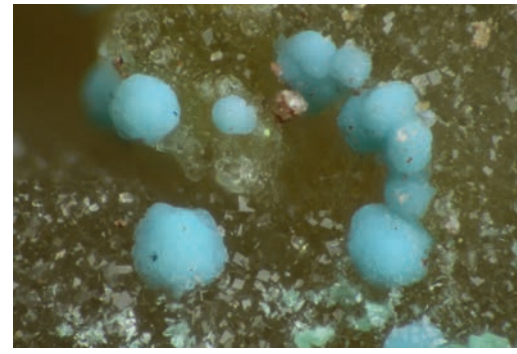

FIG. 1. Forêtite clusters with bariopharmacoalumite (colourless cubes) and chalcophyllite (green flakes) from Annex S, Cap Garonne. The field of view is ~0.2 mm across.

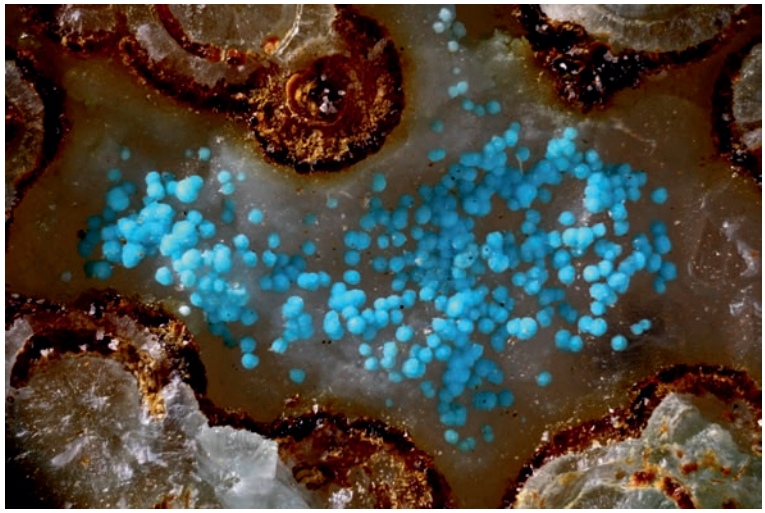

FIG. 2. Forêtite clusters with goethite on quartz from the south mine, Cap Garonne. The field of view is 5 mm across.

flattened on {010}, based on the strongest reflection in the powder X-ray diffraction (PXRD) data. Forêtite has a very pale blue streak. The individual crystals have a vitreous lustre and are transparent, but clusters of forêtite are translucent. Forêtite has one poor cleavage, parallel to the flattening of the platelets, which is visible in scanning electron microscope (SEM) images. The crystals are brittle, with an irregular fracture and have a hardness of ~3–4 on Moh's scale. The density could not be measured accurately due to the size of the crystals and the high porosity of the aggregates. The density calculated using the empirical formula is 3.286 g cm^{-3}.

Forêtite crystals are biaxial based upon their inferred triclinic symmetry. They are not pleochroic, the refractive index, n_{av}, of 1.620(5) was measured on several aggregates of forêtite crystals in white light. The 2V angle, dispersion, optical orientation and sign could not be determined because of the size and nature of the crystals. The Gladstone–Dale compatibility index (Mandarino, 2007), calculated for all the data is 0.047, which is classed as good.

Chemical composition

Six chemical analyses were carried out using a Cameca (Camebax microbeam) electron micro-

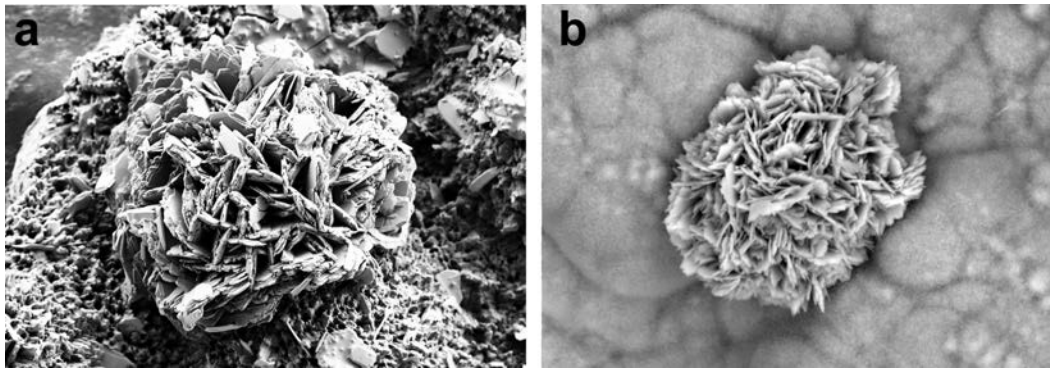

FIG. 3. Back-scattered SEM image of forêtite clusters (~50 μm across) from (*a*) Cap Garonne and (*b*) Salsigne.

TABLE 1. Electron microprobe analysis of forêtite.

Constituent	Mean (wt.%)	Range	SD	Standard
CuO	37.53	36.7–38.18	0.56	Cu metal ($K\alpha$)
Fe_2O_3	0.72	0.68–0.92	0.16	Pyrite ($K\alpha$)
Al_2O_3	24.37	23.28–25.26	0.80	Spinel ($K\alpha$)
As_2O_5	23.52	21.28–24.47	1.32	AsGa ($L\alpha$)
SiO_2	0.65	0.52–0.92	0.16	Albite ($K\alpha$)
SO_3	1.81	1.13–2.84	0.59	Pyrite ($K\alpha$)
H_2O*	11.40			
Total	100.00			

* The H_2O values were calculated by difference.

probe in wavelength dispersive X-ray spectroscopy (WDS) mode, with a 20 kV accelerating voltage, 9 nA beam current and 2 μm beam diameter on forêtite crystals from pillar 44b. Insufficient material was available for direct water determination. The H_2O content was thus calculated by difference. The presence of H_2O and OH was confirmed by Raman spectroscopy (see below). Analytical data, standards and lines used are listed in Table 1. The empirical formula (based on ten oxygen atoms per formula unit) is $Cu_{1.94}(Al_{1.96}Fe_{0.04})_{\Sigma 2.00}(As_{0.84}S_{0.09}Si_{0.04})_{\Sigma 0.97}O_{10}H_{5.19}$. The simplified formula is $4CuO{\cdot}2Al_2O_3{\cdot}As_2O_5{\cdot}5H_2O$ or $Cu_2Al_2(AsO_4)(OH,O,H_2O)_6$, which requires CuO, 37.79; Al_2O_3, 24.22; As_2O_5, 27.29; and H_2O, 10.70; total 100.00 wt.%. In the absence of a crystal structure determination, we can only speculate on how O, OH and H_2O should be apportioned in the ideal formula. There are four possible formulae: $Cu_2Al_2(AsO_4)O_3(OH){\cdot}2H_2O$, $Cu_2Al_2(AsO_3OH)O_4{\cdot}2H_2O$, $Cu_2Al_2(AsO_4)O_2(OH)_3{\cdot}H_2O$ and $Cu_2Al_2(AsO_3OH)O_3(OH)_2{\cdot}H_2O$. As the Raman spectrum (Fig. 4 and below) suggests

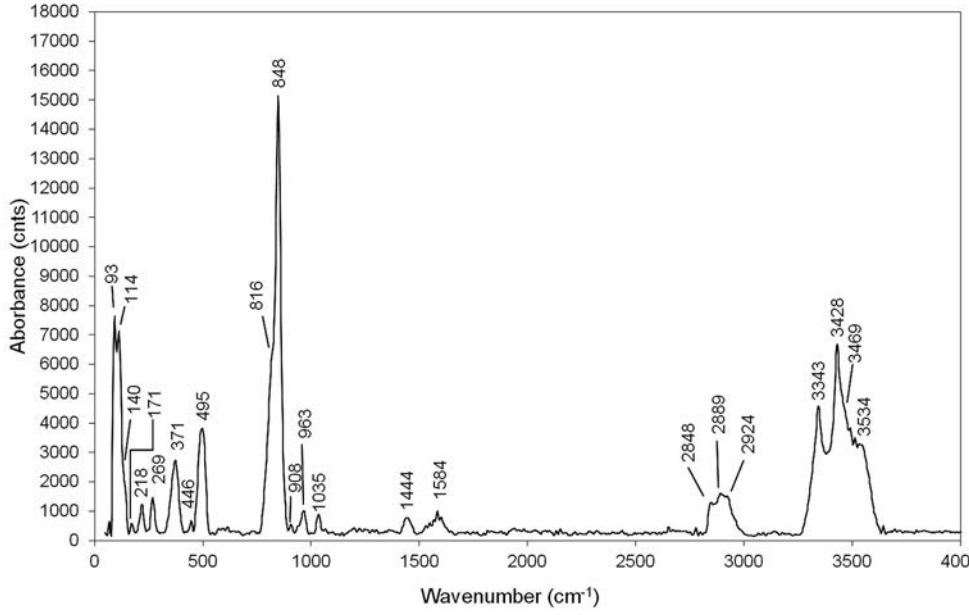

FIG. 4. The Raman spectrum of forêtite from Cap Garonne.

multiple H_2O environments, the most likely charge-balanced ideal formulae are either $Cu_2Al_2(AsO_4)O_3(OH)\cdot 2H_2O$ or $Cu_2Al_2(AsO_3OH)O_4\cdot 2H_2O$. Until crystals suitable for structure determination are found, we prefer the formula $Cu_2Al_2(AsO_4)(OH,O,H_2O)_6$.

Raman spectroscopy

The Raman spectrum (average of three 30 s spectra) of an unoriented aggregate of forêtite crystals was obtained in the range 50–4000 cm^{-1}. Data were collected in backscattered mode on a HORIBA Jobin Yvon XploRA spectrometer interfaced with an Olympus BX 41 microscope using a 100× objective, an estimated spot size 2 μm, a 1200 lines mm^{-1} grating and excitation radiation at a wavelength of 532 nm. The system was calibrated using the 521 cm^{-1} line of a silicon wafer. Peak positions and assignments are listed in Table 2. The Raman spectrum is dominated by two sharp peaks at (848 + 816) and 495 cm^{-1} (Fig. 4), corresponding to As–O symmetrical stretching and bending modes, respectively. The band at 1585 cm^{-1} corresponds to H–O–H bending and those in the regions near 3000 and 3500 cm^{-1} to O–H stretching. The number and complexity of these bands suggests several different H_2O and OH environments in the mineral, which are consistent with the formulae $Cu_2Al_2(AsO_4)O_3(OH)\cdot 2H_2O$ or $Cu_2Al_2(AsO_3OH)O_4\cdot 2H_2O$, as noted above.

Crystallography

Single-crystal X-ray studies could not be successfully carried out due to the size and nature of the forêtite plates. Conventional and synchrotron techniques were tried to obtain the unit cell or structural data, but both were unsuccessful.

The X-ray powder diffraction data were recorded using specimens from Annex S on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatic Mo$K\alpha$ radiation. The peaks were indexed using the *Crysfire* software suite (Shirley, 2002). Several programs in the suite returned an identical triclinic cell with a ~6.9, b ~7.6, c ~8.7 Å, α ~81, β ~71 and γ ~103º. Observed d spacings and intensities were then derived by profile fitting using *JADE 9.3* software. Data are given in Table 3. The unit-cell parameters refined from the powder data using *Chekcell* (Laugier and Bochu, 2004) are triclinic, space group $P\bar{1}$, a = 6.969(9), b = 7.676(9), c = 8.591(11) Å, α = 82.01(9), β = 71.68(8), γ = 102.68(8)º, V = 415(1) $Å^3$ and Z = 2.

TABLE 2. Raman band positions and assignments for forêtite.

Absorption band (cm^{-1})*	Assignments
3343, 3428, 3469, 3534 s	Stretching mode of OH groups
2848, 2889, 2924 m	Stretching mode of H_2O molecules
1585 m	H–O–H bending
1458 m	unassigned
1035 w	SO_4 symmetric stretch (ν_1)
963 w	SiO_4 symmetric stretch (ν_1)
908 vw	unassigned
848 vs	AsO_4 or $AsO_3(OH)$ symmetric stretch (ν_1)
816 s	AsO_4 or $AsO_3(OH)$ symmetric stretch (ν_1)
495 s	AsO_4 or $AsO_3(OH)$ bend (ν_4)
446 w	AsO_4 or $AsO_3(OH)$ bend (ν_4)
371 m	AsO_4 bend (ν_2)
269 m	Lattice modes
218 m	Lattice modes
171 vw	Lattice modes
140 w	Lattice modes
114 s	Lattice modes
93 s	Lattice modes

* Abbreviations are vs = very strong, s = strong, m = medium, w = weak.

TABLE 3. Powder X-ray data for forêtite.

I/I_o	d_{obs} (Å)	d_{calc} (Å)	*hkl*
100	**7.307**	**7.300**	**010, 0$\bar{1}$0**
9	6.07	6.101	011
10	5.598	5.633	$\bar{1}$10, 1$\bar{1}$0
23	**4.519**	**4.519**	**111**
18	4.277	4.272	$\bar{1}$01
7	3.894	3.874	012
13	3.648	3.650	020, 0$\bar{2}$0
17	3.455	3.492	1$\bar{1}$2
8	3.331	3.328	$\bar{1}$21
24	**3.141**	**3.174**	**200, $\bar{2}$00**
9	2.937	2.935	2$\bar{1}$2, $\bar{1}$02
24	**2.818**	**2.817**	**2$\bar{2}$0, $\bar{2}$20**
20	2.719	2.738	212
		2.707	$\bar{1}$22
13	2.496	2.520	1$\bar{3}$0, $\bar{1}$30
13	2.427	2.429	$\bar{1}$$\bar{2}$1
22	**2.343**	**2.341**	**1$\bar{3}$1**
6	2.216	2.221	
16	2.122	2.121	$\bar{1}$32
6	2.049	2.048	303
5	1.979	1.975	$\bar{3}$11
8	1.935	1.937	024
5	1.806	1.806	$\bar{1}$42
4	1.732	1.733	4$\bar{1}$2
4	1.662	1.664	$\bar{2}$42

The five strongest lines are listed in bold face.

Both the unit cell and composition of forêtite are unique and have no analogues. Due to their low quality, the powder XRD traces could not be used for *ab initio* structure determination.

Other occurrences

Forêtite has also been confirmed by PXRD and energy-dispersive X-ray spectroscopy (EDS) at the Salsigne gold mine, Salsigne, Aude, Languedoc-Roussillon, France (43º20′50"N, 2º21′20"E), but this material was not used in the characterization of the species. The similarity between the copper- and aluminium-bearing supergene mineral assemblage at Salsigne and that at Cap Garonne, led GF to have PXRD and EDS analyses performed by SJM on the Salsigne material during the study of forêtite. A second new species was identified at Cap Garonne and Salsigne as a result, as the same author provided pushcharovskite specimens to Halil Sarp while he was studying the mineral from Cap Garonne (Sarp and Sanz-Gysler, 1997).

Forêtite was identified on four specimens collected in 1995 in the oxidized upper part of the open pit at the same time as abundant chalcophyllite was found (Forner *et al*., 1997). It occurs as vitreous translucent turquoise-blue balls up to 0.1 mm across in association with chalcophyllite, mansfieldite, olivenite and goethite in a cavernous gossan which is commonly lined with siliceous crusts (Figs 3*b* and 5).

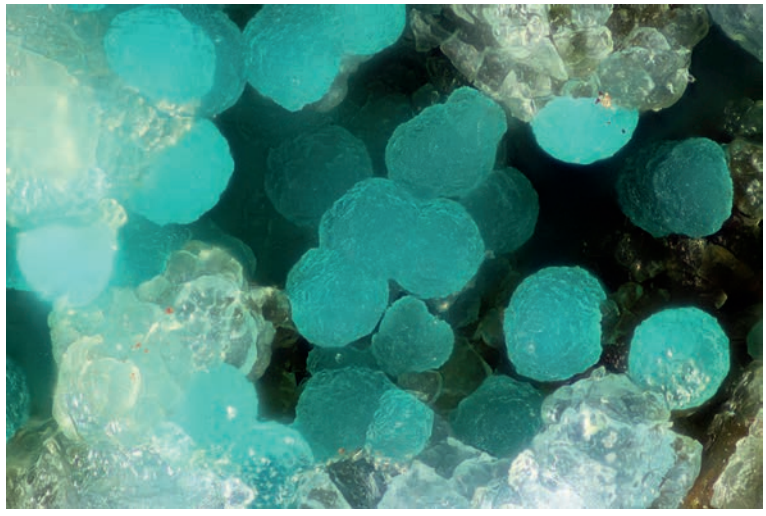

FIG. 5. Forêtite clusters with quartz from the Salsigne mine. The field of view is approximately 0.3 mm across.

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References

Chiappero, P.-J. (1993) *Les arséniates de cuivre naturels: systématique et approche des conditions de genèse par les synthèses. Application au gisement plumbocuprifère de Cap Garonne, Var (France)*. Unpublished PhD Thesis, University of Orléans, Orléans, France.

Forner, H., Favreau, G., Meisser, N. and Descouens, D. (1997) La Mine d'or de Salsigne. Les espèces minérales remarquables. *Le Règne Minéral*, **3**, 36–54.

Laugier, J. and Bochu, B. (2004) *Chekcell*: graphical powder indexing cell and space group assignment software. http://www.ccp14.ac.uk/tutorial/lmgp/.

Mandarino, J.A. (2007) The Gladstone–Dale compatibility of minerals and its use in selecting 200 mineral species for further study. *The Canadian Mineralogist*, **45**, 1307–1324.

Mari, G. and Sarp, H. (2006) Cap Garonne (Var, France). *Le Cahier des Micromonteurs*, **93**, 131–138.

Mills, S.J., Rumsey, M.S., Favreau, G., Spratt, J., Raudsepp, M. and Dini, M. (2011) Bariopharmacoalumite, a new mineral species from Cap Garonne, France and Mina Grande, Chile. *Mineralogical Magazine*, **75**, 135–144.

Sarp, H. and Chiappero, P.-J. (1992) Deloryite, $Cu_4(UO_2)(MoO_4)_2(OH)_6$, a new mineral from Cap Garonne mine near Le Pradet, Var, France. *Neues Jahrbuch für Mineralogie, Monatshefte*, **1992**, 58–64.

Sarp, H. and Sanz-Gysler, J. (1997) Pushcharovskite, $Cu(AsO_3)(OH)\cdot H_2O$, a new mineral from Cap Garonne (Var, France). *Archives des Sciences, Genève*, **50**, 177–186 [in French].

Sarp, H., Mari, G., Magnan, M.-T., Camerola, M., Delroy, B., Guarino, A. and Iltis, A. (1997) La mine de Cap Garonne (Var, France). Haut lieu de la minéralogie internationale. *Riviéra Scientifique*, **12**, 3–58.

Shirley, R. (2002) *The Crysfire 2002 System for Automatic Powder Indexing: Users Manual*. The Lattice Press, Surrey, UK.