

Phurcalite from Dartmoor, Southwest England, and its identity with 'nisaite' from Portugal

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Abstract

Yellow blades on joint surfaces in granite from Merrivale quarry, Dartmoor, Devon, are shown to be of a slightly arsenian variety of phurcalite by X-ray powder diffraction, infrared spectroscopy, electron microprobe and thermal analyses and optical methods. The results from these techniques are tabulated, including assignments for infrared absorption bands. Comparison of X-ray powder diffraction, infrared spectroscopic and optical data with those obtained from samples of 'nisaite', an incompletely described mineral from Nisa, Portugal, indicates that the latter is also phurcalite.

KEYWORDS: phurcalite, nisaite, Dartmoor, Portugal.

Introduction

'NISAITE' was described by J. de Lencastre and M. M. Vairinho (1970) as a new calcium uranyl phosphate from Nisa, Alto Alentejo, Portugal, resembling phosphuranylite, but possessing distinctive optical properties and giving a unique X-ray powder diffraction pattern. Quantitative chemical analyses and single crystal X-ray diffraction data could not be obtained, as the 'nisaite' forms thin crusts of microscopic crystals intimately associated with saleeite and other impurities, and is difficult to separate. This lack of adequate data prevented 'nisaite' from being accepted as a valid species.

Merrivale quarry, Whitchurch parish, Dartmoor, Devon, at NGR SX 546 752, works granite near the top of the Dartmoor cupola, and is a well known locality for autunite, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{--}12\text{H}_2\text{O}$, which occurs as thin crusts of yellow rectangular plates in scattered patches on joint surfaces in the granite, and as

disseminations in which it is easily recognized by its intense yellow-green fluorescence in ultraviolet radiation. One of us (RSWB) and others have noticed that patches of a deeper yellow mineral are also present. This mineral has a very weak fluorescence in ultraviolet radiation, and forms microscopic bladed crystals, often in radiating clusters. These clusters of crystals may well be the 'zippeite' noted in some popular accounts, of which no authenticated specimen from Merrivale quarry has been recorded. Initial studies indicated that this second mineral is a calcium uranyl phosphate distinct from phosphuranylite, $\text{Ca}(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, which it superficially resembles.

Phurcalite, $\text{Ca}_2(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_4 \cdot 4\text{H}_2\text{O}$, was first described by Deliens and Piret (1978) on a single small specimen from Bergen, Saxony, and was subsequently found on another single specimen from Shinkolobwe, Zaire (Deliens and Comblain, 1978). Phurcalite has also been found on

Table 1. Optical characteristics of phurcalites.

	1	2	3	4
α	(1.690, calculated)	1.690	1.670 pale yellow	1.670 pale yellow
β	1.730 very pale yellow	1.730	1.720 pale yellow	1.725 pale yellow
γ	1.749 vivid yellow	1.750	1.770 strong yellow	1.775 dark yellow
Optic sign	Biaxial -ve	Biaxial -ve	Biaxial -ve	Biaxial -ve
$2V$	68°	70°	84°	84.4° (calculated), $82 \pm 2^\circ$ (measured), $2V_g < 2V_v$
Extinction			Straight	Straight

1. Phurcalite, Bergen, Saxony. Type specimen. Deliëns and Piret (1978).
2. Phurcalite, Shale Hills, California (Crook, unpublished report).
3. "Nisaite", Nisa, Portugal (Lencastre and Vairinho, 1970).
4. Phurcalite, Merrivale quarry, Dartmoor, Devon.

diatomite at the Shale Hills, Kern Co., California by Dr R. R. Bower in 1973 and, after a preliminary investigation by Dr A. L. Kidwell, was studied in detail by W. W. Crook (unpublished report, 1980). It has also been found elsewhere in California (Chew, 1982).

The work described in this paper shows that 'nisaite' from Portugal is identical with phurcalite, and that the material described from Merrivale quarry is an arsenate-bearing variety of phurcalite. This is also of interest as the first recorded occurrence of phurcalite from the British Isles.

Description, optics

The phurcalite from Nisa is found on a flaky grey shale, and is closely associated with saleeite, while that from Dartmoor is on granite and is associated with autunite. The Shale Hills material is associated with meta-autunite, on diatomite. The type material from Saxony is on quartz-lined cavities in granite (Deliëns and Piret, 1978) and that from Zaïre on a green chloritic rock (Deliëns and Comblain, 1978). No other secondary uranium mineral was found on either of these phurcalite specimens.

Single-crystal X-ray diffraction studies (Deliëns and Piret, 1978; Piret and Declercq, 1978) have shown that phurcalite has space group *Pbca* and therefore belongs to the orthorhombic holosymmetric class *mmm*. Phurcalite crystals from Portugal and Dartmoor are similar in habit, forming blades flattened parallel to (010), elongated along [001] and terminated by the basal pinacoid and

by 'domes' formed by two prism faces (*h0l*). The 'domes' are sometimes curved as shown in the scanning electron micrographs (Figs 1 and 2). The crystals from Portugal reach about 0.1 mm in length; those from Dartmoor occasionally reach about 0.2 mm. The type phurcalite from Saxony is of similar bladed habit, but the crystals are said to be generally truncated (Deliëns and Piret, 1978) and appear to terminate in single faces of the form (*h0l*). The phurcalite from Zaïre has terminations similar to those of our specimens (Deliëns and Comblain, 1978).

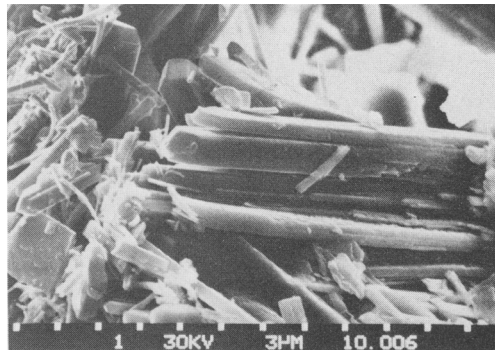
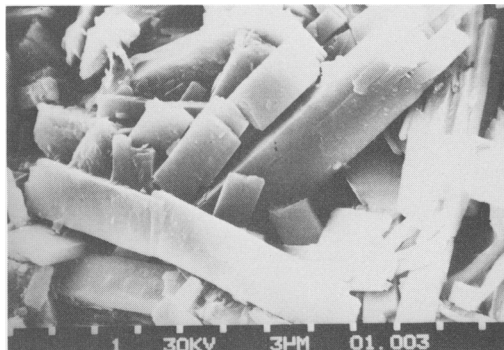
The Dartmoor phurcalite shows three cleavages, very good {100}, good {010} and very poor {001}.

The optical properties of the Dartmoor phurcalite were determined using monochromatic light of 589 nm and are given in Table 1, where they are compared with the values determined for other phurcalites, and seen to be very similar.

X-ray powder diffraction

X-ray powder diffraction data for 'nisaite' from Portugal and for the material described from Dartmoor are compared with published data for phurcalite in Table 2. The patterns of 'nisaite' and the phurcalites are similar. The strong lines correspond and the differences are minor, being confined to the weaker reflections and the resolution of lines which are close together.

The cell dimensions of the 'nisaite' from Portugal and the mineral from Dartmoor were refined using only those reflections whose indexing was



FIGS. 1 and 2. Scanning electron photomicrographs of phurcalites showing crystal habits and terminations. Field $36 \times 23 \mu\text{m}$. FIG. 1 (left). 'Nisaite' from Nisa, Portugal. FIG. 2 (right). Crystals from Merrivale quarry, Devon.

unambiguous (Table 2), although this entailed some loss of precision as the full data set was not used. The unit cells of 'nisaite' and phurcalite show only slight differences.

Chemistry

A very small sample (0.64 mg) of phurcalite from Merrivale quarry, Dartmoor, was submitted to thermogravimetric analysis by Mr Brian Philbrock in the Chemistry Department, University of Manchester Institute of Science and Technology, at a heating rate of $10^\circ\text{C min}^{-1}$ in a nitrogen atmosphere. A slow water loss from $100\text{--}150^\circ\text{C}$ was followed by a faster loss to about 200°C , almost levelling out by 250°C , by which temperature between 8–9% weight had been lost. A further slow loss took place from above about 500°C and is ascribed to oxide volatility.

A sample of the phurcalite from Merrivale quarry, Dartmoor, was quantitatively analysed by Mr D. A. Plant in the Geology Department, University of Manchester, using a modified Cambridge Geoscan electron microprobe analyser fitted with a Link Systems 290 energy dispersive analyser, utilising an operating voltage of 15 kV, and a sample current of 3 nA, measured on cobalt. The average of three analyses with good reproducibility gave the results shown in Table 3, which agree well with the published and calculated values, except in that our material from Dartmoor contains some arsenic, with a composition near $\text{Ca}_2(\text{UO}_2)_3(\text{PO}_4)_{1.85}(\text{AsO}_4)_{0.15}(\text{OH})_4 \cdot 4\text{H}_2\text{O}$.

Infrared spectroscopy

The infrared spectrum of phurcalite has not been published before. Unfortunately the type

specimen carried little phurcalite, and this was effectively destroyed in its investigation (Deliens and Comblain, 1978) and so cannot be used for infrared spectroscopy. The Shale Hills material was used for this comparison, although the amount of available material, which could not be completely separated from diatomite matrix, produced only a weak spectrum. This spectrum, however, displays nearly all the strong absorption bands seen in the spectra of the samples from Portugal and Dartmoor.

The infrared spectra of a number of samples of phurcalite from Nisa, Dartmoor, and Shale Hills, and of phosphuranylite from Tarabau and Cunha Baixa mine, Portugal, were measured in Nujol mulls, some over the $400\text{--}4000 \text{ cm}^{-1}$ range between KBr plates, others over the $670\text{--}4000 \text{ cm}^{-1}$ range between NaCl plates, using Perkin-Elmer PE 397 and PE 137 spectrophotometers respectively. Spectra of phurcalite and phosphuranylite are shown for comparison in Fig. 3, and absorption maxima and assignments are listed in Table 4.

The spectra of samples from Nisa and from Dartmoor are virtually identical, and the very weak spectrum of the Shale Hills material shows nearly all the strong absorption bands present in the others.

The spectrum of phurcalite is complex and characteristic, and easily distinguished from that of phosphuranylite. The small proportion of arsenate is not evident in the spectrum of the Dartmoor material (the arsenate ion has strong ν_3 absorption in the 800 cm^{-1} region).

The complexity of absorptions in the $950\text{--}1150 \text{ cm}^{-1}$ region suggests low symmetry and multiplicity of phosphate sites. The lowest symmetry can only produce three ν_3 absorptions for each type of phosphate anion. Although the presence

Table 2. X-ray powder diffraction data for phurcalite and "nisaite", d spacings in Å, I = relative intensities.

1		2		3		4		5		6		Indices
d	I	d	I	d	I	d	I	d	I	d	I	hkl
						~10	5					
		8.915	2									111 ²
		8.715	3	8.67	<5	8.75	3	*8.69	10	*8.68	20	200 ^{2,3}
8.05	100	8.031	100	8.02	100	8.00	10m	*7.94	100	*7.95	100	020 ^{1,2,3}
		7.659	17	7.63	10	7.60	5m	*7.50	30	7.50	20	210 ^{2,3}
						6.95	3					
6.85	5	6.914	6	6.89	10	6.85	1	6.86	15b	6.88	20	002 ¹ , 021 ^{2,3}
		6.672	3	6.63	<5							211 ^{2,3}
				6.30	<5							102 ³
				5.905	3	5.88	10	5.85	5m	*5.83	10	220 ^{2,3}
						5.37	<5					221 ³
		5.068	3	5.00	5							311 ^{2,3}
		4.972	2					4.97	3d	4.97	15b	122 ²
4.53	10	4.562	6	4.54	10	4.55	7m	*4.51	25	*4.52	20	230 ^{1,2,3}
		4.325	4									231 ²
4.24	30	4.258	17	4.24	30	4.25	7d	*4.22	50	*4.24	35	312 ^{1,2,3}
		4.205	2									410 ²
4.00	30	4.015	11	3.99	20	4.00	8m	*3.978	35	*3.967	25	040 ^{1,2,3}
		3.946	3									023 ²
3.83	25	3.851	9	3.83	20	3.82	7	3.810	35	3.816	20	041 ^{1,2} , 123 ³
		3.781	2	3.76	<5							331 ^{2,3}
		3.647	2	3.61	<5	3.64	4	*3.622	10	*3.608	15	240 ^{2,3}
								3.496	<10	3.505	15	241 ^{5,6}
3.39	50	3.398	17	3.39	30	3.39	7	3.379	45	3.378	35	004 ^{1,2} , 332 ^{1,3}
		3.335	2	3.32	<5							104 ² , 422 ³
				3.20	5							233 ³
3.10	80	3.129	17	3.10	40							521 ^{1,3} , 214 ¹ , 024 ²
								3.097	90	3.104	60	
3.09	80	3.101	24			3.09	8					502 ^{1,2}
		3.045	2									512 ²
		3.005	4	2.99	<5	3.00	1	*2.991	25	*2.982	20	043 ^{2,3}
		2.971	2									342 ²
		2.961	2									143 ²
						2.95	1					
		2.943	3	2.94	<5							251 ² , 440 ³
2.878	70	2.893	24	2.878	30	2.88	8	2.873	75	2.866	40	522 ^{1,2} , 314 ³
				2.805	<5					2.808	10	134 ³
				2.737	<5	2.74	4	2.735	15	2.737	15	353 ³
		2.677	2	2.660	<5	2.67	4	*2.660	15			060 ^{2,3}
										2.646	20	
		2.627	4	2.611	5	2.62	5					061 ^{2,3}
2.608	10	2.594	5					2.594	30	2.603	15	523 ¹ , 344 ²
2.572	10	2.584	5	2.574	10	2.58	5	*2.571	30	*2.573	20	541 ^{1,2,3}
				2.498	<5							631 ³
2.439	10	2.454	6	2.442	10	2.45	7	*2.440	20	*2.446	15	542 ^{1,2,3}
				2.404	<5					2.386	15	432 ³
				2.331	<5	2.35	1b	2.324	10			623 ³
				2.294	<5	2.25						083 ³
				2.226	5			2.223	15	2.237	15	335 ³
				2.176	<5							271 ³
2.145	10	2.158	4	2.150	10	2.16	7	2.151	20	2.156	10	510 ^{1,2} , 462 ³
		2.108	2									371 ²
		2.103	3			2.10	7d					064 ²
		2.098	4	2.098	10							561 ^{1,2,3}
2.090	15b	2.093	5					2.086	30	2.087	10	116 ^{1,2}
				2.064	<5							136 ³
		2.026	2									562 ²
						2.02	5			2.021	10	
		2.018	3	2.012	5			2.015	20			573 ² , 742 ³

1. Type phurcalite, Bergen, Saxony (Deliens and Piret, 1978). a 17.426(3); b 16.062(3); c 13.592(3) Å (from four-circle diffractometer data).
2. Powder pattern calculated from the results of the structure determination of Piret and Declercq (1978) (PDF card 30-284).
3. Phurcalite, Streuberg, near Bergen, Saxony (Roberts, 1978, quoted on PDF card 30-285). a 17.366; b 15.957; c 13.548 Å (transformed to Pbcu space-group setting).
4. "Nisaite", Nisa, Portugal (d = diffuse, b = broad, m = quarter-moon shaped as a result of preferred orientation; Lencastre and Vairinho, 1970). Unit cell not determined.
5. "Nisaite", Nisa, Portugal (this study; Philips 11.46 cm diameter camera, CuK radiation 1.5418 Å, intensities by microdensitometer). a 17.33(4); b 15.94(2); c 13.56(6) Å, refined from powder data using reflections marked *.
6. Arsenatian phurcalite, Merrivale quarry, Devon (this study; Philips 11.46 cm diameter camera, CuK radiation 1.5418 Å, intensities by microdensitometer). a 17.44(2); b 15.87(2); c 13.56(3) Å, refined from powder data using reflections marked *.

Note on indexing. The published powder patterns 1, 2 and 3 do not give the same indices for all reflections; the source of the quoted indices is shown by a superscript. Pattern 4 was unindexed. The reflection denoted 5,6 was indexed as 241 in this study by comparing observed and calculated d spacings.

The reflections used for cell refinement in 5 and 6 are free from ambiguity in their indexing.

Table 3. Analyses of phurcalites.

	1	2	3	4
CaO	6.3	9.2	8.7	9.1
UO ₂	70.9	70.3	72.0	69.8
P ₂ O ₅	11.5	11.6	9.4	10.4
As ₂ O ₅	-	-	1.4	1.9
H ₂ O	9.3 ^k	8.9	8.5 ± 0.5 ^x	8.8

1. Microprobe analysis of phurcalite, type specimen from Bergen, Saxony (Deliens and Piret, 1978)
2. Theoretical for Ca₂(UO₂)₂(PO₄)₂(OH)₄·4H₂O
3. Microprobe analysis of phurcalite, Merrivale quarry, Dartmoor, Devon. O.F. specimen R.M.
4. Theoretical for Ca₂(UO₂)₂(PO₄)_{1.8}(AsO₄)_{0.2}(OH)₄·4H₂O
- * By difference
- x From TGA results

of metal O-H bending vibrations in this region (Nakamoto, 1978) renders such conclusions unreliable, and overlap conceals the multiplicity of absorptions in the phosphate ν_4 region near 500–600 cm⁻¹, the crystal structure determination (Piret and Declercq, 1978) does show that two distinct phosphate groups are present, both of which have no symmetry.

Conclusion

The identity of the material described from Merrivale quarry, Dartmoor with the 'nisaite'

from Nisa, Portugal, has been established by X-ray powder diffraction, infrared spectroscopic and optical methods. Comparison of the X-ray and optical data with those published for the type phurcalite, and of those of the Shale Hills material show their close similarity, and the analyses of the Dartmoor material correspond with those published for phurcalite except for a small amount of arsenic substitution in the Dartmoor material.

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References

- Chew, R. T. (1982) *California Geology*, **35**(11), 246–47.
 Deliens, M. and Comblain, G. (1978) *Bull. Soc. belge Géologie*, **87**, 225–6.
 Deliens, M. and Piret, P. (1978) *Bull. Minéral.* **101**, 356–8.

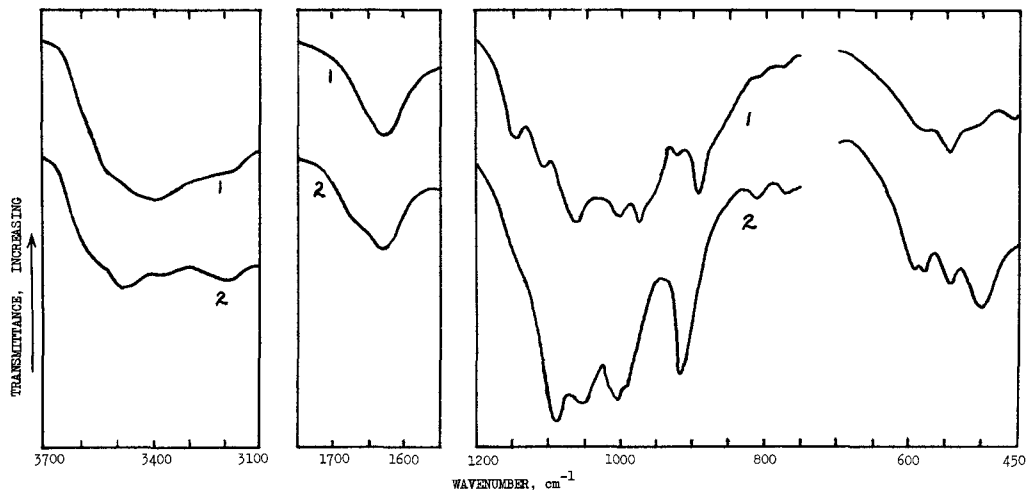


FIG. 3. Infrared spectra of phurcalite and phosphuranylite. 1. Phurcalite, Merrivale quarry, Devon. Off specimen RWT. 2. Phosphuranylite, Tarabau opencut trial, Alto Alentejo, Portugal. Off RSWB 69-247. Larger sample than 1.

TABLE 4. Infrared absorption maxima and assignments for phurcalite and phosphuranylite.

Absorption maxima, cm^{-1}			Assignments
1	2	3	
3400 s, br (3180) w	*	3470 s** 3190 m, br	} O-H stretch
1625 m, br	*	1630 m, br	
1148 m	1150	1087 vs	} H-O-H "scissor" bend
1110 ms	1105	1050 s	
1063 s	1070	1002 s	} $\text{PO}_4 \nu_3$ unsymmetrical stretch, $\text{PO}_4 \nu_1$ symmetrical stretch and metal-O-H bend
1000 s	*	(995) s	
970 s (945) w	970		
915 w		913 s	} $(\text{UO}_2)^{2+}$ unsymm. stretch
890 s	890	805 w 776 w	
(590) br		591 ms	} $\text{PO}_4 \nu_4$ unsymm. bend; coordinated water?
545 ms	540	581 ms 538 s	
		496 s	} Metal-OH ₂ vibration

* Strong matrix interference.

** Superimposed on a broad band centred near 3470 cm^{-1} .

s = strong, m = medium, w = weak, b = broad, v = very. Values in brackets are of shoulders.

1. Phurcalite, Merrivale quarry, Devon. Off specimen RWT.
2. Phurcalite, Shale Hills, California. Off RSWB 81-81. Very weak spectrum, matrix subtracted.
3. Phosphuranylite, Tarabau, Portugal. Off RSWB 69-247.

- Lencastre, J. de and Vairinho, M. M. (1970) *Estudo de um mineral uranífero da região de Nisa (Portugal)*. Presidência do Conselho, Junta de Energia Nuclear, Lisboa.
- Nakamoto, K. (1978) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. 3rd ed. John Wiley and Sons, New York.
- Piret, P. and Declercq, J.-P. (1978) *Acta Crystallogr.* **B34**, 1677–9.
- Roberts, A. C. (1978) *Powder Diffraction File Card* 30–285. International Centre for Diffraction Data. [Manuscript received 20 February 1989; revised 22 March 1989]