American Mineralogist, Volume 64, pages 359–361, 1979

Thadeuite, $Mg(Ca,Mn)(Mg,Fe,Mn)_2(PO_4)_2(OH,F)_2$, a new mineral from Panasqueira, Portugal[1]

ANDREW ISAACS, DONALD R. PEACOR AND WILLIAM C. KELLY

Department of Geology and Mineralogy, The University of Michigan
Ann Arbor, Michigan 48109

Abstract

Thadeuite occurs as a massive coarse-grained yellow-orange mineral in specimens from selvages of the hydrothermal vein system at Panasqueira, Portugal. It is associated with fluorapatite, wolfeite, the OH-bearing equivalent of isokite, althausite, topaz and quartz. It is optically biaxial, negative, $\alpha = 1.568$, $\beta = 1.597$, $\gamma = 1.600$, $2V = 33°$, non-pleochroic. The averaged formula, normalized to a total of six cations, is $Mg(Ca_{0.96}Mn^{2+}_{0.04})(Mg_{1.20}Fe^{2+}_{0.58}Mn^{2+}_{0.24})P_{1.98}O_{7.94}(OH_{1.54}F_{0.46})$. The density is 3.25 g cm^{-3} (obs), and the hardness is slightly less than 4. The mineral is orthorhombic, space group $C222_1$, with $a = 6.412(3)$, $b = 13.563(8)$, $c = 8.545(5)$A. The strongest lines in the powder pattern are: 3.61(16), 3.38(100), 3.00(31), 2.793(31), 2.626(23), 2.158(18). The name is in honor of Professor Décio Thadeu of the Instituto Superior Técnico, Lisbon, Portugal.

Introduction

The hydrothermal tin–tungsten veins of the Panasqueira mining district in central Portugal contain a variety of rare phosphate minerals that occur locally in topaz- and muscovite-rich selvages along the borders of the veins. The general geological setting is described by Thadeu (1951) and in Conde *et al.* (1971), and the general mineralogy of the veins is summarized by Bloot and de Wolf (1953), Orey (1967), and Gaines and Thadeu (1971).

Superb crystals of apatite are widespread in the veins and "triplite" has been previously reported (Gaines and Thadeu, 1971), but a relatively rare and chemically unique assemblage of other phosphates was discovered during recent electron microprobe analyses of the ores. One of the unusual phases qualitatively appeared to be a new Mg,Ca,Fe,Mn fluophosphate, and subsequent detailed studies have confirmed that it is indeed a new mineral. We have named it thadeuite in honor of Professor Décio Thadeu of the Instituto Superior Técnico, Lisbon, Portugal, in recognition of his contributions to the study of the geology and ore deposits of Portugal. The mineral and the name have been approved by the IMA Commission on New Minerals and Mineral Names. Type material is present in the collections of the Smithsonian Institution (NMNH #143141) and Department of Geology and Mineralogy, The University of Michigan, Ann Arbor, Michigan.

Physical properties

Thadeuite occurs as massive, coarse-grained cleavable material with a vitreous luster. It is translucent yellow-orange in hand specimen and is distinguished from the more common and associated wolfeite by the latter's deeper salmon-orange color. It has a very good {010} cleavage in hand specimen, and in thin section two perpendicular cleavages are observed. The grains show a low birefringence and are non-pleochroic. Thadeuite is biaxial, negative, $\alpha = 1.568$, $\beta = 1.597$, $\gamma = 1.600$, $2V = 33°$, with the crystallographic orientation $a = \gamma$, $b = \beta$, $c = \alpha$. $2V$ was measured with an accuracy of ±2° using Tobi's method as described by Bloss (1961, p. 205–206). The β and γ refractive indices were measured on a single grain mount and are accurate to ±0.002. The α refractive index was calculated from the observed values of β, γ and $2V$. The specific gravity of thadeuite is 3.21 (calc) and 3.25±0.01 (obs) (by suspension in a solution of methylene iodide and acetone; the density of the matching liquid was measured by pycnometer). The Mohs' hardness is slightly less than four, and the

---

[1] Contribution No. 346 from the Mineralogical Laboratory, Department of Geology and Mineralogy, The University of Michigan, Ann Arbor, Michigan 48109.

0003–004X/79/0304–0359$02.00

streak is white. Thadeuite is non-fluorescent in ultraviolet radiation and exhibits no cathodoluminescence in the electron microprobe, and can thus be readily differentiated from associated fluorescent apatite.

X-ray crystallography

Weissenberg and precession X-ray diffraction methods were used to determine the unit-cell parameters and space group, with the final unit-cell dimensions obtained by least-squares refinement of powder-diffraction data. Thadeuite is orthorhombic, extinctions being consistent with only one possible space group, $C222_1$. Unit-cell parameters are a = 6.412(3), b = 13.563(8), and c = 8.545(5)A. Powder-diffraction data (Table 1) were obtained with a Norelco powder diffractometer, Cu*Kα* radiation, a graphite monochrometer, and Si as an internal standard.

Table 2. Electron microprobe analyses of thadeuite

	#1		#2		#3	
	Wt %	Atoms/Cell	Wt %	Atoms/Cell	Wt %	Atoms/Cell
CaO	14.7	3.8	14.7	3.9	14.6	3.8
MnO	5.7	1.2	5.9	1.2	5.2	1.1
FeO	10.9	2.2	12.1	2.5	10.9	2.2
MgO	24.6	8.9	23.7	8.7	24.7	9.0
P_2O_5	38.9	8.0	38.4	8.0	38.9	8.0
F	2.4	1.8	2.4	2.1	2.4	1.8
OH*	7.2	6.2	6.8	5.9	7.2	6.2
	104.4		104.0		103.9	
Less O for OH,F	4.4		4.2		4.4	
	100.0		99.8		99.5	

*OH calculated assuming P:(OH,F) is 1:1.

Table 1. Powder-diffraction data for thadeuite

d(Obs)	d(Calc)	hkl	I/I_0	d(Obs)	d(Calc)	hkl	I/I_0
6.78	6.78	020	2	1.808	1.808	044	5
5.31	5.31	021	3		1.806	261	
4.79	4.80	111	4	1.770	1.771	063	5
4.25	4.27	002	4	1.720	1.720	224	8
3.68	3.69	130	5	1.701	1.701	172	10
3.61	3.61	022	16	1.696	1.696	313	11
3.38	3.39	131	100		1.696	262	
	3.39	040			1.695	080	
3.00	3.00	201	31	1.679	1.679	350	2
2.899	2.898	220	3	1.663	1.663	081	4
2.793	2.795	132	31	1.659	1.657	025	3
2.742	2.745	221	7	1.599	1.599	333	4
2.626	2.626	023	23	1.576	1.576	082	2
2.562	2.564	202	6		1.576	401	
	2.557	113			1.575	244	
2.396	2.399	222	5	1.554	1.554	173	3
	2.398	151			1.553	064	
2.328	2.330	240	4	1.535	1.535	421	4
2.249	2.248	241	5	1.509	1.508	205	2
2.185	2.185	061	18				
				1.499	1.501	402	5
2.155	2.157	152	6		1.499	280	
2.112	2.111	310	9	1.446	1.446	353	5
2.050	2.050	311	5		1.446	191	
	2.046	242					
2.031	2.032	223	7	1.412	1.414	282	6
					1.411	155	
2.005	2.005	114	7	1.399	1.401	174	4
1.931	1.932	330	5		1.397	264	
1.879	1.878	153	10		1.397	403	
1.850	1.849	134	7				

Crystal chemistry

Electron microprobe analyses of thadeuite (Table 2) were made on an ARL-EMX instrument with three wavelength-dispersive spectrometers and an Ortex current digitizer to compensate for beam current fluctuations during data collection. Standards were: apatite for Ca, P, F; clinopyroxene for Fe, Mg; synthetic tephroite for Mn. The analyses were made with a 0.02 μA specimen current and 12 kV excitation potential using LiF, PET, and TAP crystal spectrometers. Drift, atomic number, fluorescence and absorption corrections were applied to the raw data using the program EMPADR VII (Rucklidge and Gasparrini, 1969).

The cell contents were calculated from the results of the chemical analyses and measured density. The results indicated that there are 8 P per unit cell, and we therefore normalized the atomic ratios to 8P (Table 2). The ideal formula of thadeuite, with Z = 4, is $Mg(Ca,Mn)(Mg,Fe,Mn)_2(PO_4)_2(OH,F)_2$, iron and manganese divalent, Ca>Fe>Mn and OH>F. In our specimens the ratio Fe:Mn is about 2:1, and our hypothesized end-member formula for thadeuite is $MgCa(Mg,Fe)_2(PO_4)_2(OH,F)_2$.

Equipoints of space group $C222_1$ are of ranks 8 and 4. Results of a crystal-structure analysis of thadeuite (in preparation) indicate that (1) nearly half of the Mg is ordered on an equipoint of rank 4; (2) all of the Ca and some Mn occupy the other special equipoint of rank 4; (3) the remainder of the Mg and Mn and all of the Fe are on a general equipoint; (4) the P, O, and halide sites are all of rank 8. The formula we have chosen for thadeuite is consistent with these results.

The atomic ratios of thadeuite are similar to those of a number of other phosphates in that the ratio of octahedrally-coordinated cations to P is 2:1 and the ratio P:(OH,F) is unity. Other phosphates of this general formula occurring with thadeuite are wolfeite–wagnerite, the hydroxyl-bearing equivalent of isokite, and althausite. A close relation between the cell parameters of the above phases and other members of the sarkinite and tilasite groups and those of thadeuite indicates a structural relationship among these phases, in addition to the chemical similarities.

Association and paragenesis

Thadeuite occurs in only two of several hundred vein specimens gathered throughout the mine, these two samples coming from a vein located near the intersection of Panel 17 with Drift 15W, just below level 0 of the mine. Thadeuite comprises about half of the larger specimen, which is about 2 centimeters in diameter, but in the other it occurs as exceedingly small grains only detectable with the electron microprobe.

Thadeuite is intergrown with fluorapatite and the hydroxyl-containing equivalent of isokite. Other minerals in the complex assemblage include wolfeite, topaz, quartz, muscovite, sphalerite, chalcopyrite, pyrrhotite, siderite, arsenopyrite, minor chlorite, and rare althausite and vivianite. This general phosphate-rich assemblage is found frequently along the edges of the veins, but thadeuite is very rare. All phases reported have been identified using standard optical, powder X-ray diffraction and electron-microprobe techniques.

The wolfeite proved to be approximately wolfeite$_{80}$ in the solid-solution series with wagnerite. Normalized to three cations, the formula is $(Fe^{2+}_{0.86}Mn^{2+}_{0.72}Mg_{0.41}Ca_{0.01})PO_4(OH_{0.66}F_{0.34})$. In several specimens, including those with thadeuite, near end-member wagnerite rather than wolfeite is present. The hydroxyl-bearing isokite has the formula $Ca_{0.98}(Mg_{1.01}Fe^{2+}_{0.01})PO_4(OH_{0.72}F_{0.28})$, also normalized to three cations. The apatites exhibit a range of crystal form, degree of growth zonation, and color (see also Gaines and Thadeu, 1971). They are stoichiometric $Ca_5(PO_4)_3F$ to the instrumental limits of detection, using a Kevex energy-dispersive detector combined with a Northern multi-channel analyzer in conjunction with the electron microprobe. Electron microanalyses also suggest that still other new but as yet uncharacterized phosphate minerals are present in small amounts in specimens examined, which may also be related crystal-chemically to the other phosphates.

The thadeuite formed at an intermediate stage in the hydrothermal vein-filling sequence at Panasqueira and, in the specimens available, it formed after associated topaz, quartz, and sphalerite and prior to deposition of vein siderite. It is a primary phosphate in the sense that it formed by direct crystallization from the vein fluids rather than by replacement or alteration of any pre-existing phosphate or other mineral.

The new mineral contains excellent fluid inclusions, some evidently primary, and all of a simple hydrothermal type (liquid + vapor ± minute amounts of some opaque daughter mineral) similar to those found in all the hypogene vein minerals. Heating and freezing tests were not performed on these inclusions *per se,* but extensive inclusion data on the older quartz and topaz and the younger siderite (Kelly, 1974) serve to bracket the conditions of thadeuite deposition to temperatures within a range of 230–360°C and to pressures in the range of about 100–1000 bars. The vein fluids from which thadeuite crystallized were NaCl-dominant brines (*ca.* 5–10 equivalent weight percent NaCl) of very low (less than 1 mole percent) carbon dioxide content.

Acknowledgments

We are grateful to Professor Thadeu for his efforts in collecting and sending to us samples of the phosphate assemblage at Panasqueira.

References

Bloot, C. and L. C. M. de Wolf (1953) Geological features of the Panasqueira tin-tungsten ore occurrence (Portugal). *Bol. Soc. Geol. Portugal, 11,* 1–58 (Porto).

Bloss, F. D. (1961) *An Introduction to the Methods of Optical Crystallography.* Holt, Rinehart and Winston, New York.

Conde, L. N., V. Pereira, A. Ribeiro and D. Thadeu (1971) *Jazigos hipogénicos de estanho e volfrâmio.* Guidebook of excursion No. 7, Congresso Hispano-Luso-Americano de Geol. Econ., Sept. 19–25, 1971, Direcção -Geral de Minas e Serv. Geol., Lisboa.

Gaines, R. V. and D. Thadeu (1971) The minerals of Panasqueira, Portugal. *Mineral. Rec., 2,* 73–78.

Kelly, W. C. (1974) Panasqueira, Portugal—an unorthodox case of hydrothermal tin–tungsten mineralization. *Econ. Geol., 69,* 1182.

Orey, F. C. d' (1967) Tungsten–tin mineralization and paragenesis in the Panasqueira and Vale da Ermida mining districts, Portugal. *Comm. Serv. Geol. Portugal, 52,* 117–167.

Rucklidge, J. C. and E. L. Gasparrini (1969) *Specifications of a Complete Program for Processing Electron Microprobe Data: EMPADR VII.* Department of Geology, University of Toronto.

Thadeu, D. (1951) Geologia do couto mineiro de Panasqueira. *Comm. Serv. Geol. Portugal, 32,* 5–64.

Manuscript received, June 29, 1978;
accepted for publication, October 2, 1978.