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MITRIDATITE FROM THE SAN LUIS GRANITIC PEGMATITE, LA FLORIDA, ARGENTINA

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Abstract

An unusual coarse-grained sample of mitridatite from a granitic pegmatite is described. The mineral was found in three pieces of a fragmented nodule ~10–20 cm, in the dumps of the San Luis mine, La Florida, Argentina. Similar nodules of primary triphylite–lithiophilite altered to ferrisicklerite and dufrénite are included in quartz from the core-margin association of the rare-element-enriched, spodumene-bearing granitic pegmatite. Mitridatite is very dark green, almost black, has a dull pale green streak and deep ruby red internal reflections. It has very good {100} cleavage, vitreous luster, a density of 3.221 g/cm^3 and a Mohs hardness of 5 to 5.5. The three strongest X-ray powder-diffraction lines [*d* in Å(I)(*hkl*)] are: 8.70(100)(200), 2.901(80)(600), and 2.176(60)(800). The refined unit-cell parameters are: *a* 17.505(1), *b* 19.327(3), *c* 11.261(6) Å, β 96.05(1)°, *V* 3788(1) Å^3. Optically, mitridatite is transparent, with *X* pale green, almost colorless, *Y* = *Z* dark reddish brown, biaxial (–), 2*V* ~10°, α 1.775(5), β 1.843(5), γ 1.844(5), and very strong dispersion. The chemical composition gives: CaO 17.16, Mn_2O_3 1.34, Fe_2O_3 35.26, P_2O_5 32.26, H_2O^+ 8.41, H_2O^- 0.56, Rem. 4.51, which gives $Ca_{6.01}(H_2O)_6[Fe^{3+}_{8.67}Mn_{0.33}O_{6.15}(PO_4)_{8.92}]\bullet 3.17\ H_2O$. The mitridatite is considered to have formed by hydrothermal replacement of primary triphylite.

Keywords: mitridatite, nodule, granitic pegmatite, San Luis, Argentina.

Sommaire

Nous avons découvert un nodule éclaté en trois morceaux, de diamètre ~10–20 cm, contenant la mitridatite en gros grains, ce qui est assez rare dans une pegmatite. Ce nodule se trouvait dans une pegmatite granitique à la mine de San Luis, à La Florida, en Argentine. Des nodules semblables de triphylite–lithiophilite primaires altérés à ferrisicklerite et dufrénite sont inclus dans le quartz en bordure du coeur de la pegmatite granitique, enrichie en éléments rares et cristallisant le spodumène. La mitridatite est vert très foncé, presque noire, et possède une rayure vert pâle morne et des reflets internes rouge rubis foncé. Le clivage {100} est très bon, l'éclat est vitreux, la densité, 3.221, et la dureté de Mohs, entre 5 et 5.5. Les trois raies les plus intenses du spectre de diffraction X (méthode des poudres) [*d* en Å(I)(*hkl*)] sont: 8.70(100)(200), 2.901(80)(600) et 2.176(60)(800). Nous avons affiné les paramètres réticulaires: *a* 17.505(1), *b* 19.327(3), *c* 11.261(6) Å, β 96.05(1)°, *V* 3788(1) Å^3. La mitridatite est transparente, avec with *X* vert pâle, presqu'incolore, *Y* = *Z* brun rougeâtre foncé, biaxe négatif, 2*V* ~10°, α 1.775(5), β 1.843(5), γ 1.844(5), et une très forte dispersion. Une analyse chimique a donné CaO 17.16, Mn_2O_3 1.34, Fe_2O_3 35.26, P_2O_5 32.26, H_2O^+ 8.41, H_2O^- 0.56, Rem. 4.51, ce qui mène à la formule empirique $Ca_{6.01}(H_2O)_6[Fe^{3+}_{8.67}Mn_{0.33}O_{6.15}(PO_4)_{8.92}]\bullet 3.17\ H_2O$. La mitridatite se serait formée par remplacement hydrothermal de la triphylite, primaire.

Mots-clés: mitridatite, nodule, pegmatite granitique, San Luis, Argentine.

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INTRODUCTION

During the first inspection of the San Luis granitic pegmatite, located near La Florida, San Luis province, Argentina, in the dumps of the main quarry, three pieces of a nodule of a cleavable phosphate were found. According to the optical and physical properties, and the X-ray powder-diffraction pattern, the mineral was initially classified as belonging to the robertsite–mitridatite series. For its precise characterization, a chemical analysis and X-ray diffraction analysis were carried out. The data correspond to mitridatite. Because of the infrequent occurrence of coarse-grained, good-quality samples of this mineral, we document here some of its basic properties.

REVIEW

Mitridatite is a basic calcium phosphate commonly found as a thin crust or as colloidal nodular aggregates in ferric oolitic deposits of the Kertch and Taman peninsulas, Russia, known since the beginning of the century (*e.g.*, Chukhrov *et al.* 1958, and references therein). It also is found as a product of weathering of primary ferric phosphates, mainly triphylite, in granitic pegmatites; it commonly is visible as a yellowish green stain on dump samples. Owing to the cryptocrystalline nature and the impurity of the aggregates, the determination of the chemical composition and crystalline structure had to await the discovery of exceptionally well-formed crystals, in the dumps of the White Elephant pegmatite, Black Hills, South Dakota (Moore 1974). Its composition is $Ca_6(H_2O)_6Fe^{3+}{}_9O_6(PO_4)_9)\bullet 3H_2O$; it is monoclinic (pseudotrigonal) in symmetry, and crystallizes in space group Aa, $Z = 4$ (Moore & Araki 1977).

OCCURRENCE

Mitridatite was found on the dumps of the San Luis granitic pegmatite. This deposit is located at latitude 32°59'20"S and longitude 65°59'30"W, 28 km to the north of La Florida, Totoral district, Pringles department, San Luis province, Argentina. This deposit was mined intermittently for spodumene in the past, but is not presently exploited. It consists of the juxtaposition of two different types of rare-element pegmatite: an albite–spodumene type that was synkinematically emplaced and folded, and a body of complex type, spodumene subtype, called San Luis II, emplaced in the core of folds of the former (Oyarzábal & Galliski 1993). The core-margin association of the San Luis II pegmatite contains phosphate nodules of triphylite–lithiophilite solid solution, generally up to 20 cm in diameter. The primary minerals are usually hydrothermally altered to ferrisicklerite and dufrénite.

In the dumps of the mine workings of the San Luis II pegmatite, three triangular pieces of a phosphate nodule with external borders of quartz were found. The curvature of the external border of the fragments suggests that they belong to a nodule 10–20 cm in diameter. Each fragment has 5–7 cm of mitridatite. The external border of the fragments consists of a layer of brownish microcrystalline quartz, in places with crystal-lined vugs.

PHYSICAL AND OPTICAL PROPERTIES

Mitridatite occurs in massive, very dark green, almost black aggregates. It has a dull pale green streak, and perfect {100} cleavage in blades radiating from the core of the nodule. The chips show deep ruby red internal reflections, visible to the naked eye. The measured Mohs hardness is 5 to 5.5. The density, measured with a Berman balance using single fragments, is 3.221 g/cm³, in good agreement with 3.24(2) g/cm³ determined with heavy liquids by Moore (1974). The mineral has a few impurities of oxide minerals. In polished section, these seem to be coatings of secondary Mn-oxides. The mitridatite contains some apatite, as is indicated by some peaks in the X-ray-diffraction diagrams. The mineral is not fluorescent under short or longwave ultraviolet light. The optical properties were determined with a spindle stage and Cargille inmersion liquids. The data obtained are shown in Table 1.

TABLE 1. OPTICAL PROPERTIES OF MITRIDATITE FROM THE SAN LUIS GRANITIC PEGMATITE, ARGENTINA

	1	2
	Biaxial (–)	Biaxial (–)
α	1.775(5)	1.785
β	1.843(5)	1.85
γ	1.844(5)	1.85
X	very pale green	pale greenish yellow
$Y = Z$	dark reddish brown	deep greenish brown
$2V$	~10°	5° – 10°
Dispersion	very strong	—

Samples: 1. This paper, 2. Moore (1974), crystals from the White Elephant granitic pegmatite, Black Hills, South Dakota.

X-RAY DIFFRACTION

X-ray powder diagrams of mitridatite were recorded using Cu radiation (30 kV, 40 mA) with a Philips 1710 diffractometer at the Department of Geological Sciences, University of Manitoba. Annealed CaF_2 (a 5.46379 Å) was used as an internal standard. Table 2 shows the results obtained. The interplanar spacings were used for the unit-cell parameter calculations with the CELREF program (Appleman & Evans 1973). Results are compared with those of Moore (1974) for the White Elephant material in Table 2.

TABLE 2. POWDER-DIFFRACTION DATA FOR MITRIDATITE FROM THE SAN LUIS GRANITIC PEGMATITE, ARGENTINA

I_{obs}	d_{obs}	d_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	hkl
100	8.70	8.70	200	1	2.215	2.215	$\bar{5}33$
26	5.58	5.58	031	60	2.176	2.176	800
50	4.35	4.35	400	1	2.102	2.102	$\bar{3}82$
1	3.46	3.459	$\bar{2}42$	1	2.061	2.064	$\bar{7}33$
15	3.22	3.221	060	12	1.907	1.907	$\bar{5}82$
1	3.020	3.020	$\bar{2}60$	1	1.740	1.740	$\underline{10}00$
80	2.901	2.901	600	13	1.614	1.614	$\underline{10}02$
18	2.780	2.780	$\bar{1}62$	1	1.588	1.587	$\bar{9}71$
50	2.734	2.734	162	12	1.551	1.551	$\bar{3}\underline{11}3$
1	2.624	2.624	153	1	1.475	1.475	$\overline{\underline{11}}33$
20	2.570	2.569	$\bar{3}62$	1	1.451	1.450	$\underline{12}00$
1	2.464	2.463	$\bar{7}11$	1	1.408	1.408	$6\underline{12}0$

The unit-cell parameters calculated from the above data: *a* 17.505(1), *b* 19.327(3), *c* 11.261(6) Å, β 96.05(1)°, *V* 3788 Å^3. For comparison, the parameters of mitridatite from the White Elephant granitic pegmatite (Moore 1974) are: *a* 17.553(2), *b* 19.354(3), *c* 11.248(2) Å, β 95.84(1)°.

CHEMICAL ANALYSIS

According to a preliminary X-ray fluorescence spectrum, the major components were found to be Ca, Fe and Mn, whereas Sr, Zn, Cu and As are present at trace levels. A strong positive reaction was obtained with the ammonium molybdate test for phosphate. After the determination of H_2O^+ and H_2O^-, the dehydrated samples were dissolved in 1:3 HCl; the small insoluble residue was mainly granular quartz, pale pink in color. Ca, Fe, and Mn contents were established by atomic absorption spectroscopy, with La added in the first case (Ca) to minimize the interference of phosphate, and using the addition of standard solutions for the other two elements to check the matrix effect. The proportion of phosphate was determined by spectrophotometry with molybdo-vanadate. The results are presented in Table 3. The following structural formulae, based on the structure determined by Moore & Araki (1977), is $Ca_{6.01}(H_2O)_6[Fe^{3+}_{8.67}Mn_{0.33}O_{6.15}(PO_4)_{8.92}]\cdot 3.17\ H_2O$. This formula is more plausible than the one calculated according to Moore's earlier proposals (1974, 1976).

TABLE 3. CHEMICAL COMPOSITION OF MITRIDATITE, SAN LUIS GRANITIC PEGMATITE, ARGENTINA

	SL	WE		SL	WE
CaO wt.%	17.16	15.7	As_2O_5	–	–
Mn_2O_3	1.34	2.4	H_2O^+	8.41	11.5
Fe_2O_3	35.26	32.1	H_2O^-	0.56	
P_2O_5	32.26	28.4	Rem.	4.51	10.5
			Total	99.50	100.6

Analysts: San Luis (SL) material: I.L. de Upton, White Elephant (WE) material: Jun Ito.

ORIGIN

The genesis of mitridatite has been principally ascribed to alteration processes operating in low-temperature environments, such as weathering of primary iron phosphates in dumps of granitic pegmatites, alteration of oolitic sedimentary iron ore deposits, or development of stains in ferruginous soils and rocks impregnated with organic remains (Moore 1973, Moore & Araki 1977). Mitridatite also occurs as a late-stage product of porous, altered triphylite. The massive, coarse-grained appearance of the San Luis mitridatite suggests that it was formed by a late-stage hydrothermal replacement of primary triphylite.

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