

Serrabrancaite, $\text{MnPO}_4 \cdot \text{H}_2\text{O}$, a new mineral from the Alto Serra Branca pegmatite, Pedra Lavrada, Paraíba, Brazil

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ABSTRACT

Serrabrancaite is a new manganese phosphate from the Alto Serra Branca pegmatite near Pedra Lavrada, Paraíba, Brazil. The mineral occurs as dark brown to dark greenish black isometric crystals up to 0.3 mm size. The crystals have an adamantine luster and are translucent. Chemical analysis yields (in wt%) $\text{Mn}_2\text{O}_3 = 46.85$, $\text{P}_2\text{O}_5 = 42.72$, $\text{H}_2\text{O} = 9.8$, total = 99.37. The empirical formula is $\text{Mn}_{0.98}\text{P}_{1.00}\text{O}_{3.98} \cdot 0.90 \text{H}_2\text{O}$, simplified to $\text{MnPO}_4 \cdot \text{H}_2\text{O}$. Serrabrancaite is monoclinic, space group $C2/c$, with unit-cell parameters $a = 6.914(2)$, $b = 7.468(2)$, $c = 7.364(2)$ Å, $\beta = 112.29(3)^\circ$, $V = 351.8(1)$ Å³. The measured density is 3.17(1) g/cm³, the calculated density for $Z = 4$ is 3.16 g/cm³. Serrabrancaite is isostructural with the sulfates of the kieserite group. The mineral is an alteration product from a phosphate pegmatite and is accompanied by vernadite and phosphosiderite.

INTRODUCTION

The Alto Serra Branca granitic pegmatite lies approximately 10 km southwest of the village Pedra Lavrada in the state of Paraíba, Brazil. The pegmatite has been mined since the early 1940s principally for tantalite. In the course of research on the minerals of this pegmatite body a new hydrous manganese phosphate mineral was observed.

The mineral and the name were approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association (vote 98-006). The name serrabrancaite is for the type locality. Type specimens are deposited in the Mineralogical Collection of the Bergakademie Freiberg, Germany (No. 78025) and in the Mineralogical Collection of the Martin-Luther Universität Halle, Institut für Geologische Wissenschaften (No. 010355).

OCCURRENCE AND PARAGENESIS

The Alto Serra Branca pegmatite intruded into biotite schist of the Precambrian Equador Formation. The complete extent of this pegmatite is not known, as the western part is cut by a hillside, whereas the eastern continuation of the body is hidden within the same hill with no outcrop exposed. The center of the pegmatite is visible today with an estimated diameter of about 25 m across.

The pegmatite consists mainly of quartz (sometimes of bluish colour), microcline and muscovite, with minor amounts of

albite and amblygonite. Additional minerals are apatite, beryl, uraninite, elbaite, members of the tantalite group, and secondary uranium minerals. Also, in the central part of the body isolated pods and masses occur of either primary Mn-poor triphylite or Fe-poor triplite, each of them up to several tons of weight. Purpurite, rockbridgeite, tavorite, barbosalite, hureaulite, eosphorite, phosphosiderite, and several others were observed as alteration products of these phosphates. An unusual association of carlhintzeite, colquiriite, pachnolite, ralstonite, and fluellite is also observed. Serrabrancaite is an alteration product of triplite and was found in close association with vernadite.

PHYSICAL AND OPTICAL PROPERTIES

Serrabrancaite occurs as equant or short-prismatic crystals up to 0.3 mm size (Figs. 1 and 2). The color of the mineral is dark brown to dark greenish black, the streak is olive green. The crystals have an adamantine luster and are translucent in thin fragments. Serrabrancaite is brittle and shows an uneven fracture. No cleavage was discernible. The Mohs hardness is 3½. The density, measured by the float-sink method using sodiumpolytungstate solution, is 3.17(1) g/cm³ (mean of four determinations on one crystal), which is very near the calculated density 3.16 g/cm³.

Refractive indices $\alpha = 1.75(1)$ and $\beta = 1.79(1)$ were measured at a wavelength 589 nm using immersion liquids. The third refractive index γ is > 1.79 , but could not be measured with accuracy. Serrabrancaite shows pleochroism from dark brown to olive greenish-brown.

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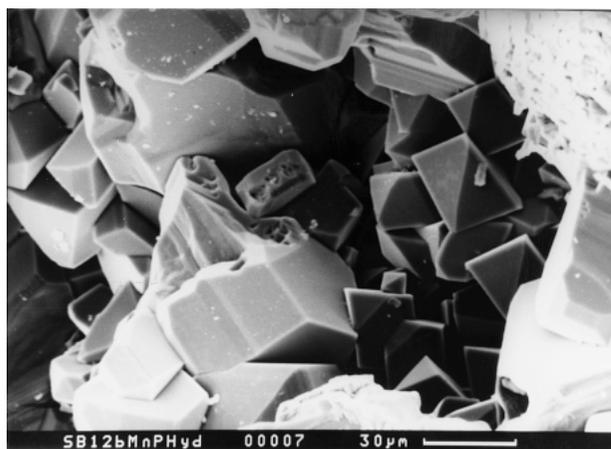


FIGURE 1. SEM micrograph of serrabrancaite.

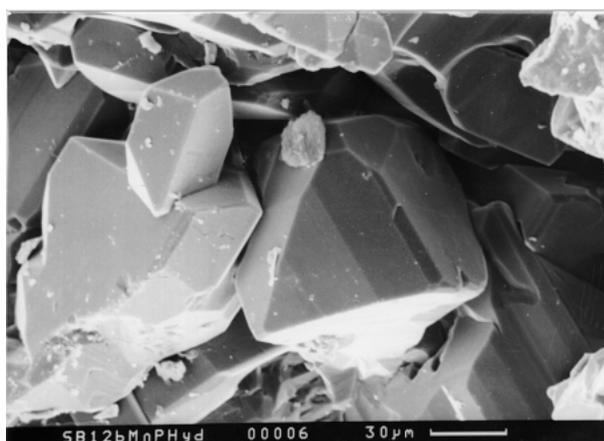


FIGURE 2. SEM micrograph of serrabrancaite.

MINERAL CHEMISTRY AND THERMAL ANALYSIS

Chemical analyses of the new mineral have been performed by means of energy-dispersive (EDS) as well as wavelength-dispersive (WDS) X-ray spectrometry. An EDS spectrum revealed Mn, P, and O as the only elements present (measured at the Institut für Geologische Wissenschaften, Halle, Germany). Traces of Fe were observed in a few crystals. A sample virtually free from Fe was chosen for WDS analysis. The data were obtained with a CAMECA SX 100 electron microprobe operated at an acceleration voltage of 15 kV and a beam current of 10 nA with rhodonite (Mn) and apatite (P) as standards (Institut für Mineralogie, Kristallographie und Materialwissenschaft, Leipzig, Germany). For data reduction the PAP corrections (Pouchou and Pichoir 1988) were used. The analyses were performed on four different spots of the selected grain. The results of the analyses are given in Table 1.

The thermal analysis of serrabrancaite was done at the Institut für Geologische Wissenschaften, Halle, Germany. The mineral shows a weight loss of 14.6 wt% at 520 °C in one step (Fig. 3). The weight loss is accompanied by a change of colour from dark greenish black to pale yellowish white. X-ray diffraction analysis showed that the reaction product is $Mn_2P_2O_7$. According to the reaction



the theoretical weight loss is 15.48% (4.76% from O_2 and 10.72% from H_2O). This corresponds well with the observed weight loss of 14.6 wt% (4.8% from O_2 and 9.8% from H_2O) of the Serra Branca material. For synthetic $MnPO_4 \cdot H_2O$, a similar weight loss reaction and transformation into $Mn_2P_2O_7$ is also

TABLE 1. Chemical composition in wt% of serrabrancaite

Component	I	II	III	IV	Average	Theoretical
Mn_2O_3	46.73	46.89	47.21	46.57	46.85	47.01
P_2O_5	41.16	43.22	43.22	43.29	42.72	42.27
H_2O^*					9.80	10.72
Total					99.37	100.00

* From thermal analysis.

described by Lightfoot et al. (1987).

The empirical formula for serrabrancaite calculated on $P = 1$ from the microprobe and thermal analyses is $Mn_{0.98}P_{1.00}O_{3.98} \cdot 0.90 H_2O$. This is near the ideal composition $MnPO_4 \cdot H_2O$.

X-RAY POWDER DIFFRACTION

The X-ray powder diffraction pattern was recorded by a Siemens D5000 diffractometer with $CuK\alpha$ radiation and a secondary monochromator. Peaks were indexed using the data from synthetic material (Lightfoot et al. 1987). Analysis of the powder diffraction data from the Serra Branca sample (Table 2) yields a monoclinic cell with $a = 6.914(2)$, $b = 7.468(2)$, $c = 7.364(2)$ Å, $\beta = 112.29(3)^\circ$, $V = 351.8(1)$ Å³.

A structure analysis of synthetic material yielded the space group $C2/c$ and a cell $a = 6.912(1)$, $b = 7.470(1)$, $c = 7.357(1)$ Å, $\beta = 112.3^\circ$, and $Z = 4$ (Lightfoot et al. 1987). The structure analysis of a crystal from the Alto Serra Branca pegmatite confirmed the space group $C2/c$ and the lattice parameters (Schuckmann and Joswig, personal communication).

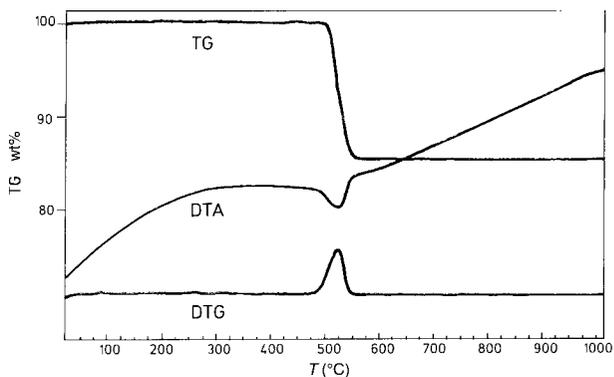


FIGURE 3. Thermal analysis of serrabrancaite. TG = thermogravimetry, DTG = derivative thermogravimetry, DTA = differential thermal analysis. The vertical scale applies only to the TG analysis.

TABLE 2. Powder diffraction data of serrabrancaite

<i>hkl</i>	serrabrancaite, MnPO ₄ ·H ₂ O			MnPO ₄ ·H ₂ O, synthetic	
	<i>l</i> _{meas.}	<i>d</i> _{meas.}	<i>d</i> _{calc.}	<i>l</i> _{meas.}	<i>d</i> _{meas.}
1 1 0	12	4.856	4.858	36	4.866
1 1 1	15	4.633	4.637	52	4.647
0 2 0	2	3.732	3.734	7	3.735
1 1 1	100	3.503	3.506	100	3.511
0 2 1	10	3.271	3.275	36	3.273
2 0 2	10	2.957	2.958	35	2.961
2 2 1	9	2.530	2.530	19	2.534
0 2 2	19	2.516	2.517	47	2.518
1 1 2				3	2.478
2 2 0	1	2.429	2.429	5	2.433
1 3 0				2	2.324
1 3 1	3	2.296	2.295	8	2.297
3 1 1	5	2.197	2.197	12	2.201
2 2 1	12	2.104	2.104	20	2.108
3 1 0	2	2.054	2.050	5	2.055
2 0 2	5	1.985	1.986	7	1.988
0 2 3	1	1.939	1.940	2	1.943
3 1 3	5	1.906	1.907	11	1.909
1 1 3	5	1.861	1.862	8	1.864
2 2 2	6	1.753	1.753	5	1.755
1 3 3	1	1.742	1.747		
4 0 2	2	1.720	1.720	3	1.724
0 0 4	1	1.702	1.703	2	1.705
0 4 2	3	1.638	1.637		
2 2 4	7	1.633	1.633	16	1.635
3 3 0	2	1.620	1.619		
2 4 0	4	1.613	1.612	8	1.615
4 0 0	4	1.599	1.599	6	1.602
2 4 2				2	1.581
4 2 2	3	1.562	1.562	5	1.565
4 2 1	1	1.533	1.533		
3 3 3	4	1.546	1.546	8	1.548
1 3 3	7	1.521	1.522		
2 4 1	1	1.506	1.506		
4 2 3	1	1.495	1.495		
3 3 1	2	1.483	1.482		
4 2 0	1	1.470	1.470		
2 2 3	1	1.462	1.462		
1 5 0	1	1.454	1.455		
0 4 3	2	1.443	1.442		
1 1 5	1	1.426	1.423		
1 5 1	1	1.399	1.398		
3 1 5	1	1.393	1.393		
4 2 4	2	1.375	1.375		

* Aranda (1993).

RELATIONSHIP TO OTHER MINERALS

Serrabrancaite shows no isostructural relation to any natural phosphate, arsenate, or vanadate mineral. Besides the above described synthetic equivalent of serrabrancaite, there also exists a synthetic arsenate analogue (Aranda 1993). According to Lightfoot (1987) the sulfates of the kieserite group are isostructural with the MnPO₄·H₂O. Kieserite, MgSO₄·H₂O, as well as the related Mn, Fe, Ni, Cu, and Zn minerals szmikite, szmolnokite, dwornikite, poitevinite, and gunningite, are monoclinic, space group *C2/c* (or in another orientation *A2/a*). The X-ray diffraction patterns of these sulfates are similar to that of serrabrancaite. The relation of serrabrancaite to synthetic MnPO₄·H₂O, synthetic MnAsO₄·H₂O, and kieserite is shown in Table 3.

TABLE 3. Relationship of serrabrancaite to synthetic MnPO₄·H₂O, synthetic MnAsO₄·H₂O and kieserite

	Serrabrancaite MnPO ₄ ·H ₂ O	Synthetic* MnPO ₄ ·H ₂ O	Synthetic* MnAsO ₄ ·H ₂ O	Kieserite† MgSO ₄ ·H ₂ O
space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	6.914	6.928	7.041	6.921
<i>b</i> (Å)	7.468	7.478	7.838	7.611
<i>c</i> (Å)	7.364	7.372	7.477	7.511
β	112.29°	112.30°	112.14°	116.17°
Z	4	4	4	4

* Aranda (1993).

† Powder diffraction role no. 33-882.

The structure of MnPO₄·H₂O is built up of chains of corner-sharing (MnO₆)-octahedra running in the [101] direction. The chains are connected by (PO₄)-tetrahedra (Lightfoot et al. 1987). Schubnelite, FeVO₄·H₂O, is triclinic and has a different arrangement of the (FeO₆)-octahedra and vanadate tetrahedra (Schindler and Hawthorne 1999).

ORIGIN OF THE MINERAL

The Serra Branca pegmatite is characterized by two different phosphate associations. Triphylite and its secondary minerals, like hureaulite, tavorite and barbosolite, are very rich in iron and poor in manganese, whereas triplite and its secondary minerals are very rich in manganese and poor in iron. The minerals represent almost the end-member or near end-member compositions. This is significantly different to the Hagendorf/Germany or Mangualde/Portugal phosphate pegmatites with solid solutions between Mn and Fe analogues (Wegner et al. 1998).

Serrabrancaite is an alteration product of triplite and therefore shows a very low iron content. The vernadite in this paragenesis is also practically free of iron.

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