Staringite, a new Sn–Ta mineral from north-eastern Brazil

E. A. J. BURKE

Institute for Earth Sciences, Free University, Amsterdam

C. KIEFT

Netherlands Organization for the Advancement of Pure Research

R. O. FELIUS

Geological and Mineralogical Institute, University of Leiden

MARIA S. ADUSUMILLI

Escola de Geologia, Recife

SUMMARY. Staringite, $(Fe,Mn)_{0.5}(Sn,Ti)_{4.5}(Ta,Nb)_{1.0}O_{12}$, occurs as inclusions in tapiolite from pegmatites at Seridózinho and Pedra Lavreda, Paraiba State, NE. Brazil. An indexed powder pattern is presented. The mineral is tetragonal with a 4·742 Å and c 9·535 Å, and most probably has a 'tri-rutile' structure. Electron-microprobe analysis yielded Ta_2O_5 21·5 %, Nb_2O_5 1·8, SnO_2 73·3, TiO_2 0·03, FeO 3·7, MnO 0·3, sum 100·6 %. D_{calc} 7·17. Micro-indentation hardness (load 100 g) 1033–1187 kg/mm^2; reflectivity at 470 nm (R_o) 12·8 to (R_e') 14·5 %, at 546 nm 12·1–13·9, at 589 nm 12·0–13·7, and at 650 nm 11·8–13·6; staringite is uniaxial positive.

QUALITATIVE and semi-quantitative X-ray fluorescence analyses were performed by the fourth author at the University of Lisbon on a series of Nb–Ta minerals from pegmatites in NE. Brazil. Some samples proved to contain minor tin. After a short visit to the department of mineralogy and petrology of the Institute for Earth Sciences of the Free University at Amsterdam, Mrs. Adusumilli left some samples for further study.

Subsequent investigation by light-optical, X-ray diffraction, and electron-microprobe methods showed the tin-content to be due partly to the rare mineral wodginite, partly to a new Sn–Ta mineral. This mineral was named staringite (pronounced stä-ring-ite) in honour of Dr. W. C. H. Staring (1808–77), founder of geology and mineralogy in The Netherlands. The name was approved before publication by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Type locality (Seridózinho) material is preserved at the Institute for Earth Sciences, Free University, Amsterdam, and at the Escola de Geologia, Recife.

Occurrence. The geology of the Paraiba and Rio Grande do Norte pegmatite district has been described by de Almeida *et al.* (1944) and Johnston (1945). Pre-cambrian schists and quartzites are intruded by granites, which are accompanied by thousands

of pegmatitic dikes. One type of pegmatites shows pronounced internal zoning. The Ta–Nb minerals are associated with large crystals of microcline, which occur between the muscovite walls and the quartz core of the dikes.

Tapiolite from the Seridózinho and Pedra Lavreda pegmatites (about 10 km north of the city of Joazeiro, Paraiba State) contains inclusions of staringite. This mineral usually occurs as small exsolution bodies (20–50 μm) in tapiolite (fig. 1). At Seridózinho tapiolite is intergrown with wodginite in alternating layers. Staringite then occurs as elongated exsolution fringes 10–20 μm wide and sometimes several hundred micrometres long along the contacts between tapiolite and wodginite (fig. 2).
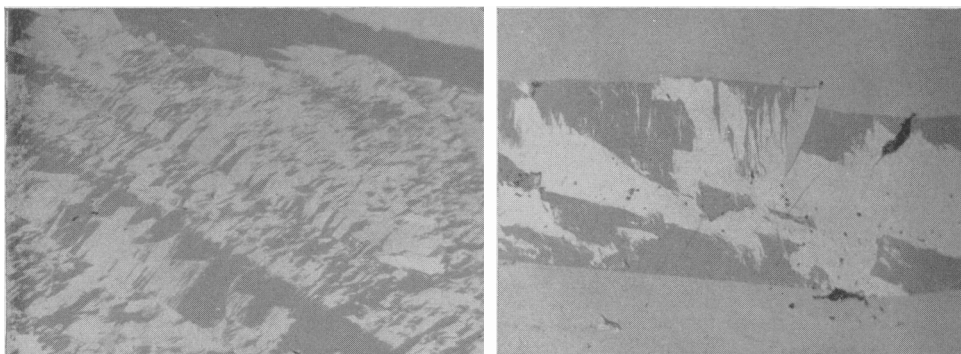
FIGS. 1 and 2: Fig. 1 (left). Seridózinho, Paraiba, Brazil. Staringite (dark grey) as exsolution bodies in tapiolite (light grey). Reflected light, oil immersion, ×220. Fig. 2 (right). Seridózinho, Paraiba, Brazil. Exsolution bodies of staringite (dark grey) in a lamella of tapiolite (light grey) included in wodginite (medium grey). Reflected light, oil immersion, ×220.

Physical and optical properties. Since staringite only was found as small inclusions in tapiolite the density could not be determined experimentally. It was calculated from the unit-cell data and the chemical analysis: $D_{calc} = 7 \cdot 17$. Under the microscope, in reflected light, staringite is dark grey (in oil); the colour is very similar to that of cassiterite; bireflection is moderately strong, the colour varying from lighter to darker grey, and the anisotropy is very distinct (different shades of grey). The internal reflections are abundant in oil (yellowish-orange to brownish-red), and sometimes obscure the anisotropy. The polishing hardness is higher than for tapiolite and wodginite. Staringite is optically homogeneous, even at the highest magnifications (up to ×2000). The associated tapiolite shows a strong bireflection, with colours varying from yellowish grey to grey with a bluish tint, and a very strong anisotropy with greenish-yellow to deep blue interference colours. The internal reflections are deep red. Twinning is present.

Micro-indentation hardness (VHN) was measured with the Leitz Durimet-Pol (Uytenbogaardt, 1966); the applied load was 100 g, and the indentation time 15 sec VHN of staringite from Seridózinho (mean minimum and maximum values of 5 indentations): 1033–1187 kg/mm². Tapiolite has a VHN of 893–959 kg/mm².

The spectral reflectivity of staringite was measured with the Leitz MPV Microscope

Photometer (Weber, 1965). Monochromatic light was obtained with a Schott continuous-running filter, type Veril B-200. The reflectivity was measured at 10 wavelengths (including the 4 standard wavelengths proposed by the IMA-Commission on Ore Microscopy) on a grain showing maximum bireflection. As standard the carborundum NPL N.2538.30 was used. For comparison the spectral reflectivities of cassiterite and tapiolite were measured (table I). Prior to the measurements the apparatus was checked for primary and secondary glare (Piller, 1967), none of which was found to be present.

TABLE I. *Reflectivities of staringite* (1) *and tapiolite* (3), *both from Seridózinho, Brazil, and of a commercial cassiterite concentrate* (2). λ *in nanometres*

λ	1		2		3		λ	1		2		3	
	R_0	R'_e	R_0	R'_e	R_0	R'_e		R_0	R'_e	R_0	R'_e	R_0	R'_e
470	12·8	14·5	11·3	13·0	16·2	17·0	570	12·1	13·8	10·8	12·3	—	—
490	12·6	14·3	11·2	12·7	—	—	589	12·0	13·7	10·7	12·1	15·2	17·1
510	12·4	14·1	11·1	12·7	—	—	610	11·9	13·7	10·7	12·1	—	—
530	12·3	13·9	11·1	12·6	—	—	630	11·9	13·6	10·7	12·1	—	—
546	12·1	13·9	10·9	12·4	15·5	17·2	650	11·8	13·6	10·5	11·9	15·0	17·0

The method described by Cameron (1963) was followed to determine the optical sign. Staringite is uniaxial positive, which is also the case for cassiterite and tapiolite.

Chemistry. Electron-microprobe[1] analyses were carried out by the second author. The following standards were used: tantalum metal for Ta, analysed lueshite for Nb, tin metal for Sn, TiO for Ti, iron metal for Fe, and analysed rhodonite for Mn. The analytical results were corrected for absorption, atomic number, and secondary fluorescence. Absorption correction was applied according to the formula of Philibert (1963) with the σ of Duncumb and Shields (1966); in this correction, the mass-absorption coefficients of Heinrich (1966) were used. Atomic number correction was divided into back-scatter factor R and retardation factor S. R was calculated by following the data of Bishop (1967), while for S the expression of Reed (1964) was applied. The formula of Reed (1965) was used for the correction of secondary fluorescence. Nine analyses were made of staringite and two of the associated tapiolite and gave (average and range):

	Ta_2O_5	Nb_2O_5	SnO_2	TiO_2	FeO	MnO	Sum
Staringite	21·5 (20·1–22·4)	1·8 (1·7–1·9)	73·3 (72·2–75·2)	0·03	3·7 (3·5–3·9)	0·3	100·6
Tapiolite	77·5 (76·7–78·3)	7·3 (7·2–7·4)	1·8 (1·3–2·3)	0·2	13·2 (13·0–13·4)	1·0 (0·9–1·0)	101·0

Crystallography. The X-ray powder diffraction diagrams were obtained with Straumanis-type 57·54-mm and 114·83-mm diameter Debye–Scherrer cameras, which were mounted on a Philips PW 1008 X-ray generator. Ni-filtered Cu-$K\alpha$ radiation (λ = 1·5418 Å) was used with 40 kV and 14 mA, and varying exposure times

---

[1] Geoscan, Cambridge Instrument Company Ltd., Cambridge, Great Britain.

(up to 24 hours). In order to reduce darkening by fluorescence the film was wrapped in Al-foil.

The small dimensions of the inclusions of staringite in tapiolite presented many problems in obtaining the powder pattern. Only one grain was sufficiently large to be drilled out without contamination with tapiolite. The small amount of powder was mixed with a drop of rubber solution and then rolled into a ball and mounted on a

TABLE II. *X-ray powder diffraction diagrams of cassiterite, staringite, and tapiolite*

Cassiterite				Staringite				Tapiolite			
I	d_{meas}	hkl	d_{calc}	I	d_{meas}	hkl	d_{calc}	I	d_{meas}	hkl	d_{calc}
—	—	—	—	2	4·75 Å	002	4·77 Å	2	4·61 Å	002	4·61 Å
—	—	—	—	3	4·23	101	4·24	3	4·24	101	4·23
8	3·36 Å	110	3·34 Å	10	3·36	110	3·35	10	3·36	110	3·36
—	—	—	—	½	2·738	112	2·743	1	2·710	112	2·715
7	2·64	011	2·64	8	2·644	103	2·640	9	2·582	103	2·582
3	2·37	020	2·36	4	2·374	200	2·371	5	2·378	200	2·376
½	2·30	111	2·30	1	2·307	113	2·307	1	2·270	113	2·269
½	2·12	120	2·11	½	2·125	210	2·120	½	2·115	210	2·125
—	—	—	—	½	2·070	211	2·070	1	2·069	211	2·071
10	1·762	121	1·761	9	1·762	213	1·764	8	1·748	213	1·748
4	1·672	220	1·672	4	1·677	220	1·676	5	1·680	220	1·680
—	—	—	—	—	—	—	—	½	1·579	222	1·579
2	1·590	002	1·590	2	1·590	006	1·589	3	1·538	006	1·538
4	1·497	130	1·496	4	1·499	310	1·499	4	1·503	310	1·503
—	—	—	—	—	—	—	—	½	1·428	312	1·429
3	1·437	112	1·435	4	1·438	116	1·436	4	1·409	303	1·408
5	1·412	031	1·412	4	1·415	303	1·415	3	1·399	116	1·399
2	1·318	022	1·319	2	1·319	206	1·320	2	1·290	206	1·291
5	1·212	231	1·212	4	1·214	323	1·215	3	1·212	323	1·211
2	1·181	040	1·183	1	1·186	400	1·186	2	1·188	400	1·188
3	1·152	222	1·151	3	1·152	226	1·153	3	1·135	226	1·135
2	1·116	330	1·115	1	1·118	330	1·118	2	1·120	330	1·120
	a 4·73 Å				*a* 4·742 Å				*a* 4·752 Å		
	c 3·18 Å				*c* 9·535 Å				*c* 9·229 Å		
	c/a 0·672				*c/a* 2·011				*c/a* 1·942		

Cassiterite, Cornwall, England. Berry and Thompson (1962).
Staringite, Seridózinho, Paraiba, Brazil.
Tapiolite, Seridózinho, Paraiba, Brazil.

capillary tube in the camera. This rubber solution, however, caused intense dark banding of the film in the region of about 3–6 Å. For the measurement of the low-angle diffractions, therefore, films of mixtures of tapiolite and staringite had to be used.

The films of these mixtures showed a characteristic doubling of the diffraction lines of tapiolite, so that from the beginning it was thought that staringite might have the same crystal structure as tapiolite. Using Bunn charts the X-ray powder pattern of staringite, which is shown in table II along with those of tapiolite and cassiterite, could readily be indexed on a tetragonal cell. The unit-cell dimensions were calculated from the powder data by the least squares method as described by Zussman (1967):

a 4·742 Å, c 9·535 Å, c/a 2·011; the associated tapiolite has a 4·752 Å, c 9·229 Å, c/a 1·942. The d-spacings were then calculated from the lattice dimensions for the indices obtained from a Bunn chart. The calculated values are in fair agreement with the measured d-spacings.

No single-crystal study could be made, but because of the evident similarities of the powder pattern and the unit-cell dimensions of staringite to those of tapiolite, it seems highly probable that the new mineral has the same 'trirutile' structure as tapiolite. A strong argument for this opinion is the presence in the pattern of staringite of the same lines (002, 101, 112, 211) as are found in the pattern of tapiolite, and which are caused by the 'trirutile' structure.

Crystal chemistry. Assuming a 'trirutile' structure for staringite, the unit-cell contains 12 oxygen atoms (in accordance with tapiolite, $FeTa_2O_6$, with $Z = 2$). On the basis of the analysis the formula of staringite from Seridózinho can then be written as $(Fe_{0.47}Mn_{0.04})_{0.51}(Sn_{4.47}Ti_{0.004})_{4.47}(Ta_{0.90}Nb_{0.12})_{1.02}O_{12}$. The mineral is chemically intermediate between SnO_2 (cassiterite) and $(Fe,Mn)(Ta,Nb)_2O_6$ (tapiolite). Its composition can be considered as being the result of the substitution $3(Sn,Ti)^{4+} \rightleftharpoons 1(Fe, Mn)^{2+}+2(Ta,Nb)^{5+}$; consequently the formula can be written as $(Fe,Mn)_x(Sn,Ti)_{6-3x}(Ta,Nb)_{2x}O_{12}$. In the case of the Seridózinho staringite $x = 0.51$. The associated tapiolite shows as formula $(Fe_{1.78}Mn_{0.14})_{1.92}(Sn_{0.12}Ti_{0.02})_{0.14}(Ta_{3.39}Nb_{0.53})_{3.92}O_{12}$; in the substitution formula then $x = 1.92-1.96$. It is proposed that the name staringite should be used for compounds having 'trirutile' structure and $x < 1$, and tapiolite for $x > 1$.

Discussion. Since no studies have been undertaken in the complex (Fe,Mn)–(Sn,Ti)–(Ta,Nb)–O system, it is not known whether or not a continuous series exists from the staringite composition to a composition with $x = 2$ (tapiolite), nor is the minimum value of x for compounds with a 'trirutile' structure known (when $x = 0$ the composition is SnO_2, but cassiterite has a 'monorutile' structure).

Natural material with a chemical composition similar to that of staringite has not hitherto been reported. Edwards (1940) described a specimen from Ubini, Western Australia, containing 79·2 % SnO_2, 17·5 % $(Ta_2O_5+Nb_2O_5)$, and 2·7 % FeO, but examination of polished sections showed it to consist of a mixture of cassiterite and tapiolite or tantalite. Edwards (1940) suggests that at high temperatures cassiterite can form a solid solution with the isomorphous tapiolite molecules, to an unknown extent, but that at lower temperatures the tapiolite molecules are precipitated. He also presumes that somewhat similar conditions hold when tapiolite is the dominant mineral in the solid solution, although no such specimens had been observed. Such a specimen seems to have been found at Seridózinho; however, no cassiterite exsolved from the tapiolite, but a compound with 'trirutile' structure.

Åmark (1941) carried out some experiments with SnO_2 and $ZnSb_2O_6$ to find out the isodimorphous solubility of these compounds of 'monorutile' and 'trirutile' type respectively. The results indicated that, from a mineralogical point of view, up to about 25 mol % of tapiolite eventually might enter isomorphically the cassiterite structure.

The Seridózinho staringite chemically consists of SnO_2 with somewhat more than 25 mol % dissolved tapiolite. Taking in account the theories of Edwards (1940) and Åmark (1941), and because of the 'trirutile' structure of staringite, the possibility of this mineral being metastable cannot be excluded.

REFERENCES

ÅMARK (KARIN), 1941. *Geol. Fören. Förhandl.* **63,** 295–9.

BERRY (L. G.) and THOMPSON (R. M.), 1962. *Mem. Geol. Soc. Amer.* **85,** 178.

BISHOP (H. E.), 1967. In *X-ray Optics and Microanalysis,* 153–8.

CAMERON (E. N.), 1963. *Amer. Min.* **48,** 1070–9.

DE ALMEIDA (S. C.), JOHNSTON (W. D., JR.), LEONARDOS (O. H.), and SCORZA (E. P.), 1944. *Econ. Geol.* **39,** 206–23.

DUNCUMB (P.) and SHIELDS (P. K.), 1966. In *The Electron Microprobe,* 284–96.

EDWARDS (A. B.), 1940. *Australasian Inst. Mining Met. Proc.* **120,** 731–44.

HEINRICH (K. F. J.), 1966. In *The Electron Microprobe,* 296–378.

JOHNSTON (W. D., JR.), 1945. *Bull. Geol. Soc. Amer.* **56,** 1015–70.

PILLER (H.), 1967. *Min. Mag.* **36,** 242–59.

PHILIBERT (J.), 1963. In *X-ray Optics and X-ray Microanalysis,* 379–92.

REED (S. J. B.), 1964. Ph.D. Thesis, Cambridge, England.

—— 1965. *Brit. Journ. Appl. Phys.* **16,** 913–26.

UYTENBOGAARDT (W.), 1966. *Leitz Mitt. Wiss. Techn.* **3,** 218–19.

WEBER (K.), 1965. Ibid. 103–7.

ZUSSMAN (J.), 1967. In *Physical Methods in Determinative Mineralogy,* chap. 6.