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## «JOHNSTRUPITE»: A CHEMICAL AND STRUCTURAL STUDY

**Abstract** - Chemical (EPM analyses), crystallographic and structural (single crystal X-Ray diffraction) investigations carried out on a specimen of «johnstrupite» from the Barkevik skerry, taken from Brøgger's own collection, pointed to its identity with rinkite and indicated the ideal crystal chemical formula  $Ti(Na_2Ca)(Ca_3REE)(Si_2O_7)_2(F_3O)$ .

**Key words** - «Johnstrupite», Mosandrite, Rinkite, Langesundsfjord.

**Riassunto** - *Studio cristallografico e strutturale della «johnstrupite»*. Analisi chimiche in microsonda elettronica e studi cristallografici e strutturali condotti mediante diffrazione di raggi X da cristallo singolo su un campione di «johnstrupite» dallo «scoglio» di Barkevik, preso dalla collezione personale di Brøgger, hanno suggerito l'identità con la rinkite ed hanno indicato la seguente formula cristallografica ideale:  $Ti(Na_2Ca)(Ca_3REE)(Si_2O_7)_2(F_3O)$ .

**Parole chiave** - «Johnstrupite», Mosandrite, Rinkite, Langesundsfjord.

### INTRODUCTION

The chemical composition of mosandrite has been recently redefined on the basis of new chemical (EPM analyses) and TG-DSC studies, as well as structural (single crystal X-ray diffraction) investigations, which confirmed the results of the old wet-chemical analysis of H. Bäckström, as reported by Brøgger (1890) and pointed to the crystal chemical formula  $Ti[\square_2(Ca,Na)](Ca_3REE)(Si_2O_7)_2[(OH)_2F(H_2O)] \cdot 1H_2O$  (Bellezza *et al.*, 2009). In the same paper devoted to the description of mosandrite, Brøgger (1890) described also the related mineral «johnstrupite» from the Barkevik skerry, Langesundsfjord, Norway.

Mosandrite [Erdmann, as reported in Berzelius (1841); Bellezza *et al.*, 2009], rinkite (Lorenzen, 1884; Galli & Alberti, 1971) and nacarenite-(Ce) (Petersen *et al.*, 1989; Sokolova & Hawthorne, 2008) are presently the three members of the rinkite group with recognized validity (Tab. 1). As regards «johnstrupite» it is not reported among the valid species in the list of the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC); different authors and different compilations indicate its identity with rinkite or mosandrite; the ambiguity is largely due to the Fleischer's

suggestion (Fleischer, 1958; Fleischer, 1987) to drop the names rinkite and johnstrupite (and rinkolite and lovchorrite, as well) in favour of mosandrite.

An interesting question is raised by the contrasting results obtained by Bellezza *et al.* (2009) in their study of mosandrite and by Sokolova & Cámara (2008) in their investigations on a specimen of «mosandrite» they received on loan from the American Museum of Natural History (New York, USA) and found identical with rinkite, on the basis of chemical and structural data. We suspect that the specimen was previously labelled rinkite or johnstrupite, and that a re-labelling occurred when mosandrite was assumed as the only valid species. Aim of the present work is actually to definitely solve the recalled ambiguity, namely the identity of «johnstrupite» with rinkite or mosandrite, through single-crystal X-ray diffraction studies and electron probe analyses. The study has been carried out using a specimen of «johnstrupite» from Brøgger's own collection (stored in the Natural History Museum, University of Oslo, Norway). We have obtained sound indications of its identity with rinkite and a noteworthy correspondence of the observed cationic distribution with that obtained by Sokolova & Cámara (2008) in the specimen of «mosandrite» which was the object of their work.

### EXPERIMENTAL

Four quantitative chemical analyses were done on a fragment of johnstrupite in wavelength-dispersive (WDS) mode by means of a JEOL JXA-8600 electron microprobe. The operating voltage was 15 kV, the beam current was 20 nA and the beam diameter was 20  $\mu$ m. Standards used were kaersutite (SiK $\alpha$ , CaK $\alpha$ , FeK $\alpha$ ), albite (NaK $\alpha$ ), ilmenite (TiK $\alpha$ ), monazite (CeL $\alpha$ , LaL $\alpha$ ), bustamite (MnK $\alpha$ ), cubic zirconia (ZrK $\alpha$ , YK $\alpha$ ), metal Nb (NbK $\alpha$ ) and fluorite (FK $\alpha$ ).

The average values (with ranges) are reported here: SiO<sub>2</sub> 30.61 (30.04-31.29), TiO<sub>2</sub> 7.25 (7.21-7.31), CaO 30.08 (30.04-30.12), MnO 0.14 (0.10-0.18), FeO 0.22 (0.17-0.30), Na<sub>2</sub>O 8.14 (7.95-8.21), Y<sub>2</sub>O<sub>3</sub> 2.03 (1.89-2.11), La<sub>2</sub>O<sub>3</sub> 3.79 (3.76-3.80), Ce<sub>2</sub>O<sub>3</sub> 8.32 (8.15-8.51), ZrO<sub>2</sub> 1.34 (1.32-1.44), Nb<sub>2</sub>O<sub>5</sub> 1.25 (0.99-1.35), F 6.81 (6.44-7.45), O = F 2.87, total 97.11 wt. %. The low total has to be attributed to the presence of some elements not analysed for, such as Al, Pr, Nd, Sm, Gd, Dy, Er, and Th which have been found in mosandrite (Bellezza

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Tab. 1 - Crystal chemical formulas and unit cell parameters for the three valid species in the rinkite group.

	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$
Mosandrite (Bellezza <i>et al.</i> 2009) Ti[□ <sub>2</sub> (Ca,Na)](Ca <sub>3</sub> REE)(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> [(OH) <sub>2</sub> F(H <sub>2</sub> O)] · 1H <sub>2</sub> O	7.398	5.595	18.662 Å	101.37°
Rinkite (Galli & Alberti 1971) (Ti,Nb)[Na <sub>2</sub> (Na,Ca)](Ca <sub>3</sub> REE)(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (F <sub>3</sub> O)	7.437	5.664	18.843	101.38
Nacareniobsite-(Ce) (Sokolova & Hawthorne 2008) Ti(Na <sub>2</sub> Ca)(Ca <sub>3</sub> REE)(Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (F <sub>3</sub> O)	7.468	5.689	18.891	101.37

*et al.* 2009) and in rinkite (Tê-Yü *et al.* 1965; Petersen *et al.* 1989). The empirical formula, based on 4 Si atoms, is (Ti<sub>0.71</sub>Zr<sub>0.09</sub>Nb<sub>0.07</sub>)<sub>Σ0.87</sub>(Na<sub>2.06</sub>Ca<sub>0.92</sub>Mn<sub>0.02</sub>Fe<sub>0.02</sub>)<sub>Σ3.02</sub>(Ca<sub>3.29</sub>REE<sub>0.58</sub>Y<sub>0.14</sub>)<sub>Σ4.0</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(O<sub>0.73</sub>F<sub>2.81</sub>)<sub>Σ3.54</sub>, or ideally Ti(Na<sub>2</sub>Ca)(Ca<sub>3</sub>REE)(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(F<sub>3</sub>O) which is closely similar to that of rinkite (Galli & Alberti 1971; Sokolova & Cámara 2008).

Single-crystal rotation and Weissenberg photographs of johnstrupite show the mineral is monoclinic, space group *P2<sub>1</sub>/c* with cell parameters very close to those of rinkite and quite distinct from those of mosandrite. A crystal with dimension of 0.29 x 0.15 x 0.10 mm<sup>3</sup> was chosen for X-ray single-crystal data collection. The intensity data were collected with an Ital Structure automatic four-circles diffractometer using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). The measured reflections were corrected for Lorentz, polarization and absorption factors. This last correction was made according to the method of North *et al.* (1968) using 3 reflections; the least-squares method, based on the angular parameters of 42 reflections in the range  $18^\circ \leq 2\theta \leq 30^\circ$ ,

gives the unit-cell parameters *a* 7.421(2), *b* 5.709(1), *c* 19.019(7) Å,  $\beta$  101.23(4)°. The structure was refined in the space group *P2<sub>1</sub>/c* starting from the atomic coordinates reported by Galli & Alberti (1971) for rinkite. The refinement of the structure was carried out using the SHELXL97 program package (Sheldrick, 1997). The distribution of the cations over the five non-equivalent «octahedral» sites M(1) to M(5) was established taking into account the corresponding electron densities and the bond valence balance; in assessing the cationic distribution in the polyhedral sites, Ce represents all the REE. The occupancies were subsequently refined and, after introduction of the anisotropic thermal parameters for all the cations, the final reliability index was *R* = 0.057 for 1133 reflections with  $F_o > 4\sigma(F_o)$ . As regards the occupancies of the two anionic sites not linked to the Si atoms, OF(1) and OF(2), they were assumed as O<sub>0.5</sub>F<sub>0.5</sub> during the refinement and were subsequently established as F<sub>0.55</sub>O<sub>0.45</sub> and F<sub>0.80</sub>O<sub>0.20</sub>, respectively, on the basis of the valence bond balance. Final positional coordinates of the atomic sites, isotropic displacement

Tab. 2 - Atomic coordinates and isotropic (*B*) or equivalent isotropic (*B<sub>eq</sub>*) displacement parameters in «johnstrupite» (standard deviations in parentheses).

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> / <i>B<sub>eq</sub></i>
M(1)	0	0	0	3.45(7)
M(2)	1/2	0	0	3.34(16)
M(3)	0.7547(3)	0.5010(5)	0.00110(17)	4.21(9)
M(4)	0.0935(1)	0.6624(2)	0.19121(6)	3.07(3)
M(5)	0.5972(2)	0.6660(3)	0.19122(8)	3.16(4)
Si(1)	0.3511(3)	0.1560(5)	0.13998(14)	2.67(5)
Si(2)	0.7845(3)	0.1554(5)	0.13785(14)	2.68(5)
O(1)	0.2197(9)	0.1511(14)	0.06120(39)	3.93(14)
O(2)	0.8309(8)	0.1419(13)	0.05804(38)	3.64(13)
O(3)	0.3379(9)	0.3972(13)	0.18387(39)	3.67(14)
O(4)	0.8429(9)	0.4018(13)	0.17807(42)	4.04(15)
O(5)	0.3334(8)	0.9352(13)	0.19159(37)	3.39(13)
O(6)	0.8561(8)	0.9386(12)	0.19143(36)	3.25(13)
O(7)	0.5585(9)	0.1415(13)	0.12134(38)	3.79(14)
OF(1)	0.0308(8)	0.7012(11)	0.06006(36)	3.71(19)
OF(2)	0.5279(9)	0.6555(12)	0.06071(39)	4.44(21)

Tab. 3 - Occupancies and average bond distances for the cationic sites in «johnstrupite» and corresponding sites in rinkite and in «mosandrite» of Sokolova and Cámara. The last two rows report the anionic distribution in OF(1), OF(2) and the corresponding sites in rinkite and in «mosandrite» of Sokolova and Cámara.

Site	«Johnstrupite» (this work)		Rinkite (Galli & Alberti, 1971)		«Mosandrite» of Sokolova & Cámara (2008)*	
	occupancies	average bond distance	occupancies	average bond distance	occupancies	average bond distance
M(1)	Ti <sub>0.86</sub> Zr <sub>0.09</sub> Nb <sub>0.05</sub>	2.014 Å	Ti <sub>0.51</sub> Nb <sub>0.33</sub> Al <sub>0.09</sub> Zr <sub>0.05</sub>	2.00 Å	Ti <sub>0.87</sub> Nb <sub>0.08</sub> Zr <sub>0.05</sub>	1.994 Å
M(2)	Na <sub>0.90</sub> Ca <sub>0.10</sub>	2.501	Na <sub>0.66</sub> Ca <sub>0.19</sub> □ <sub>0.13</sub> K <sub>0.02</sub>	2.50	Na <sub>1.00</sub>	2.496
M(3)	Na <sub>0.46</sub> Ca <sub>0.54</sub>	2.380	Na <sub>0.76</sub> Ca <sub>0.22</sub> K <sub>0.02</sub>	2.39	Na <sub>0.50</sub> Ca <sub>0.42</sub> □ <sub>0.08</sub>	2.375
M(4)	Ca <sub>0.71</sub> Ce <sub>0.29</sub>	2.466	Ca <sub>0.68</sub> Ce <sub>0.26</sub> Fe <sub>0.03</sub> Mg <sub>0.02</sub> Th <sub>0.01</sub>	2.45	Ca <sub>0.68</sub> REE <sub>0.32</sub>	2.452
M(5)	Ca <sub>0.84</sub> Ce <sub>0.16</sub>	2.499	Ca <sub>0.68</sub> Ce <sub>0.26</sub> Fe <sub>0.03</sub> Mg <sub>0.02</sub> Th <sub>0.01</sub>	2.47	Ca <sub>0.82</sub> REE <sub>0.17</sub> Sr <sub>0.01</sub>	2.484
OF(1)	F <sub>0.55</sub> O <sub>0.45</sub>		F <sub>0.75</sub> O <sub>0.25</sub>		F <sub>0.60</sub> O <sub>0.40</sub>	
OF(2)	F <sub>0.80</sub> O <sub>0.20</sub>		F <sub>0.75</sub> O <sub>0.25</sub>		F <sub>1.00</sub>	

\*The sites indicated M(1), M(2), M(3), M(4), M(5), OF(1), OF(2) in «johnstrupite» and rinkite correspond to the sites indicated M<sup>o</sup>(1), M<sup>o</sup>(2), M<sup>o</sup>(3), M<sup>h</sup>, A<sup>p</sup>, X<sup>o</sup><sub>M</sub> and X<sup>a</sup>, respectively, in «mosandrite» of Sokolova and Cámara.

factors for the anions and equivalent isotropic displacement factors for the cations are given in Table 2. The refined site populations for the cationic sites M(1) to M(5) and the calculated occupancies at anionic sites OF(1) and OF(2) are reported in Table 3, together with the average bond distance in the various polyhedra, and are compared with the corresponding values found by Galli & Alberti (1971) for rinkite and by Sokolova & Cámara (2008) for their specimen of «mosandrite». By looking at Table 3 we may easily conclude that the structures of «johnstrupite» and of the «mosandrite» specimen studied by Sokolova & Cámara (2008) are «topologically and chemically identical to that of rinkite from type locality of Kangerdluarssuk, Greenland» (Sokolova & Cámara, 2008).

In conclusion «johnstrupite», firstly described by Brøgger in 1890, closely corresponds to rinkite, firstly described by Lorenzen in 1884 and therefore its name should be definitely dropped in favour of rinkite, not mosandrite which actually displays a peculiarly distinct composition and crystallography, as indicated in Table 1.

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