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RALSTONITE RENAMED HYDROKENORALSTONITE, COULSELLITE RENAMED FLUORNATROCOULSELLITE, AND THEIR INCORPORATION INTO THE PYROCHLORE SUPERGROUP

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Abstract

Ralstonite is renamed hydrokenoralstonite, ideally $\square_2Al_2F_6(H_2O)$. "Atroarite" and the "AHF" phase (hydrated aluminum hydroxy-fluoride, a "ralstonite-like mineral") are also hydrokenoralstonite. The name ralstonite is transferred to the group, where M^{3+} cations are dominant at the B site, and Al is dominant among them, and F^{1-} is the dominant anion at the X site. Hydrokenoralstonite from the Pitinga mine, Presidente Figueiredo, Amazonas, Brazil, is intimately associated with galena and sphalerite. It forms chemically homogeneous octahedral crystals, from 0.1 to 1 mm in size. The mineral is colorless with white streak, vitreous luster, transparent, density (calc.): 2.554 g/cm^3. Its empirical formula is $(\square_{1.87}Na_{0.12}Rb_{0.01})_{\Sigma 2.00}(Al_{1.86}Mg_{0.14})_{\Sigma 2.00}[F_{3.46}(OH)_{2.54}]_{\Sigma 6.00}(H_2O)$. The mineral is cubic, $Fd\overline{3}m$ (#227), a 9.8455(7) Å, V 954.36 (12) Å^3, $Z = 8$. Hydrokenoralstonite exhibits (Al,Mg) cations with octahedral coordination and Na cations located within distorted cubes. Coulsellite, a rhombohedral pyrochlore-supergroup mineral, ideally $(Na,Ca)_2(Mg,Al)_2F_6F$, is renamed fluornatrocoulsellite, and the name coulsellite is transferred to the group, where M^{2+} cations are dominant at the B site, and Mg is dominant among them, and F^{1-} is the dominant anion at the X site. This nomenclature proposal was approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association.

Keywords: hydrokenoralstonite, fluornatrocoulsellite, Pitinga mine, Presidente Figueiredo, Amazonas, pyrochlore supergroup.

Introduction

Ralstonite and coulsellite have a pyrochlore structure and were forgotten in the recent classification of the pyrochlore supergroup (Atencio *et al*. 2010). The general formula of the pyrochlore-supergroup minerals is $A_2B_2X_6Y$. The names are composed of two prefixes and one root name (identical to the name of the group). The first prefix refers to the dominant anion (or cation) of the dominant valence [or H_2O or $\square$] at the Y site. The second prefix refers to the dominant cation of the dominant valence [or H_2O or $\square$] at the A site. The fact that ralstonite probably belongs to the pyrochlore group was previously mentioned by Pabst (1939a).

The study of the mineral "atroarite" (Minuzzi *et al*. 2003) from the Pitinga mine, Presidente Figueiredo, Amazonas, Brazil, led to the conclusion that it is identical to ralstonite [originally described by Brush (1871) from the Ivigtut cryolite deposit, Ivittuut (Ivigtut), Arsuk Fjord, Sermersooq, Greenland]. Following the established naming rules for pyrochlore

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[§] *Corresponding author e-mail address*: datencio@usp.br supergroup minerals (Atencio *et al*. 2010), ralstonite should be renamed hydrokenoralstonite. The name ralstonite should be transferred to the group (ralstonite group), where M^{3+} cations are dominant at the *B* site, and Al is dominant among them, and F^{1-} is the dominant anion at the *X* site.

Coulsellite, a rhombohedral pyrochlore mineral (Mumme *et al*. 2010), with formula $Na_3CaMg_3AlF_{14}$ $[(Na_{1.5}Ca_{0.5})_{\Sigma2}(Mg_{1.5}Al_{0.5})_{\Sigma2}F_6F$ or $(Na,Ca)_2(Mg,Al)_2F_6F$ in order to compare with the pyrochlore supergroup minerals] should be renamed fluornatrocoulsellite, and the name coulsellite should be transferred to the group (coulsellite group), where M^{2+} cations are dominant at the *B* site, and Mg is dominant among them, and F^{1-} is the dominant anion at the *X* site. Birch & Pring (1990) published an incomplete description of a mineral from the same occurrence and referred to it as "a calcian ralstonite-like mineral" which corresponds to "hydroxynatrocoulsellite".

This nomenclature proposal was approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA).

Hydrokenoralstonite from the Pitinga Mine

Hydrokenoralstonite occurs in thin veins in the core subfacies of the albite-enriched granite in the Madeira deposit, Pitinga mine (0°44′43″S 60°7′40″W), Presidente Figueiredo, Amazonas, Brazil. The Madeira granite, which is hosted by A-type volcanic rocks (Iricoumé Group, ~1880 Ma), formed in a caldera complex. The albite-enriched granite facies corresponds to the Madeira world-class Sn-Nb-Ta (Y, REE, F, Zr, Li, and Th) deposit, with 130 million tons of disseminated ore. In addition, in the central portion of the albite-enriched granite facies, there is a massive cryolite deposit of 10 million tons with a grade of 31.9% of Na_3AlF_6. This association of Sn with several rare metals in the same albite-enriched granite that hosts a massive cryolite deposit is unique in the world. The directly associated mineral is halloysite. Minerals in the albite-enriched granite are quartz, K-feldspar, albite, riebeckite, biotite, muscovite, cryolite, zircon, polylithionite, cassiterite, pyrochlore-group minerals, "columbite", thorite, lead, galena, fluorite, xenotime-(Y), gagarinite-(Y), fluocerite-(Ce), genthelvite-helvite, topaz, "illite", kaolinite, and "chlorite". At the magmatic stage, the high F content in the melt was buffered by crystallization of cryolite. Tin, Nb, and REE were homogeneously dispersed throughout the deposit, transported by F-bearing complexes in the melt, and concentrated in the forms of cassiterite, a U-Pb-rich pyrochlore-group mineral, and xenotime-(Y), respectively. Zircon crystallization, inhibited at the early magmatic stage by high F activity, intensified at the late magmatic stage owing to a decrease in alkalinity associated with riebeckite crystallization, forming concentrations, together with xenotime-(Y) and polythionite, in pegmatitic zones. Yttrium and REE mineralization in the lower portion of the deposit is represented by gagarinite-(Y), with fluocerite-(Ce) inclusions formed by exsolution of the early gagarinite. There is no evidence for either silicate–fluoride liquid immiscibility or for a continuous transition from volatile-rich silicate melt to solute-rich fluids. The abrupt magmatic–hydrothermal transition triggered three processes: (1) albitization accompanied by the crystallization of hydrothermal cryolite in the rock matrix; (2) conversion of pyrochlore to a columbite-group mineral, characterized by gradual loss of Pb and enrichment in U and Nb; and (3) formation of the massive cryolite deposit, made up of crystals of twinned cryolite (87%) with subordinate quartz, K-feldspar, and zircon from an aqueous saline (1.7 to 22.4 wt.% equiv. NaCl) hydrothermal fluid, starting at a minimum temperature of 400 °C and continuing down-temperature. The evolution of parameters (REE-total, La/Lu, LREE/HREE, Y) in cryolite is continuous from the magmatic stage to the low-temperature hydrothermal stage (Bastos Neto *et al*. 2009). This is the type locality for waimirite-(Y) (Atencio *et al*. 2015).

Hydrokenoralstonite is intimately associated with galena and sphalerite. It forms chemically homogeneous octahedral crystals, from 0.1 to 1 mm in size (Figs. 1 and 2). No twinning is observed. The mineral is colorless with white streak, vitreous luster, transparent, density (calc.): 2.554 g/cm^3.

Chemical Data

Chemical analyses (11) were carried out using a Cameca SX100 electron microprobe in WDS mode; 15 kV; 10 nA; beam diameter 10 μm (Table 1). H_2O was calculated from the crystal structure. The empirical formula [based on 6 (F+OH) anions a*pfu*)] is $(\square_{1.87}Na_{0.12}Rb_{0.01})_{\Sigma2.00}(Al_{1.86}Mg_{0.14})_{\Sigma2.00}[F_{3.46}(OH)_{2.54}]_{\Sigma6.00}(H_2O)$. The simplified formula is $\square_2Al_2F_6(H_2O)$. The latest analysis for ralstonite from the type locality (RRUFF Project, R060012) resulted in the formula $(\square_{1.30}Na_{0.70})_{\Sigma2.00}(Al_{1.30}Mg_{0.70})_{\Sigma2.00}[F_{4.18}(OH)_{1.82}]_{\Sigma6.00}(H_2O)$. All chemically analyzed ralstonite samples from the literature are hydrokenoralstonite, with the *A* site dominantly empty, the *B* site populated predominantly by Al, the *X* site dominantly occupied by F, and the *Y* site occupied by H_2O. The "AHF" phase (hydrated aluminum hydroxy-fluoride), a "ralstonite-like mineral" (Desborough & Rostad

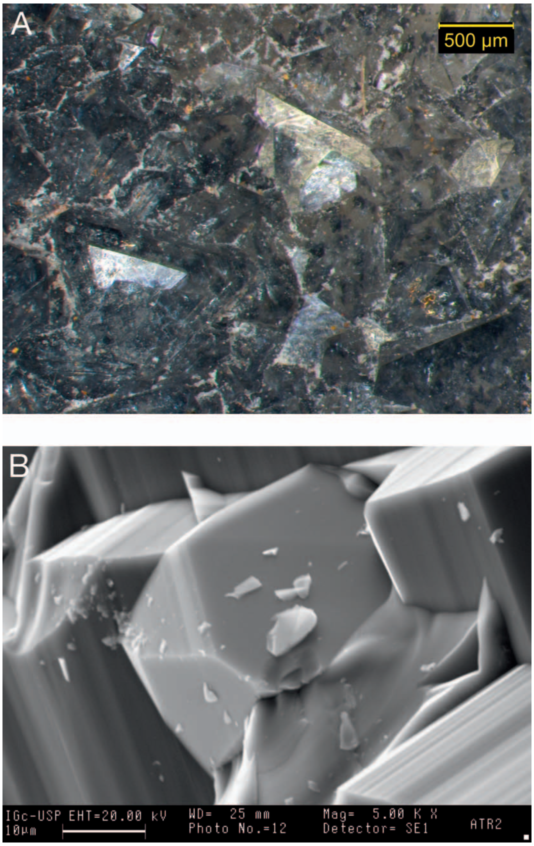

FIG. 1. Hydrokenoralstonite from Presidente Figueiredo Co., Amazonas State, Brazil.

TABLE 1. ANALYTICAL DATA FOR HYDROKENORALSTONITE FROM THE PITINGA MINE

Constituent	wt.%	Range	Standard deviation	Electron microprobe standard
Na_2O	2.14	0.99–2.98	0.80	albite
K_2O	0.02	0.01–0.04	1.14	orthoclase
Rb_2O	0.55	0.34–0.73	0.10	synthetic $RbTiPO_4$
MgO	3.20	1.20–4.86	1.31	olivine
CaO	0.01	n.d.–0.02	0.01	anorthite
Al_2O_3	52.63	50.87–54.99	1.14	anorthite
F	36.46	33.82–38.44	1.50	MgF_2
H_2O	22.70			
O=F	–15.35			
Total	102.36			

1980, Keith 1991, Rosenberg 2006) is also hydrokenoralstonite. Table 2 lists the published hydrokenoralstonite formulae.

CRYSTALLOGRAPHY

Single-crystal X-ray studies were carried out using an Bruker X8 APEX2 CCD 4-circle diffractometer with graphite-monochromated Mo*K*α ($\lambda = 0.71073$ Å) radiation. The mineral is cubic, $Fd\bar{3}m$ (#227), *a* 9.8455(7) Å, *V* 954.36 (12) Å^3, $Z = 8$.

Powder XRD data for hydrokenoralstonite from Pitinga (Table 3) were obtained with a D8 Advance DaVinci diffractometer using Cu*K*α radiation at the X-ray Diffraction Laboratory, Geosciences Institute, University of São Paulo. Unit-cell parameters refined

TABLE 2. PUBLISHED HYDROKENORALSTONITE FORMULAE

$(Mg,Na_2)Al_3(F\text{-}OH)_{11}\bullet 2H_2O$	Penfield & Harper (1886)
$(Na_2,Mg)F_2.3Al(F,OH)_3\bullet 2H_2O$	Pabst (1939a)
$Na_x(Al_{2-x},Mg_x)(F,OH)_6\bullet H_2O$	Pabst (1950)
$NaMgAl(F,OH)_6\bullet H_2O$	Pauly (1965)
$Na_xMg_xAl_{2-x}(F,OH)_6\bullet H_2O$	Hitchon *et al.* (1976)
$Na_{2.8}(Al,Mg)_{16}(F,OH)_{48}\bullet 7H_2O$	Effenberger & Kluger (1984)
$Na_x[Mg_xAl_{2-x}F_{6-y}(OH)_y]\bullet zH_2O$	Effenberger & Kluger (1984)
$Na_xMg_xAl_{2-x}F_{6-y}(OH)_y\bullet nH_2O$	Rosenberg (2006)
$Al_2F_{6-y}(OH)_y\bullet nH_2O$ *	Rosenberg (2006)
$Al_{16}(F,OH)_{48}\bullet 12–15H_2O$ *	Rosenberg (2006)
$\square_2Al_2F_6(H_2O)$	This paper

Note: * AHF phase (hydrated aluminum hydroxy-fluoride, a "ralstonite-like mineral").

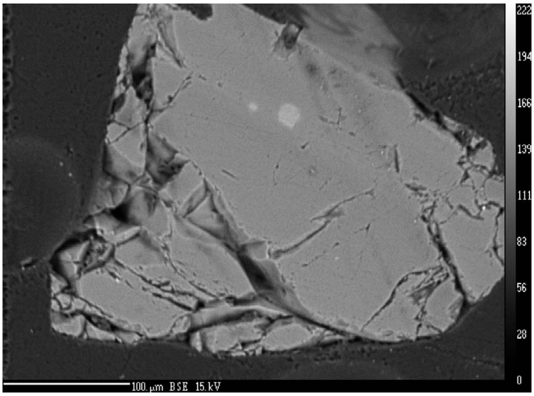

FIG. 2. BSE image of hydrokenoralstonite from Presidente Figueiredo Co., Amazonas State, Brazil. The lighter areas are due to beam damage.

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR HYDROKENORALSTONITE FROM THE PITINGA MINE

$I_{meas.}$ (%)	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)*	*h*	*k*	*l*
100	**5.687**	**5.686**	**1**	**1**	**1**
18	**2.973**	**2.969**	**3**	**1**	**1**
28	**2.841**	**2.843**	**2**	**2**	**2**
3	2.466	2.462	4	0	0
2	2.262	2.259	3	3	1
3	2.013	2.010	4	2	2
36	**1.893**	**1.895**	**3**	**3**	**3**
3	1.726	1.741	4	4	0
1	1.666	1.665	5	3	1
1	1.559	1.557	6	2	0
1	1.504	1.502	5	3	3
1	1.487	1.485	6	2	2

Note: * Calculated data were obtained using CELLCALC software (Miura 2003). Lines with strongest intensities in **bold**.

from powder data using CellCalc software (Miura 2003) are as follows: *a* 9.849(9) Å, *V* 955(3) Å^3.

The crystal structure was solved and refined using SHELX97 (Sheldrick 2008): $R_1 = 0.016$, $wR = 0.050$, with 106 observed reflections ($F_o > 4\sigma(F_o)$). Goodness-of-fit = 1.25. The refined formula is: $Na_{0.13}(Al_{1.85}Mg_{0.15})_{\Sigma 2}[F_{3.44}(OH)_{2.56}]_{\Sigma 6}(H_2O)$ (see Table 4 for atomic coordinates and Table 5 for bond distances and bond valence values). Hydrokenoralstonite exhibits (Al,Mg) cations with octahedral coordination and Na cations located within distorted cubes (Fig. 3). Note that the major cations Al, Mg, and Na were included in the structure refinement. For simplicity, Rb was ignored, due to the negligible effect on the final results. It was not possible to locate the H positions during the structure refinements. These results agree with those in the literature (Pabst 1939b, Effenberger & Kluger 1984).

CONCLUSIONS

The incorporation of hydrokenoralstonite and fluornatrocoulsellite into the pyrochlore supergroup modifies the definition of the supergroup as follows:

If M^{6+} cations are dominant at the *B* site, and W is dominant among them, and O^{2-} is the dominant anion at the *X* site, then the group is elsmoreite.

If M^{5+} cations are dominant at the *B* site, and Nb is dominant among them, and O^{2-} is the dominant anion at the *X* site, then the group is pyrochlore.

If M^{5+} cations are dominant at the *B* site, and Ta is dominant among them, and O^{2-} is the dominant anion at the *X* site, then the group is microlite.

TABLE 4. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR HYDROKENORALSTONITE

Atom	*x*	*y*	*z*	Occ.	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al	0	0	0	0.93(2)	0.0067(2)	0.0067(2)	0.0067(2)	0.0067(2)	−0.00088(11)	−0.00088(11)	−0.00088(11)
Mg	0	0	0	0.07(2)	0.0067(2)	0.0067(2)	0.0067(2)	0.0067(2)	−0.00088(11)	−0.00088(11)	−0.00088(11)
Na	1/2	1.2	1/2	0.065(8)	0.032(8)	0.032(8)	0.032(8)	0.032(8)	0.000	0.000	0.000
F	0.31268(8)	1/8	1/8	0.573(17)	0.0116(3)	0.0114(4)	0.0116(3)	0.0116(3)	0.000	0.000	0.0038(3)
OH	0.31268(8)	1/8	1/8	0.427(17)	0.0116(3)	0.0114(4)	0.0116(3)	0.0116(3)	0.000	0.000	0.0038 (3)
OW	3/8	3/8	3/8	1	0.0423(8)	0.0423(8)	0.0423(8)	0.0423(8)	0.000	0.000	0.000

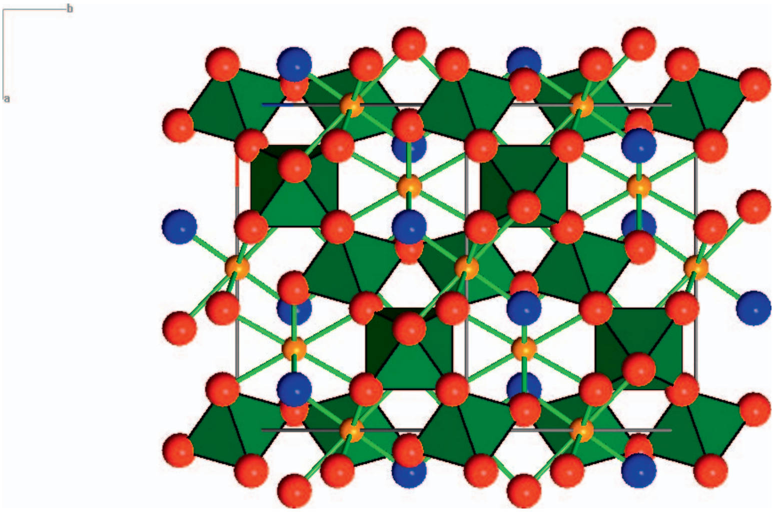

FIG. 3. Crystal structure of hydrokenoralstonite. Green: (Al,Mg)–(F,OH) octahedra; orange: Na; blue: H_2O; and red: F. $(Al,Mg)(F,OH)_6$ octahedra share corners to form a three-dimensional framework, with eight-coordinated Na occupying the cavities in the framework.

If M^{5+} cations are dominant at the *B* site, and Sb is dominant among them, and O^{2-} is the dominant anion at the *X* site, then the group is roméite.

If M^{4+} cations are dominant at the *B* site, and Ti is dominant among them, and O^{2-} is the dominant anion at the *X* site, then the group is betafite.

If M^{3+} cations are dominant at the *B* site, and Al is dominant among them, and F^{1-} is the dominant anion at the *X* site, then the group is ralstonite.

If M^{2+} cations are dominant at the *B* site, and Mg is dominant among them, and F^{1-} is the dominant anion at the *X* site, then the group is coulsellite.

As a mineral group consists of two or more minerals (Mills *et al.* 2009), ralstonite and coulsellite cannot really be considered, for now, as mineral groups. Hydrokenoralstonite and fluornatrocoulsellite should be designated as unassigned members of the pyrochlore supergroup, because there is no other member to allow a group to be established.

TABLE 5. SELECTED BOND LENGTHS AND BOND VALENCES FOR HYDROKENORALSTONITE USING THE PARAMETERS PUBLISHED BY BRESE & O'KEEFFE (1991)

Bond	Bond length	BV (*vu*)	Σ
Na–F	2.5358(6)	0.003673(×6)	0.022037
Na–OH	2.5358(6)	0.003855(×6)	0.023130
Na–Ow	2.1316(1)	0.026887(×2)	0.053774
Σ			0.098941
Al–OH	1.8466(3)	0.214895(×6)	1.28937
Al–F	1.8466(3)	0.23500(×6)	1.41000
Mg–OH	1.8466(3)	0.02048(×6)	0.12288
Mg–F	1.8466(3)	0.020101(×6)	0.12060
Σ			2.94285

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