Canadian Mineralogist
Vol. 29, pp. 355-358 (1991)

PERRAULTITE, A NEW HYDROUS Na–K–Ba–Mn–Ti–Nb SILICATE SPECIES FROM MONT SAINT-HILAIRE, QUEBEC

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ABSTRACT

Perraultite is a new mineral species from the De-mix quarry, Mont Saint-Hilaire, Quebec. It occurs as small prismatic crystals up to 0.5 mm in pegmatite dikes in nepheline syenite, associated with kupletskite, catapleiite, microcline, albite, aegirine, rhodochrosite, natrolite, tetranatrolite, lorenzenite, polylithionite, ancylite, fluorite, calcite and pyrochlore. The mineral is orange brown with a pale brown streak, vitreous, slightly waxy, opaque to translucent, transparent in small fragments, very brittle, and nonfluorescent in ultraviolet light. Cleavage {001} very good; fracture uneven to irregular. Mohs hardness about 4; D(meas.) 3.71(5), D(calc.) 3.808 g/cm^3. The mineral is not affected by HCl, H_2SO_4 and HNO_3. Optically biaxial (-), α 1.785(2), β 1.81(1), γ 1.82(1) (λ 589 nm), $2V$(meas.) 66(1)°, $2V$(calc.) 64°, strong dispersion, $r \ll v$. Orientation: $X = b$, $Y \wedge a = 19°$ in the obtuse β angle. Pleochroism pronounced: Z = dark brown, $X = Y$ = light yellow. Perraultite is monoclinic, $C2/m$, Cm or $C2$, a 10.820(2), b 13.843(4), c 20.93(1) Å, β 95.09(2)°, Z = 4. An $I2/m$ subcell with $a' = \frac{1}{2}a$, $b' = \frac{1}{2}b$, $c' = c$ and $\beta' = \beta$ is very pronounced. Crystals are prismatic and flattened on {010}, with elongation along [100], bound by {001}, {010}, {100} and a $\{\bar{h}0l\}$ form, possibly $\{\bar{1}01\}$. "Swallow-tail" contact twins are common, with {001} as twin plane and composition plane. The strongest seven X-ray powder-diffraction lines [d in Å(I)(hkl)] are: 10.43(42)(002), 3.573(11)(025), 3.474(100)(006), 3.186(15)(224), 2.867(13)(241), 2.606(40)(008), 2.084(15)(00•10). Electron-microprobe analyses gave: SiO_2 27.32, Al_2O_3 0.03, MnO 31.14, FeO 1.12, MgO 0.06, TiO_2 9.44, Nb_2O_5 13.35, ZrO_2 0.12, BaO 8.88, K_2O 2.68, Na_2O 3.52, F 0.84, H_2O (by TGA) 3.49, $-O \equiv F$ 0.35, total 101.64 wt. %, corresponding to $Na_{2.02}K_{1.00}Ba_{1.02}(Mn_{7.73}Fe_{0.27}Mg_{0.03})(Ti_{2.08}Nb_{1.77}Zr_{0.02})(Si_{8.01}Al_{0.01})O_{32.00}[(OH)_{5.62}F_{0.78}(H_2O)_{0.60}]_{\Sigma 7.00}$. The tentative ideal formula is $Na_2KBaMn_8(Ti,Nb)_4Si_8O_{32}(OH,F,H_2O)_7$. TGA showed a two-stage weight loss with a break at 450°C. The infrared-absorption spectrum confirms the presence of H_2O and OH. The name honors Professor Guy Perrault.

Keywords: perraultite, new mineral species, silicate, Mont Saint-Hilaire, Quebec, occurrence, properties, X-ray data, chemical composition.

SOMMAIRE

La perraultite est une nouvelle espèce minérale découverte à la carrière De-mix, au mont Saint-Hilaire, Québec. Elle forme de petits cristaux prismatiques atteignant 0.5 mm dans des filons pegmatitiques dans la syénite néphélinique, en association avec kupletskite, catapleiite, microcline, albite, aegyrine, rhodocrosite, natrolite, tétranatrolite, lorenzenite, polylithionite, ancylite, fluorite, calcite et pyrochlore. Elle est orange brun avec une rayure brune pâle, à l'aspect hyalin, légèrement cireux; elle est opaque à translucide, transparente en petits fragments, extrêmement cassante, et non fluorescente en lumière ultra-violette. Le clivage {001} est très bon; la cassure est inégale à irrégulière. Le dureté de Mohs est d'environ 4; la densité est 3.71(5) (mesurée) et 3.808 (calculée). Le minéral n'est pas affecté par HCl, H_2SO_4 et HNO_3. Optiquement biaxe négatif, α 1.785(2), β 1.81(1), γ 1.82(1) (λ 589 nm), $2V$ 66(1)° (mesuré), 64° (calculé), forte dispersion, $r \ll v$. Orientation: $X = b$, $Y \wedge a = 19°$ dans l'angle β obtus. Le pléochroïsme est prononcé: Z brun foncé, $X = Y$ jaune pâle. La perraultite est monoclinique, $C2/m$, Cm ou $C2$, a 10.820(2), b 13.843(4), c 20.93(1) Å, β 95.09(2)°, Z = 4. Une sous-maille $I2/m$ ayant $a' = \frac{1}{2}a$, $b' = \frac{1}{2}b$, $c' = c$ et $\beta' = \beta$ est très évidente. Les cristaux sont prismatiques, applatis sur {010}, allongés sur [001], et délimités par {001}, {010}, {100} et une forme $\{\bar{h}0l\}$, possiblement $\{\bar{1}01\}$. Les macles de contact "en queue d'hirondelle" sont courantes; elles ont {001} comme plan de macle et plan de composition. Les sept raies les plus intenses du cliché de diffraction [méthode des poudres; d en Å(I)(hkl)] sont: 10.43(42)(002), 3.573(11)(025), 3.474(100)(006), 3.186(15)(224), 2.867(13)(241), 2.606(40)(008), 2.084(15)(00•10). Les analyses à la microsonde électronique ont donné: SiO_2 27.32, Al_2O_3 0.03, MnO 31.14, FeO 1.12, MgO 0.06, TiO_2 9.44, Nb_2O_5 13.35, ZrO_2 0.12, BaO 8.88, K_2O 2.68, Na_2O 3.52, F 0.84, H_2O (par analyse thermogravimétrique) 3.49, $-O \equiv F$ 0.35, total 101.64% par poids, ce qui correspond à $Na_{2.02}K_{1.00}Ba_{1.02}(Mn_{7.73}Fe_{0.27}Mg_{0.03})(Ti_{2.08}Nb_{1.77}Zr_{0.02})(Si_{8.01}Al_{0.01})O_{32.00}[(OH)_{5.62}F_{0.78}(H_2O)_{0.60}]_{\Sigma 7.00}$. La formule idéale serait $Na_2KBaMn_8(Ti,Nb)_4Si_8O_{32}(OH,F,H_2O)_7$. L'analyse thermogravimétrique a révélé une perte en poids en deux étapes, avec une discontinuité à 450°C. Le spectre d'absorption infra-rouge confirme la présence de H_2O et de OH. Le nom honore M. Guy Perrault.

(Traduit par la Rédaction)

Mots-clés: perraultite, nouvelle espèce minérale, silicate, mont Saint-Hilaire, Québec, propriétés, données de diffraction X, composition chimique.

INTRODUCTION

The formerly unidentified mineral UK17 from Mont Saint-Hilaire, Quebec (Chao *et al.* 1967) has been established as a new mineral species on the basis of X-ray-diffraction studies and electron-micropobe analyses. The mineral is named *perrault-*

ite, in honor of Emeritus Professor Guy Perrault, of Ecole Polytechnique, Montreal, Quebec, in recognition of his contributions to the study of mineralogy of the nepheline syenite at Mont Saint-Hilaire. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names, IMA. The type specimens of perraultite are deposited at the Canadian Museum of Nature, Ottawa, Ontario (CMN #50037) and the Royal Ontario Museum, Toronto, Ontario (M41005).

Occurrence and Properties

The mineral occurs in pegmatite dikes in the nepheline syenite at the De-mix quarry, Mont Saint-Hilaire, in close association with kupletskite, rhodochrosite, catapleiite, microcline, pyrochlore, ancylite, natrolite, tetranatrolite, albite, polylithionite, aegirine, lorenzenite, calcite and fluorite.

Perraultite is orange brown with a pale brown streak. The luster is vitreous on fresh surfaces and slightly waxy on the exposed faces. Small fragments of the mineral are transparent, and larger grains are translucent to opaque. The mineral is very brittle, with a Mohs hardness about 4. It has a very good {001} cleavage and uneven to irregular fracture. The density determined using a Berman balance is 3.71(5) g/cm^3. Perraultite is nonfluorescent in ultraviolet light and is not affected by cold 1:1 HCl, H_2SO_4 or HNO_3. Crystals of perraultite (up to 0.5 mm long) are prismatic and flattened on {010}, with elongation along [100], bound by {001}, {010}, {100} and a {$\bar{h}0l$} form , perhaps {$\bar{1}01$}. "Swallow-tail" type, simple, contact twins are common, with {001} as twin plane and composition plane.

Optically, perraultite is biaxial (–), with α 1.785(2), β 1.81(1), γ 1.82(1), $2V$(meas.) 66(1)° (all measured in Na light, λ 589 nm) and $2V$(calc) 64°. Dispersion is strong, with $r << v$. The optic orientation is X = b, $Y \wedge a$ = 19° in the obtuse β angle. Pleochroism is pronounced with Z = dark brown, X = Y = light yellow.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR PERRAULTITE

	Perraultite[1]			Jinshajiangite[2]	
hkl	d_{calc}	d_{obs}	*I*	d_{obs}	*I*
002	10.422	10.43	42	10.2	7
110	8.504	8.45	2		
021	6.569	6.57	3		
$\bar{2}01$	5.333	5.33	6		
004	5.211	5.21	3		
201	5.108	5.11	2		
023	4.903	4.90	3		
$\bar{2}03$	4.454	4.45	2	4.4	3
220	4.252	4.25	4		
203	4.086	4.09	4	4.05	3
222	3.8439	3.847	2	3.80	2
025	3.5710	3.573	11		
006	3.4739	3.474	100	3.44	10
$\bar{2}24$	3.4134	3.415	8		
224	3.1869	3.186	15	3.15	8
$\bar{2}41$	2.9030	2.899	4		
241	2.8651	2.867	13	2.85	7
$\bar{2}26$	2.7875	2.789	10	2.77	3
027	2.7353	2.736	6		
$\bar{4}02$	2.6665	2.664	7		
243	2.6408	2.640	10	2.63	7
008	2.6054	2.606	40	2.570	8
402	2.5542	2.556	1		
$\bar{4}04$	2.4849	2.486	3		
046	2.4517	2.450	3	2.450	3b
245	2.3352	2.336	3	2.320	2
$\bar{4}06$	2.2268	2.227	5	2.202	4
$\bar{2}47$	2.1336	2.133	3		
00·10	2.0844	2.084	15	2.062	3
406	2.0431	2.042	4	2.020	2
264	1.9409	1.941	1		
04·10	1.7855	1.787	1		
249	1.7717	1.772	8	1.755	4
00·12	1.7370	1.737	10		
$\bar{4}0$·10	1.7243	1.726	7	1.715	5b
$\bar{6}24$	1.6935	1.693	1		
622	1.6915				
$\bar{4}65$	1.6499	1.651	1		
$\bar{2}4$·11	1.6242	1.625	5		
$\bar{6}41$	1.5992	1.599	5	1.587	3
$\bar{2}0$·13	1.5754	1.575	8	1.570	2
24·11	1.5545	1.553	2		
04·12	1.5524				
$\bar{6}28$	1.5072	1.507	2		

1. Diffractometer data, Cu$K\alpha_1$ radiation, λ = 1.54059Å.
2. Fe radiation, 57.3 mm camera (Hong & Fu 1982).

X-Ray Crystallography

Single-crystal X-ray precession photographs of perraultite showed the mineral to be monoclinic. The cell parameters obtained from the single-crystal photographs and refined by a least-squares method using X-ray powder-diffraction data (Table 1) are: a 10.820(2), b 13.843(4), c 20.93(1) Å, β 95.09(2)° and Z = 4. There is a very pronounced subcell with $a' = \frac{1}{2}a$, $b' = \frac{1}{2}b$ and $c' = c$, $\beta' = \beta$, as the odd level a-axis and b-axis precession photographs show very weak reflections with strong streaking along c^*. The reflection conditions are very unusual: for all reflections where $k = 2(2n)$ and $h = 2(2n)$, $l = 2n$; where $k = 2(2n)$ and $h = 2(2n+1)$, $l = 2n+1$; where $k = 2(2n+1)$ and $h = 2(2n)$, $l = 2n+1$; where $k = 2(2n+1)$ and $h = 2(2n+1)$, $l = 2n$; where $k = 2n+1$ and $h = 2n+1$, l = all. These conditions are consistent with those for space groups $C2/m$, Cm or $C2$, but with extra conditions added. If the weak reflections with $h = 2n+1$ and $k = 2n+1$ are ignored, the space group for the subcell becomes $I2/m$.

The X-ray powder-diffraction data for perraultite are compared with those for a closely related mineral, jinshajiangite, in Table 1. The powder data were indexed using single-crystal photographs as a guide. Indices of the relatively strong reflections were assigned to the powder-diffraction lines. Owing to the limit of the least-squares program used, d values below 1.941 Å were not used in the refinement of the cell parameters.

Chemical Composition

Perraultite was analyzed using wavelength dispersion on a Cambridge Microscan MK5 electron microprobe with an operating voltage of 15 kV and a beam current of 20 nA and a slightly defocused beam. Rhodonite (Mn$K\alpha$), aenigmatite (Si$K\alpha$, Ti$K\alpha$), biotite (K$K\alpha$, Al$K\alpha$), synthetic fluorphlogopite (F$K\alpha$), pyroxene (Mg$K\alpha$), olivine (Fe$K\alpha$), ZrO_2 (Zr$L\alpha$), $NaNbO_3$ (Na$K\alpha$, Nb$L\alpha$), and $BaFe_{12}O_{19}$ (Ba$L\alpha$) were used as standards. H_2O was determined by weight loss in a thermogravimetric analysis (to 1000°C) after deducting F. The average results of three analyses on different spots of the same grain are given in Table 2. Preliminary calculations of the cell contents using the measured density, cell volume and results of the electron-microprobe analyses indicate that the cell contains approximately 8 (Si + Al) and 39(O + F + OH + H_2O). The composition was, therefore, recalculated on the basis of 39(O + F + OH + H_2O) to yield the following empirical formula: $Na_{2.02}K_{1.00}Ba_{1.02}(Mn_{7.73}Fe_{0.27}Mg_{0.03})_{\Sigma 8.03}(Ti_{2.08}Nb_{1.77}Zr_{0.02})_{\Sigma 3.87}(Si_{8.01}Al_{0.01})_{\Sigma 8.02}O_{32.00}[(OH)_{5.62}F_{0.78}(H_2O)_{0.60}]_{\Sigma 7.00}$. Other ways of expressing the anion groups are possible, but without knowledge of the crystal structure, it is difficult to determine which is the correct way. A tentative idealized formula may be given as $Na_2KBaMn_8(Ti,Nb)_4Si_8O_{32}(OH,F,H_2O)_7$. The calculated density for the mineral is 3.808 g/cm^3, close to the measured density of 3.71 g/cm^3.

Thermal and Infrared-Absorption Data

Thermal gravimetric analysis of perraultite, carried out to 1000°C on a 14.7-mg sample, showed a two-stage weight loss (2.74% and 1.59%), with a break at 450°C. The first stage is probably due to the release of H_2O and a part of OH groups, and the second stage is interpreted as due to the loss of the rest of OH groups and F.

The infrared-absorption spectrum of perraultite was obtained using a KBr pellet containing 1 mg of sample and 200 mg KBr. The spectrum shows absorption bands at 475, 525, 590, 625, 680, 870, 935, 1025, 1095, 1160, 1625 and 3410 cm^{-1}. The bands at 1625 and 3410 cm^{-1} confirm the presence of H_2O and OH in perraultite.

Discussion

Perraultite is closely related to jinshajiangite, $(Ba,Ca)_4(Na,K)_5(Fe^{2+},Mn)_{15}(Ti,Fe^{3+},Nb,Zr)_8Si_{15}O_{64}(F,OH)_6$, in composition. A probable structural relationship of perraultite to jinshajiangite may be inferred from their identical space-group symmetry, comparable cell-parameters, similar powder-diffraction patterns and essential physical properties (Table 3). The similarity in composition becomes apparent if the formula of jinshajiangite is recalculated from the original chemical analysis, on the basis of 38 anions, as follows: $Na_{1.81}K_{0.87}(Ba_{1.14}Ca_{0.93}REE_{0.10}Sr_{0.01})_{\Sigma 2.18}(Fe^{2+}_{4.73}Mn_{3.25}Mg_{0.12})_{\Sigma 8.10}(Ti_{3.55}Fe^{3+}_{0.37}Nb_{0.14}Zr_{0.10})_{\Sigma 4.16}(Si_{8.04}Al_{0.12})_{\Sigma 8.16}O_{32.00}[O_{2.83}F_{2.49}(OH)_{0.12}(H_2O)_{0.56}]_{\Sigma 6.00}$. The formula may be idealized to $Na_2KBaCa(Fe,Mn)_8Ti_4Si_8O_{32}(O,F,H_2O,OH)_6$. The charge balance could also be satisfied by the anion group $O_{32}(F,OH)_7$, which is similar to that in perraultite. Thus, perrault-

TABLE 2. CHEMICAL COMPOSITION OF PERRAULTITE

	Emperical[1]	Calculated[2]
SiO_2 wt.%	27.32	26.79
Al_2O_3	0.03	
MnO	31.14	30.57
FeO	1.12	1.08
MgO	0.06	
TiO_2	9.44	9.62
Nb_2O_5	13.35	13.63
ZrO_2	0.12	
BaO	8.88	8.55
K_2O	2.68	2.63
Na_2O	3.52	3.45
F	0.84	0.83
H_2O	3.49	3.20
-O=F	0.35	0.35
Total	101.64	100.00

1. Average of three electron-microprobe analyses.
2. Calculated for $Na_2KBa(Mn_{7.73}Fe_{0.27})(Ti_{2.16}Nb_{1.84})Si_8O_{32}[(OH)_{6.06}F_{0.78}(H_2O)_{0.16}]$.

TABLE 3. PROPERTIES OF PERRAULTITE AND JINSHAJIANGITE

	Perraultite	Jinshajiangite[1]
Space group	*C2/m, Cm, C2*	*C2/m, Cm, C2*
a (Å)	10.820(2)	10.732
b	13.843(4)	13.847
c	20.93(1)	20.817
β (°)	95.09(2)	95.05
$D_{meas.}$ g/cm^3	3.71	3.61
$D_{calc.}$	3.808	3.56
Hardness	4 (Mohs)	430 kg/mm^2 (Vicker)
Color	orange brown	black red, brownish red or golden red
Streak	brown	light yellow
Habit	tabular prissmatic, elongation [100]	tabular prismatic elongation [001][2]
Cleavage	{001} v. good	{010}, {100} perfect
Optics		
α	1.785(2)	1.729
β	1.81(1)	1.802
γ	1.82(1)	1.852
$2V_{meas.}$ (°)	(-) 66(1)	(+) 72
$2V_{calc.}$	(-) 64	(-) 76[3]
Dispersion	*r* << *v*	*r* < *v*
Orientation	*X* = *b* *Y* ∧ *a* = 19°	
Pleochroism		
X	light yellow	light golden yellow
Y	light yellow	brownish yellow
Z	dark brown	brownish red

(1). Hong & Fu 1982.
(2). Inferred by GYC from the reported extinction angle, *c* ∧ *X* = 13°.
(3). Calculated by GYC.

ite may be considered as a Mn- and Nb-rich analogue of jinshajiangite. The major cationic substitutions involved are Mn ↔ Fe^{2+} and 2Nb ↔ 2Ti + Ca. The additional Ca atom in jinshajiangite is probably accommodated in an interstitial site.

In perraultite the number of Ti atoms and that of Nb atoms are both close to 2, which suggests the possibility of an ordered arrangement. The presence of a supercell with a pronounced subcell is probably the result of this ordering.

Gladstone–Dale calculations for perraultite gave $1-(K_P/K_C) = 0.036$, using measured density and indices of refraction and constants given by Mandarino (1981). Thus the compatibility of the chemical and physical data of perraultite is excellent, and if the calculated density is used, $1-(K_P/K_C) = 0.062$, the compatibility becomes fair (Mandarino 1981).

Acknowledgements

I thank Judith Baker for technical assistance, Peter C. Jones for electron-microprobe analyses, J. A. Mandarino, an anonymous referee, and R. F. Martin for constructive suggestions for improvement of the manuscript. The work was supported by NSERC operating grant A5113.

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Received November 6, 1990, revised manuscript accepted January 7, 1991.