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VOGGITE, A NEW HYDRATED Na–Zr HYDROXIDE–PHOSPHATE–CARBONATE FROM THE FRANCON QUARRY, MONTREAL, QUEBEC[1]

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ABSTRACT

Voggite, ideally $Na_2Zr(PO_4)(CO_3)(OH)\cdot 2H_2O$, is found at the margins of an altered amygdaloidal basalt dyke that has intruded a silicocarbonatite sill exposed at the Francon quarry, Montreal, Quebec. It occurs as mm-sized matted nests of colorless to white transparent acicular crystals within cavities, associated with quartz, dawsonite and calcite. Other minerals found within similar cavities are mordenite, analcime, dolomite, barite, fluorite and albite. Individual crystals are colorless, average 1 × 0.01 × 0.01 mm in size, and are elongate [010], with forms {100} major, {$\bar{1}$01} major, and {001} minor. The average length-to-width ratio exceeds 100:1. The streak is white; tenacity brittle; luster vitreous; cleavage {010} poor; D (meas.) 2.70(2), D (calc.) 2.704 g/cm³ for the theoretical formula; nonfluorescent in ultraviolet light. Voggite is biaxial positive, α 1.569 (1), β 1.594 (1), γ 1.622 (1), $2V$ (meas.) 81 (5)°, $2V$ (calc.) 88°; $r \ll v$, strong; indicatrix orientation $X = b$, $Z \wedge a = 22°$ in the obtuse β angle. The symmetry is monoclinic, space-group $I2/m$, with a 12.251(5), b 6.557(3), c 11.755(5) Å, β 116.12(4)°, V 848(1) Å³, $a{:}b{:}c$ 1.8684:1:1.7927, Z = 4. The strongest seven lines of the X-ray powder-diffraction pattern [d in Å (I) (hkl)] are 10.2 (100) ($\bar{1}$01), 5.58(80) (110, 011, 200), 4.06 (60) ($\bar{3}$01), 3.89 (65) ($\bar{1}$03), 3.281 (60) (020), 2.546 (40) ($\bar{4}$04) and 2.039 (40) (204, $\bar{5}$05, $\bar{6}$02). The physical characteristics of the mineral precluded an accurate quantitative electron-microprobe result. TGA–EGA gave CO_2 12(2), H_2O 15(2) wt.%. The idealized formula, derived from a crystal-structure study, requires Na_2O 17.95, ZrO_2 35.69, P_2O_5 20.56, CO_2 12.75, H_2O 13.05, total 100.00 wt.%. The new species is named for Adolf Vogg who first discovered the mineral.

Keywords: voggite, new mineral species, sodium zirconium hydroxide–phosphate–carbonate hydrate, Francon quarry, Montreal, Quebec, X-ray data, chemical composition.

SOMMAIRE

Nous avons découvert la voggite, de composition idéale $Na_2Zr(PO_4)(CO_3)(OH)\cdot 2H_2O$, dans les bordures d'un filon basaltique amygdulaire altéré qui recoupe un sill de silicocarbonatite dans la carrière de Francon, à Montréal (Québec). La voggite forme des agrégats nattés de cristaux aciculaires millimétriques blancs ou transparents dans des cavités, en association avec quartz, dawsonite et calcite. Aussi retrouvés dans la même paragenèse sont mordenite, analcime, dolomite, barytine, fluorite et albite. Les cristaux individuels sont incolores, d'une taille moyenne de 1 × 0.01 × 0.01 mm, et allongés sur [010]; ils montrent les formes {100} et {$\bar{1}$01} prominentes, et {001} d'importance moindre. Le rapport de longueur à largeur surpasse 100:1. La rayure est blanche, sa ténacité, cassante, et son éclat, vitreux; le clivage {010} est de piètre qualité. Densité 2.70(2) mesurée, 2.704 (calculée selon la formule idéale). Elle est non fluorescente en lumière ultra-violette. Elle est biaxe positive, α 1.569(1), β 1.594(1), γ 1.622(1), $2V$ 81(5)° (mesuré), 88° (calculé), $r \ll v$, intense. L'orientation de l'indicatrice est $X = b$, $Z \wedge a = 22°$ dans l'angle β obtus. Sa symétrie est monoclinique, groupe spatial $I2/m$, avec a 12.251(5), b 6.557(3), c 11.755(5) Å, β 116.12(4)°, V 848(1) Å³, $a{:}b{:}c$ 1.8684:1:1.7927, Z = 4. Les sept raies les plus intenses du cliché de diffraction (méthode des poudres) [d en Å(I)(hkl)] sont: 10.2(100)($\bar{1}$01), 5.58(80)(110,011,200), 4.06(60)($\bar{3}$01), 3.89(65)($\bar{1}$03), 3.281(60)(020), 2.546(40)($\bar{4}$04) et 2.039(40)(204,$\bar{5}$05,$\bar{6}$02). Les propriétés physiques de la voggite n'ont pas permis une détermination quantitative précise de sa composition chimique par microsonde électronique. Une analyse thermogravimétrique, avec détermination des gaz libérés, a donné: CO_2 12(2), H_2O 15(2)% (par poids). La formule idéale, dérivée d'une ébauche de la structure cristalline, requiert Na_2O 17.95, ZrO_2 35.69, P_2O_5 20.56, CO_2 12.75, H_2O 13.05, pour un total de 100.00% par poids. Le nom de la nouvelle espèce honore M. Adolf Vogg, qui l'a découverte.

(Traduit par la Rédaction)

Mots-clés: voggite, nouvelle espèce minérale, hydroxyde-

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phosphate–carbonate de sodium et de zirconium hydraté, carrière de Francon, Montréal, Québec, données de rayons X, composition chimique.

INTRODUCTION

The silicocarbonatite sills exposed at the Francon limestone quarry, Montreal, Quebec have been the source of several new minerals since investigation of the unique mineral assemblage began in 1966. A complete list of references related to the mineralogy and chemistry of the quarry can be found in Roberts *et al.* (1986). While on a visit to the quarry in June, 1985, Adolf Vogg, a local amateur mineralogist, collected vuggy-looking rock specimens near the contact between a sill and an intruding darker-colored dyke. Megascopic examination revealed that several vugs contain some clear transparent hair-like needles, which were unidentifiable. Subsequent X-ray powder-diffraction studies at the Geological Survey of Canada confirmed the presence of a potential new mineral species in one vug of each of two hand specimens. This new phase was designated unknown #15. Later that same year, one of us (A.P.S.) collected additional material from the same contact; two hand specimens were found to contain the same new phase, a sodium zirconium hydroxide–phosphate–carbonate hydrate. We name this new mineral *voggite* after Adolf Vogg, who had collected the original material from which the mineral was identified and characterized.

The mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA. Type specimens are housed in the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, under catalogue number NMC 65631.

OCCURRENCE AND ASSOCIATED MINERALS

Voggite is a very rare constituent found within cm-sized cavities of an altered amygdaloidal basalt dyke exposed at the Francon quarry, Montreal, Quebec. Only four specimens, containing an estimated 10 mg of sample, have been identified to date. The dyke has intruded a silicocarbonatite sill, and the voggite-bearing vugs are located within a few centimeters of the contact margin. It seems that the mineral formed by reaction between the intruding dyke and the Zr-rich sill material. Colorless crystalline masses of quartz and dawsonite also are found associated with the voggite as cavity linings and infillings. In addition, microglobules of quartz and calcite, attached to voggite needles, have been identified by X-ray powder-diffraction. Other cavity-bearing minerals within the dyke rock that have been identified by X-ray powder-diffraction are mordenite, analcime, dolomite, barite, fluorite and albite. Some of the mordenite closely resembles voggite in appearance.

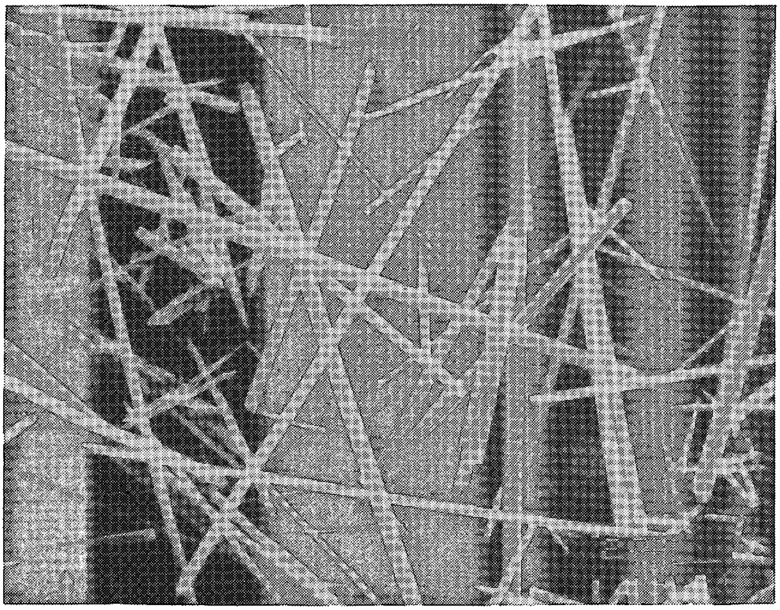

FIG. 1. Scanning-electron photomicrograph of voggite showing typical habit of crystals. Scale bar 20 μm.

TABLE 1. X-RAY POWDER DATA FOR VOGGITE

*I*est	*d*Åmeas	*d*Åcalc	*hkl*
100	10.2	10.2	$\bar{1}01$
80	5.58	5.63 5.57 5.50	110 011 200
30	5.29	5.28	002
60	4.06	4.06	$\bar{3}01$
65	3.89	3.88	$\bar{1}03$
20	3.480	3.479	112
5	3.395	3.392	$\bar{3}03$
60	3.281	3.279	020
35	3.181	3.200 3.173	310 202
20	3.110	3.120 3.100	$\bar{1}21$ 013
35	3.051	3.050	$\bar{4}02$
10	2.938	2.936	$\bar{2}04$
30	2.814	2.816	220
5	2.776	2.785	022
10	2.732	2.730	$\bar{4}11$
20	2.625	2.629 2.624	$\bar{1}14$ $\bar{4}13$
40	2.546	2.544	$\bar{4}04$
30	2.360	2.363 2.357	$\bar{3}12$ $\bar{3}23$
20	2.263	2.266	$\bar{1}05$
10	2.234	2.233	$\bar{4}22$
20	2.205	2.206	114
10	2.192	2.187	$\bar{2}24$
20	2.141	2.140	031
15	2.120	2.116	303
20	2.093	2.093 2.091	$\bar{4}15$ 402
40	2.039	2.053 2.035 2.031	$\bar{2}04$ $\bar{5}05$ $\bar{6}02$
25	1.940	1.942 1.937	$\bar{2}06$ 231
15	1.917	1.922 1.922 1.913	105 $\bar{5}21$ $\bar{4}06$
20	1.875	1.877 1.876 1.864	$\bar{3}30$ $\bar{6}11$ $\bar{1}25$
10	1.857	1.857	033
15	1.832	1.833	600
10	1.799	1.798	$\bar{1}16$
10	1.774	1.777 1.767	$\bar{3}23$ $\bar{4}31$
15	1.749	1.750	$\bar{7}03$
20	1.731	1.738 1.729	$\bar{1}34$ $\bar{5}25$
15	1.672	1.671	$\bar{7}12$
15	1.657	1.658 1.655 1.652	$\bar{7}05$ $\bar{3}32$ $\bar{4}26$
15	1.637	1.639	040
20	1.619	1.620	$\bar{5}07$
15	1.599	1.598	134
10	1.579	1.581	116

- 114.6 mm Debye – Scherrer powder camera employing Ni-filtered Cu radiation (λCu*K*a 1.54178 Å)
- indexed with a 12.251, *b* 6.557, *c* 11.755 Å, ß 116.12°
- intensities visually estimated

PHYSICAL AND OPTICAL PROPERTIES

Voggite occurs as mm-sized matted nests of colorless to white acicular fibers within amygdaloidal cavities. Individual crystals are needle-shaped prisms that are colorless, transparent and elongate along [010], with forms {100} major, {$\bar{1}$01} major, and {001} minor. The crystals possess a poor {010} cleavage and can exceed 1 mm in length. Most needles are less than 0.01 mm in width and have an average length-to-width ratio greater than 100:1 (Fig. 1). Voggite is brittle, with a white streak, a vitreous luster, and is nonfluorescent under both long- and short-wave ultraviolet radiation. However, the mineral exhibits a blue cathodoluminescence under the electron-microprobe beam. The hardness could not be determined because of the physical size of the individual crystals. The specific gravity measured in heavy liquids is 2.70(2) g/cm^3; the calculated density, assuming the theoretical formula derived from the crystal-structure determination (Szymański & Roberts 1990) and $Z = 4$, is 2.704 g/cm^3. Voggite is nonreactive in 1:1 HCl both at room temperature and elevated temperatures and also is nonreactive in concentrated HNO_3.

Optical measurements were made on a spindle stage using sodium light (λ 589 nm). Voggite is biaxial positive, α 1.569 (1), β 1.594 (1), γ 1.622 (1), $2V$ (meas.) 81 (5)° and $2V$ (calc.) 88°. The dispersion is strong with r very much less than v. The optical orientation is $X = b$, $Z \wedge a = 22°$ in the obtuse β angle. Neither pleochroism nor absorption was observed.

X-RAY CRYSTALLOGRAPHY

Precession single-crystal studies of two crystal fibers, employing Zr-filtered Mo radiation, showed that voggite is monoclinic, with measured and calculated unit-cell parameters a 12.3, b 6.54, c 11.8 Å, β 116.95°. The following levels were photographed: $hk0 \rightarrow hk3$, $0kl \rightarrow 2kl$, $h0l \rightarrow h2l$, $101^* \wedge b^*$, $\bar{1}01^* \wedge b^*$, $\bar{2}01^* \wedge b^*$ and $\bar{3}01^* \wedge b^*$. The space-group extinction conditions are compatible with the space groups *I*2/*m*, *I*2 or *Im* (diffraction aspect *I**/*). The correct space-group is *I*2/*m* based on the crystal-structure determination (Szymański & Roberts 1990). The X-ray powder-diffraction data are presented in Table 1. The unit-cell parameters were refined using 25 powder reflections between 4.06 and 1.579 Å for which unambiguous indexing was possible, based on visual inspection of precession single-crystal films. The refined unit-cell parameters are: a 12.251(5), b 6.557(3), c 11.755(5) Å, β 116.12(4)°, V 848(1) Å^3, a:b:c 1.8684:1:1.7927. The powder data are unique and bear no resemblance to any other inorganic phase listed in the Powder Diffraction File. This is the first reported sodium zirconium hydroxide–phosphate–carbonate hydrate in either a natural or synthetic form.

CHEMISTRY

Voggite decomposes rapidly under the electron beam at typical operating conditions for electron microprobes (5 to 25 kV, 5 to 40 nA). Under such conditions, the decomposition of minerals that contain volatile elements can be retarded to a manageable rate by defocusing the electron beam (Autefage & Fontan 1985, Ercit, unpub. data). For such cases, decay curves can be plotted and extrapolated to give the original composition of the undecomposed sample. However, because crystals of voggite are acicular and extremely slender, typically less than 0.01 mm in diameter, it was not possible to sufficiently defocus the beam to slow the rates of change to levels at which highly precise results could be obtained.

The problem was further complicated by the fact that samples of voggite decompose differently under the electron beam depending upon their orientation (Fig. 2). Acicular crystals oriented parallel to the electron beam showed less total variation in their count rates than crystals oriented perpendicular to the electron beam. To the best of our knowledge, the style of the change in the Na count rate for crystals in the perpendicular orientation (Fig. 2C) is unique; the count rate increases by over 700% after only three minutes of exposure of the sample to the electron beam.

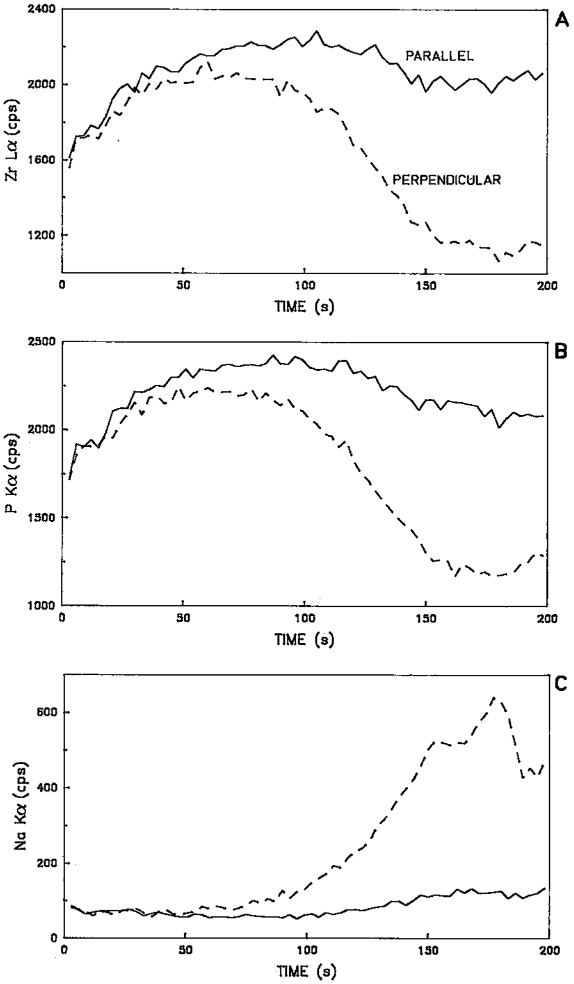

FIG. 2. Decomposition curves for voggite under electron bombardment (15 kV, 10 nA). (A) Zr$L\alpha$, (B) P$K\alpha$, (C) Na$K\alpha$. Solid lines represent data for crystals in a parallel orientation to the beam, and broken lines represent data for crystals in a perpendicular orientation to the beam.

TABLE 2. VOGGITE: MEASURED AND CALCULATED COMPOSITIONS

	Meas. (wt. %)	Calc. (wt. %)
Na_2O	7.4	17.95
ZrO_2	43.3	35.69
P_2O_5	25.9	20.56
CO_2	12	12.75
H_2O	15	13.05
Total	103.6	100.00

– Na, Zr, P by electron microprobe; CO_2, H_2O by TGA – EGA

A JEOL 733 electron microprobe with Tracor Northern TASK automation, housed at the National Museum of Natural Sciences, was used for the microprobe analyses. Because of the rapid decomposition, relatively "gentle" operating conditions were selected for analysis: 15 kV, 10 nA. Similarly, rapid changes in count rates necessitated short counting times which, combined with the low beam-current, gave analytical results of low precision. For each crystal, counts for P, Zr and Na were measured simultaneously on three separate wavelength-dispersion spectrometers; the three largest crystals in the probe mount were used for the measurements (each with a diameter slightly exceeding 0.01 mm). Even with short counting times of 5 seconds each for peak and background measurements, only three measurements of the count rate for each of P, Zr and Na could be made on each crystal before the slopes of the decomposition curves first changed sign (Fig. 2). The three measurements were fitted to exponential curves and extrapolated to the intercept at time = 0 seconds to obtain pre-decay count rates, which were then reduced with a conventional ZAF routine to give elemental weight percents. Albite (Na$K\alpha$), ZrO_2 (Zr$L\alpha$) and apatite (P$K\alpha$) were used as standards.

The resulting average composition, as determined by electron-microprobe analysis, is given in Table 2. The low analytical sum of $Na_2O + ZrO_2 + P_2O_5$ was assumed to indicate the presence of light elements with an atomic number less than 11. Using a lead stearate crystal and operating conditions of 5 kV and 100 nA, carbon was detected, but owing to the small size of the remaining crystals, and to the broad diameter of the beam and large excitation volume at these conditions, carbon could not be measured quantitatively. No other elements with atomic number greater than 4 were detected.

TGA – EGA determinations for H_2O and CO_2 were made on 0.362(4) mg of hand-picked sample using the Mettler thermal analyzer and integrated mass-spectrometer at the Royal Ontario Museum. The sample experienced two major weight losses; a 15(2) wt.% H_2O loss occurred between 140 and 250°C with a pressure maximum at 215°C, and a 12(2) wt.% CO_2 loss between 480 and 600°C.

The ideal composition of the mineral (Table 2) was calculated from the formula resulting from the crystal-structure analysis (Szymański & Roberts 1990), *i.e.*, $Na_2Zr(PO_4)(CO_3)(OH){\bullet}2H_2O$. The TGA – EGA data for H_2O and CO_2 match the calculated composition to within 1 σ. However, the electron-microprobe data differ radically; Na_2O is significantly lower, and ZrO_2 and P_2O_2 are significantly higher than the ideal concentrations. We take this as an indication that: (1) the simple exponential curves fitted to the microprobe data points failed to adequately predict changes in the count rate that took place during the first few seconds of analysis; this was expected, as the change in count rate was too rapid for adequate modeling; (2) the weakly bound H_2O molecules, indicated by structural analysis, have been driven off upon impingement of the electron beam; this loss increases the quantitative values for ZrO_2 and P_2O_5; decarbonation also may have occurred concurrently with dehydration, compounding the problem; (3) the Na atoms have migrated through the open channels within the structure and also have been boiled off: this accounts for the very low Na_2O value. As the samples are extremely homogeneous (energy-dispersion spectra of eight crystals, all with perpendicular orientation, were found to be identical), there is no doubt that the crystal selected for structural study was initially identical to the material used for the electron-microprobe analysis.

From Figure 2, it is obvious that the count rates for P and Zr are inversely dependent upon the count rate for Na. Note that although the cationic ratio Na:(Zr + P) for the microprobe data significantly deviates from ideality, the ratio of Zr:P(0.96:1) is quite close to the expected 1:1 ratio. Both of these features support a structural model involving mobile Na in a relatively immobile Zr–P–O framework, when the mineral undergoes electron bombardment.

Calculations using the Gladstone - Dale relationship and the ideal composition derived from the structure analysis give $K_C = 0.218$ and $K_P = 0.220$ for the constants of Mandarino (1981); hence $1 - (K_P/K_C)$ is $- 0.009$, indicating superior compatibility (Mandarino 1979).

Since the voggite structure appears to display high mobility of Na, it deserves further study as a potential low-temperature solid electrolyte. Another Zr-phosphate, $Na_3Zr_2PSi_2O_{12}$, possesses a framework structure with a three-dimensional network of tunnels occupied by mobile Na atoms (West 1984, p 479). It was named NASICON (for sodium superionic conductor). We hope to examine this synthetic compound as a potential Na microprobe standard for minerals such as voggite.

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