*American Mineralogist, Volume 73, pages 1191–1194, 1988*

# Calciohilairite: $CaZrSi_3O_9{\cdot}3H_2O$, the calcium analogue of hilairite from the Golden Horn batholith, northern Cascades, Washington

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## ABSTRACT

Calciohilairite, $CaZrSi_3O_9{\cdot}3H_2O$, occurs associated with microcline, quartz, albite, fluorite, chlorite, bastnaesite, zircon, and malachite in miarolitic cavities in peralkaline granite of the Eocene Golden Horn batholith, northern Cascades, Washington. The crystals are white to pale blue, trigonal, up to 2 mm long, and show the forms $a'$ $\{11\bar{2}0\}$, $'a$ $\{2\bar{1}\bar{1}0\}$, $r$ $\{10\bar{1}2\}$, and $-r$ $\{01\bar{1}2\}$. The probable space group is $R32$; with $a = 20.870(4)$ and $c = 16.002(4)$ Å. The Mohs' hardness is 4, and there is a conchoidal fracture and no cleavage. The density is 2.68(2) g/cm³ (meas.), 2.74 g/cm³ (calc.). The optical properties are uniaxial (−), $\epsilon = 1.619(1)$, $\omega = 1.622(1)$. The X-ray powder-diffraction pattern, which is very similar to that of hilairite ($Na_2ZrSi_3O_9{\cdot}3H_2O$), shows the following strongest eight lines [$d$ (Å),$I$,$hkl$]: 5.99,12,202; 5.23,100,220; 3.14,14,422; 3.02,34,205,600; 2.606,8,440,612,244; 1.817,31,381,725,734; 1.671,17,930,482; 1.668,15,482,384. An average of six electron-microprobe analyses yields the empirical formula

$$(Ca_{0.89}Zr_{0.15}Na_{0.03}Cu_{0.03})(Zr_{0.99}Fe_{0.01})(Si_{2.82}Al_{0.09})O_9{\cdot}3.30H_2O.$$

The name is for the Ca content and the relationship to hilairite.

## INTRODUCTION

The Eocene Golden Horn batholith drops out over 310 km² in the northern Cascade Mountains in Washington. Four granite types occur in the batholith, a peralkaline arfvedsonite granite, an alaskitic border granite, a hypersolvus biotite granite, and a subsolvus biotite granite (Stull, 1969; Boggs, 1984a, 1984b). Several suites of uncommon minerals occur in miarolitic cavities and small pegmatites in the different granite types and have been described by Dunn et al. (1977) and Boggs (1980, 1984a, 1984b).

Calciohilairite is the third new species to be described from the Golden Horn batholith. The previously described species are zektzerite, $NaLiZrSi_6O_{15}$ (Dunn et al., 1977) and okanoganite, $(Na,Ca)_3(Y,Nd,Ce)_{12}Si_6B_2O_{27}F_{14}$ (Boggs, 1980). All three species occur in miarolitic cavities in the batholith, zektzerite and okanoganite in the arfvedsonite granite and calciohilairite in the border granite (Boggs, 1984a, 1984b). The mineral has been accepted and the name approved by the IMA Commission on New Minerals and Mineral Names. The name is for the Ca content and the relationship to hilairite ($Na_2ZrSi_3O_9{\cdot}3H_2O$). Co-type material has been deposited in the National Museum of Natural History, Smithsonian Institution, Washington, D.C. (NMNH no. 161901 and 162182) and in my own collection (no. T990 to T996).

## OCCURRENCE

Calciohilairite has been found in two occurrences in boulders of border granite on a talus slope on the north side of Liberty Bell Mountain, Okanogan County, Washington (lat 48°31′4″N, long 120°39′7″W). Both occurrences have been collected by Robert M. Boggs, who provided the material for this study. The first occurrence, discovered in September 1982, consisted of white altered trigonal prismatic crystals up to 2 mm associated with microcline, quartz, albite, fluorite, and chlorite in a zone of small miarolitic cavities. The second, discovered in October 1984, consisted of smaller (up to 1 mm) white to pale blue unaltered crystals in a larger isolated miarolitic cavity associated with microcline, quartz, albite, bastnaesite, zircon, chlorite, and malachite. Less than 500 mg of material has been collected from the two occurrences. Other minerals found in miarolitic cavities in the border granite in the same area but not associated with calciohilairite include allanite, kainosite, gadolinite, and beta-fergusonite (Boggs, 1984a, 1984b).

## PHYSICAL PROPERTIES

The material from the first find consisted of white altered crystals with a hardness of about 1. Owing to the altered nature of these crystals, it was not possible to measure other physical properties. The crystals from the second occurrence are unaltered and thus permit their physical and optical properties to be measured. These unaltered crystals have a Mohs' hardness of 4. The crystals do not show any cleavage. The density is 2.68(2) g/cm³ (measured by flotation in heavy liquids) or 2.74 g/cm³ (calc.). The crystals are uniaxial (−), with $\epsilon = 1.619(1)$ and $\omega = 1.622(1)$. The crystals have a vitreous luster and show no fluorescence under either long-wave or short-wave ultraviolet light.

0003–004X/88/0910–1191$02.00

TABLE 1. X-ray powder-diffraction data for calciohilairite and hilairite

| Calciohilairite (altered) | | | | Calciohilairite (unaltered) | | | | Hilairite* | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $I$ | $d_{obs}$ | $d_{calc}$ | $hkl$ | $I$ | $d_{obs}$ | $d_{calc}$ | $hkl$ | $d_{obs}$ | $I$ | $hkl$ |
| 12 | 5.989 | 5.990 | 202 | 12 | 5.993 | 6.003 | 202 | 6.00 | 60 | 012 |
| 100 | 5.228 | 5.217 | 220 | 100 | 5.231 | 5.225 | 220 | 5.28 | 100 | 110,003 |
| | | | | 4 | 3.917 | 3.916 | 104 | | | |
| | | | | | | | | 3.64 | 5 | 104 |
| | | | | 6 | 3.197 | 3.186 | 511 | | | |
| | | | | | | 3.146 | 422 | | | |
| 14 | 3.139 | 3.141 | 422 | 20 | 3.137 | | | 3.17 | 50 | 122 |
| | | | | | | 3.134 | 134 | | | |
| | | 3.017 | 205 | | | 3.016 | 600 | | | |
| 34 | 3.017 | | | 30 | 3.013 | | | 3.05 | 40 | 300 |
| | | 3.012 | 600 | | | 3.013 | 152 | | | |
| | | 2.898 | 125 | | | | | | | |
| 4 | 2.890 | | | 7 | 2.900 | 2.898 | 520 | 2.994 | 30 | 024 |
| | | 2.894 | 520 | | | | | | | |
| | | | | | | | | 2.639 | 30 | 200,033 |
| | | 2.609 | 440 | | | | | | | |
| | | | | | | 2.610 | 612 | | | |
| 8 | 2.606 | 2.606 | 612 | 9 | 2.607 | | | 2.604 | 5 | 214 |
| | | | | | | 2.603 | 244 | | | |
| | | 2.598 | 244 | | | | | | | |
| | | | | | | | | 2.146 | 10 | 312 |
| | | | | | | 2.395 | 262 | | | |
| 3 | 2.386 | 2.385 | 434 | 4 | 2.393 | | | 2.362 | 5 | 116 |
| | | | | | | 2.390 | 434 | | | |
| | | | | | | 2.173 | 217 | | | |
| | | | | 4 | 2.172 | | | 2.197 | 10 | 042 |
| | | | | | | 2.173 | 354 | | | |
| | | 2.128 | 722 | | | | | | | |
| 3 | 2.128 | | | | | | | 2.135 | 15 | 134 |
| | | 2.124 | 624 | | | | | | | |
| | | | | 3 | 2.050 | 2.048 | 182 | | | |
| | | 2.009 | 075 | | | | | | | |
| | | | | | | 2.007 | 327 | | | |
| 5 | 2.009 | 2.008 | 900 | 4 | 2.005 | | | 2.027 | 30 | 232 |
| | | | | | | 2.007 | 544 | | | |
| | | 2.007 | 642 | | | | | | | |
| | | 1.988 | 018 | | | | | | | |
| | | | | | | 1.976 | 265 | | | |
| 5 | 1.980 | 1.973 | 265 | 5 | 1.976 | | | 1.996 | 30 | 410,306 |
| | | | | | | 1.975 | 820 | | | |
| | | 1.972 | 820 | | | | | | | |
| | | | | | | | | 1.866 | 5 | 226 |
| | | | | | | | | 1.852 | 10 | 324 |
| | | 1.823 | 381 | | | 1.826 | 381 | | | |
| 31 | 1.817 | 1.817 | 725 | 4 | 1.820 | 1.821 | 725 | 1.820 | 5 | 208 |
| | | 1.813 | 734 | | | 1.816 | 437 | | | |
| | | 1.740 | 645 | | | | | | | |
| | | | | | | 1.743 | 645 | | | |
| 5 | 1.738 | 1.739 | 660 | 4 | 1.744 | | | 1.759 | 40 | 330 |
| | | | | | | 1.742 | 660 | | | |
| | | 1.738 | 292 | | | | | | | |
| | | | | | | | | 1.719 | 5 | 128 |
| | | 1.671 | 930 | | | | | | | |
| 17 | 1.671 | | | | | | | 1.688 | 20 | 422 |
| | | 1.670 | 482 | | | | | | | |
| | | 1.670 | 482 | | | | | | | |
| 15 | 1.668 | | | | | | | 1.661 | 20 | 054 |
| | | 1.668 | 384 | | | | | | | |
| | | | | 3 | 1.640 | 1.637 | 0.11.1 | | | |
| | | | | | | 1.597 | 933 | | | |
| | | 1.591 | 10.2.2 | | | | | | | |
| | | | | | | 1.595 | 835 | | | |
| 3 | 1.589 | 1.589 | 574 | 4 | 1.594 | | | 1.607 | 10 | 152 |
| | | | | | | 1.593 | 850 | | | |
| | | 1.588 | 277 | | | | | | | |
| | | | | | | 1.593 | 10.2.2 | | | |
| | | | | | | | | 1.584 | 10 | 244 |
| | | 1.560 | 11.1.1 | | | | | | | |
| 3 | 1.558 | 1.558 | 2.1.10 | | | | | 1.562 | <5 | 318,1.0.10 |
| | | 1.556 | 295 | | | | | | | |
| | | | | | | | | 1.524 | 5 | 600 |
| | | | | | | | | 1.516 | 10 | 514 |
| | | 1.461 | 862 | | | | | | | |
| 3 | 1.461 | | | | | | | 1.476 | 10 | 342 |
| | | 1.460 | 494 | | | | | | | |
| | | | | | | 1.449 | 592 | | | |
| 3 | 1.443 | 1.443 | 10.1.6 | 4 | 1.446 | 1.445 | 10.1.6 | 1.464 | 30 | 520 |
| | | | | | | 1.442 | 648 | | | |
| | | | | | | | | 1.441 | 10 | 238,2.1.10 |
| | | | | | | | | 1.373 | 10 | 612 |
| | | | | | | | | 1.344 | 5 | 508,1.3.10 |
| | | | | | | | | 1.319 | 15 | 440,606 |
| | | | | | | | | 1.288 | 10 | 072,532 |

* Chao et al. (1974).

Applying the Gladstone-Dale relationship with the constants of Mandarino (1981) and the observed average composition gives a $K_C$ of 0.2274. The measured indices of refraction and density give a $K_P$ of 0.2317. This gives a value of the compatibility expression $1 - (K_P/K_C)$ of $-0.0189$, which indicates superior compatibility among density, indices of refraction, and chemical composition.

## X-RAY AND MORPHOLOGICAL CRYSTALLOGRAPHY

The crystals are very similar in habit to those of hilairite and show only four forms. These are two trigonal prisms $a'$ $\{11\bar{2}0\}$ and $'a$ $\{2\bar{1}\bar{1}0\}$ and a right and left rhombohedron $r$ $\{10\bar{1}2\}$ and $-r$ $\{01\bar{1}2\}$. No twinning, as seen in hilairite, was observed. Figure 1 is a drawing of a typ-

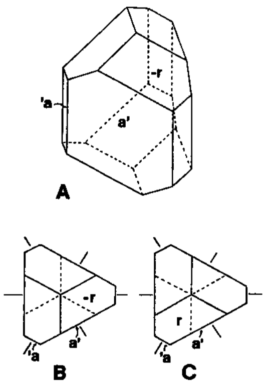

Fig. 1. Crystal drawings of calciohilairite. Forms shown are *a'* {$01\bar{1}2$}, *'a* {$2\bar{1}\bar{1}0$}, *r* {$10\bar{1}2$}, and −*r* {$01\bar{1}2$}. (**A**) Left-handed crystal. (**B** and **C**) Projections down the **c** axis of a left- and right-handed crystal, respectively.

ical crystal along with two projections down **c** showing the development of right- and left-handed crystals. This interpretation of the morphological crystallography differs from that described for hilairite by Chao et al. (1974), who described the morphology in terms of a hexagonal prism {$11\bar{2}0$} and a rhombohedron {$01\bar{1}2$}. All hilairite crystals seen by me show a habit very much like that shown in Figure 1. This suggests that out of the possible space groups reported by Chao et al. (1974), the space group of both calciohilairite and hilairite is most likely *R*32. This space group was confirmed for hilairite by the crystal-structure determination of Ilyushin et al. (1981).

The X-ray powder-diffraction pattern of calciohilairite, obtained on a Phillips diffractometer using Cu*K*$\alpha$ radiation ($\lambda$ = 1.54178 Å) and quartz as an internal standard, is very similar to that of hilairite. Table 1 shows the data for calciohilairite (both the altered and unaltered material) compared with the data from Chao et al. (1974) for hilairite. The powder pattern obtained on the altered crystals shows an unidentified line at 7.17 Å. This line is not present in the pattern of an unaltered crystal obtained using a Gandolfi camera and is attributed to an unidentified phase in the altered material. Initially, a least-squares refinement of the powder data for the altered material (based on the relationship to hilairite and Weissenberg photographs) gave cell dimensions of $a$ = 10.415(4) Å and $c$ = 16.01(3) Å. Later single-crystal diffractometer work, using the unaltered material (Subrata Ghose, pers. comm., July 1987), indicated that the above cell was a subcell and that the actual cell has dimensions of $a$ = 20.887(4) Å and $c$ = 15.914(3) Å. A refinement of the powder data for the altered material based on this new cell gave cell dimensions of $a$ = 20.870(4) Å and $c$ = 16.002(4) Å. A refinement of powder data from the unaltered material (obtained both with a Gandolfi camera and a Picker diffractometer) gave cell dimensions of $a$ = 20.90(1) Å and $c$ = 16.05(2) Å. The poorer quality of this refinement is due to the lack of enough unaltered material to obtain a better pattern.

## COMPOSITION

Crystals of calciohilairite were embedded in epoxy, ground to expose their centers, and coated with 200 Å of C. Analyses were done by a combination of wavelength-dispersive (for Na) and energy-dispersive techniques on an ARL EMX electron microprobe equipped with a Tracor Northern TN-2000 energy-dispersive analyzer. Energy-dispersive spectra were corrected for peak overlap using the program SUPERML, and the combined energy- and wavelength-dispersive data were corrected for generation, absorption, and fluorescence effects using a modified version of the program ZAF (both programs supplied by Tracor Northern). The results of six analyses are shown in Table 2. Water was not analyzed for owing to the altered nature of most of the crystals and the small amount of material available. An average of these analyses gives the empirical formula $(Ca_{0.89}Na_{0.03}Cu_{0.03})(Zr_{1.14}Fe_{0.01})(Si_{2.82}Al_{0.09})O_9 \cdot 3.30H_2O$, or ideally $CaZrSi_3O_9 \cdot 3H_2O$ with minor substitution of $Na^+$ and $Cu^{2+}$ for $Ca^{2+}$. Water was determined by difference. The Si:Zr ratio is consistently slightly lower than the ideal 3.00 (in the range of 2.80–2.90). This lower ratio could be accounted for in two ways. The first would be a systematic error in the determination of the Si:Zr ratio, and the second that some of the Zr is substituting for Ca. The first of these seems to be ruled out by the fact that other Zr-bearing silicates analyzed along with calciohilairite (zektzerite, sogdianite, calcium catapleiite, and elpidite) do not show such systematic errors (Boggs, 1984a).

TABLE 2. Composition of calciohilairite (wt%)

| | $CaZrSi_3O_9 \cdot 3H_2O$ | 1 | 2 | 3 | 4 | 5 | 6† |
|---|---|---|---|---|---|---|---|
| $Na_2O$ | — | 0.20 | 0.22 | 0.24 | 0.13 | 0.20 | 0.19 |
| CaO | 13.56 | 11.25 | 10.74 | 10.70 | 11.62 | 11.41 | 14.10 |
| CuO | — | 0.19 | 0.77 | 1.12 | 0.42 | 0.74 | n.d. |
| FeO* | — | 0.03 | 0.70 | 0.03 | 0.12 | 0.09 | 0.00 |
| $SiO_2$ | 43.58 | 38.81 | 39.03 | 39.74 | 41.16 | 41.37 | 37.35 |
| $ZrO_2$ | 29.79 | 31.64 | 32.37 | 33.39 | 33.58 | 32.02 | 33.97 |
| $TiO_2$ | — | 0.09 | 0.09 | 0.04 | 0.04 | 0.02 | 0.00 |
| $Al_2O_3$ | — | 2.61 | 2.59 | 1.06 | 0.05 | 0.28 | 0.00 |
| Sum | 86.93 | 84.82 | 86.51 | 86.32 | 87.12 | 86.13 | 85.61 |
| $H_2O$ | 13.07 | 15.18** | 13.49** | 13.68** | 12.88** | 13.87** | 14.39** |
| Sum | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

* Total Fe as FeO.
** $H_2O$ by difference.
† Altered material.

The second possibility is supported by the fact that the sum of Ca, Na, and Cu is less than one atom calculated with respect to nine oxygens, and the additional Zr brings this total close to one and improves the site occupancies in the Ca and Zr sites. This assumption gives the empirical formula $(Ca_{0.89}Zr_{0.15}Na_{0.03}Cu_{0.03})(Zr_{0.99}Fe_{0.01})(Si_{2.82}Al_{0.09})O_9 \cdot 3.30H_2O$. The substitution of $Zr^{4+}$ for $Ca^{2+}$ may seem somewhat unlikely, but their ionic radii do not differ greatly (0.79 and 0.99 Å, respectively), and similar substitutions are known to take place in, for example, the pyrochlore group, where $Na^+$, $Ca^{2+}$, $Pb^{2+}$, $U^{4+}$, etc., substitute for one another. This substitution would lead to a generalized formula of $(Ca,Na,Zr,Cu)_{1-2}ZrSi_3O_9 \cdot 3H_2O$ for calciohilairite.

## ACKNOWLEDGMENTS

I wish to thank William S. Wise for use of the electron microprobe at the University of California, Santa Barbara, and Robert M. Boggs, who collected the specimens that made this study possible. Felix Mutschler reviewed the manuscript and contributed helpful suggestions. Subrata Ghose contributed useful single-crystal diffractometer data.

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MANUSCRIPT RECEIVED MARCH 4, 1987
MANUSCRIPT ACCEPTED MAY 24, 1988