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Junitoite, a new hydrated calcium zinc silicate from Christmas, Arizona

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Abstract

Junitoite occurs in the retrogressively altered tactite zone at Christmas, Arizona, where it is associated with kinoite, apophyllite, and smectite. Its occurrence is closely tied to the breakdown of sphalerite in the ores. Junitoite may alter to a tyrolite-like phase. Found as large crystals (4–5 mm), sp gr (meas) = 3.5. Cleavages on {100} (poor), {101} (poor), {010} (good). Crystals are strongly pyroelectric and morphologically hemimorphic, orthorhombic *mm*2. Morphological axial ratio $a : b : c = 0.506 : 1 : 0.688$. X-ray cell $a = 6.309$, $b = 12.503$, $c = 8.549$Å (giving 0.505 : 1 : 0.684); space group *Bbm*2. Sp gr (calc) = 3.516 for $Z = 4$.

Chemical analysis gave CaO 15.5, ZnO 44.8, SiO_2 31.0, H_2O 5.8, total 97.1 percent giving $Ca_{0.98}Zn_{1.96}Si_{1.84}O_{6.6} \cdot 1.13H_2O$, or $CaZn_2Si_2O_7 \cdot H_2O$.

Indices are $\alpha = 1.656$, $\beta = 1.664$, $\gamma = 1.672$, $2V_z = 86°$. Dispersion is very weak. $X = a$, $Y = b$, $Z = c$. Resembles hemimorphite or bertrandite in thin section.

Named for Dr. Jun Ito, prominent American mineral chemist.

Introduction

Junitoite was first noted by Joe Ana Ruiz and called to my attention by R. A. Jenkins, a geologist for Phelps Dodge Corporation. He had noted crystals of the mineral in samples collected as kinoite specimens and submitted one of them for identification. The first sample came from the collection of Joe Ruiz and was collected at the open pit of the Christmas mine, a porphyry copper deposit in Gila County, Arizona. After the initial discovery, further samples were obtained by Mr. Jenkins from the collection of Mssrs. Ruiz and Raymond Diaz, who kindly loaned them for study.

The deposit has been previously described by Eastlick (1968) and by Perry (1969), and is known for its ores occurring in tactites derived from Paleozoic carbonate rocks by thermal metamorphism. Those samples carrying kinoite and junitoite differ markedly from the usual tactites occurring at Christmas, however, for they have suffered very strong retrograde metamorphic effects. The tactite originally consisted of garnet, wollastonite, and diopside, with minor vesuvianite, scattered in a calcitic base. Chalcopyrite and sphalerite disseminated in the tactite seem to have been partly oxidized and altered during retrograde effects, and have yielded to a mesogene assemblage including kinoite and junitoite. The argument for a mesogene origin is strengthened by the observation that the kinoite-bearing assemblage is confined to certain layers in the limestones, and these layers are overlain by others carrying fresh sulfide ores (Dave Cook, personal communication). A similar origin for kinoite has been implied by Anthony and Laughon (1970) for the type locality.

The retrograde rock-forming minerals occurring with kinoite and junitoite include apophyllite, a smectite, calcite, and xonotlite. Junitoite usually occurs along fractures where they cut pods of disseminated sphalerite. Typically it is seen as sprays of crystals embedded in smectite and forming open rings around the host sphalerite that has been exposed by the fracture. The smectite is invariably pink and shows strong emission lines for cobalt and manganese.

Junitoite may alter; in some samples it becomes milky-white, tinged lilac or greenish in places. At this stage it gives an unchanged powder pattern. Further corrosion, however, leads to replacement by a species similar to tyrolite, an alteration that may well be supergene.

Physical properties

Junitoite was seen only as crystals, usually as a jumble of randomly oriented tablets perched on and in the matrix. Dimensions of crystals vary, but plates are commonly 4–5 mm across and 0.5 mm thick.

TABLE 1. Chemical analysis of junitoite

	1	2	3
CaO	15.5%	.276	15.71%
ZnO	44.8	.551	45.58
SiO_2	31.0	.516	33.66
H_2O	5.8	.322	5.05
	97.1		100.00

1) CaO, average of two analyses, 11.0% and 11.1% on 0.859 and 0.970 mg respectively;

ZnO, average of five analyses, 35.7%, 36.2%, 36.2%, 35.9%, 36.0% Zn on 0.859, 0.970, 1.035, 0.734 and 0.856 mg respectively.

SiO_2, one analysis of 14.5% Si on 0.734 mg.

All above analyses by M. Duggan, Phelps Dodge Corporation.

H_2O on 3.220 mg by Penfield method (by SAW)

2) Ratios

3) Theory for $CaZn_2Si_2O_7 \cdot H_2O$.

The Mohs hardness is 4½ and crystals are brittle. Pressed with a needle normal to the plane of flattening they repeatedly part on {010}, breaking eventually into a pile of shimmering scales. The luster is glassy, but distinctly brighter than the apophyllite with which it occurs. Crystals are perfectly transparent and colorless. As noted above, however, the color may be milky-white or tinged in various colors with the onset of alteration. This change is also indicated by a tendency of the crystals to become semisectile.

No fluorescence was observed in long or short wavelength ultraviolet. Crystals are strongly pyroelectric, however, and give an effect as marked as that given by hemimorphite when dusted with Kundt's powder during cooling.

The symmetry was established as orthorhombic methods in diluted Clerici solution at 23°C. It was found to be 3.5 ± 0.1, matching measured hemimorphite (3.505) exactly in behavior.

Chemistry

Spectrographic analysis of junitoite showed only traces of copper in addition to strong lines for calcium, silicon, and zinc. The absence of carbonate and halogens (Cl, Br, I) was demonstrated by microchemical tests. Fluorine was sought by analysis and not found. This is mildly surprising, since the associated apophyllite gave a value of 2.1 percent.

Junitoite is easily soluble in cold 10 percent HCl or 1 : 7 HNO_3 but is insoluble in water. It is slowly decomposed by hot 40 percent KOH. Heated in the closed tube it quickly turns milky-white, spalling into flakes that separate on {010}. Water is lost during the process, and it fuses to a clear glassy bead.

For chemical analysis, junitoite was taken into solution in 1N HCl and zinc determined by atomic absorption. Calcium was determined colorimetrically as the arsenazo-III complex at a pH of 9.7, and silicon was determined as β-silicomolybdate (extracted into ethyl acetate from 3M H_2SO_4) at 335 mμ in ultraviolet. Water was determined by the Penfield method and was clearly visible in the tube during early stages of heating. The low results for Ca, Zn, and Si, and high value for H_2O may all be due to minute amounts of smectite inextricably mixed with the junitoite picked for analysis. There was too little to recover as insoluble residue following wet analysis.

The analytical results, presented in Table 1, provide empirical cell contents $Ca_{0.98}Zn_{1.96}Si_{1.84}O_{6.6} \cdot 1.13H_2O$, which can be written $CaZn_2Si_2O_7 \cdot H_2O$.

Crystallography

Fine crystals were readily obtained for study with the two-circle goniometer, and four were measured. A typical example is shown in Figure 1.

Forms are not abundant, and all are listed in Table 2; all shown were seen on each crystal with the exception of {191}, seen only on one. The only pair of

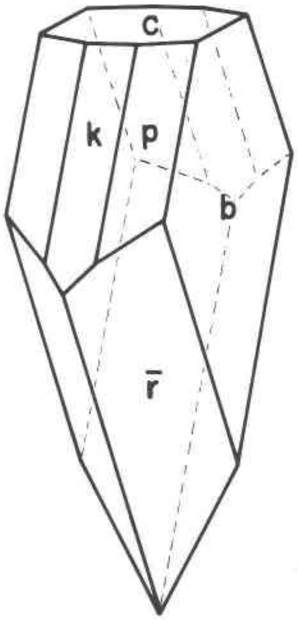

FIG. 1. Typical junitoite crystal.

TABLE 2. Angle table for junitoite, orthorhombic *mm*2
$a{:}b{:}c$ = 0.505:1:0.684 $p_0{:}q_0{:}r_0$ = 1.335:0.684:1
$q_1{:}r_1{:}p_1$ = 0.505:0.738:1 $r_2{:}p_2{:}q_2$ = 1.462:1.981:1

Form	khl	ø	ρ = c	ø$_1$	ρ$_1$ = A	ø$_2$	ρ$_2$ = B
c	001	.....	0°00'	0°00'	90°00'	90°00'	90°00'
b	010	0°00'	90 00	90 00	90 00	.....	0 00
k	101	90 00	53 34	0 00	36 26	36 26	90 00
p	111	63 13	56 37	34 22	41 48	36 26	67 54
r	131	33 26	67 52	64 01	59 18	36 26	39 22
$\bar{r}$	$13\bar{1}$	33 26	112 08	115 59	59 18	-36 26	39 22
$\bar{g}$	$19\bar{1}$	12 25	99 01	99 14	77 44	-36 26	15 18

like forms found at each pole is $r/\bar{r}$; *r* is rare and a mere line when seen. Doubtless $\bar{p}$ and $\bar{k}$ could also be found given enough measurements for, like hemimorphite, the polarity of [*c*] is probably best shown by the size and perfection of most forms, not their complete absence or dominance. No attempt was made to study vicinal forms that modify the surface of {010}. These are merely crenulations that meet in a wishbone pattern pointed at the antilogous pole. The analogous pole was chosen as morphologically positive to provide the most pleasing setting. The axial ratio used in Table 2 is derived from the refined X-ray cell. The morphological ratio is close, $a : b : c$ = 0.506:1:0.688.

The symmetry was established as orthorhombic *mm*2 not only by pyroelectricity and morphology but also by etching. The best reagent was 10 percent HCl (cold), which produces isoceles triangles in abundance on {010}, all aligned with their blunt (unique) angles pointing toward the analogous pole. A solution of 1:7 HNO_3 produces a similar effect, but dissolution is too rapid to be satisfactory.

Weissenberg and rotation X-ray patterns, using CuKα radiation, established the cell dimensions as follows: a = 6.309, b = 12.503, c = 8.539Å(all ± 0.006Å). The cell edges were refined from the powder data in Table 3. Similar dimensions were obtained from partly altered, lilac-colored crystals and are: a = 6.307, b = 12.497, c = 8.546Å(all ± 0.006Å).

Taken with physical and morphological evidence, the X-ray results give criteria for space group *Bbm*2. The cell volume is 674.4Å^3, giving a calculated specific gravity of 3.516 if Z = 4.

Optics

In thin section junitoite bears a strong resemblance, at least upon casual inspection, to hemimorphite, bertrandite, or even prehnite. Detailed observations would distinguish it from these minerals,

TABLE 3. X-ray powder data for junitoite (Cr*K*α radiation, 114 mm camera)

I/I_{est}	d_{meas}	d_{calc}	hkl
4	6.253	6.252	020
5	4.703	4.704	111
4	4.272	4.275	002
10	3.528	3.529	022
4	3.221	3.221	131
½	3.162	3.155	200
1	3.126	3.126	040
10	2.816	2.816	220
10	2.540	2.538	202
		2.543	113
5	2.521	2.515	230
		2.523	042
7	2.352	2.352	222
2	2.243	2.243	151
1	2.201	2.204	133
4	2.021	2.015	311
		2.022	024
3	1.970	1.970	242
2	1.872	1.873	062
1	1.833	1.834	331
½	1.802	1.801	153
3	1.768	1.764	044
		1.769	204
3	1.739	1.739	260
3	1.703	1.703	224
3	1.677		
2	1.611		
4	1.577		
1	1.565		
6	1.540		
2	1.492		
3	1.440		
1	1.408		
1	1.390		
4	1.338		
3	1.331		
1	1.318		
3	1.298		
3	1.271		
4	1.244		

however. Basal plates give a flash figure, and crystals may be either length-slow or length-fast seen on edge.

The indices for NaD are $\alpha = 1.656$, $\beta = 1.664$, $\gamma = 1.672$ and $2V_z$ is 86° (calc) Dispersion is $\nu > \rho$ and is very weak. The optic orientation is $a = X$, $b = Y$, $c = Z$.

Cleavage was noted in measured crystals but is best seen in thin section, enhanced by grinding. The side pinacoid {010} is a plane of parting and good cleavage; {100} is a poor cleavage and {101} is poor.

Additional comments

Junitoite is named in honor of Dr. Jun Ito, a prominent American mineral chemist. It was he who first noted the compound (Ito, 1968) in a series of experiments of synthesis of Pb–Ca–Zn silicates. His powder data show excellent agreement with mine, and it is fortunate that they were published. The formula assigned tentatively to the artificial material, phase X_3 of Ito, was based on a best guess from results of experimental runs (Ito, personal communication, 1975).

Junitoite does not appear to be isostructural with any other Ca–Mg or Ca–Zn silicates. It is interesting to note, however, that it shows strong polarity like its brethern hemimorphite and clinohedrite. The synthetic conditions attending the appearance of phase X_3 correlate well with the supposed retrograde mesogene origin of junitoite, and it seems probable that it would not form under most supergene conditions. In a recent letter Dr. Ito reports a new hydrothermal synthesis at 206°C. He reports as follows: "The starting material used for the synthesis of phase X_3 was chemically precipitated sparingly soluble amorphous $CaZn_2Si_2O_7 \cdot nH_2O$ at pH 11.8 by NaOH from the aqueous solution. Excess Na was removed by the repeated centrifuge-washing with distilled water. Final pH was 10.2. (The) Na_2O content in the phase X_3 thus prepared was 0.01 wt %."

Mr. Jenkins reported no difficulty in finding samples of junitoite in collections of Christmas mine specimens. It is not uncommon in the kinoite-bearing zone, and some dozens of specimens are now known. During a recent visit to the locality, we found junitoite with relative ease in a particular brecciated limestone bed, but in other beds (also carrying kinoite) it was lacking or very rare.

Type specimens will be provided the University of Arizona, British Museum (Natural History), and The University of Paris.

Acknowledgments

I am grateful to R. A. Jenkins for bringing the original specimen to my attention and his assistance in procuring working material. Mssrs. Ruiz and Raymond Diaz kindly provided specimens. The mine geologist, Dave Cook, kindly assisted us during a recent visit to the locality. Ms. Marjorie Duggan provided her usual excellent analyses which I am happy to acknowledge.

The mineral and its name have been approved by the Commission on New Minerals and Mineral Names, IMA.

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