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Ruizite, a new silicate mineral from Christmas, Arizona

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SUMMARY. Ruizite is a new mineral found in the mesogene calc-silicate assemblage at the Christmas mine, Gila County, Arizona. Occurs with kinoite, apophyllite, smectite, and junitoite. Colour is orange inclining to brown with pale streak, H = 5, Sp. Gr. meas. = 2·9. Crystals monoclinic $2/m$, elongate on [010]; $a = 11{\cdot}95$ Å, $b = 6{\cdot}17$, $c = 9{\cdot}03$, $\beta = 91^\circ\ 22\frac{1}{2}'$. Probable space group $P2_1/c$ with $Z = 4$ giving $D_{calc} = 2{\cdot}997$. Strongest lines are 11·951 Å (10), 4·190 (7), 3·116 (6), 5·092 (5), 3·644 (4), 2·951 (4), 2·591 (4), 2·132 (4). Indices are $\alpha = 1{\cdot}663$, $\beta = 1{\cdot}715 \parallel [010]$, $\gamma = 1{\cdot}734$, 44° to [001] in obtuse β; $2V_\alpha = 60{\cdot}2^\circ$; inclined dispersion $\rho > v$ strong. Twinned on {100}. Analysis by wet methods gave CaO = 20·57 %, $Mn_2O_3 = 23{\cdot}42$, $SiO_2 = 39{\cdot}14$, $H_2O = 16{\cdot}0$ leading to $Ca_{1\cdot06}Mn^{3+}_{0\cdot86}(SiO_3)_{1\cdot89}(OH)_{1\cdot03}2{\cdot}06H_2O$ or $CaMn^{3+}(SiO_3)_2(OH).2H_2O$.

Named for its discoverer, Joe Ana Ruiz of Mammoth, Arizona.

DURING the course of investigation of junitoite at the Christmas mine, Gila County, Arizona, an unidentifiable brown mineral was found by Joe Ana Ruiz and Robert Jenkins. Better samples were quickly found by Dave Cook, the mine geologist. Since subsequent study showed it to be a new species it was named for its discoverer, Joe Ana Ruiz, an amateur mineralogist and collector keenly interested in the mineralogy of the Christmas mine. Ruizite is abundant at the mine. Type specimens will be provided to the British Museum (Natural History) and The University of Arizona.

Occurrence. Ruizite occurs as spherules of radially arranged acicular crystals, rarely as scattered and isolated euhedra, in veinlets and on fracture surfaces in meta-limestones at the mine. The limestones have been converted to calc-silicate rocks during contact metamorphism attendant upon intrusion of the porphyry copper stock at Christmas. The calc-silicate assemblage includes wollastonite, grossular, diopside, and minor vesuvianite, in an excess of calcite as a matrix. Most of the mineralization took place during this event, and in the area where ruizite is found chalcopyrite, bornite, and sphalerite are the dominant sulphides.

Ruizite formed during retrograde metamorphism and oxidation as part of a mesogene assemblage including junitoite (Williams, 1976), kinoite, apophyllite, smectite, xonotlite, and sepiolite. It is commonly found in fractures embedded on or in smears of smectite or sepiolite. On the surface of open fractures it occurs as free spherules, but more often these are enveloped in large limpid tablets of apophyllite.

Physical properties. Ruizite is typically an orange colour, varying from RHS-170B to 170D depending on the size of the spherules. The colour inclines to brown in exceptionally large spherules and to white as surficial alteration to sepiolite and calcite proceeds. The streak is pale apricot (near 170D). The Mohs hardness was difficult to determine owing to the minute size of crystals but tightly knit spherules appear to be approximately five.

The specific gravity was estimated as 2·9 ± 0·1 in Clerici solution at 23 °C. This value appears to be low and may well owe to entrapment of minute bubbles among the fibres. Finer grinding of material increased the apparent specific gravity but when fibres were completely separated, the resultant fragments were judged to be too minute to give reliable results.

Crystallography. Spherules of ruizite are 0·5 mm in diameter or less, and only exceptionally attain 1·0 mm. One remarkable piece found by Robert A. Jenkins carried tiny (0·2 mm long) but highly perfect, isolated crystals. A few were doubly terminated.

Crystals are monoclinic 2/*m* and two were examined on the two-circle goniometer. Prisms are elongate on [010] and somewhat flattened on *a*{100}. The forms found on the two crystals are *a* {100}, *q* {102}, *s* {$10\bar{2}$}, *p* {111}, and *d* {011}. The crystal pictured in fig. 1 is drawn with +[010] vertical. Twinning is common on *a*{100} with re-entrants bounded by *q* or *s*; such twinning always appears to involve only two individuals.

One of the two measured crystals was retained for single crystal X-ray study. Rotation and Weissenberg photographs indicate the space group $P2_1/c$. Cell dimensions were taken from powder data by refinement and are: $a = 11·95$ Å, $b = 6·17$, $c = 9·03$, $\beta = 91° 22\frac{1}{2}'$. No comparable results were calculated as an axial ratio from the morphological work owing to the poor reflections caused by the minuteness of the crystals.

The powder photographs taken in a 114 mm Straumanis camera using Cr-K_α radiation were unusually crisp and complete. The powder data are given in Table I but an additional 28 lines down to about 1·2 Å are omitted, none having $I_{est} > 3$.

Chemistry. An emission spectrogram of ruizite showed only Ca, Mn, and Si as major constituents as well as the usual trace of Cu. Microchemical tests were employed to demonstrate the absence of carbonate and halogens other than fluorine. Less than 0·1 % fluoride was detected using a fluoride-ion-specific electrode technique.

We report the analysis of ruizite in detail here because a preliminary literature search for analysis of comparable silicates was very disappointing. In most cases analysis of silicates with

TABLE I

I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl	I	d_{meas}
10	11·951	11·946	100	1	2·704	2·704	013	4	2·132
1	5·974	5·973	200	3	2·649	2·650	$11\bar{3}$	1	2·092
5	5·092	5·092	011	2	2·624	2·625	113	1	2·027
1	4·704	4·708	$11\bar{1}$	4	2·591	2·592	$41\bar{1}$	3	1·982
3	4·513	4·513	002	3B	2·547	2·546	022	½	1·928
7	4·190	4·189	102	4	2·519	2·519	$40\bar{2}$	½	1·911
3	3·982	3·982	300	2	2·486	2·483	122	1	1·891
1	3·851	3·860	211			2·484	213	½B	1·868
4	3·644	3·642	012	1	2·445	2·444	213	1	1·823
		3·643	$20\bar{2}$	½	2·392	2·389	500	2	1·782
1	3·563	3·560	202	3	2·331	2·331	222	2	1·755
6	3·116	3·116	311			2·332	$41\bar{2}$	2	1·735
1	3·084	3·084	020	½	2·208	2·208	104	2	1·708
		3·083	212	½	2·175	2·174	$51\bar{1}$	2	1·674
1	2·986	2·986	120	½	2·154	2·154	023	5	1·646
		2·987	400			2·152	511		
4	2·951	2·951	302			2·158	$32\bar{2}$		
3	2·740	2·740	220						

TABLE II

	1	2
CaO	20·57	18·68
Mn_2O_3	23·42	26·29
SiO_2	39·14	40·03
H_2O	16·0	15·00
Sum	99·13	100·00

1. Ca and total Mn on 1·113 mg, Si on 1·978 mg, H_2O on 1·772 mg.
2. Theory for $CaMn^{3+}(SiO_3)_2OH.2H_2O$.

mixed valences for Mn, including tervalent, has not been reported, or the valence of Mn has been merely assumed from crystallochemical considerations.

Silica was determined by the solvent extraction procedure of D. R. Schink (1965). A milligram or less of ruizite was decomposed by fusion with sodium hydroxide in a platinum crucible at 450 °C for one hour. Dilute hydrochloric acid was added to dissolve and acidify the melt. After the manganese oxides formed had dissolved, the solution was adjusted to about pH2 with dilute sodium hydroxide solution. The sample solution was made to volume in a 50 ml volumetric flask. An aliquot containing 6 to 10 μg of silica was diluted to 30 ml with water in a 60 ml glass-stoppered separatory funnel having a Teflon stopcock; 1·0 ml molybdate solution was added and after 20 min the silicomolybdic acid formed was extracted with 10·0 ml ethyl acetate, immediately after addition of 15·0 ml 1:1 sulphuric acid. The absorbance of the ethyl acetate extract was read spectrophotometrically at 335 nm.

Calcium and total manganese were determined by atomic absorption spectroscopy using a laminar-flow premixed air-acetylene flame. For this purpose, ruizite was decomposed with 40 % HF in a platinum crucible, and after complete evaporation, solution was effected with 10 % HNO_3. Standard curves were also prepared with 10 % HNO_3.

To determine tervalent manganese, approximately 1 mg of ruizite was decomposed in a covered, 6 ml platinum crucible by adding 1 ml of 2*M* KF and a few ml of 40 % HF. Digestion was carried out for about three hours on a hot plate at 60–70 °C. The lid was then removed and the heat increased to 110 °C and the solution evaporated to about one-half ml. This material was brought to volume in a 25 ml polyethylene volumetric flask with 0·4*M* KF. An aliquot containing about 40–80 μg of Mn^{3+} was transferred to a polyethylene test tube and adjusted to 10 ml with 0·4 KF; 2 ml of freshly prepared 10 % KI were added and mixed. A portion of this solution was immediately transferred to a 1 cm light-path polystyrene spectrophotometer cell and read at 375 nm. Standardization utilized commercially available MnF_3 subjected to the same dissolution technique.[1] The tervalent manganese content of ruizite determined by this method was within 0·1 % of the total manganese.

Water in ruizite was determined by the Penfield method, and was clearly visible in the tube. All water was lost only upon ignition.

Ruizite was difficult to prepare for analysis. Literally hundreds of spherules were used; each was split open and disemboweled with a needle to remove the calcite or apophyllite nucleus commonly present. Nevertheless, some contamination by these species probably occurred, and the major effect would be to raise CaO and lower Mn_2O_3 values.

The results of analytical work are summarized in Table II, and lead to the formula $CaMn^{3+}(SiO_3)_2(OH).2H_2O$. The empirical formula is $Ca_{1\cdot06}Mn^{3+}_{0\cdot86}(SiO_3)_{1\cdot89}(OH)_{1\cdot03}2\cdot06H_2O$. The theoretical formula gives a calculated density of 2·997 using a cell volume of 665·23 Å^3 with $Z = 4$. The difference (3 %) from the measured specific gravity is thought to be due to poor measured values.

The effect of 1:1 HNO_3, 1:1 HCl, and 40 % KOH on ruizite is negligible when cold; it readily dissolves in all three reagents when heated.

Optics. In this section ruizite might be confused with some varieties of phlogpite or stilpnomelane when coarse grained. It also resembles piemontite in its red to yellow pheochroism although the colours are not quite right. The pleochroic formula is $\beta > \gamma \gg \alpha$ with β approximately Mars orange (RHS-31C) and γ Dresden yellow (5C). α is the same colour as β but much paler. These judgements were made by holding the colour chart by the microscope barrel and are surely subject to error.

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[1] We also analysed braunite from Bisbee, Arizona, finding Mn^{3+} in almost exactly the amount required by theory for $Mn^{2+}Mn^{3+}_6SiO_{12}$.

The indices, measured for the D line at 23·4 °C are $\alpha = 1{\cdot}663$, $\beta = 1{\cdot}715$, $\gamma = 1{\cdot}734$ (all $\pm 0{\cdot}002$). The $2V_\alpha$ measured (for D) is 60·2°, calculated as 60·7°. The dispersion is inclined and strong with $\rho > v$. Since an optic axis is nearly normal to *a* {100}, single crystals lying on this face do not extinguish completely. A further cause of non-extinction in this orientation is the twinning so commonly seen in {100}.

The optic orientation is $\beta \parallel [010]$, $\gamma{:}[001] = 44°$ in obtuse β. In thin section or fragment mounts, of course, ruizite usually shows parallel extinction and is length fast or slow. The optic orientation sketched in fig. 1 is misleading unless one recalls that crystals are elongate on *b* [010].

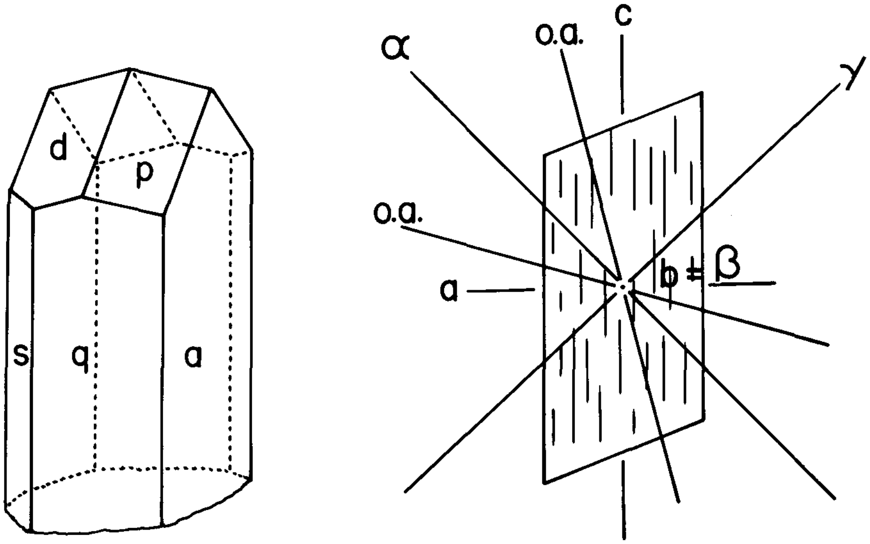

FIG. 1

Additional comments. There are several Ca–Mn silicates already known and all appear to be well characterized, including X-ray data. Ruizite is clearly none of these. No analogous compound with ferric iron rather than tervalent manganese is known as a mineral. Ruizite evidently originated during cooling of a higher temperature calc-silicate assemblage under high oxidizing conditions. The manganese may have been liberated from local sphalerite during its mesogene oxidation to junitoite; several sphalerites in the assemblage were checked and found rich in manganese. Manganese is lacking in the diopside in the wallrocks.

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