

## Mineralogical studies of the nitrate deposits of Chile: VII. Two new saline minerals with the composition $K_6(Na,K)_4Na_6Mg_{10}(XO_4)_{12}(IO_3)_{12} \cdot 12H_2O$ : Fuenzalidaite (X = S) and carlosruizite (X = Se)

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### ABSTRACT

Two new isostructural saline minerals from the nitrate deposits of northern Chile have the composition  $K_6(Na,K)_4Na_6Mg_{10}(XO_4)_{12}(IO_3)_{12} \cdot 12H_2O$ : fuenzalidaite (FNZ, X = S) and carlosruizite (CLR, X = Se, S, Cr). They are trigonal,  $P\bar{3}c1$ ; for FNZ  $a = 9.4643(4)$ ,  $c = 27.336(6)$  Å; for CLR  $a = 9.5901(8)$ ,  $c = 27.56(2)$  Å. The crystals form thin hexagonal plates on {0001} up to 0.2 mm across, beveled at the edges by {10 $\bar{1}$ 2}. The crystals are transparent and pale yellow; optics are uniaxial negative with  $\omega = 1.622(5)$ ,  $\epsilon = 1.615(5)$  (FNZ), and  $\omega = 1.655(3)$ ,  $\epsilon = 1.642(1)$  (CLR). The crystal structure ( $R_w = 0.043$  for FNZ, 0.053 for CLR) consists of two complex slabs normal to the c axis, each having a double layer of iodate groups ( $IO_3$ ), bounded at the top and bottom by layers of  $SO_4$  or  $SeO_4$  groups. The strongest X-ray powder lines [ $d$ , ( $hkl$ )] for FNZ are 13.67 (50,002), 7.05 (40,102), 3.927 (100,202), 3.023 (41,212,117), 2.681 (33,302); for CLR, 13.75 (30,002), 7.10 (20,102), 3.561 (100,204), 3.082 (32,206), 3.058 (39,212,117), 2.715 (39,302).

### INTRODUCTION

The two new minerals, fuenzalidaite (fwen-za-leed'-a-ite) and carlosruizite (kar-los-ru-eez'-ite), are members of a solid solution series,  $K_6(Na,K)_4Na_6Mg_{10}(XO_4)_{12}(IO_3)_{12} \cdot 12H_2O$ , for which the end-members have X = S for the former and X = Se for the latter. With the exception of Se, the components of these minerals are widespread constituents of the Chilean nitrate ores. Se was not known to occur in these ores until it was discovered as a major component in carlosruizite by X-ray spectroscopy in the scanning electron microscope (SEM). Subsequent analyses of several specimens of nitrate ore from scattered localities in the Chilean nitrate fields showed them all to contain Se in amounts ranging from a few parts per million to nearly 50 ppm.

The new minerals are named for Humberto Fuenzalida P. (1904–1966) and Carlos Ruiz F. (b. 1916); both played major roles in the 20th century development of geology in Chile. Ruiz planned and directed the first national geological institution (inaugurated in 1957), the Instituto de Investigaciones Geológicas, now the Servicio Nacional de Geología y Minería, which began the first systematic geologic mapping and study of mineral deposits in Chile. Similarly, Fuenzalida planned and directed the first school of geology in Chile (inaugurated in 1958) at the University of Chile. The two new mineral species and names have been approved by the Commission on New Minerals and Mineral Names of the IMA.

### OCCURRENCE AND ASSOCIATED MINERALS

Small amounts (a few tens of milligrams each) of fuenzalidaite and carlosruizite were found in nitrate ore from two localities in the Chilean nitrate fields. Fuenzalidaite occurs as blebs and flattened aggregates of bright yellow micaceous material in veins and veinlets of white nitrate ore, called *caliche blanco*, in a former nitrate mine about 1 km south of the former plant site of Oficina Santa Luisa. Carlosruizite was found as ~200  $\mu$ m platy crystals in samples of iquiqueite,  $Na_4K_3Mg(CrO_4)B_{24}O_{39}(OH) \cdot 12H_2O$  (Erickson et al., 1986), obtained by leaching *caliche amarillo* (yellow nitrate ore) from samples in the Iquique office of the former Servicio de Minas del Estado of Chile, now the Servicio Nacional de Geología y Minería. The field locality of these samples is not precisely known but probably is in the vicinity of Zapiga, where *caliche amarillo* is especially abundant.

Among the 25 species of saline minerals that have been identified in the Chilean nitrate ores (Erickson, 1993), 11 are known to be associated with the two new minerals reported here. Veins and veinlets containing fuenzalidaite consist chiefly of a fine-grained mixture of nitratine ( $NaNO_3$ ) and halite; tiny blebs of fibrous probertite [ $NaCaB_5O_{10}(OH)_4 \cdot 3H_2O$ ] and platy darapskite [ $Na_3(NO_3)(SO_4) \cdot H_2O$ ] occur in cavities. The fractured bedrock in which these veins occur also contains abundant veinlets of anhydrite ( $CaSO_4$ ). The dense *caliche amarillo* containing carlosruizite consists chiefly of a fine-grained mix-

TABLE 1. Crystallographic data for fuenzalidaite and carlosruizite

	Fuenzalidaite	Carlosruizite
Formula	$K_6M_4Na_6Mg_{10}(XO_4)_{12}(IO_3)_{12} \cdot 12H_2O$	
Cations M	$(K_{1.2}Na_{2.8})$	$(K_{1.4}Na_{2.6})$
X	$(S_{0.95}Se_{0.05})$	$(Se_{0.51}S_{0.36}Cr_{0.10})$
Formula weight	4225.8	4520.1
$D_{calc}$ g/cm <sup>3</sup>	3.284	3.400
Optical properties	transparent, pale yellow	
Color		
Character	uniaxial (-)	uniaxial (-)
Refractive indices		
$\omega$	1.622(5)	1.655(3)
$\epsilon$	1.615(5)	1.642(1)
Crystallography		
Space group	$P\bar{3}c1$	$P\bar{3}c1$
Unit cell data		
$a$ (Å)	9.4643(4)	9.5901(8)
$c$ (Å)	27.336(6)	27.56(2)
$V$ (Å <sup>3</sup> )	2120.5(4)	2195.(1)
Z	1	1
$c/a$	2.888	2.877
Morphology	thin, hexagonal plates {0001} bounded by {10 $\bar{1}$ 2}	
Structure analysis		
Diffractometer	modified Picker automatic	
Radiation	Nb-filtered MoK $\alpha$ (0.7107 Å)	
Absorption coeff. $\mu$ (cm <sup>-1</sup> )	52	76
Crystal dim. (mm)	0.12 × 0.12 × 0.020	0.24 × 0.12 × 0.013
Range of 2 $\theta$ (°)	4–40	4–50
Reflections Measured	2078	3864
Independent	704	1325
For refinem.	520	691
Reliability factors		
R	0.083	0.087
$R_w$ (1/ $\sigma$ wt)	0.043	0.053
Goodness of fit	1.76	1.86

ture of nitratine, halite, and darapskite. The residues of leaching this material in cold water contain dietzeite [Ca<sub>2</sub>(IO<sub>3</sub>)<sub>2</sub>(CrO<sub>4</sub>)], brüggenite [Ca(IO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O], tarapacaita (K<sub>2</sub>CrO<sub>4</sub>), lopezite (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), ulexite [NaCaB<sub>5</sub>O<sub>6</sub>(OH)<sub>6</sub>·5H<sub>2</sub>O], probertite, and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

### PHYSICAL AND OPTICAL PROPERTIES

Fuenzalidaite and carlosruizite occur as thin, colorless to pale yellow, transparent, euhedral, platy crystals with hexagonal outline, generally <200  $\mu$ m in diameter and 20  $\mu$ m thick. The crystals have a pseudorhombohedral habit, flattened on {0001} with beveled edges {10 $\bar{1}$ 2} (Fig. 1). They are slowly soluble in H<sub>2</sub>O. Scanning electron micrographs (Fig. 1) show that some crystals have regular fractures parallel to {11 $\bar{2}$ 0} that may mark cleavage planes. Surfaces of some crystals show abundant round or elongate cavities (Fig. 1B), which probably were formerly filled with saline fluids. The crystals are brittle and break easily into multiple fragments. Hardness could not be measured, but to judge from the ease of breaking, it is on the order of 2–3. The luster is vitreous.

Both minerals are uniaxial negative. Their refractive indices, measured with Na light by immersion on the spindle stage, are given in Table 1. Determined on the basis of the structural formulas defined in Table 1 and the molar refractivities listed by Mandarino (1976), the Gladstone-Dale compatibility for fuenzalidaite is good, and for carlosruizite, fair (Mandarino, 1981).

### CRYSTALLOGRAPHY AND STRUCTURE ANALYSIS

Although the crystal morphology of both fuenzalidaite and carlosruizite is rhombohedral, single-crystal X-ray precession photography shows a primitive trigonal lattice. The two crystals are isomorphous, with the same flat, hexagonal habit (Fig. 1) and very similar crystallographic properties. The precession patterns show symmetry and extinctions of the space groups  $P\bar{3}c1$  or  $P3c$ ; the former centrosymmetric group (no. 165) was fully confirmed by the subsequent structure determination. Unit-cell parameters (Table 1) were refined from X-ray powder data obtained with the Guinier-Hägg focusing camera (Table 2).

Single-crystal intensity data for both crystals were collected with a Krisel-modified Picker automated diffractometer. After application of the usual corrections for Lorentz-polarization and absorption (by Gaussian quadrature) and normalization to  $E$  values, the  $F$  data for carlosruizite were used for a structure analysis. At the outset, the chemical formula was unknown, but an X-ray spectroscopic test in the SEM showed the presence of I, S, K, Mg, Na, Cr, and even Se.

Starting with the Se-rich carlosruizite crystal, the first  $E$  map derived from a Multan analysis at once revealed the position of the I atom. Subsequently, each of the constituent atoms (identified from electron density and coordination considerations), K, Na, Mg, and finally O, appeared in turn, in structure-factor electron-density cycles, until the whole structure was clearly revealed. This pro-

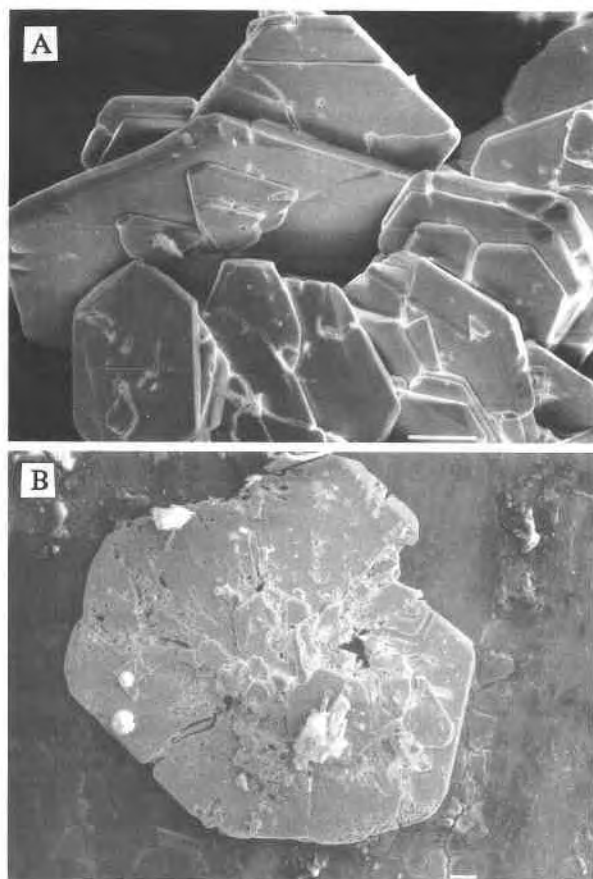


Fig. 1. Scanning electron micrographs of (A) fuenzalidaite, and (B) carlosruizite. The scale bars at the lower right corners represent 10  $\mu\text{m}$ .

cess led to the chemical formula  $\text{K}_{10}\text{Na}_6\text{Mg}_{10}(\text{XO}_4)_{12}(\text{IO}_3)_{12} \cdot 12\text{H}_2\text{O}$ , where  $\text{XO}_4$  represents a tetrahedral anionic group. As indicated in a later probe analysis, Cr was fixed at 1.2 atoms in the 12-fold tetrahedral site, S and Se were introduced into the tetrahedral site as  $[\text{xSe} + (0.9 - \text{x})\text{S}]$ , and refinement continued with weights based on counting statistics. In the final refinement, the occupancy factor  $x$  was found to be 0.54(2), showing that selenate dominates the tetrahedral anion component of this crystal. A similar refinement procedure for fuenzalidaite was started with the carlosruizite model and the assumption of full tetrahedral occupancy by S, as indicated by an SEM EDX estimate.

The above structure refinements were based on a considerable excess of K over that found in the microprobe analysis. Large displacement parameters for K2 suggested some replacement by Na in this site. Refinement of site occupancy by K and Na showed that K1 is fully occupied by K, but that in site K2 (now designated M), K is replaced by Na to the extent of  $68 \pm 8$  mol% in carlosruizite and  $72 \pm 11$  mol% in fuenzalidaite.

Final anisotropic refinements, with a total of 75 varied

TABLE 2. X-ray powder data for fuenzalidaite and carlosruizite

hkl	Fuenzalidaite			Carlosruizite		
	$d_{\text{calc}}$ (Å)	$d_{\text{obs}}$ (Å)	$I/I_0$	$d_{\text{calc}}$ (Å)	$d_{\text{obs}}$ (Å)	$I/I_0$
002	13.67	13.67	50	13.79	13.75	30
102	7.03	7.05	40	7.11	7.10	20
104	5.249	5.254	4	5.303		
111	4.663	4.665	13	4.724		
113	4.200	4.200	3	4.251		
200	4.098	4.099	9	4.153		
202	3.926	3.927	100	3.976	3.974	16
204	3.515	3.515	24	3.557	3.561	100
210	3.098	3.099	16	3.139		
211	3.078	3.078	8	3.119	3.112	3
206	3.047	3.048	8	3.080	3.082	32
212	3.021	3.023	41	3.061	3.058	39
117	3.012			3.043		
214	2.822	2.822	4	2.857	2.860	2
0,0,10	2.734	2.731	1	2.756		
300	2.732			2.768		
302	2.679	2.681	33	2.714	2.717	39
208	2.624	2.624	2	2.651		
304	2.537	2.537	10	2.569	2.570	12
217	2.4270	2.4269	<1	2.454		
220	2.3661	2.3665	2	2.398		
222	2.3314	2.3273	21	2.362	2.361	14
223	2.2901	2.2905	6	2.320	2.323	4
311	2.2654	2.2654	9	2.2955	2.2948	5
312	2.2424	2.2434	2	2.2719	2.2713	4
224	2.2359	2.2348	<1	2.2641		
313	2.2056	2.2060	<1	2.2343	2.2378	2
219	2.1688	2.1691	<1	2.1919		
314	2.1570	2.1575	1	2.1254	2.1256	2
308	2.1339	2.1329	1	2.1579		
315	2.0990	2.0993	2	2.1254	2.1256	2
2,1,10	2.0497	2.0490	<1	2.0710		
402	2.0264	2.0261	<1	2.0531	2.0543	4
2,0,12	1.9911	1.9957	1	2.0097		
404	1.9628	1.9634	2	1.9884	1.9879	4
320	1.8804	1.8802	3	1.9054	1.0925	1
406	1.8688	1.8692	2	1.8920		
322	1.8628	1.8624	12	1.8869	1.8875	12
323	1.8416	1.8415	<1	1.8657		
2,1,12	1.8353	1.8354	<1	1.8534		
324	1.8130	1.8124	5	1.8364	1.8362	3
2,2,10	1.7890	1.7890	4	1.8088		
411	1.7848	1.7842	7	1.8085	1.8077	10
325	1.7781	1.7782	2	1.8008	1.8012	5
412	1.7735	1.7727	2	1.7969	1.7959	4
413	1.7551	1.7545	4	1.7781	1.7768	4
3,1,10	1.7479	1.7488	1	1.7674		

Note:  $d_{\text{obs}}$  was measured from Guinier-Hägg patterns made with  $\text{CuK}\alpha$  radiation, Si internal standard; intensities were measured with a Nonius Model II microdensitometer.

parameters, including anisotropic displacement parameters for all cations and extinction parameters (O atoms isotropic, anomalous dispersion applied), using  $1/\sigma$  weights based on counting statistics, led to the reliability factors shown in Table 1. The structural parameters for fuenzalidaite and carlosruizite are listed in Table 3. Table 4<sup>1</sup> lists anisotropic thermal parameters for I, S(Se), and K, and Tables 5<sup>1</sup> and 6<sup>1</sup> list observed and calculated structure amplitudes. All calculations were carried out using the XTAL 2.4 system of Hall and Stewart (1988).

<sup>1</sup> To obtain Tables 4, 5, and 6 order Document AM-94-563 from the Business Office, Mineralogical Society of America, 1130 17th Street, NW, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

**TABLE 3.** Structural parameters for fuenzalidaite and carlosruizite

Atom	Site		x	y	z	u
I	12g	FNZ	0.3904(3)	0.2218(2)	0.4551(1)	0.075(8)
		CLR	0.3911(2)	0.2199(2)	0.4560(1)	0.105(5)
O1	12g	FNZ	0.195(2)	0.035(2)	0.4557(7)	0.11(2)
		CLR	0.201(2)	0.039(2)	0.4585(6)	0.10(2)
O2	12g	FNZ	0.490(2)	0.159(2)	0.4057(6)	0.11(2)
		CLR	0.489(2)	0.168(2)	0.4097(7)	0.13(2)
O3	12g	FNZ	0.481(2)	0.169(2)	0.5085(7)	0.13(2)
		CLR	0.482(2)	0.174(2)	0.5060(7)	0.14(2)
S(Se)	12g	FNZ	0.3184(8)	0.2986(8)	0.3245(3)	0.10(2)
		CLR	0.3188(5)	0.2992(5)	0.3243(2)	0.11(1)
O4	12g	FNZ	0.288(2)	0.416(2)	0.2992(6)	0.11(2)
		CLR	0.286(2)	0.427(2)	0.2975(7)	0.14(2)
O5	12g	FNZ	0.220(2)	0.135(3)	0.3044(7)	0.16(2)
		CLR	0.223(2)	0.126(2)	0.3031(6)	0.11(2)
O6	12g	FNZ	0.500(2)	0.354(3)	0.3212(7)	0.15(2)
		CLR	0.507(2)	0.365(2)	0.3204(7)	0.14(2)
O7	12g	FNZ	0.274(2)	0.295(2)	0.3805(7)	0.12(2)
		CLR	0.274(2)	0.294(2)	0.3801(7)	0.14(2)
K1	6f	FNZ	0.3789(10)	0	1/4	0.15(3)
		CLR	0.3834(10)	0	1/4	0.17(2)
M(Na,K)	4e	FNZ	0	0	0.1238(7)	0.19(3)
		CLR	0	0	0.1212(5)	0.15(3)
Na1	4d	FNZ	1/3	2/3	0.3336(7)	0.14(3)
		CLR	1/3	2/3	0.3338(7)	0.15(2)
Na2	2a	FNZ	0	0	1/4	0.11(5)
		CLR	0	0	1/4	0.11(3)
Mg1	4d	FNZ	1/3	2/3	0.1394(5)	0.12(3)
		CLR	1/3	2/3	0.1391(6)	0.12(2)
Mg2	4d	FNZ	1/3	2/3	0.4478(6)	0.12(3)
		CLR	1/3	2/3	0.4480(6)	0.12(2)
Mg3	2b	FNZ	0	0	0	0.07(7)
		CLR	0	0	0	0.13(4)
O8(H <sub>2</sub> O)	12g	FNZ	0.667(2)	0.504(2)	0.1020(6)	0.04(6)
		CLR	0.662(2)	0.497(2)	0.0987(7)	0.14(2)

Note: FNZ = fuenzalidaite; CLR = carlosruizite, *u* = rms displacement (Å).

### CHEMICAL COMPOSITION

After the crystal structure analysis of carlosruizite was completed, the chemical compositions of fuenzalidaite and carlosruizite were determined by electron microprobe analysis of single crystals (Table 7). The crystals were too soft to be embedded in plastic and polished in the usual manner and were mounted flat on an Al stub, thus providing a uniform, horizontal surface for electron probe analysis.

The lack of precision in these analyses probably results from the use of soft, unpolished crystals, the presence of H<sub>2</sub>O of crystallization, and volatilization of material caused by exposure to a vacuum and heating in the electron beam, the last being the most important (see Erickson et al., 1986). Molar ratios for Mg, S, Se, and I are not significantly different from those predicted by the crystal structure analysis, but those for K and Na are considerably less than expected. The low values found for K are attributed to extensive substitution by Na at a putative K site (M), and the low values for Na are attributed to volatilization.

### CRYSTAL CHEMISTRY

The crystal structure of fuenzalidaite and carlosruizite may be viewed as a double layer of iodate groups en-

**TABLE 7.** Compositions of fuenzalidaite and carlosruizite

	Fuenzalidaite			Carlosruizite				
	<i>m</i>	Theor.	Probe*	<i>m</i>	Theor.	Probe*		
K <sub>2</sub> O	26	7.2	8.0	5.9(2)	26	7.4	7.7	6.7(2)
Na <sub>2</sub> O		8.8	6.5	5.2(1.2)		8.6	5.9	4.7(4)
MgO		10	9.5	10.0(5)		10	8.9	9.2(3)
SO <sub>3</sub>	12	11.00	20.7	20.9(9)	12	4.4	7.8	7.9(5)
SeO <sub>3</sub>		0.3	1.1	0.1(2)		6.4	18.0	19.0(8)
CrO <sub>3</sub>		0.7	1.7	0.2(1)		1.2	2.6	2.5(2)
I <sub>2</sub> O <sub>5</sub>	12	47.4	49.3(1.0)	12	44.3	45.6(9)		
H <sub>2</sub> O	12	5.1		12	4.8			
Total			91.6			95.6		

Note: *m* denotes cations per unit cell from structure analysis based on formulas given in Table 1. Probe analyses showed trace amounts of Ca, Al, and Si. Standards for probe analysis; Na,Al,Si; albite (Tiburón); Mg,Cr, chromite (Tibaghi); S, anhydrite; Ca,I, brüggenite; K, orthoclase; Se, Se<sub>2</sub> (synthetic).

\* Electron microprobe analyses (wt%) average of ten spot analyses each, standard deviations of ten observations in parentheses.

closed by layers of sulfate groups above and below. These compound layers are separated by K cations, and the layer complex itself is held together by Na and Mg cations (Fig. 2). All the cations have normal coordination and bond lengths with O (Table 8). The average S-O bond length in fuenzalidaite is 1.505 Å, close to the value of 1.489 Å in thenardite (Mehrotra et al., 1978). In carlosruizite the tetrahedral bond length is 1.590 Å, about 2/3 of the difference between the S-O length of 1.489 Å and the Se-O length of 1.633 Å in Na<sub>2</sub>SeO<sub>4</sub> (thenardite structure: Mehrotra et al., 1978).

The trigonal-pyramidal IO<sub>3</sub> group has an average I-O bond distance of 1.863 Å in fuenzalidaite and 1.797 Å in carlosruizite, as compared with 1.806 Å in NaIO<sub>3</sub> (Svensson and Ståhl, 1988). The average pyramidal angle is 96.7° in fuenzalidaite, 97.3° in carlosruizite (Table 8), and 100.5° in NaIO<sub>3</sub> (Svensson and Ståhl, 1988). The pyramidal iodate groups stand in a layer with one base edge nearly parallel to the *c* axis (Fig. 2). In this structure, as in those of other iodates, a large cavity is present in the iodate layer centered opposite the I atom at the apex of the IO<sub>3</sub> pyramid, which accommodates an unshared electron pair. The nearest I-O distances opposite the pyramid vertices are >2.70 Å.

The Na atoms have octahedral coordination at sites Na1 and Na2, with an average Na-O distance of 2.37 Å (Table 8). Mg is also octahedrally coordinated at Mg1, Mg2, and Mg3, with an average Mg-O distance of 2.09 Å. The unexpected appearance of Na in the M site is actually quite reasonable. Although the eightfold coordination of site K1 is less than that of ninefold-coordinated M, the average K-O distance in the former (2.90, 2.93 Å) is normal for K atoms; the average distance at the M site (2.79, 2.71 Å), however, is substantially less than expected for K and is consistent with partial occupancy by Na. Thus it is apparent that it is the Na content that is deficient in the microprobe analysis (Table 7), not the K content.

The H<sub>2</sub>O molecules form the face shared by the Na1

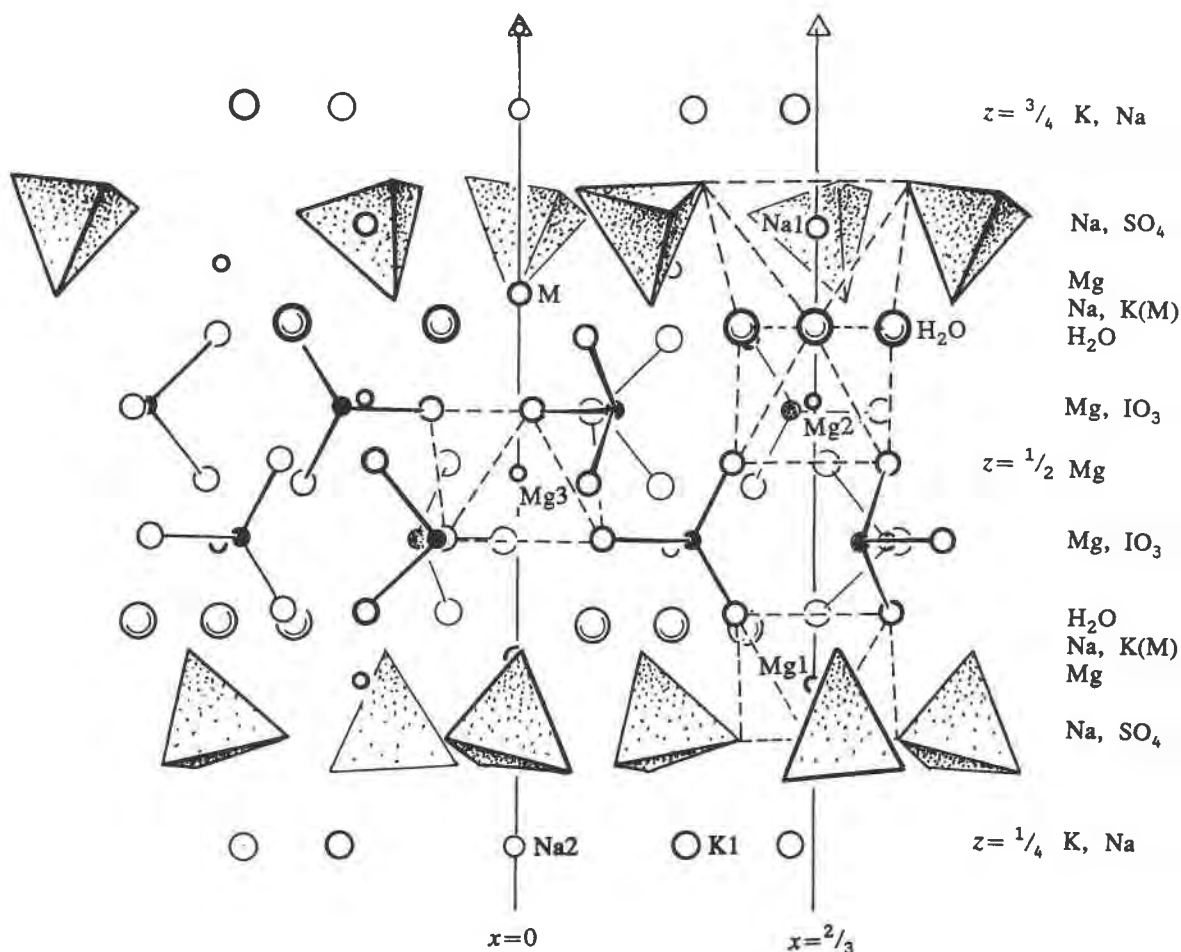


Fig. 2. One layer of the fuenzalidaite and carlosruizite structure viewed along the *a* axis. Solid circles are I (in IO<sub>3</sub>); SO<sub>4</sub> (SeO<sub>4</sub>) groups are represented by shaded tetrahedra. The octahedral coordination of Na and Mg cations on the threefold axes is shown by dashed lines; layers are separated by K1 and Na2 atoms.

TABLE 8. Bond lengths (Å) and angles (°) in fuenzalidaite (FNZ) and carlosruizite (CLR)

	FNZ	CLR		FNZ	CLR
I-O1	1.81(2)	1.79(2)	O1-I-O2	97(1)	100(1)
-O2	1.88(2)	1.80(2)	O2-I-O3	97(1)	95(1)
-O3	1.90(2)	1.80(2)	O3-I-O1	96(1)	97(2)
Av.	1.863	1.797	Av.	96.7	97.3
S(Se)-O4	1.45(2)	1.60(2)	O4-S(Se)-O5	112(1)	114(1)
-O5	1.46(2)	1.56(2)	O4-S-O6	109(1)	107(1)
-O6	1.53(2)	1.59(2)	O4-S-O7	109(1)	108(1)
-O7	1.58(2)	1.60(2)	O5-S-O6	111(1)	110(1)
Av.	1.505	1.588	O5-S-O7	109(1)	109(1)
			O6-S-O7	108(1)	108(1)
			Av.	109.7	109.3
K1-O5[×2]	2.84(2)	2.80(2)	Mg1-O6[×3]	1.98(2)	2.04(2)
-O4[×2]	2.90(2)	2.88(2)	-O2[×3]	2.09(2)	2.13(2)
-O6[×2]	2.93(2)	2.86(2)	Mg2-O3[×3]	2.02(2)	2.04(2)
-O4[×2]	3.06(2)	3.06(2)	-O8[×3]	2.14(2)	2.10(2)
M-O5[×3]	2.67(2)	2.80(2)	Mg3-O1[×6]	2.11(2)	2.11(2)
-O7[×3]	2.70(2)	2.74(2)	O8-O2*	2.66(2)	2.79(3)
-O1[×3]	2.76(2)	2.82(2)	-O7*	2.63(2)	2.75(3)
Na1-O4[×3]	2.36(2)	2.33(2)	-O8[×2]	2.79(3)	2.76(3)
-O8[×3]	2.44(2)	2.46(2)	O2-O8-O7	110(2)	108(2)
Na2-O5[×6]	2.35(2)	2.37(2)			

\* Probable H bond.

and Mg2 coordination octahedra (see Fig. 2). They are apparently strongly H bonded to O2 in the IO<sub>3</sub> group and O7 in the SO<sub>4</sub> group (Table 8). Three H<sub>2</sub>O molecules form a tight triangle in the a-b plane but are probably not bonded by H atoms.

Fuenzalidaite and carlosruizite have structures that bear a distant resemblance to those of the alunite group. These structures are rhombohedral or trigonal, with *a* axial lengths of about 7 Å, and contain layers consisting of sheets of tetrahedral sulfate anions joined to an <sup>61</sup>Al (or <sup>61</sup>Fe) sheet, including OH groups, and the layers are separated by K (or Na) ions. The minerals described here are the first of this type in which a layer of IO<sub>3</sub> groups occurs.

The phase systems in which these minerals form have not been studied, and an attempt to obtain fuenzalidaite from a stoichiometric solution at room temperature was not successful.

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