THE CRYSTAL STRUCTURE OF KAINITE

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ABSTRACT

Kainite, $KMg(SO_4)Cl \cdot 2\ 3/4H_2O$, is monoclinic $C\ 2/m$ with $a = 19.72 \pm .02$, $b = 16.23 \pm .01$, $c = 9.53 \pm .01$ Å, $\beta = 94°55' \pm 5'$, and $Z = 16$. The structure was solved by the symbolic addition procedure utilizing 1693 intensity data, collected with a Buerger automated diffractometer and CuKα radiation. A full-matrix least-squares refinement, with anisotropic temperature factors for cations and chlorine ions, yielded a final R-index of 0.047. The structure can be envisioned as polyhedral layers composed of corner–sharing Mg-octahedra and S–tetrahedra. The negatively charged layers are balanced by positively charged Mg and K ions which, together with chlorine ions and water molecules, occupy the spaces between the layers. The layers are parallel to (100), thus responsible for the perfect {100} cleavage. The geometry of the magnesium octahedra and sulphur tetrahedra is close to ideal. Two of the three independent K ions are in irregular 8-fold coordination while the third has nine ligands. The mean cation–anion distances are: S–O = 1.47, Mg–O,Ow = 2.07, K–O = 2.87, and K–Cl = 3.23 Å.

INTRODUCTION

Kainite, $KMg(SO_4)Cl \cdot 2\ 3/4H_2O$, distinguishes itself among other K–Mg sulphates (such as langbeinite, leonite, and picromerite) by virtue of its Cl content and its commercial importance. First noted in the much studied salt deposits of Stassfurt, Germany, the mineral is also found abundantly in the Zechstein Formation of Europe and the Salado Formation of Texas and New Mexico, both Permian in age, and noted potash deposits of oceanic origin.

Two questions concerning the mineral, aside from the fact that its structure was unknown, prompted our study. First, the water content of the mineral is listed in Dana's System of Mineralogy (Palache *et al.*, 1951) as $3H_2O$. However, Kühn and Ritter (1958) reported a water content of $2\ 3/4H_2O$, based on chemical analyses of natural as well as synthetic kainite. Second, the relatively low birefringence of

the mineral is suggestive of a framework structure; yet a perfect {100} cleavage is observed. Herein we present the structure of kainite which provides the answers to the aforementioned questions.

A large transparent crystal of kainite from Stassfurt, Germany was obtained from the U. S. National Museum, Smithsonian Catalogue No. C–4613. Precession photographs and measurements with a Buerger single–crystal diffractometer yielded the following lattice constants: $a = 19.72 \pm .02$ Å, $b = 16.23 \pm .01$ Å, $c = 9.53 \pm .01$ Å, $\beta = 94°55' \pm 5'$, space group $C\ 2/m$, and $Z = 16$.

The transformation matrix from the morphological cell of Groth[1] to our structure cell is 002/010/$\frac{1}{2}$00. After transformation (ours $\rightarrow$ Groth) our axial ratio becomes 1.174:1.0:0.607, in good agreement with the ratio reported by Groth of 1.1727:1.0:0.6093. In addition, our cell dimensions are in good agreement with those reported by Evans[1] who also gave the space group as $C\ 2/m$. The calculated specific gravity of 2.176 is in reasonably good agreement with the measured value of 2.15 reported.[1]

A 0.22 mm diameter sphere was used for data collection. From the 2085 reciprocal lattice points scanned, a total of 1693 "observable", non–equivalent reflections were obtained utilizing a Buerger automated diffractometer (Weissenberg geometry) with Ni–filtered CuKα radiation, a proportional detector, and a pulse height analyzer. A reflection was considered observed if $I - B \geq 3^*\sqrt{I + B}$ where I = total counts accumulated during the scan and B = total background. Standard reflections were carefully monitored to insure system stability. The data were corrected for Lp and spherical absorption ($\mu r = 1.378$).

Experimental normalized structure–factor statistics, along with the theoretical values for centrosymmetric and noncentrosymmetric crystals calculated by Karle *et al.* (1965), are given in Table 1. They correspond to those for a centrosymmetric crystal and accordingly $C\ 2/m$ was used throughout the determination.

The crystal structure was solved by the symbolic addition procedure, using the semi–automatic SORTE program of Bednowitz (1970). The distribution of intensities indicated a pseudo–face centered cell making the determination somewhat less than straightforward. However, by careful, manual manipulation of the data and the acceptance of lower probability values for the interactions of the weaker reflections, a sufficient number of phases were determined to yield an E–map which showed the complete structure. It should be mentioned that the fully automated program of R. E. Long (1965) failed to reveal the structure.

Three cycles of full–matrix least–squares refinement employing the RFINE program of Finger (1969) lowered the isotropic R–index to 0.066. The coefficients for the analytical form factors for K^{1+}, Mg^{2+}, S^0, Cl^{1-}, and O^{1-} were obtained from Cromer and Mann (1968). The weights were calculated from the variance for each structure factor:

[1] As quoted in Palache *et al.*, 1951.

$$\sigma^2(F) = \frac{F^2}{4(T - B)^2}[T + B + 0.0009 \ (T - B)^2]$$

where T = total count, B = average background count, and the additional term involving $(T - B)$ is to allow for errors proportional to the net count, such as variation in the beam and absorption errors (Brandle and Steinfink, 1969).

TABLE 1. EXPERIMENTAL AND THEORETICAL VALUES OF
NORMALIZED STRUCTURE FACTORS

	Experimental	Centrosymmetric	Non-Centrosymmetric
Av. $\lvert E \rvert$	0.733	0.798	0.886
Av. $\lvert E^2 - 1 \rvert$	0.985	0.968	0.736
$\lvert E \rvert \geq 3.0$	.25%	0.3%	0.01%
$\lvert E \rvert \geq 2.0$	5.1%	5.0%	1.8%
$\lvert E \rvert \geq 1.0$	25.2%	32.0%	37.0%

An experimental value for the extinction parameter, s

$$F^2_{corr} = F^2_{uncorr}/(1 - sF^2_{uncorr})$$

was determined by examination of twenty large, low angle reflections obviously suffering from extinction. Refinement of s (initial value = 0.40×10^{-5}; final value = 0.448×10^{-5}) and all other parameters lowered R to 0.058. In the last cycle, the isotropic temperature factors of the cations and the Cl atoms were converted to anisotropic temperature factors and all parameters were again varied, yielding a final R of 4.7 percent. A final difference Fourier map revealed only background ripples, thereby confirming the H_2O content to be as reported by Kühn and Ritter (1958). The final atomic coordinates and temperature factors are given in Tables 2 and 3. Observed and calculated structure factors are listed in Table 4 which has been deposited with the National Auxiliary Publications Service.[1]

DISCUSSION OF THE STRUCTURE

The structure of kainite is illustrated in the polyhedral drawing of Figure 1. The sheet–like structure of kainite is apparent; the Mg(3) octahedra serve as links between the octahedral–tetrahedral sheets. The alternate arrangement of the positively charged Mg(3) and K cations and the negatively charged octahedral-tetrahedral sheets, parallel to (100), accounts for the perfect {100} cleavage.

Table 5 lists selected interatomic distances and angles for kainite. The shape of the two sulphate tetrahedra approaches the ideal, with

[1] To obtain a copy of this material, order NAPS Document Number 01858 The present address is National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 866 Third Avenue, New York, New York 10022, and price $2.00 for microfiche or $5.00 for photocopies, payable in advance to CCMIC-NAPS. Check a recent issue of the journal for current address and price.

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Table 2. Atomic Coordinates and Isotropic Temperature Factors
for Kainite[a]

Atom	Equipoint	x	y	z	B(Å^2)
K(1)	4i	.19158(8)	1/2	.4203(2)	1.80(4)[b]
K(2)	4i	.19318(8)	0	.9398(2)	1.56(4)[b]
K(3)	8j	.19487(6)	.3064(1)	.8483(1)	2.00(4)[b]
S(1)	8j	.09695(5)	.3308(1)	.5175(1)	0.69(4)[b]
S(2)	8j	.09805(5)	.1672(1)	.0136(1)	0.75(4)[b]
Mg(1)	2d	0	1/2	1/2	0.87(7)[b]
Mg(2)	2a	0	0	0	1.00(8)[b]
Mg(3)	4f	1/4	1/4	1/2	1.14(5)[b]
Mg(4)	8j	.00026(7)	.2484(1)	.2481(1)	1.00(4)[b]
Cl(1)	4i	.21470(12)	0	.2730(2)	2.45(5)[b]
Cl(2)	4i	.13985(10)	0	.6231(2)	2.27(5)[b]
Cl(3)	8j	.17890(7)	.3892(1)	.1357(1)	2.35(4)[b]
O(1)	8j	.0710(2)	.2317(3)	.9152(3)	1.30(6)
O(2)	8j	.0707(2)	.2694(3)	.4142(3)	1.37(6)
O(3)	8j	.0749(2)	.3107(2)	.6569(3)	1.29(7)
O(4)	8j	.0734(2)	.4133(2)	.4744(4)	1.52(7)
O(5)	8j	.0715(2)	.0859(2)	.9646(4)	1.56(7)
O(6)	8j	.0760(2)	.1844(2)	.1552(3)	1.14(6)
O(7)	8j	.1721(2)	.3316(3)	.5261(3)	1.25(6)
O(8)	8j	.1722(2)	.1668(3)	.0183(3)	1.34(6)
Ow(1)	4i	.0399(2)	0	.2197(5)	1.65(9)
Ow(2)	4i	.0193(2)	1/2	.7192(5)	1.42(9)
Ow(3)	8j	.2133(2)	.1727(3)	.6510(4)	2.19(8)
Ow(4)	8j	.0259(2)	.3588(3)	.1468(4)	1.48(7)
Ow(5)	8j	.0200(2)	.1354(3)	.6489(4)	1.74(7)
Ow(6)	8j	.1963(2)	.1849(3)	.3438(4)	1.80(7)
Ow(7)	4i	.1454(4)	1/2	.8430(8)	4.49(16)

[a]Standard errors in parentheses.
[b]Anisotropic temperature factors converted to equivalent isotropic.

an average S–O distance of 1.471 Å and a range of only 0.016 Å. All
sulphate oxygens, with the exception of O(8), are also coordinated to
Mg, resulting in the small spread of the S–O distances. The thermal
motion of the S atoms is practically isotropic (Table 3). The Mg–O,Ow
distances range from 2.023 Å to 2.173 Å with the Mg–O distances tend-
ing to be slightly shorter, as expected.

Two of the three non-equivalent K atoms are surrounded by four
oxygens and four chlorine ligands whereas the third K is in nine–fold
coordination. These coordination numbers are low relative to those
found in the K–Fe hydrated sulphates where the numbers are 10 and
11 (Graeber and Rosenzweig, 1971). Also, the K–O distances are much
longer (mean = 3.03 Å, range = 0.70 Å) than those of kainite which
has a mean K–O distance of 2.870 Å and a range of 0.19 Å. The average
K–Cl distance in kainite is 3.225 Å, slightly longer than the ionic

Table 3. Magnitudes and Orientation of Principal Axes of
Thermal Ellipsoids in Kainite

| Atom, axis	rms displacement Å(σ)	Angle, in degrees, with respect to			Atom, axis	rms displacement Å(σ)	Angle, in degrees, with respect to		
		+a(σ)	+b(σ)	+c(σ)			+a(σ)	+b(σ)	+c(σ)
S(1), 1	.085(3)	25(13)	106(14)	75(11)	K(1), 1	.135(3)	156(3)	90	61(3)
2	.096(3)	66(16)	72(52)	153(48)	2	.137(6)	90	180	90
3	.099(6)	82(23)	24(45)	68(54)	3	.177(3)	66(3)	90	29(3)
S(2), 1	.093(3)	115(46)	94(19)	21(47)	K(2), 1	.126(3)	167(4)	90	72(4)
2	.096(3)	153(45)	101(21)	110(48)	2	.141(6)	90	180	90
3	.104(6)	79(21)	169(21)	90(16)	3	.154(3)	77(4)	90	18(4)
Mg(1), 1	.081(8)	172(6)	90	77(7)	K(3), 1	.135(2)	84(15)	84(8)	13(17)
2	.102(16)	90	180	90	2	.140(2)	26(5)	66(3)	103(17)
3	.127(6)	82(7)	90	13(7)	3	.195(3)	65(2)	155(2)	90(2)
Mg(2), 1	.097(7)	153(10)	90	58(10)	Cl(1), 1	.152(7)	90	0	90
2	.114(14)	90	180	90	2	.159(3)	95(2)	90	170(2)
3	.126(6)	63(10)	90	32(10)	3	.211(3)	175(2)	90	80(3)
Mg(3), 1	.110(5)	173(16)	90	78(16)	Cl(2), 1	.158(3)	174(5)	90	79(5)
2	.122(4)	97(16)	90	168(16)	2	.167(6)	90	180	90
3	.128(8)	90	0	90	3	.182(3)	84(5)	90	11(5)
Mg(4), 1	.094(4)	44(14)	83(7)	51(13)	Cl(3), 1	.141(2)	163(3)	107(4)	82(4)
2	.105(4)	47(14)	108(7)	136(13)	2	.163(3)	84(5)	122(3)	148(3)
3	.134(6)	98(6)	161(7)	72(6)	3	.207(3)	74(2)	143(3)	59(3)
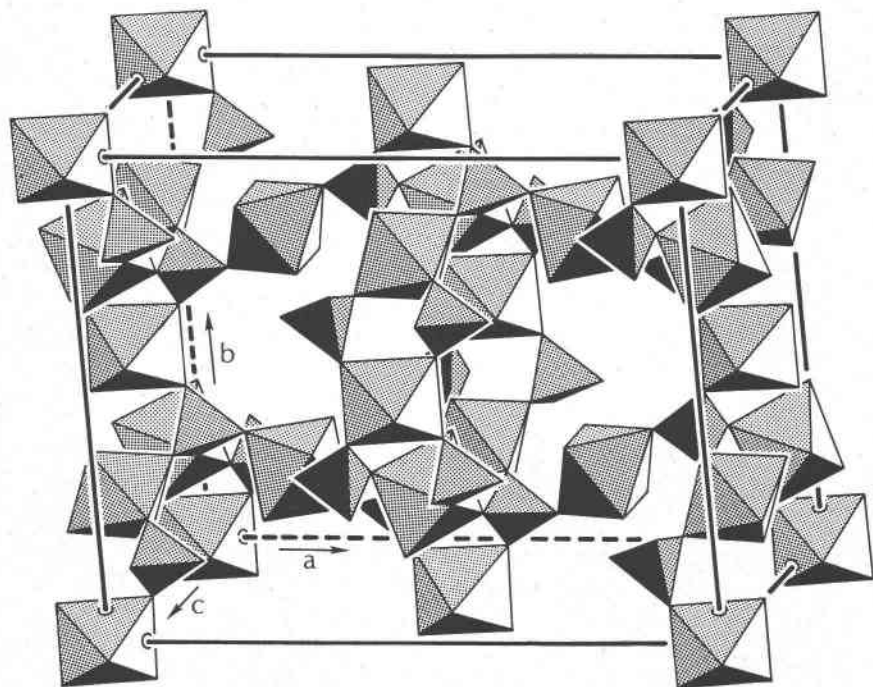
FIG. 1. A polyhedral representation of the kainite structure (K and Cl atoms omitted).

Table 5. Selected Interatomic Distances and Angles[a]

Tetrahedral coordination around S						
S(1)-O(2)	1.464(4) Å	O(2)-O(3)	2.402(5) Å	O(2)-S(1)-O(3)	110.0(2)°
S(1)-O(3)	1.469(3)	O(2)-O(4)	2.405(6)	O(2)-S(1)-O(4)	110.4(2)
S(1)-O(4)	1.465(4)	O(2)-O(7)	2.407(5)	O(2)-S(1)-O(7)	109.8(2)
S(1)-O(7)	1.478(3)	O(3)-O(4)	2.407(5)	O(3)-S(1)-O(4)	110.3(2)
		O(3)-O(7)	2.398(5)	O(3)-S(1)-O(7)	109.0(2)
		O(4)-O(7)	2.372(5)	O(4)-S(1)-O(7)	107.5(2)
Mean	1.469 Å	Mean	2.398 Å	Mean	109.5°
S(2)-O(1)	1.474(4) Å	O(1)-O(5)	2.412(6) Å	O(1)-S(2)-O(5)	109.4(2)°
S(2)-O(5)	1.480(4)	O(1)-O(6)	2.406(4)	O(1)-S(2)-O(6)	109.2(2)
S(2)-O(6)	1.479(3)	O(1)-O(8)	2.393(5)	O(1)-S(2)-O(8)	109.3(2)
S(2)-O(8)	1.460(3)	O(5)-O(6)	2.414(5)	O(5)-S(2)-O(6)	109.4(2)
		O(5)-O(8)	2.399(5)	O(5)-S(2)-O(8)	109.3(2)
		O(6)-O(8)	2.411(4)	O(6)-S(2)-O(8)	110.2(2)
Mean	1.473 Å	Mean	2.406 Å	Mean	109.5°

Octahedral coordination around Mg						
Mg(1)-O(4)	2.048(4) Å [X4]	O(4)-O(4)	2.976(7) Å [X2]	O(4)-Mg(1)-O(4)	93.2(2)° [X2]
Mg(1)-Ow(2)	2.091(2) [X2]	O(4)-O(4)	2.813(8) [X2]	O(4)-Mg(1)-O(4)	86.8(2) [X2]
		O(4)-Ow(2)	2.998(5) [X4]	O(4)-Mg(1)-Ow(2)	92.8(1) [X4]
		Ow(2)-O(4)	2.854(6) [X4]	Ow(2)-Mg(1)-O(4)	87.2(1) [X4]
Mean	2.062 Å	Mean	2.916 Å	Mean	90.0°
Mg(2)-O(5)	2.032(4) Å [X4]	O(5)-O(5)	2.790(8) Å [X2]	O(5)-Mg(2)-O(5)	86.7(2)° [X2]
Mg(2)-Ow(1)	2.173(5) [X2]	O(5)-O(5)	2.956(7) [X2]	O(5)-Mg(2)-O(5)	93.3(2) [X2]
		O(5)-Ow(1)	2.916(6) [X4]	O(5)-Mg(2)-Ow(1)	87.7(1) [X4]
		Ow(1)-O(5)	3.033(6) [X4]	Ow(1)-Mg(2)-O(5)	92.3(1) [X4]
Mean	2.079 Å	Mean	2.941 Å	Mean	90.0°
Mg(3)-O(7)	2.060(4) Å [X2]	O(7)-Ow(6)	2.791(5) Å [X2]	O(7)-Mg(3)-Ow(6)	85.7(1)° [X2]
Mg(3)-Ow(3)	2.085(4) [X2]	Ow(6)-O(7)	3.011(6) [X2]	Ow(6)-Mg(3)-O(7)	94.3(1) [X2]
Mg(3)-Ow(6)	2.046(4) [X2]	Ow(3)-Ow(6)	2.917(6) [X2]	Ow(3)-Mg(3)-Ow(6)	89.8(1) [X2]
		Ow(6)-Ow(3)	2.924(5) [X2]	Ow(6)-Mg(3)-Ow(3)	90.2(1) [X2]
		O(7)-Ow(3)	2.926(6) [X2]	O(7)-Mg(3)-Ow(3)	89.8(1) [X2]
		Ow(3)-O(7)	2.934(5) [X2]	Ow(3)-Mg(3)-O(7)	90.2(1) [X2]
Mean	2.064 Å	Mean	2.917 Å	Mean	90.0°
Mg(4)-O(1)	2.023(4) Å	O(1)-O(3)	2.783(5) Å	O(1)-Mg(4)-O(3)	85.8(1)°
Mg(4)-O(2)	2.043(4)	O(1)-O(6)	3.017(5)	O(1)-Mg(4)-O(6)	94.7(1)
Mg(4)-O(3)	2.067(4)	O(1)-Ow(4)	2.839(5)	O(1)-Mg(4)-Ow(4)	86.6(1)
Mg(4)-O(6)	2.079(4)	O(1)-Ow(5)	3.075(5)	O(1)-Mg(4)-Ow(5)	95.3(2)
Mg(4)-Ow(4)	2.116(4)	O(2)-O(3)	2.970(5)	O(2)-Mg(4)-O(3)	92.6(1)
Mg(4)-Ow(5)	2.135(4)	O(2)-O(6)	2.838(5)	O(2)-Mg(4)-O(6)	87.0(1)
		O(2)-Ow(4)	2.998(5)	O(2)-Mg(4)-Ow(4)	92.2(2)
		O(2)-Ow(5)	2.848(5)	O(2)-Mg(4)-Ow(5)	85.9(1)
		O(3)-Ow(4)	2.950(5)	O(3)-Mg(4)-Ow(4)	89.7(1)
		O(3)-Ow(5)	3.044(6)	O(3)-Mg(4)-Ow(5)	92.8(2)
		O(6)-Ow(4)	2.996(6)	O(6)-Mg(4)-Ow(4)	91.2(1)
		O(6)-Ow(5)	2.882(5)	O(6)-Mg(4)-Ow(5)	86.3(2)
Mean	2.077 Å	Mean	2.937 Å	Mean	90.0°

Coordination around K					
K(1)		K(2)		K(3)	
K(1)-O(4)	2.808(4) Å [X2]	K(2)-O(5)	2.803(4) Å [X2]	K(3)-O(8)	2.843(4) Å
K(1)-O(7)	2.949(4) [X2]	K(2)-O(8)	2.848(4) [X2]	K(3)-O(8)	2.847(3)
K(1)-Cl(3)	3.246(2) [X2]	K(2)-Cl(3)	3.229(2) [X2]	K(3)-O(1)	2.848(4)
K(1)-Cl(1)	3.322(3)	K(2)-Cl(1)	3.167(2)	K(3)-O(3)	2.861(3)
K(1)-Cl(2)	3.385(2)	K(2)-Cl(2)	3.110(3)	K(3)-Ow(3)	2.914(4)
				K(3)-Ow(6)	2.941(4)
				K(3)-Cl(3)	3.092(2)
				K(3)-O(7)	3.092(3)
				K(3)-Ow(7)	3.290(3)

[a]Standard errors in parentheses.

radius sum of $1.33 + 1.81 = 3.14$ Å. This is probably due to the fact that the Cl atoms are located in rather spacious voids.

There are three non-equivalent Cl atoms in the structure, two of which are in special positions. Aside from being bonded to the K atoms, the Cl atoms have some water neighbors which are close enough to conceivably be hydrogen bonded to Cl. These are: $Cl(1)-Ow(7) = 3.059$ Å, $Cl(1)-Ow(6) = 3.715$ Å $[\times 2]$, $Cl(2)-Ow(3) = 3.156$ Å $[\times 2]$, $Cl(3)-Ow(3) = 2.987$ Å, and $Cl(3)-Ow(4) = 3.068$ Å. No further study of the H–bonding scheme was attempted.

STRUCTURES OF OTHER K–Mg SULPHATES

The most abundant chemical compounds in marine evaporites are calcium sulphate hydrates and sodium chloride. However, of greater interest are the rare deposits of the more soluble salts obtainable from seawater—the chlorides and sulphates of magnesium and potassium. They are: langbeinite–$K_2Mg_2(SO_4)_3$, leonite–$K_2Mg(SO_4)_2 \cdot 4H_2O$, picromerite (or schönite)—$K_2Mg(SO_4)_2 \cdot 6H_2O$, and kainite. It is of interest to make structural comparisons among these minerals.

The octahedral–tetrahedral arrangement in langbeinite is a 3–dimensional framework, with all S–tetrahedral and Mg–octahedral corners shared (Zemann and Zemann, 1957). The K is coordinated to seven sulphate oxygens. This 3–dimensional linkage of T and O polyhedra is morphologically manifested by a lack of cleavage (and the presence of a conchoidal fracture). In leonite (Schneider, 1961), the linkage is altered because of the introduction of four water molecules in the formula. All the water surrounds the octahedral cation as usual and the remaining two corners are made up of sulphate oxygens. The water ligands of Mg make the 3–dimensional $\cdots$ T–O–T–O $\cdots$ linkage impossible, and three out of the four independent sulphate oxygens are unshared with the Mg–octahedra. The structural formula can thus be written as $K_2[Mg(H_2O)_4](SO_4)_2$. Leonite also shows no cleavage and possesses low birefringence. These characteristics cannot be explained in terms of the T–O linkage. However, the structure becomes a framework type when the K coordination (6 oxygen and 3 water ligands) is considered to be an integral part of the linkage. The highest hydrate in this series is picromerite (Kannan and Viswamitra, 1965), the structural formula being $K_2[Mg(H_2O)_6](SO_4)_2$. Here the number of water molecules is just sufficient to surround the octahedral cation and no sharing between the S–tetrahedra and Mg–octahedra takes place. The structure thus consists of isolated T or O groups. Accordingly, one might expect no cleavage to develop, as in soda alum. However, the K coordination again plays an important role in picromerite. The 9–

fold coordinate K polyhedra form infinite sheets parallel to $(20\bar{1})$ and, as a result, the mineral exhibits a perfect $\{20\bar{1}\}$ cleavage. Thus one sees a contrasting role played by K polyhedra in leonite and picromerite. In the former the K polyhedra give rise to a framework structure, whereas in the latter mineral, the K polyhedra impart a sheet structure. In kainite, there also exist K polyhedra. However, the role played by these polyhedra is reduced to secondary importance, for the cleavage in this mineral is the consequence solely of the octahedral–tetrahedral topology in the structure.

It is apparent that the spatial arrangement of coordination polyhedra, other than those of tetrahedra and octahedra, can be an important controlling factor of the cleavages in sulphate minerals.

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