Kieserite, $Mg(SO_4)(H_2O)$, a Titanite-Group Mineral

By

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With 6 figures and 7 tables in the text

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Abstract: The crystal structure of kieserite, $MgSO_4 \cdot H_2O$, monoclinic, $a = 6.891(2)$, $b = 7.624(2)$, $c = 7.645(2)$, $\beta = 117.70(2)$, $V = 355.6(2)$, $Z = 4$, space group C2/c, has been refined by a least-squares method to an R index of 2.3 % using 509 observed ($I > 2.5\sigma I$) reflections collected on an automated four-circle diffractometer using MoKα x-radiation. Mixed tetrahedral-octahedral chains of the form $[Mg(SO_4)\phi_3]$ (ϕ: unspecified ligand) run parallel to the Z-axis. Tetrahedra bridge across to adjacent chains to form a tetrahedral-octahedral $[Mg(SO_4)(H_2O)]$ framework that is isostructural with the $[Ti(SiO_4)O]$ framework in titanite and graphically identical to the $[Al(PO_4)F]$ framework in amblygonite.

Kieserite is an important rock-forming mineral in many marine salt deposits, and is frequently associated with other (alkali metal) magnesium sulphate minerals in very complex assemblages. A generalized paragenetic scheme is set up for the more common magnesium sulphate minerals, and the crystal structures of the various phases are examined in terms of the arguments of Hawthorne (1985). There is a gradual depolymerization of the structure module with progressive evolution through the general paragenetic sequence, facilitated by the incorporation of increasing amounts of (H_2O) into the mineral as a component of the structure module. This depolymerization is also accompanied by a decrease in the module basicity of the minerals, which has the effect of decreasing the acidity of the extra-module cations until, in the latest parts of the sequence, there are no extra-module cations and the structure modules are neutral.

Key words: Kieserite, crystal structure, sulphate, paragenesis.

Introduction

Kieserite, $MgSO_4 \cdot H_2O$, is an abundant rock-forming mineral in marine salt deposits around the world. It typically occurs in the upper parts of such deposits, where it is generally associated with halite, polyhalite or anhydrite, and sometimes shows alteration to leonite, polyhalite or epsomite. The crystal structure of kieserite was first solved by Leonardt & Weiss (1957) and refined by Brégeault et al. (1970). Baur (1959a) examined the relationship between the structures of kieserite, titanite and amblygonite, showing that kieserite and

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titanite are isostructural, and that both structures are graphically identical to that of amblygonite. The current work was undertaken to provide more precise structure parameters for kieserite, and to more fully explore some of the structural aspects of these 7 Å $M\phi_5$ chain minerals (Moore, 1970).

Experimental

The crystals used in this work are from the Wathlingen, Hanover, Germany, and were supplied through the courtesy of the Department of Mineralogy and Geology, Royal Ontario Museum, Toronto, collection number M23594. Cell dimensions (Table 1) were determined by least-squares refinement of the setting angles for 25 intense reflections automatically aligned on a 4-circle diffractometer. Intensity data were collected according to the procedure described by Hawthorne & Eby (1985); relevant information concerning data collection and refinement is given in Table 1. The ψ-scan absorption correction reduced the R index for the azimuthal data from 1.1 % to 0.9 %; the data were corrected for Lorentz, polarization and background effects, and reduced to structure factors; of the 560 unique reflections, 506 were classed as observed [$I > 2.5\sigma(I)$].

Table 1. Miscellaneous Information: Kieserite.

a	=	6.912(2)	Crystal size (mm) =	0.16 × 0.17 × 0.24
b	=	7.624(2)	Rad/Mono	MoKα/Graphite
c	=	7.642(2)	Total Unique $\lvert F_o \rvert$	598
β	=	118.09(2)	No. of $\lvert F_o \rvert > 4\sigma$	509
V	=	355.6(2)	R (observed)	2.3 %
Space Group C2/c			R_w (observed)	2.5 %

Unit cell contents: $4[MgSO_4 \cdot H_2O]$
$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$
$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$, $w = 1$

Structure Refinement

Systematic absences confirmed the space group C2/c assigned by previous workers. Scattering curves for neutral atoms together with anomalous dispersion coefficients were takem from Cromer & Mann (1968) and Cromer & Lieberman (1970). R indices are of the form given in Table 1 and are expressed as percentages.

From the starting coordinates of Brégeault et al. (1970), least-squares refinement converged rapidly to an R index of 4.1 %. Conversion to anisotropic temperature factors resulted in convergence at an R index of 2.3 % and a ωR index of 2.5 %. Final parameters are given in Table 2, selected interatomic distances are given in Table 3, and an empirical bond-valence analysis is given in Table 4.

Table 2. Atomic positions and temperature factor coefficients for kieserite.

Site	x	y	z	U^*_{equiv}	U^*_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg	0	1/2	0	95(3)	81(3)	98(4)	101(4)	−5(3)	38(3)	4(3)
S	0	0.15490(8)	1/4	79(2)	59(3)	77(3)	92(3)	0	29(2)	0
O(1)	0.1761(2)	0.0447(2)	0.3943(2)	146(5)	93(6)	156(7)	171(7)	37(5)	46(5)	65(5)
O(2)	0.0916(2)	0.2676(2)	0.1491(2)	128(5)	121(7)	125(6)	167(7)	12(5)	92(5)	43(5)
O(3)	0	0.6353(3)	1/4	120(7)	100(10)	136(9)	119(9)	0	47(7)	0
H	0.120(3)	0.693(3)	0.296(3)	100	–	–	–	–	–	–

$U = U \times 10^4$.

Table 3. Selected interatomic distances (Å) and angles° in kieserite.

S–O(1)	× 2	1.466(1)	Mg–O(1)	× 2	2.019(2)
S–O(2)	× 2	1.478(2)	Mg–O(2)	× 2	2.041(1)
<S–O>		1.472	Mg–O(3)	× 2	2.172(1)
			<Mg–O>		2.077
O(1)–O(1)a		2.404(2)	O(1)–S–O(1)a		110.1(1)
O(1)–O(2)	× 2	2.393(2)	O(1)–S–O(2)	× 2	108.7(1)
O(1)–O(2)a	× 2	2.415(2)	O(1)–S–O(2)a	× 2	110.2(1)
O(2)–O(2)a		2.405(2)	O(2)–S–O(2)a		108.9(1)
<O–O>S		2.404	<O–S–O>		109.5
O(1)b–O(2)	× 2	2.762(2)	O(1)b–Mg–O(2)	× 2	85.7(1)
O(1)b–O(2)d	× 2	2.975(2)	O(1)b–Mg–O(2)d	× 2	94.3(1)
O(1)b–O(3)	× 2	2.995(2)	O(1)b–Mg–O(3)	× 2	91.1(1)
O(1)b–O(3)d	× 2	2.936(2)	O(1)b–Mg–O(3)d	× 2	88.9(1)
O(2)–O(3)	× 2	3.050(2)	O(2)–Mg–O(3)	× 2	92.7(1)
O(2)–O(3)d	× 2	2.909(2)	O(2)–Mg–O(3)d	× 2	87.3(1)
<O–O>Mg		2.938	<O–Mg–O>		90.0
O(3)–H	× 2	0.86(2)			
O(3)–O(2)		2.741(2)	O(3)–H–O(2)		162 (3)
H–O(2)		1.92(3)			
H–H		1.47(5)	H–O(3)–H		118 (6)

a: −x,y,1/2−z; b: 1/2−x,1/2+y,1/2−z; c: −1/2+x,1/2−y,−1/2+z; d: x,y, 1/2−z.

Table 4. Bond-valence table for kieserite*.

	Mg	S	H	Σ
O(1)	$0.391^{\times 2}{\downarrow}$	$1.543^{\times 2}{\downarrow}$		1.934
O(2)	$0.373^{\times 2}{\downarrow}$	$1.490^{\times 2}{\downarrow}$	0.20	2.063
O(3)	$0.286^{\times 2}{\downarrow}{\rightarrow}$		$0.80^{\times 2}{\rightarrow}$	2.172
Σ	2.100	6.066	1.00	

* calculated from the curves of Brown (1981).

Discussion

The structure is as found by previous studies. Corner sharing $[Mg\phi_5]$ chains (ϕ: unspecified ligand) extend parallel to the Z-axis, and are further linked along their lengths by (SO_4) tetrahedra to form type I $[Mg(SO_4)\phi_3]$ chains (Moore, 1970), as shown in Fig. 1. The tetrahedral vertices not linked to the central octahedral chain cross-link to adjacent chains (Fig. 3 a) to form a mixed

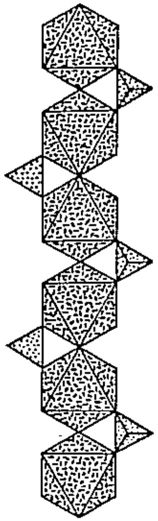

Fig. 1. Type 1 [$Mg(SO_4)\phi_3$] chain (Moore, 1970).

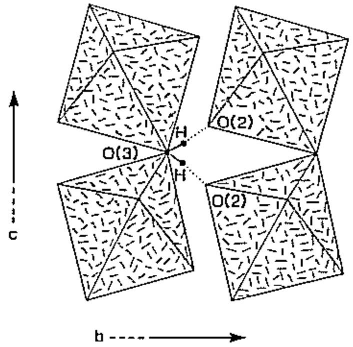

Fig. 2. The hydrogen bond arrangement around O(3) in kieserite.

tetrahedral-octahedral framework. The O(3) anion that bridges along the length of the ($M\phi_5$) octahedral chain is the (H_2O) group; as this group is bonded to two Mg cations, it must form two reasonably strong hydrogen bonds (Table 4). Fig. 2 shows the local arrangement around the O(3) anion; hydrogen bonds link to O(2) anions of an adjacent chain, further increasing interchain linkage.

Related Structures

Kieserite is isostructural with the common silicate mineral titanite Ca(Ti,Al, Fe^{3+})(SiO_4)(O,OH); this is perhaps more easily seen when the formula of kieserite is written as $Mg(SO_4)(H_2O)$. The cell dimensions of these minerals are compared in Table 5, and the structures are shown in Figs. 3 a and 3 b. There is a considerable difference in the relative sizes of the tetrahedra and octahedra in each structure, but the heteropolyhedral framework is very flexible and can ac-

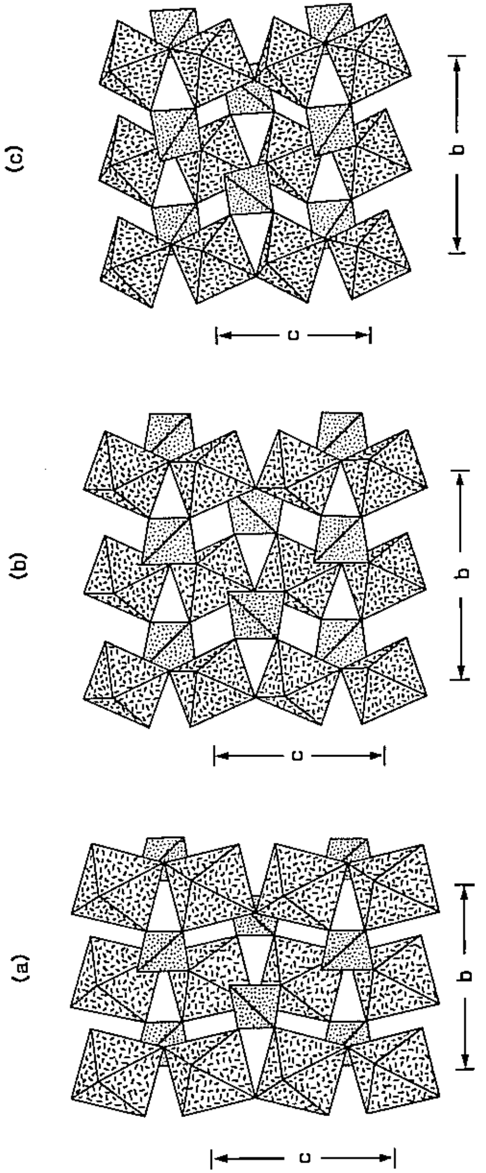

Fig. 3. Polyhedral representations of the crystal structures of (a): kieserite; (b): titanite; (c): amblygonite.

Table 5. Minerals structurally related to kieserite.

Mineral	Formula	a(Å)	b(Å)	c(Å)	β(°)	Sp.Gr.	Ref.
Dwornikite	$[Ni(SO_4)(H_2O)]$	6.839	7.582	7.474	117.85	C2/c	(1)
Gunningite	$[Zn(SO_4)(H_2O)]$	6.954(8)	7.586(8)	7.566(8)	115.93(3)	C2/c	(2)
*Kieserite	$[Mg(SO_4)(H_2O)]$	6.912(2)	7.624(2)	7.642(2)	117.70(2)	C2/c	(3)
Poitevinite	$[Cu(SO_4)(H_2O)]$	7.176(10)	7.426(10)	7.635(10)	116.15(3)	C2/c	(2)
Szmikite	$[Mn(SO_4)(H_2O)]$	7.120(1)	7.666(1)	7.766(1)	115.85(1)	C2/c	(4)
Szomolnokite	$[Fe^{2+}(SO_4)(H_2O)]$	7.123	7.468	7.624	115.9	C2/c	(1)
Durangite	$Na[Al(AsO_4)F]$	6.574(1)	8.505(2)	7.019(1)	115.34	C2/c	(5)
Isokite	$Ca[Mg(PO_4)F]$	6.52(5)	8.75(5)	7.16	109.8	C2/c	(6)
Lacroixite	$Na[Al(PO_4)F]$	6.414	8.207	6.885	115.47	C2/c	(7)
Malayaite	$Ca[Sn(SiO_4)O]$	6.668(4)	8.895(9)	7.156(6)	113.4(1)	C2/c	(8)
Panasqueiraite	$Ca[Mg(PO_4)OH]$	6.535(3)	8.753(4)	6.919(4)	112.33(4)	C2/c	(6)
Tilasite	$Ca[Mg(AsO_4)F]$	6.688(2)	8.944(2)	7.560(2)	121.16(2)	Cc	(9)
Titanite-$P2_1/c$	$Ca[Ti(SiO_4)O]$	6.562(1)	8.714(3)	7.068(1)	113.82	$P2_1/c$	(10)
*Titanite-C2/c	$Ca[Ti,Al,Fe^{3+})(SiO_4)O]$	6.555(2)	8.718(5)	7.073(4)	113.97(5)	C2/c	(11)
*Amblygonite†	$Li[Al(PO_4)F]$	6.659(1)	7.734(2)	6.923(2)	117.47(2)	$C\bar{1}$	(12),(13)
Montebrasite†	$Li[Al(PO_4)(OH)]$	6.709(5)	7.725(6)	7.041(15)	117.75(8)	$C\bar{1}$	(12),(14)
Natromontebrasite	$Na[Al(PO_4)(OH)]$	–	–	–	–		
Tavorite	$Li[Fe^{3+}(PO_4)(OH)]$	–	–	–	–		(15)

References: (1): Pistorius (1960); (2): Pistorius (1961a); (3) this study; (4): Pistorius (1961b); (5): Foord et al. (1985); (6): Isaacs & Peacor (1981); (7): Pajunen & Lahti (1985); (8): Higgins & Ribbe (1977); (9): Bladh et al. (1972); (10): Taylor & Brown (1970); (11): Mongiorgi & Riva di Sanseverino (1968); (12): Cerna et al. (1973); (13): Simonov & Belov (1958); (14): Baur (1959b); (15): Lindberg & Pecora (1955).

†amblygonite: $\alpha = 89.9(1)$, $\gamma = 88.95(2)°$; montebrasite: $\alpha = 89.4(1)$, $\gamma = 88.32(5)°$; both transformed to C-centred orientation.

Table 6. Site-occupancies in kieserite-related groups.

Group	VII	VI	IV	II
Kieserite	□	Mg,Fe^{2+},Mn,Ni,Zn	S	H_2O
Titanite	Ca,Na (REE)	Ti,Sn^{4+},Al,Mg $(Ta^{5+},Nb^{5+},Fe^{3+})$	Si,P,As	O,F,OH
Amblygonite	Li,Na	Al,Fe^{3+}	P	OH,F

comodate these differences within unit cells of very different relative dimensions. The flexibility of this atomic arrangement is apparent from the considerable number of minerals of wide chemical variability that crystallize with this structure (Table 5). The site-occupancies of the general structure are summarized in Table 6. The [7]-co-ordinate site can be completely occupied by Ca,Na or a vacancy (□). The [6]-co-ordinate site can be completely occupied by Ti^{4+}, Al^{3+} or Mg^{2+}, the [4]-co-ordinate site can be occupied by Si^{4+}, P^{5+} or S^{6+} and the bridging anion position can be occupied by O^{2-}, $(OH)^-$ or $(H_2O)^0$; in addition, considerable amounts of pentavalent cations (Ta,Nb) have been found to substitute at the [6]-co-ordinate sites (Clarke, 1974; Paul et al., 1981; Groat et al., 1985). There is some variation in space group symmetry within these monoclinic minerals. Most have symmetry C2/c, but fairly pure titanite has symmetry $P2_1/c$ and tilasite has symmetry Cc. Adequate explanations for these symmetry differences have not yet been proposed.

As indicated by Baur (1959 a), the structures of kieserite and titanite are graphically identical to the structure of amblygonite. This is more apparent if the amblygonite structure is transformed to the space group $C\bar{1}$, when the dimensional similarity of the unit cells can be recognized (Table 5). The amblygonite structure is shown in Fig. 3 c, in which the similarity of the three structures is very apparent. The reason for the difference in symmetry between the titanite and amblygonite groups is not entirely obvious. The presence of Li as the "large" cation in amblygonite might suggest that the relaxation in symmetry occurs to allow a closer coordination around Li than would be possible in the titanite-type structure. However, natromontebrasite, $Na[Al(PO_4)(OH)]$, is also triclinic, whereas lacroixite, $Na[Al(PO_4)F]$, is monoclinic, and so the situation obviously involves more than just the coordination around the non-framework cation. Further work on this point is desirable.

Paragenesis as a function of structure

Kieserite is an important rock-forming mineral in many marine salt deposits, and is frequently associated with other (alkali metal) magnesium sulphate minerals in parageneses that can be very complex. Moore (1980, 1982) and Hawthorne (1979, 1985) have suggested that complex mineral parageneses may be susceptible to interpretation in terms of the crystal structures of the constituent minerals. Here we examine a general paragenetic scheme for the more common magnesium sulphate minerals, characterizing the structural variation as a function of progressive crystallization. Obviously this is not complete, but a reasonable degree of success would indicate it worthwhile to expand the minerals considered to all magnesium sulphate minerals (and others) and include explicitly the effects of pH and temperature.

The minerals considered here are listed in Table 7. Their phase relations (in aqueous solutions) and occurrence were examined, and the paragenetic scheme of Fig. 4 was constructed. The vertical scale (uncalibrated) is temperature, and

Table 7. Common magnesium sulphate minerals.

Mineral	Formula	Module type	Module basicity (v.u.)
Langbeinite	$K_2Mg_2(SO_4)_3$	Infinite framework	0.11
Loeweite	$Na_{12}Mg_7(SO_4)_{13} \cdot 15H_2O$	Infinite framework	0.14
Vanthoffite	$Na_6Mg(SO_4)_4$	Infinite sheet	0.14
Polyhalite	$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$	Finite cluster	0.21
Kieserite	$Mg(SO_4) \cdot H_2O$	Framework	0.00
Leonite	$K_2Mg(SO_4)_2 \cdot 4H_2O$	Finite cluster	0.14
Bloedite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$	Finite cluster	0.14
Pentahydrite	$Mg(SO_4) \cdot 5H_2O$	Infinite chain	0.00
Hexahydrite	$Mg(SO_4) \cdot 6H_2O$	Isolated polyhedra	0.00
Picromerite	$K_2Mg(SO_4)_2 \cdot 6H_2O$	Isolated polyhedra	0.13
Epsomite	$Mg(SO_4) \cdot 7H_2O$	Isolated polyhedra	0.00

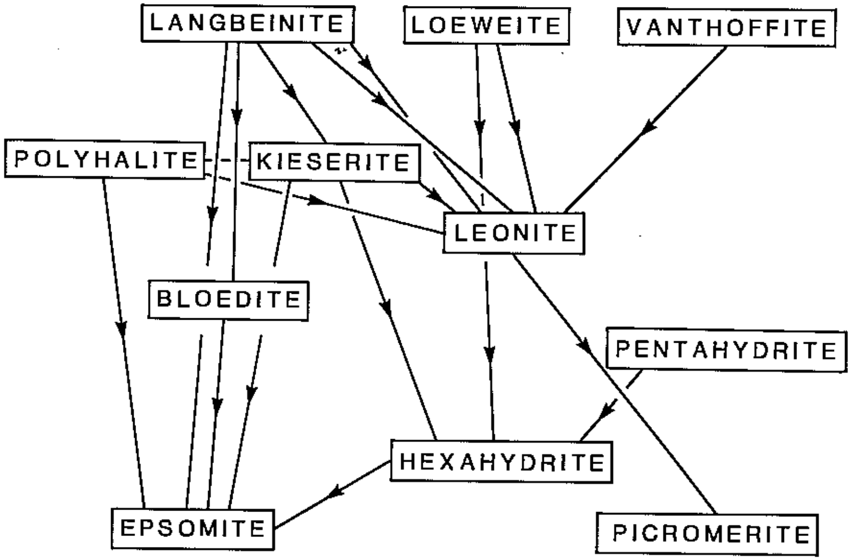

Fig. 4. Paragenetic scheme for common magnesium sulphate minerals.

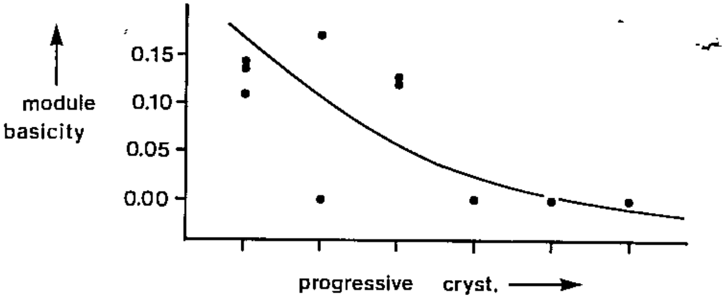

Fig. 5. Variation in module basicity with progressive crystallization for the magnesium sulphates of Fig. 4.

the arrows indicate a change in the crystallizing phase from an aqueous solution of the bulk composition of the higher temperature mineral, and/or an alteration with decreasing temperature. Obviously these equilibria will also be dependent on bulk composition and pH, but we hope that the scheme shown in Fig. 4 is not too distorted from reality.

Hawthorne (1983, 1985, in prep.) has suggested that crystal structures can be ordered into hierarchies according to the polymerization of those co-ordination polyhedra with higher bond valences, and has applied this idea to the structural classification of minerals with tetrahedrally and octahedrally co-ordinated cations. The fundamental building block of a structure is a heteropolyhedral cluster of tetrahedra and octahedra that is repeated (often polymerized) by translational symmetry operators to form the structure module, a complex (usually) anionic array whose excess charge is balanced by the presence of large low-valence cations. The basicity and character of the structure modules of the magnesium sulphate minerals is given in Table 7, in which the minerals are ordered according to their position in the paragenetic scheme of Fig. 4. It is immediately apparent that there is a gradual de-polymerization of the structure module through the paragenetic sequence. In this regard, the progressive evolution of structure type resembles the more complex changes documented by Moore (1973) for a generalized sequence of pegmatitic phosphate minerals. This de-polymerization is facilitated by the incorporation of increasing amounts of H_2O into the mineral as a component of the structure module. In this role, each H_2O replaces as polymerization linkage, leading to a break in the linkage in that direction. This de-polymerization is also accompanied by a decrease in the module basicity of the minerals (Table 7). This has the effect of

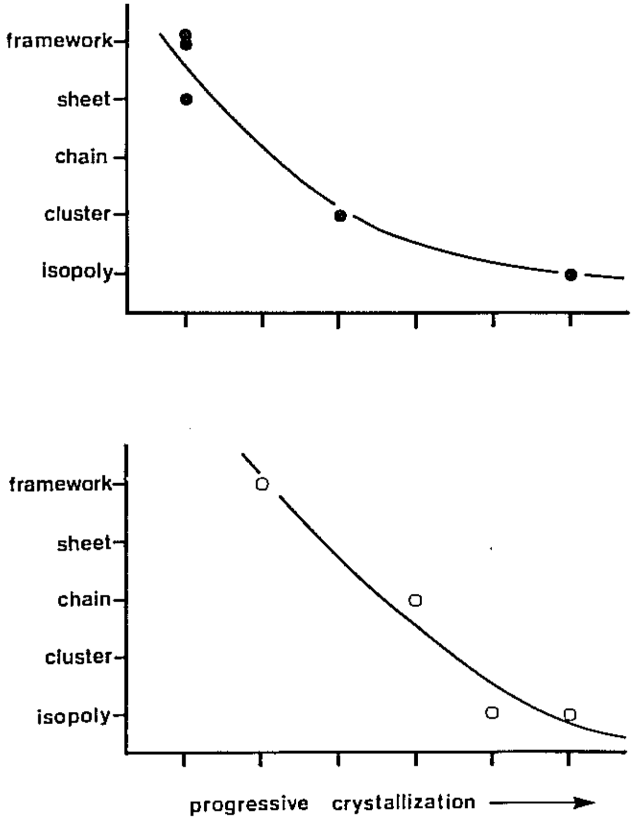

Fig. 6. Variation in module type with progressive crystallization for magnesium sulphate minerals with structure modules of similar basicities.

gradually changing the character of the extra-module cations, which exhibit a gradually decreasing acidity until, in the latest (most recent or last) parts of the sequence, there are no extra-module cations and the structure modules are neutral.

The decrease in module basicity with progressive crystallization is shown in Fig. 5. There is considerable scatter that close inspection of Table 7 shows to be related to the type of the structure module. The complete structural variation through this series of minerals can be understood by considering the effect of module basicity. Fig. 6 shows the variation in module type as a function of progressive crystallization for structure modules of about 0.14 and 0.00 v.u. basicity respectively. For a specific module basicity, there is a gradual depolymerization of the structure modules with progressive crystallization.

There are a considerable number of rarer minerals that also occur together with the minerals discussed here. As an example, uklonskovite [$NaMg(SO_4)OH(H_2O)_2$] is found together with bloedite, epsomite, hexahydrite and other associated salt minerals (Slyusareva, 1964), and its structure (Sabelli, 1985) module consists of kieserite-like [$Mg(SO_4)OH]^-$ 7 Å chains. However, the detailed paragenesis is not known and, like many of the rarer minerals, it cannot be exactly positioned in a paragenetic sequence for this reason. Thus a more detailed examination of the paragenesis of these minerals would seem to be warranted.

Acknowledgements

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Moldanubian granulites: Source material and petrogenetic considerations

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With 12 figures and 6 tables in the text

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Abstract: The study presents geochemical characteristics (contents of Th, U, K, Rb, Sr, Ba, Y, Zr, V, Cr, Ni and major oxides) of the Moldanubian granulites obtained on the basis of 106 samples. The studied granulites form three groups representing various pregranulitic source materials: acid pyroxene-free granulites (group A) correspond to metaigneous rocks of granite/rhyolite composition; subacid to intermediate pyroxene-bearing granulites (group B_1) represent metamorphosed members of a "normal" calc-alkaline igneous rock series; subacid pyroxene-free granulites (group B_2) are probably metamorphosed arenitic sediments. In comparison to upper crustal equivalents the Moldanubian granulites are not depleted in K and Rb, which does not point to a substantial participation of syngranulitic anatexis in the process of metamorphism. The observed low Th, U, Zr, and Sr contents may be explained by their selective removal into a fluid phase during granulite metamorphism.

Key words: Granulites, geochemistry, petrography, major element analyses, trace element analyses, Th, U, K, heat production, metamorpbism, Bohemian Massif, Moldanubicum, genesis, source material, geotectonic setting.

1. Introduction

Recent opinions on the genesis of Moldanubian granulites diverge and can be roughly divided into two main streams. The Czechoslovak authors ZOUBEK (1946, 1965), VESELÁ (1967), LOSERT (1971), and SUK (1974) mostly follow the original concept of SUESS (1926) and consider the granulites as an autochthonous metamorphosed volcano-sedimentary unit, which occupies a distinct stratigraphic position within the Moldanubian complex. On the other hand, Austrian authors assume Moldanubian granulites to be mainly metamorphosed arkosic sediments (SCHARBERT, 1964) and their position to be allochthonous within the Moldanubian complex that is incorporated as a vast granulite nappe (FUCHS, 1976; THIELE, 1976; TOLLMANN, 1985). Petrological studies of Moldanubian granulites by SCHARBERT & KURAT (1974) reveal a high-pressure type of the primary granulite metamorphism (above 1.1 GPa, 760 °C

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