

Alumino-magnesiohulsite, a new member of the hulsite group, in kotoite marble from east of Verkhoyansk, Sakha-Yakutia, Russia

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Abstract: Alumino-magnesiohulsite, the Al- and Mg-dominant analogue of hulsite, $(\text{Fe}^{2+}, \text{Mg})_2(\text{Fe}^{3+}, \text{Sn}, \text{Mg})\text{O}_2\text{BO}_3$, is a new, optically spectacular mineral with pleochroism from brown to blue-green discovered in a magnesian skarn from northeastern Siberia. It forms prismatic, twinned crystals in a spinel-bearing kotoite marble at the contact of a Mesozoic granosyenite against Palaeozoic dolomite marbles. EMP analyses give: MgO 33.94; FeO 15.97; Al_2O_3 15.86; SnO_2 11.88; TiO_2 0.75; MnO 0.42; CaO 0.11; B_2O_3 (calc.) 17.07; total 96.00 wt.%, which can be recalculated to the formula $(\text{Mg}_{1.55}\text{Fe}^{2+}_{0.45})_{\Sigma 2.00}(\text{Al}_{0.63}\text{Mg}_{0.17}\text{Mn}_{0.01}\text{Ti}_{0.02}\text{Sn}_{0.16})_{\Sigma 0.99}\text{O}_2(\text{BO}_3)$. Optically, it is biaxial (+), α' about 1.78, γ' about 1.805, $2V_z$ (measured from extinction data) = 33(5)°, α is parallel to the prism axis **b**. Alumino-magnesiohulsite is monoclinic, space group $P2/m$, with $a = 5.3344(7)$, $b = 3.0300(5)$, $c = 10.506(1)$ Å, $\beta = 94.46^\circ$, $V = 169.29(4)$ Å³, $Z = 2$ and $D_{\text{calc}} = 3.84$ g/cm³. Its cell parameters are significantly smaller than those of previously studied members of the hulsite group. A single-crystal X-ray study provided a pattern of cation distribution over the five distinct octahedral sites (M1–M5), which is not consistent with the formula given above. Despite this discrepancy, the IMA-Commission on New Minerals and Mineral Names agreed for nomenclature and classification purposes with using the conventional stoichiometric formula in which the amount of R^{2+} cations attributed to the tin-bearing unit equals that of the tetravalent ions, so that this attains an overall charge of 3.0⁺. Taking into account variable tin contents as usual in hulsites, an ideal general formula of alumino-magnesiohulsite is $\text{Mg}_2(\text{Al}_{1-2x}\text{Mg}_x\text{Sn}_x)\text{O}_2(\text{BO}_3)$ with x expected to be in the range 0.15–0.20.

Alumino-magnesiohulsite occurs within bimineralic aggregates in the rock together with aluminous, tin-bearing ludwigite of the formula $(\text{Mg}_{1.62}\text{Fe}^{2+}_{0.38})(\text{Fe}^{3+}_{0.50}\text{Al}_{0.31}\text{Fe}^{2+}_{0.07}\text{Mn}_{0.01}\text{Ca}_{0.01}\text{Sn}_{0.05}\text{Ti}_{0.05})\text{O}_2(\text{BO}_3)$. These aggregates may be pseudomorphs after a pre-existing high-temperature mineral intermediate in composition between ludwigite and alumino-magnesiohulsite. The reason for the exceptionally high Al-content of the new hulsite-group mineral can only partly be due to its Al-saturation by coexisting spinel, because hulsites from other localities also coexisting with spinel contain much less Al.

Key-words: new mineral: alumino-magnesiohulsite, borates, chemical analysis (mineral), crystal structure, ludwigite, Siberia.

Introduction

Hulsite, a tin-bearing iron borate, was first described from the Seward Peninsula, Alaska, by Knopf & Schaller (1908) with an addition by Schaller (1910). Leonard *et al.* (1962) recognized that tin is a major and necessary component, by which hulsite can be distinguished from the otherwise chemically similar minerals of the ludwigite-vonsenite series. In addition, Clark (1965) found hulsite to be monoclinic in contrast to orthorhombic ludwigite and vonsenite. Vlisidis & Schaller (1974) gave the hulsite formula as $(\text{Fe}^{2+}, \text{Mg})_2(\text{Fe}^{3+}, \text{Sn}^{4+})\text{BO}_3\text{O}_2$, compared to end-member ludwigite, $\text{Mg}_2\text{Fe}^{3+}\text{BO}_3\text{O}_2$, and vonsenite, $\text{Fe}^{2+}_2\text{Fe}^{3+}\text{BO}_3\text{O}_2$. Note that, with tin-being tetravalent, their hulsite formula does not balance. Yang *et al.* (1985) found a tin-bearing ana-

logue of ferrous ludwigite. This mineral was accepted as a new species with the name magnesiohulsite, $(\text{Mg}, \text{Fe}^{2+})_2(\text{Fe}^{3+}, \text{Sn}, \text{Mg})(\text{BO}_3)\text{O}_2$, in which some Mg was placed in the Sn-bearing unit for charge balance.

With the first crystal structure determination of hulsite by Konnert *et al.* (1976) it became clear that the structural relationships are far more complicated than expected from the stoichiometric formulae given above. These authors found as many as five crystallographically distinct octahedral sites (M1–M5), which are shared by the three elements Fe, Mg and Sn. Thus, the simple 2:1 ratio between divalent and higher valent cations of earlier formulae is questioned. Nevertheless, the Konnert *et al.* (1976) results imply that there is a 2:1 cation ratio between two different structural units (sheets), respectively (M2+M3+M5) and (M1+M4). How-

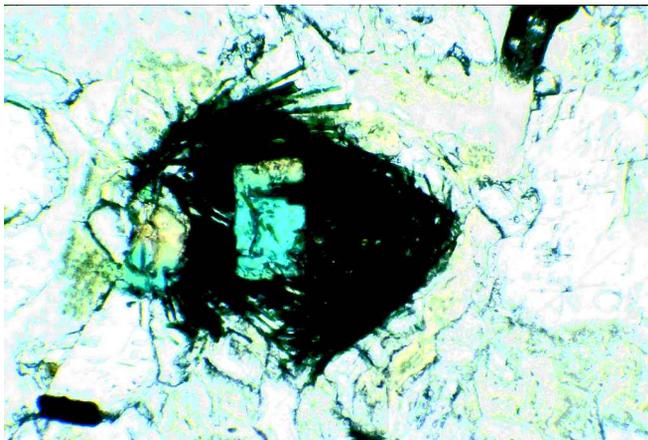


Fig. 1. Thin section photograph of a bimineralic aggregate consisting of needles of opaque ludwigite and two prisms of translucent aluminomagnesian hulsite lying in a matrix of mainly calcite. Note rhombic outline of aggregate (pseudomorph?). Plane polarized light. (Long edge of figure equals 0.45 mm).

ever, the valence distribution does not follow this scheme. The structural formula of a hulsite from the Alaska locality was given by Konnert *et al.* (1976) as $[\text{Sn}^{4+}_{0.20}\text{Fe}^{3+}_{0.27}\text{Fe}^{2+}_{0.36}\text{Mg}^{2+}_{0.16}]_{\Sigma 0.99}[\text{Fe}^{3+}_{0.40}\text{Fe}^{2+}_{1.10}\text{Mg}^{2+}_{0.48}]_{\Sigma 1.98}\text{O}_2(\text{BO}_3)$, where the $\Sigma 0.99$ unit comprises the sites M1 and M4, and the $\Sigma 1.98$ unit the sites M2, M3 and M5. A second crystal structure determination by Yamnova *et al.* (1978) resulted in a very similar cation distribution. Notice that in the hulsite structure the octahedral positions M1-M4 are on the special positions $2/m$ whereas M5 has only local symmetry m . For this reason M5 has twice the multiplicity of M1-M4, which becomes important for formula calculation.

In later papers reporting chemical data on hulsite minerals (*e.g.* Aleksandrov *et al.*, 2000a) including the new species magnesiohulsite by Yang *et al.* (1985), these complexities were largely ignored, obviously because of the lack of structure analyses for the crystals analyzed. Aleksandrov *et al.* (2000a) recalculated their electron microprobe analyses on the basis of $B = 1.0$ per formula unit (p.f.u) and continued to distinguish a unit M^{2+} containing only divalent cations from a unit M^{3+} , which not only included all trivalent ions plus Sn^{4+} and Ti^{4+} , but also contained Mg^{2+} or Fe^{2+} or both, in amounts equivalent to Sn and Ti so as to keep the overall charge of the whole M^{3+} unit as 3.0^+ . Thus, their calculated hulsite formulae always followed the traditional scheme $\text{M}^{2+}_2\text{M}^{3+}\text{O}_2(\text{BO}_3)$, which is also used for the ludwigite-vonsente series.

In the present paper we describe an optically spectacular hulsite mineral which is characterized by significant Mg and the highest Al-content ever measured. Because Al makes up more than 50% of the M^{3+} unit of Aleksandrov *et al.* (2000a), we expected that this mineral can be used to define a new hulsite end member. In order to clarify the role of Al and Mg in hulsite crystal chemistry we endeavoured to obtain a crystal structure analysis of our crystal as well. The crystal used by Konnert *et al.* (1976) for structural analysis was nearly free of Al and relatively poor in Mg, and thus no

site distribution for these two elements in hulsite minerals could be predicted from their study.

The new mineral and its name were approved by the IMA-Commission on New Minerals and Mineral Names (CNMMN – 2002 – 038). Type material has been deposited at the Mineralogical Collection of the Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Germany, catalogue number 25164.

Occurrence

Alumino-magnesiohulsite occurs as a rare component in a kotoite marble of considerable mineralogical complexity, which carries the new mineral pertsevite as well (Schreyer *et al.*, 2003). The sample was collected by NNP in 1964 along the Tas-Khayakhtakh ridge in the Chersky Mountain System, some 250 km east of Verkhojansk in what is now the Republic of Sakha-Yakutia in the Russian Federation. The exact locality lies near the mouth of Kebirin'ya creek, a northern tributary of Dogdo river, which cuts through the ridge. The approximate coordinates are 67.5°N , 139°E . The locality represents one of many small occurrences of magnesian skarns with boron mineralization that is extensively developed along contacts between Palaeozoic marbles and Mesozoic granosyenite massifs, apparently belonging to the Verkhne-Tirekhtyakh batholith. Specifically, the type locality for the two new minerals is situated at the SW-contact of the Nalyednyi granitoid massif. Altogether, the region is part of the extensive Mesozoic belt of Sn-Au-B mineralization of northeastern Asia, which extends into Alaska. Descriptions of the enormous wealth of minerals and rock types in the area were presented by Pertsev (1971) and, especially regarding the hulsite minerals, by Rudnev (1996) and Aleksandrov *et al.* (2000b). More than 20 Ca- and Mg-borate minerals are known from the region. Here are the type localities for sakhaitite, borcarite, and olshanskyite. Pertsev (1971, p. 105-106) described danburite from the very locality of the sample studied here. The kotoite and kotoite marble zones occupy the outermost position within the sequence of magnesian skarns around the granitic intrusions. Crystallization took place under conditions of low load and fluid pressures, low CO_2 fugacity, but widely varying temperatures (from 800°C to several tens of degrees only).

Our study was confined to a single thin section (no. B-1048), because the original sample is no longer available. In addition to the new hulsite phase, the following minerals were identified: calcite, kotoite, forsterite, clinohumite, spinel, ludwigite and the new Mg-silicoborate mineral pertsevite described separately (Schreyer *et al.*, 2003). Secondary minerals of minute grain size mainly replacing kotoite are szaibelyite and brucite or mixtures thereof.

Alumino-magnesiohulsite generally occurs within aggregates of very thin, opaque or – in extremely thin portions – very dark brown to very dark green pleochroic needles of ludwigite (Fig. 1). There it forms euhedral or semi-euhedral stout prisms with lengths of up to $90\ \mu\text{m}$ and a spectacular pleochroism from brown to blue-green. Fig. 1 conveys the frequent observation that the bimineralic aggregates of lud-

Table 1. Electron microprobe analyses of alumino-magnesiohulsite (1-4) and ludwigite (5-6) from sample B 1048.

	ALUMINO-MAGNESIOHULSITE					LUDWIGITE			
	1	2	3	4	Mean	s.d.	5	6	Mean
MgO	34.10	34.05	33.79	33.83	33.94	.16	32.53	32.01	32.27
FeO	15.98	15.81	16.21	15.89	15.97	.17	15.86	16.76	16.31
Fe ₂ O ₃	-	-	-	-	-	-	20.23	19.54	19.89
Al ₂ O ₃	16.03	15.87	15.97	15.57	15.86	.20	8.01	7.45	7.73
SnO ₂	11.95	11.85	11.58	12.13	11.88	.23	3.24	3.98	3.61
TiO ₂	.79	.72	.78	.70	.75	.04	1.75	1.97	1.86
MnO	.47	.41	.36	.44	.42	.05	.29	.31	.30
CaO	.09	.10	.13	.12	.11	.02	.35	.30	.33
Total 1	79.41	78.81	78.82	78.68	78.93	.33	82.26	82.32	82.30
B ₂ O ₃ cl	17.17	17.07	17.07	16.98	17.07	.08	17.31	17.16	17.24
Total 2	96.58	95.88	95.89	95.66	96.00	.40	99.57	99.48	99.54

Atoms per formula unit based on 5 oxygens, 1 boron and 3 cations

Mg	1.549	1.551	1.540	1.547	1.547	.006	1.623	1.611	1.617
Fe ²⁺	.451	.449	.460	.453	.453	.005	.377	.389	.383
M I	2.000	2.000	2.000	2.000	2.000	-	2.000	2.000	2.000
Al	.637	.635	.639	.626	.634	.006	.316	.296	.306
Fe ³⁺	-	-	-	-	-	-	.509	.496	.503
Fe ²⁺	-	-	-	-	-	-	.066	.084	.073
Mg	.165	.171	.169	.174	.170	.005	-	-	-
Mn ²⁺	.013	.012	.010	.013	.012	.001	.008	.009	.008
Ca	.003	.004	.005	.004	.005	.001	.012	.011	.012
Ti ⁴⁺	.020	.018	.020	.018	.020	.001	.044	.050	.047
Sn ⁴⁺	.161	.160	.157	.165	.161	.003	.043	.054	.048
M II	0.999	1.000	1.000	1.000	1.002	-	0.998	1.000	0.997

cl = calculated, s.d. = standard deviation

wigite and the hulsite phase actually seem to represent pseudomorphs after an earlier euhedral mineral with trigonal or orthorhombic(?) morphology. Only in very rare cases, smaller crystals (< 40 µm) of alumino-magnesiohulsite were also found directly included in calcite and independent from the ludwigite aggregates.

Because thin section B-1048 was embedded in Canada balsam, a portion of the rock slice was removed by means of a microdrill, cleaned, re-embedded in epoxy and polished for work under the electron microprobe, as done previously (for technical details see Schreyer *et al.*, 1998). A small single crystal of alumino-magnesiohulsite could be separated from the polished slide for the structural study.

Physical properties

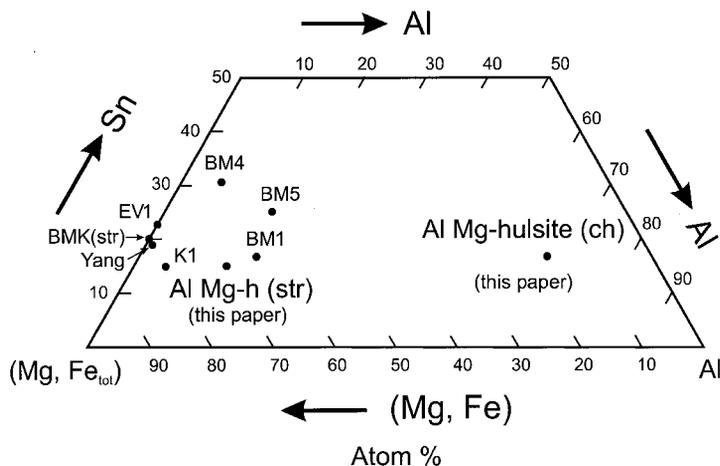
The small amount of material available as well as the dark color of the immersion media in the range required for the hulsite phase studied, did not allow high-precision measurements of the refractive indices with standard immersion methods by means of a spindle stage. Thus, these values were calculated from reflectance measurements in air and standard immersion oil using SiC as a standard on a grain showing maximum birefractance in the polished thin section. The absence of internal reflections was carefully checked prior to the measurements. From the data set, the values calculated for $\mu = 546$ nm are $\alpha' = 1.78$, $\gamma' = 1.805$ leading to a minimum birefringence Δn of about 0.025.

In addition, the small crystal, which was also used for the structure analysis, was measured on a spindle stage in diiodomethane ($n = 1.74$) for extinction data to calculate $2V$, and to check the optical orientation as well as the pleochroic scheme. Though the difference in refraction between immersion medium and crystal prohibited accurate determinations, the value of $2V_z = 33(5)^\circ$ is reliable. Thus the mineral is optically biaxial positive. The optical orientation is $\alpha = \mathbf{b}$, which is the direction of the prism elongation; the pleochroic colors are $\alpha =$ brown, $\beta =$ brown, $\gamma =$ blue-green. A centered axial figure for determination of the dispersion of $2V$ could not be found.

All crystals are twinned, which could easily be recognized by color effects due to the marked pleochroism. The spindle stage investigation showed that the twins are narrow lamellae parallel to $\{h0l\}$. Calculated density is 3.84 g/cm³; the compatibility index (Mandarino, 1979) is -0.049 , which places alumino-magnesiohulsite into the category "Good".

Chemical properties

In the present paper we restrict our chemical discussion to the new mineral alumino-magnesiohulsite and to the directly adjacent mineral ludwigite. Electron microprobe analyses were performed using the CAMECA SX 50 electron microprobe of the Ruhr-Universität Bochum. Most analytical details and standards are described in the companion paper by Schreyer *et al.* (2003). The standard used for tin in the



Brooks Mountain samples. Yang represents the magnesiohulsite as described by Yang *et al.* (1985). EV1 is part of analysis B-1442 of a hulsite from East Verkhoyan'ye listed by Rudnev (1996), and K1 of analysis 141/1-Ka of a hulsite from Karelia also listed by Rudnev (1996).

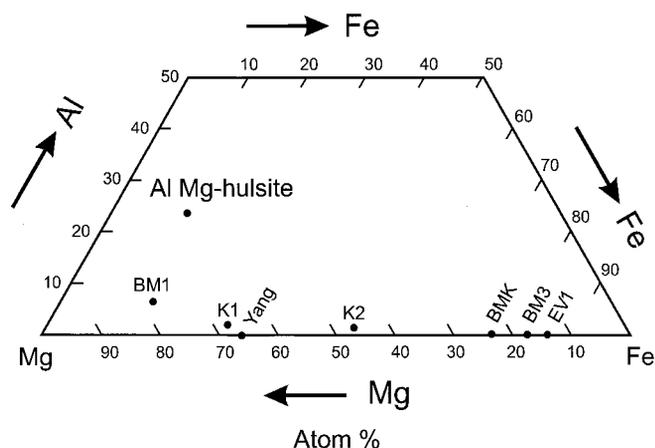


Fig. 3. Ternary plot of Mg - Fe_{tot} - Al present in all structural sites, or in the chemical bulk analyses, of selected minerals of the hulsite group. The new mineral alumino-magnesiohulsite is abbreviated here as AlMg-hulsite. Its point represents the composition listed in Table 1, Mean 1-4. For abbreviations and characterization of other data points see Fig. 2. Additional analyses used only in this figure are: BM3, of a so-called "paigeite" (Fe-rich hulsite) from Brooks Mountain, Alaska, analysis 9-11-11 as reported by Aleksandrov *et al.* (2000a, Table 6); K2 is the analysis 147/4-Ka of a hulsite from Karelia listed by Rudnev (1996). For a discussion of the name "paigeite" see section on "classification" in the text.

present analyses was cassiterite (Sn L_α). Boron was not analyzed here, but its presence was taken into account for matrix correction. The formulae were calculated on the basis of 1 B, 5 oxygens and 3 octahedral cations, which leads directly to the amounts of divalent and trivalent iron present.

In Table 1 the results of four analyses on two different crystals of alumino-magnesiohulsite are listed, together with mean values and standard deviations. The crystals are evidently homogeneous without any signs of zonation. In addition to the major elements Mg, Al, Fe and Sn, only small amounts of Ti, Mn and Ca were found. Iron is exclusively divalent. Surprisingly, the totals including the B₂O₃

Fig. 2. Ternary plot of elements (Mg+Fe_{tot}) - Al - Sn present in the tin-bearing unit of selected hulsite-group minerals. For the new mineral alumino-magnesiohulsite described in this paper two compositions are plotted: 1) as calculated from chemical data to be present in stoichiometric unit M II [=Al Mg-hulsite (ch)] (see Table 1, Mean 1-4); 2) as determined from the cation distribution found by single-crystal structural analysis of the same new mineral in the structural sites M1+M4 [=Al Mg-h (str)] (see Table 4, this study). The remaining data points are taken from the literature: BMK(str) represents the (M1+M4) occupancy of the hulsite from Brooks Mountain, Alaska, studied by single-crystal work by Konnert *et al.* (1976). All other data points are based on stoichiometric calculations as in Table 1 (only M II unit), but published by earlier authors: BM1, BM4, and BM5 are taken from analyses 19-3-19, 21-13-15, and 19-6-5, respectively, as reported by Aleksandrov *et al.* (2000a, Table 2) also on

as calculated stoichiometrically are only near 96 wt.%, but no other elements with atomic numbers greater than 6 could be detected.

Following the method of Aleksandrov *et al.* (2000a), in the mineral formulae calculated an M I-unit with an occupancy of 2.0 p.f.u. was chosen to consist of only divalent cations including all the iron and most of the Mg. The remaining Mg was allocated, together with Al, Mn, Ca, Ti and Sn to the second unit M II with the occupancy of 1.00 p.f.u., where the sums of divalent cations (Mg+Mn²⁺+Ca) are equal to those of the tetravalent ones (Sn+Ti) making the total charge of this unit 3.0⁺ as it should be. The Mg, Fe²⁺ allocations are, of course, hypothetical.

In order to appreciate the unusual chemistry of the new hulsite-type mineral from sample B-1048 having both high Mg like magnesiohulsite and high Al, two triangular plots (Fig. 2-3) were constructed in which its composition, here abbreviated as AlMg-hulsite, is compared with those of relevant "normal" or even extreme hulsite-type compositions from the literature, all with SnO₂ > 11 wt.%. Although, especially for iron-rich hulsites, a distinction between Fe²⁺ and Fe³⁺ is critical, we combine them here in order to keep the diagrams planar and, in particular, to show the role of Al in the new mineral. Most impressive is the (Mg, Fe_{tot}) - Al - Sn plot (Fig. 2) of the elements allocated to the M II unit (=M³⁺ of Aleksandrov *et al.*, 2000a). With about 66 % Al, alumino-magnesiohulsite is by far the most aluminous hulsite-type mineral. The literature value nearest to it with 40 % Al, listed as 19-4-32 by Aleksandrov *et al.* (2000a) in their Table 2 of "magnesian borates", is probably a ludwigite, because it contains only 0.94 wt.% SnO₂. It was, therefore, omitted from Fig. 2. All the remaining analyses of Fig. 2 with "normal" Sn (of about 15 % in M II) to very high values (near 30 % Sn of M II) have Al < 20 % in the stoichiometric unit thus defined.

In order to avoid any bias in element distribution to the two stoichiometric units of the formulae chosen, the plot of Fig. 3 takes into account all the major cations of the two octahedral units except for Sn. Even in this relevant part of the

Table 2. Details of X-ray data collection of alumino-magnesiohulsite.

Space group	$P2/m$ (No. 10)
a, b, c (Å)	5.3444(7), 3.0300(5), 10.506(1)
β (°)	94.46(1)
V (Å ³)	169.29(4)
Z	2
Diffractometer	Enraf Nonius CAD4
X-ray radiation	MoK α
X-ray power	55 kV, 40 mA
Temperature	293 K
Crystal size	20 × 20 × 50 μm^3
Upper θ limit	28°
h, k, l limit	$-7 \leq h \leq 7, -1 \leq k \leq 3, -13 \leq l \leq 12$
μ (mm ⁻¹)	3.22
Reflections measured	566
Reflections > 4 σ (F)	330
Absorption correction	Not applied
Twinning	Non-merohedral (0.77(1)/0.23)
R (σ) %	11.5
Number of least square parameters	25
Goof	1.041
$R1$ %, $F_o > 4\sigma(F_o)$	6.17
$R1$ %, all data	16.2
wR % (on F^2)	18.2

Mg – Fe_{tot} – Al triangle the alumino-magnesiohulsite of B-1048 with about 23 % Al (atomic) is clearly separated from the rest with Al < 7 %. This includes the so-called “paigeites” of Aleksandrov *et al.* (2000a, b), which are the Fe-richest hulsites. A comment on this name will follow in a later section.

In summary and prior to a discussion of the cation occupancies of the new aluminous hulsite phase of sample B-1048 on its sites M1-M5, the mineral described here is – purely on chemical grounds relative to the formula chosen – best called alumino-magnesiohulsite. An ideal general formula could be given as Mg₂(Al_{1-2x}Mg_xSn_x)_{Σ=1}BO₃O₂. Note that with x being 0.18 (given by Sn+Ti) in the alumino-magnesiohulsite studied here, Al with 0.63 p.f.u. has practically reached the maximum value for this particular (Sn+Ti) content (Table 1).

Structural properties

X-ray data collection and refinement

Single-crystal X-ray data collection on a crystal fragment of the alumino-magnesiohulsite from thin section B-1048, about 0.02 × 0.02 × 0.05 mm³ in size, was performed with an ENRAF NONIUS CAD4 single-crystal X-ray diffractometer using graphite monochromated MoK α X-radiation. Cell dimensions were refined from the setting angles of 20 reflections with $8^\circ < \theta < 15^\circ$ yielding monoclinic symmetry with $a = 5.3344(7)$, $b = 3.0300(5)$, $c = 10.506(1)$ Å, $\beta = 94.46(1)^\circ$, $V = 169.29(4)$ Å³ (Table 2). Experimental details are given in Table 2. Diffraction data were collected up to θ

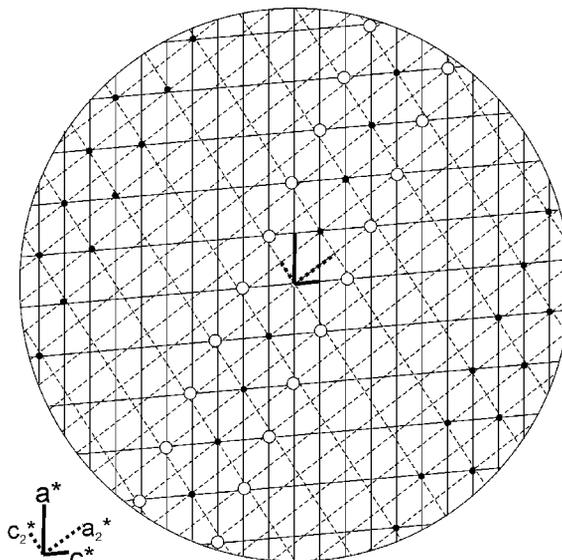


Fig. 4. Reciprocal space drawing of the observed twinning in alumino-magnesiohulsite. The reciprocal lattice of the dominant twin component is represented by solid lines whereas the reciprocal lattice of the minor twin component has dashed lines. The two twin individuals have b^* and $[101]^*$ in common. Reflections for which complete overlap between both individuals was found are indicated by black dots. Reflections for which partial overlap was observed are indicated by open circles; these reflections were eliminated from the data set.

$= 28^\circ$ using an X-ray exposure time of 10 minutes for each reflection yielding 712 intensities of which only 423 had $F_o > 4\sigma(F_o)$. Data reduction, including background and Lorentz polarization correction, was carried out with the SDP program system (Enraf Nonius, 1983). In analogy to other hulsite refinements the space group $P2/m$ was chosen (Konert *et al.*, 1976; Yamnova *et al.*, 1978). The structure was solved by direct methods with the program SHELXS-97 (Sheldrick, 1997). Subsequent refinement cycles with neutral atom scattering factors (program SHELXL-97 by Sheldrick, 1997) were accompanied by difference Fourier maps yielding five octahedrally coordinated cation sites, one trigonal boron position, and 5 oxygen positions. The subsequent difference Fourier map displayed ‘ghost peaks’ *ca.* 4 electrons/Å³ in intensity for which no structural explanation could be given, so it was suspected that the crystal was twinned. Twinning was confirmed by collection of a limited X-ray data set on a BRUKER SMART CCD system. Reciprocal space plots indicated that the twinned individuals had b^* and $[101]^*$ in common (Fig. 4) where $[101]^*$ acted as a mirror line in a^*c^* reciprocal layers (non-merohedral twinning). Fig. 4 was used to analyse for which reflections the reciprocal lattices of the twin individuals completely overlapped and for which reflections partial overlap had to be assumed. Partially overlapping reflections were eliminated and overlapping reflections were indexed in the settings of both twin individuals (HKL5 option in SHELXL-97). The final data set consisted of 566 reflections for which a twin ratio of 0.77/0.23 was subsequently refined. Cation assignment was based on interatomic dis-

Table 3. Atomic positional parameters and isotropic displacement parameters for alumino-magnesiohulsite.

Site	x/a	y/b	Z/c	B (Å ²)
M1	0	0	0	0.57(4)*
M2	½	0	½	0.57(4)*
M3	0	0	½	0.57(4)*
M4	½	½	0	0.57(4)*
M5	0.2163(7)	½	0.2802(4)	0.57(4)*
O1	0.309(2)	0	-0.1099(9)	0.6(2)
O2	0.495(2)	0	0.3069(9)	0.5(2)
O3	0.054(2)	0	0.6947(9)	0.4(2)
O4	0.179(2)	½	0.0934(9)	0.4(2)
O5	0.247(2)	½	0.476(1)	1.1(2)
B	0.289(3)	0	0.758(1)	0.4(2)

* Starred atoms were refined isotropically but constrained to a common displacement parameter. For occupancies of M sites consult Table 4.

tances and scattering power. Isotropic displacement parameters were refined for all atoms in the last cycles and to reduce the number of variables a common displacement parameter was constrained for all octahedral M sites. The labeling of atomic sites conforms to Konnert *et al.* (1976). Notice that Yamnova *et al.* (1978) use a different labeling in their original study. The refinement results are represented in Table 3. In addition, selected bond lengths and cation assignments are compared (Konnert *et al.*, 1976; Yamnova *et al.*, 1978; this study) in Table 4.

Discussion of the structure

The refined structure of alumino-magnesiohulsite is actually of low quality because of the small crystal size and the additional non-merohedral twinning. The twinning with b^* in common for both twin individuals and $[101]^*$ acting as mirror line in a^*c^* reciprocal layers may be interpreted as caused by a (101) twin plane in direct space.

It is of importance that all the cell parameters are smaller relative to those of the earlier structure analyses: the cell volume of the new Siberian hulsite mineral is 6.1 % smaller than that of the crystal studied by Konnert *et al.* (1976) and 5.8 % smaller than that of the one of Yamnova *et al.* (1978). Undoubtedly this is due to the smaller Al ion replacing Fe^{3+} , and Mg partly substituting for Fe^{2+} .

As in the case of hulsite, the structure of alumino-magnesiohulsite consists of (001) sheets of edge-sharing octahedra (M1 and M4) formed by alternating M1 and M4 stripes extending parallel to **b**. These sheets are corner-connected by a zig-zag-like folded sheet of edge-sharing octahedra (M2, M3, M5) where the M5 octahedron links the zig-zag sheet to the planar sheet. This arrangement leads to triangular channels parallel to **b** which are occupied by three-coordinated boron (Fig. 5). All octahedra (M1-M5) have very similar mean M-O distances between 2.03 and 2.09 Å (Table 4). The triangular channels parallel to **b** are lined with edge-sharing double chains of M5-M3, M5-M2, and M1-M4 octahedra. In order to provide a planar trigonal coordination with O-B-O angles of 120°, the octahedral edges exposed on

Table 4 Selected bond distances (Å) for alumino-magnesiohulsite compared to literature data on hulsite. In addition, the assumed (refined) cation occupancy is given for each M site.

	This study	Konnert <i>et al.</i> , 1976	Yamnova <i>et al.</i> , 1978
M1-O4 (4x)	2.005(6)	2.059	2.052
M1-O1 (2x)	2.084(9)	2.106	2.115
Mean	2.031	2.075	2.073
	0.3Sn, 0.4Fe, 0.3Al	0.4Sn, 0.54Fe ³⁺	0.35Sn, 0.65 Fe ³⁺
M2-O2 (2x)	2.027(9)	2.086	2.085
M2-O5 (4x)	2.032(7)	2.086	2.094
Mean	2.030	2.086	2.091
	0.5Al, 0.5Mg	0.6Fe ²⁺ , 0.4Fe ³	Fe ²⁺
M3-O5 (4x)	2.036(7)	2.090	2.081
M3-O3 (2x)	2.044(9)	2.086	2.091
Mean	2.039	2.089	2.084
	0.5Al, 0.5 Mg	0.6Fe ²⁺ , 0.4Fe ³⁺	0.5Fe ³⁺ , 0.4Mg ²⁺ , 0.1Sn
M4-O4 (2x)	2.040(9)	2.070	2.032
M4-O1 (4x)	2.118(7)	2.190	2.177
Mean	2.092	2.150	2.129
	0.90 Mg, 0.10Fe	0.7 Fe ²⁺ , 0.3Mg	0.59Fe ²⁺ , 0.41Mg
M5-O3 (2x)	2.123(7)	2.197	2.186
M5-O2 (2x)	2.127(7)	2.192	2.183
M5-O4	1.957(10)	1.960	1.952
M5-O5	2.052(12)	2.072	2.085
Mean	2.085	2.135	2.129
	0.90 Mg, 0.10Fe	0.5 Fe ²⁺ , 0.5Mg	0.67Fe ²⁺ , 0.33Mg
B-O3	1.369(16)	1.389	1.382
B-O2	1.381(16)	1.368	1.383
B-O1	1.387(17)	1.376	1.376
Mean	1.379	1.378	1.380

Refined formula: $Sn_{0.15}Fe_{0.35}Mg_{1.85}Al_{0.65}O_2BO_3$. The Sn concentration was constrained according to the electron microprobe analyses of Table 1, the total Fe-concentration was refined. Mg and Al cannot be distinguished by their scattering power. Mg, Al assignment was done based on bond lengths. All atomic site labels are according to Konnert *et al.* (1976); notice that Yamnova *et al.* (1978) use a different labeling in their original study.

the channel surface must be similar. X-ray scattering power for M2 and M3 octahedra indicates that these sites are filled with light elements (Mg, Al). The mean M2-O and M3-O bond lengths of ca. 2.03 Å suggest that M2 and M3 octahedra are occupied by Mg and Al in approximately equal amounts. In contrast, M4 and M5 octahedra have ca. 10 % Fe in addition to light elements, and the longer mean M4-O and M5-O distances (2.09 Å) suggest that these sites are dominated by Mg²⁺. The structure refinements on hulsite (Konnert *et al.*, 1976 and Yamnova *et al.*, 1978) led to mean M4-O and M5-O distances of 2.15, 2.14 Å, and 2.13, 2.13 Å, respectively, and different ratios of Fe²⁺/Mg were attributed to these sites. The M1 octahedron of alumino-magnesiohulsite has the strongest X-ray scattering power and after assignment of 30 % Sn, according to the chemical analyses, the remaining occupancy converged to 40 % Fe and 30 % (Al,Mg). We have assigned 30 % Al rather than Mg to this

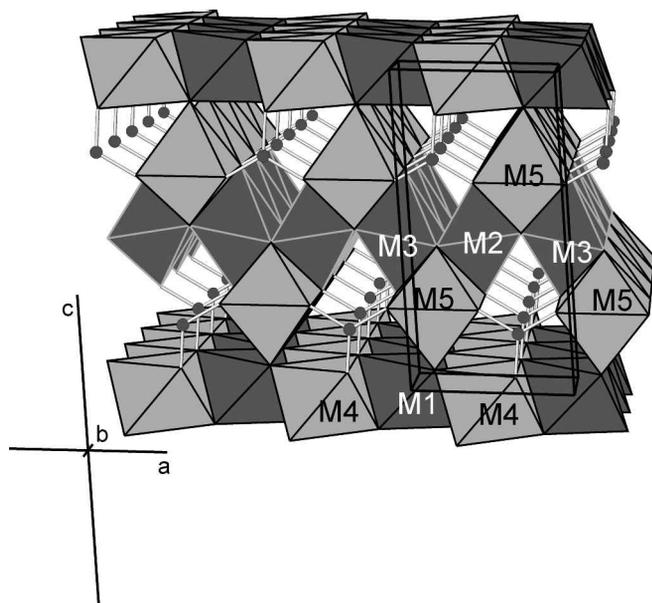


Fig. 5. Polyhedral representation with unit cell outlines of the structure of alumino-magnesiohulsite projected approximately along **b**. Labeling of octahedra conforms to Konnert *et al.* (1976). Mixed-valence octahedra are dark, and octahedra occupied by divalent cations (M4 and M5) are light. The M1 octahedron has 0.3 Sn in addition to 0.4 Fe and 0.3 Al. M2 and M3 octahedra with light rims are occupied by approximately equal amounts of Mg and Al. Boron (grey dots) occupies the triangular interspace.

site for two reasons: (1) to be in agreement with the bulk chemical analysis and (2) to explain the relatively short mean M1-O distance of 2.03 Å. Comparison with hulsite structure refinements by Konnert *et al.* (1976) and Yamnova *et al.* (1978) indicated (Table 4) that the mean M1-O distances in these previous studies were 2.07 Å and the refined occupancy was 40 % and 35 % Sn, respectively, with the remaining assigned to Fe³⁺. All structure refinements (Konnert *et al.*, 1976; Yamnova *et al.*, 1978; this study) have in common that the double-chains M5-M3, M5-M2, and M4-M1, lining the trigonal channels, are formed by alternating small and large octahedra. This is emphasized in Fig. 5 by different color codes. If as shown above, M4 and M5 are occupied by divalent cations it is suggested that M1, M2, and M3 have a mixed-valence occupation. Any substantial valence ordering on M1, M2, and M3 would lead to uneven B-O distances, which does not agree with the observed distances. Each oxygen bonded to B participates in three octahedra of which two are occupied by divalent cations and one by mixed-valence cations.

Definition and classification of hulsite-type minerals

The discrepancy between structural and stoichiometric formulae

The question now arises, how the structural results just reported can be reconciled with the traditional way of presenting the chemical data of hulsite-group minerals as given in

Table 1 and plotted in Fig. 2. Among the literature analyses shown in Fig. 2, only BMK, *i.e.* that of the hulsite studied by Konnert *et al.* (1976), was located on the basis of its cation distribution determined by crystal structure analysis for the two sites M1 and M4, that make up one structural unit (see Fig. 5 and Introduction). When the data of Table 4 are used to treat the alumino-magnesiohulsite of B-1048 accordingly, it plots far away from the Al-corner (Fig. 2), because Mg and Fe are the dominant cations in the (M1+M4)-sheet. Thus, on this basis, the alumino-magnesiohulsite described in the present paper would not seem to deserve special attention. Closer inspection of Table 4 shows that actually none of the five octahedral positions M1-5 have a predominance of Al-occupancy over the remaining cations. Even in M2 and M3 about equal amounts of Al and Mg are envisioned, because the slightly longer M3-O distance does not exceed the limits of error. Thus the clear stoichiometric enrichment of Al in the B-1048 alumino-magnesiohulsite based on the traditional formula $M_2M_1O_2BO_3$ is masked structurally by distributing it over the three sites (M1-M3). Structurally, this is apparently necessary in order to provide the planar trigonal coordination for the boron site as discussed before.

Discrepancies between stoichiometric and structural formulae become particularly evident, when the sums of charges of the respective units are compared. While the stoichiometric formulae with their 2 : 1 atomic ratios are arranged to have a charge ratio of 4⁺ : 3⁺ (see Table 1), the cation distributions found by X-ray diffraction analyses in the two structural units having 2 : 1 atomic ratios as well, are 4.36⁺ to 2.65⁺ for the Konnert *et al.* (1976) hulsite (see Introduction) and 4.50⁺ to 2.45⁺ for alumino-magnesiohulsite (Table 4).

Because up to now only three structure analyses on hulsite-type minerals exist, but – on the other hand – there is a multitude of chemical analyses in the literature (*e.g.* Aleksandrov *et al.*, 2000 a, b), we proposed to the IMA-Commission CNMMN, when submitting our case, that with the present state of knowledge the stoichiometric results should be given priority over the structural ones. This was accepted by CNMMN with a 20:1:1 vote, thus confirming the formula $(Mg_{1.55}Fe_{0.45})_{\Sigma 2.00}(Al_{0.63}Mg_{0.17}Mn_{0.01}Ti_{0.02}Sn_{0.16})_{\Sigma 0.99}O_2(BO_3)$ and the name alumino-magnesiohulsite.

Nevertheless, the situation remains unsatisfactory, and future studies should be directed toward a better solution. E. S. Grew (personal communication, 2003), who acted as journal reviewer for the first version of this manuscript submitted, suggested that a new structural formula for hulsite-type minerals be established. This should no longer be based on the prominent geometric features of the structure (sheets and chains), but rather on the distribution of cations with different valences on the five sites M1-M5, *i.e.*, distinguishing M4+M5, which contain only divalent cations, from M1-M3, which combine cations with valences 2⁺, 3⁺ and 4⁺, as can be seen by the different shadings of Fig. 5. This distribution is consistent in the three hulsite-type structures determined thus far (Table 4). Thus, a stoichiometric formula $(M4+M5)_{1.5}(M1+M2+M3)_{1.5}O_2(BO_3)$ might also reflect much of the real site distribution of cations in hulsite minerals. In the present paper, we prefer not to apply this new method, not only because the data base for crystal structures of hulsite-type phases is still rather meagre, but also in order

to publish the data on the new mineral aluminomagnesiophulsite as they were accepted by the IMA Commission. An additional paper is being planned for presenting the new formula $(M4+M5)_{1.5}(M1+M2+M3)_{1.5}O_2(BO_3)$ as a basis for distinguishing the known minerals related to hulsite and for recognizing any new ones.

Classification

In the new Mineralogical Tables by Strunz & Nickel (2001), hulsite and magnesiophulsite are included in the pinakiolite group. This is somewhat unfortunate as pinakiolite, $Mg_2Mn^{3+}O_2(BO_3)$, does not contain tin, which is a characteristic element in hulsite minerals. We, therefore, propose to define a separate hulsite group, which comprises the minerals hulsite, magnesiophulsite and the new mineral aluminomagnesiophulsite. Using the Strunz & Nickel (2001) formulation they are: hulsite, $(Fe^{2+},Mg)_2(Fe^{3+},Sn,Mg)[O_2/BO_3]$; magnesiophulsite, $(Mg,Fe^{2+})_2(Fe^{3+},Sn,Mg)[O_2/BO_3]$; and aluminomagnesiophulsite, $(Mg,Fe^{2+})_2(Al,Sn,Mg)[O_2/BO_3]$. All three minerals have the same space group and very similar cell parameters, whereas those of pinakiolite with a different space group are at variance.

An unusual classification scheme for Al-free hulsite minerals was used by Aleksandrov *et al.* (2000a, Fig. 3), in which – in addition to magnesiophulsite (Yang *et al.*, 1985) and hulsite – the name paigeite is applied to the Fe-richest members. This name, originally given by Knopf & Schaller (1908), had been discredited by Vlisidis & Schaller (1974), because the “paigeites” studied by them turned out to be identical to vonsenite. In addition, the nomenclature scheme by Aleksandrov *et al.* (2000a) violates the IMA rule of naming only end members of solid solution series. Applying this to Aleksandrov’s *et al.* (2000a) series magnesiophulsite – hulsite – paigeite, would imply that hulsite, actually the traditional group name, should be abandoned. It is suggested, therefore, not to revive “paigeite” but restrict classification of Al-free phases to magnesiophulsite – hulsite with the division at $Mg/(Mg+Fe^{2+}) = 0.5$.

The role of tin in hulsite-group minerals and their distinction from ludwigite-vonsenite

Hulsite-group minerals are distinguished from those of the ludwigite-vonsenite series by their respective symmetries, monoclinic *versus* orthorhombic. Nevertheless, the literature contains many cases in which a clear attribution has not been made, so that chemical analyses are reported under the general name “magnesian borates” (*e.g.* Aleksandrov *et al.*, 2000a, Tables 2 and 4). Especially in Fe-rich members of the two series the distinction is controversial (“paigeite” *versus* vonsenite; Aleksandrov *et al.*, 2000a, Table 6 and page 782). This is probably due to the difficulty to obtain critical X-ray diffraction data on small crystals or crystal aggregates in thin section, although their chemistry could be determined readily by electron microprobe analysis. In other cases where a distinction has been made (*e.g.* Aleksandrov *et al.*, 2000b, Tables 2-3; Aleksandrov & Troneva, 2000, Tables 1 and 2), hulsite-group minerals consistently have higher tin

contents than those of the ludwigite-vonsenite group. Evidently, the hulsite structure is stabilized by the presence of tin, but the minimum amounts necessary seem to vary widely. At any rate, tin seems to be an essential element for hulsite-group minerals and must be included in their formulae.

The thin section B-1048 studied here, which contains tin-bearing ludwigite coexisting with aluminomagnesiophulsite, allowed to determine the fractionation of tin between the two minerals. There will be more discussion on these miscibility relations in subsequent sections.

Another question is a possible upper limit for tin in hulsite-group minerals. Considering the general formula of aluminomagnesiophulsite, $Mg_2(Al_{1-2x}Mg_xSn_x)O_2(BO_3)$, which implies the substitution $Mg^{2+} + Sn^{4+}$ for $2Al^{3+}$, the absolute end member with $x = 0.5$ would be $Mg_2(Mg_{0.5}Sn_{0.5})O_2(BO_3)$, that is a hypothetical hulsite-phase without any trivalent cations but with maximum tin contents.

Chemistry of coexisting ludwigite

Electron microprobe analyses of the ludwigite needles coexisting with aluminomagnesiophulsite in the biminerale aggregates of thin section B-1048 (Fig. 1) yielded the same spectrum of elements as for the hulsite-group phase, although in different proportions (Table 1). The recalculation scheme of the two ludwigite analyses corresponds to that used for aluminomagnesiophulsite, although its general formula, $(Mg,Fe^{2+})_2Fe^{3+}O_2BO_3$, considers only trivalent cations to be present in the second stoichiometric unit. The data of Table 1 show, however, that the ludwigite is quite high in Sn and Ti, so that additional divalent cations are necessary for charge balance. The B-1048 ludwigite carries considerable Al as well. The ferrous/ferric ratios of Table 1 result from recalculation on the basis of 3.0 cations.

Table 1 indicates that there is a characteristic element distribution pattern between the two coexisting borate minerals of the biminerale aggregates (Fig. 1) of sample B-1048: Fe^{3+} is exclusively, and Ti and Ca are preferentially fractionated into ludwigite, whereas Al, Sn and – to a lesser degree – Mg predominate in aluminomagnesiophulsite. With about 0.1 atoms (Sn+Ti) p.f.u., ludwigite contains only about half the amount of tetravalent cations present in aluminomagnesiophulsite.

Relative to the overall chemical variations of ludwigites known from the literature, the Al-content found here (Table 1) is within the limits found earlier: Ludwigites described by Schaller & Vlisidis (1961) as well as by Pertsev & Aleksandrov (1964) have Al_2O_3 near 11 wt.%, one listed by Aleksandrov & Troneva (2000) nearly 12 wt.%. Tin is relatively high in our sample due to Sn-saturation by the neighboring aluminomagnesiophulsite. But Vlisidis & Schaller (1974) in their chemical study of the ludwigite-vonsenite series also list a vonsenite with nearly 5 wt.% SnO_2 .

Speculation on an intermediate precursor phase and the hulsite-ludwigite miscibility gap

As indicated in an earlier section, the partly opaque aggregates of ludwigite and aluminomagnesiophulsite occurring

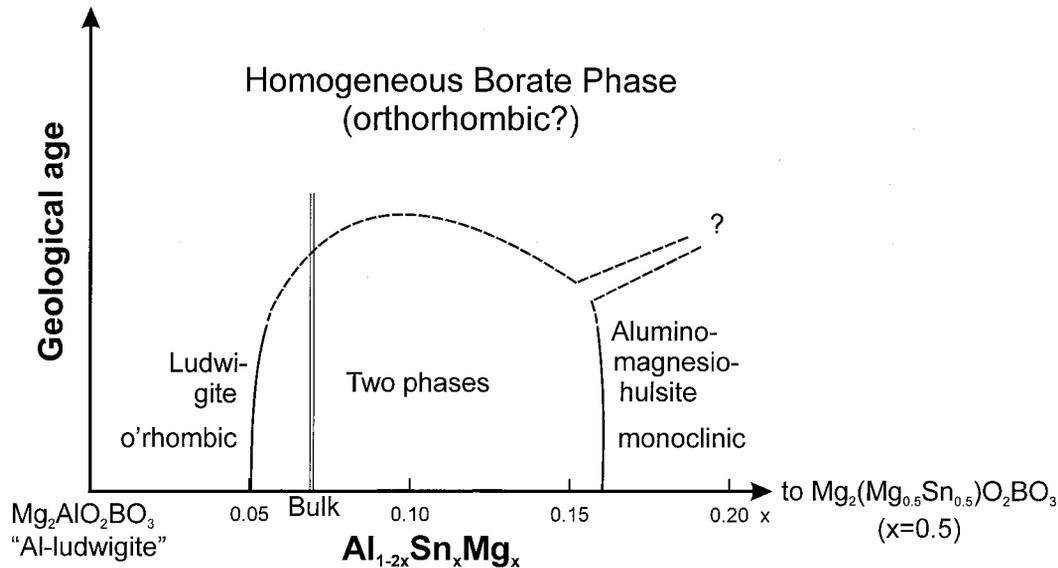


Fig. 6. Sketch of hypothetical phase relations involving potential miscibility between alumino-magnesiohulsite and ludwigite. For simplification, only Mg,Al,Sn-borate formulae are considered. The ordinate is a reversed time axis indicating that a homogeneous borate phase may, under different petrogenetic conditions, have preceded the two-phase aggregates (pseudomorphs) now observed in thin section B-1048 (Fig. 1). The abscissa follows the general formula of alumino-magnesiohulsite, $Mg_2(Al_{1-2x}Sn_xMg_x)O_2(BO_3)$, as given in the text. At $x = 0$ the phase “Al-ludwigite” (Pertsev, 1971 and Fig. 7 here) appears, while the end member at $x = 0.5$ is a hypothetical MgSn-borate. The bar shown as “Bulk” denotes the estimated total composition of the bimineralic aggregates in sample B-1048 based only on tin contents. The delineation of all theoretically necessary two-phase fields in the middle portion of the plot was omitted.

in sample B-1048 seem to represent pseudomorphs after a pre-existing euhedral (trigonal or orthorhombic?) mineral phase (Fig. 1). The idea of a pre-existing phase, which contained the ludwigite and alumino-magnesiohulsite compositions measured, does not seem unlikely in view of their strong chemical similarities (Table 1). Because the internal textures of the bimineralic aggregates do not provide any evidence for an exsolution or breakdown process, *e.g.* lamellae or symplectites, complete recrystallization of the two minerals would have to be assumed.

If so, mutual miscibility between hulsite and ludwigite phases would strongly depend on environmental conditions, and the coexistence now observed (Fig. 1) would represent an equilibrium attained late during petrogenesis, while the pre-existing homogeneous phase may have formed at an earlier higher-temperature(?) stage. The sketch of Fig. 6 is highly speculative, confined to an idealized ludwigite-hulsite system containing only the cations Sn, Al and Mg, and is modelled loosely after the miscibility relations of alkali-feldspars. The bulk composition of the pseudomorphs was estimated from the ratio of the two phases observed to contain 0.07 atoms Sn p.f.u., being split into ludwigite with 0.05 and alumino-magnesiohulsite with 0.16 atoms Sn p.f.u. The orthorhombic symmetry of the potential high-temperature phase is hypothetical. Its estimated SnO_2 weight percentage of some 5% is not unusual for unspecified “magnesian borates” (Aleksandrov *et al.*, 2000a), and it equals that of the vonsenite of Vlisisid & Schaller (1974).

Phase relations and element distribution relative to other minerals in the rock

In the sample containing the new mineral alumino-magnesiohulsite and aluminous ludwigite, the only other Al-bearing mineral is pure end-member spinel $MgAl_2O_4$ (for analysis see Schreyer *et al.*, 2003), which occurs as euhedral crystals in close proximity to the bimineralic aggregates and may be taken to belong to the stable assemblage. Phase relations within the partial system $(Mg,Fe)O - Al_2O_3 - B_2O_3$ are shown in Fig. 7 in the relevant portion of the triangle projected from Fe_2O_3 and SnO_2 . Al-free members of the hulsite group plot along the left side of the triangle very close to ideal ludwigite-vonsenite, but at somewhat higher $(Mg,Fe)O$ because of the necessary charge balancing relative to the tetravalent cations. An ideal end member $Mg_2AlBO_3O_2$, an “Al-ludwigite” (Pertsev, 1971, p. 38), lies exactly on the join kotoite – spinel (“Al-lu” in Fig. 7). The analyzed ludwigite from sample B-1048 plots along a theoretical line of solid solution between this end member and Al-free ludwigite. The alumino-magnesiohulsite described plots somewhat below this line, but at a higher Al_2O_3 value. Both alumino-magnesiohulsite and ludwigite from the sample coexist with spinel and are, therefore, saturated with regard to Al. Al-saturation with corundum is impossible due to the intervening tie line kotoite-spinel (Fig. 7). Kotoite occurs near the bimineralic aggregates as well, so that the stable assemblage of borate minerals from rock B-1048 can be characterized by the four-phase volume in space of alumino-magnesiohulsite + ludwigite + spinel + kotoite (Fig. 7). For the as-

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Received 30 January 2003

Modified version received 30 June 2003

Accepted 6 October 2003