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NEW DATA ON SZAIBELYITE FROM THE TYPE LOCALITY, BĂIŢA BIHOR, ROMANIA

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ABSTRACT

At Băiţa Bihor (formerly Rézbánya), Romania, the type locality szaibelyite occurs in magnesian skarns hosted by the dolomitic marbles of Mesozoic age, near the contact with a granite – granodiorite body of Upper Cretaceous – Paleogene age. Associated minerals include calcite, dolomite, magnesite, kotoite, suanite, ludwigite, fluoborite, fluorite, chondrodite, norbergite, magnetite, brucite, chrysotile, lizardite, clinochlore, lepidocrocite and goethite. Szaibelyite from Băiţa Bihor is extremely close to the end-member composition [$Mg_2(B_2O_4OH)(OH)$]. Up to 0.88 mol.% sussexite (the Mn end-member), 1.06 mol.% $Fe_2(B_2O_4OH)(OH)$ and 0.20 mol.% $Ca_2(B_2O_4OH)(OH)$ may be deduced on the basis of combined wet-chemical and electron-microprobe analyses. The mineral exhibits very slight fluorine contents [$X_F = F/(F + OH) \leq 0.01$]. Selected-area electron imaging supported by X-ray powder patterns indicate that the szaibelyite from Băiţa Bihor is monoclinic, space group $P2_1/a$. The mean unit-cell parameters are a 12.559(18), b 10.402(12), c 3.132(8) Å and β 95.77(33)°. Thermogravimetric curves gave a smooth and continuous weight-loss of up to 3.39 wt.% H_2O between 150 and 600°C, in reasonable agreement with the results obtained by loss on ignition. The complete dehydration occurs between 650 and 700°C, the breakdown product being the monoclinic ($P2_1/a$) polymorph of $Mg_2(B_2O_5)$. Two OH-stretching bands in the infrared absorption spectra of the mineral, at ~3560 and ~2510 cm^{-1}, respectively, are indicative of two distinct hydrogen positions in the structure. The IR spectra do not systematically show absorption systematically at ~1630 cm^{-1} (bending mode of H_2O), suggesting that the mineral does not contain molecular H_2O. Szaibelyite from Băiţa Bihor is estimated to have developed at temperatures of 160–450°C, pressures of 0.6–3 kbar, at relatively high activity of fluorine, and at low potentials of iron and manganese.

Keywords: szaibelyite, magnesian skarns, scanning-electron microscopy, physical parameters, X-ray data, thermal behavior, infrared-absorption data, crystal chemistry, Băiţa Bihor, Romania.

SOMMAIRE

A Băiţa Bihor (anciennement Rézbánya), en Roumanie, localité type de cette espèce minérale, la szaïbelyite est localisée dans des skarns magnésiens cantonnées dans des marbres dolomitiques d'âge Mésozoïque, proche du contact avec un corps de granite – granodiorite d'âge Crétacé supérieur – Paléogène. Parmi les minéraux associés, on trouve la calcite, la dolomite, la magnésite, la kotoïte, la suanite, la ludwigite, la fluoborite, la fluorite, la chondrodite, la norbergite, la magnétite, la brucite, le chrysotile, la lizardite, le clinochlore, la lépidocrocite et la goethite. La szaïbelyite de Băiţa Bihor a une composition extrêmement proche de celle correspondant au pôle $Mg_2(B_2O_4OH)(OH)$. En s'appuyant sur l'analyse chimique par voie humide et sur l'analyse à la microsonde électronique, on voit que la szaïbelyite contient jusqu'à 0.88 mol.% de sussexite (le pôle manganésifère), 1.06 mol.% de $Fe_2(B_2O_4OH)(OH)$ et 0.20 mol.% de $Ca_2(B_2O_4OH)(OH)$ dans la solution solide. Le minéral contient de très faibles teneurs en fluor [$X_F = F/(F + OH) \leq 0.01$]. Les images de diffraction d'électrons sur aire restreinte étayées par des données de diffraction X sur poudres montrent que la szaïbelyite de Băiţa Bihor est monoclinique (groupe spatial $P2_1/a$). Les paramètres réticulaires sont a 12.559(18), b 10.402(12), c 3.132(8) Å et β 95.77(33)°. Les courbes d'analyse thermogravimétrique montrent une perte continue de poids, de jusqu'à 3.39 % de la masse initiale, entre 150 et 600°C; cette perte est due à l'élimination d'eau et est proche des résultats obtenus par perte au feu. La déshydratation complète se produit entre 650 et 700°C, et le produit de décomposition est le polymorphe monoclinique (groupe spatial $P2_1/a$) de $Mg_2(B_2O_5)$. Deux bandes de vibration des groupes OH dans les spectres d'absorption infrarouge (à ~3560 et ~2510 cm^{-1}, respectivement) montrent la présence de deux positions distinctes de l'hydrogène dans la structure. Dans les spectres IR, la bande d'absorption à ~1630 cm^{-1} (vibration de déformation plane OH) n'est pas présente de manière systématique, ce qui fait penser que le minéral ne contient pas de molécules de H_2O. A Băiţa Bihor, la szaïbelyite s'est apparemment développée à une température de 160–450°C, entre 0.6 et 3 kbar, à une activité relativement élevée du fluor, et à de faibles potentiels du fer et du manganèse.

Mots-clés: szaïbelyite, skarns magnésiens, microscopie électronique à balayage, paramètres physiques, données de diffraction X, analyse thermique, spectrométrie d'absorption infrarouge, chimie cristalline, Băiţa Bihor, Roumanie.

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INTRODUCTION

Szaibelyite, ideally $Mg_2(B_2O_4OH)(OH)$, is characteristic of boron-bearing magnesian skarns and some evaporites. The mineral was named and first described by Peters (1861, 1863) from the skarns from Băiţa Bihor, Bihor Mountains, Romania. In much of the early literature (*e.g*., Peters 1861, Watanabe 1939, Palache *et al.* 1951), the locality is referred by its former Hungarian name of Rézbánya.

Peters (1863) offered the sole chemical information known so far. Since 1861, szaibelyite from Băiţa Bihor has, however, received extensive attention (*i.e.*, Watanabe 1939, Stoicovici & Stoici 1969, Stoici 1974, 1983). The abundance of the mineral in the boron-bearing magnesian skarns from this occurrence is remarkable; Watanabe (1939) and Stoici (1974) gave extensive accounts of szaibelyite as the principal skarn-forming mineral. However, the present state of knowledge is far from satisfactory. All previous studies on szaibelyite from Băiţa Bihor have been confined to limited topics, *e.g*., parageneses and physical properties (Watanabe 1939, Stoicovici & Stoici 1969, Stoici 1974), or position of the szaibelyite-bearing skarn in the general context (Stoici 1983). In a few cases, optical and morphological data and X-ray powder patterns were offered; however, no new chemical data have been reported, accurate values for the unit-cell parameters and optical data are scarce, and thermal and infrared absorption data are lacking. A structural investigation of the holotype material, deposited in the collection of Eötvös Lorand University (Budapest, Hungary), was recently undertaken by Lovas & Dodony (1997) and offers accurate unit-cell parameters.

In this work, I present results of a re-investigation of the material from the type locality in order to improve on the optical, chemical, thermal, infrared and X-ray database.

GEOLOGICAL SETTING

The contact-metamorphic zone at Băiţa Bihor, about 90 km south–east from Oradea, Romania, is developed over a wide area (many square kilometers) owing to the influence of a unexposed intrusive body, the Bihor batholith. The batholith consists mainly of granodiorite and granite porphyry with subordinate quartz monzodiorite and diorite (Stoici 1983, Ştefan *et al*. 1988). A whole-rock Rb–Sr isochron age of 70 ± 5 Ma has been reported for granodioritic rocks of the Bihor batholith (Pavelescu *et al*. 1985). This is some 10 Ma younger than a K–Ar age of 81 Ma reported for similar rocks in satellite bodies by Bordea *et al*. (1988), but older than other K–Ar ages (in the range 50–61 Ma) mentioned by the same authors (Bordea *et al*. 1988). The intrusion may be consequently assigned to the most important magmatic event in the region, the "banatitic" one, of Upper Cretaceous – Paleocene age.

Extensive boron metasomatism affected the rocks in the contact-metamorphic zone and is locally manifested in magnesian skarns developed at the expense of sequences of dolostone of Anisian – Carnian or Carnian – Norian age (Bordea *et al*. 1988). Such skarns are commonly boron-bearing and occur in well-expressed metasomatic columns, or "skarn bodies" (*i.e.*, those at Baia Roşie, Antoniu, Hoanca Moţului and Bolfu–Tony). The skarn bodies, now mostly removed by intensive mining for base-metal sulfides, extended downward to more than 400 m below the surface; only small exposures may now be observed at the surface. A geological sketch of the Băiţa Bihor area is given in Figure 1. Stoici (1974, 1983) gave additional details concerning the geology and mining operations in the area, as well as extensive cartographic descriptions.

Magnesian borates (*i.e*., kotoite, suanite, ludwigite, fluoborite, szaibelyite) are found in the outer zones of the metasomatic columns, whose inner zones generally consist of diopside-bearing skarns. The boron-bearing skarn is always located at the very contact of the dolomite marble. The abundance of kotoite is remarkable; for this reason, Watanabe (1939) gave the name "kotoite marble" to this rock. In fact, the internal zoning of the boron-bearing skarn is more complex, including an external zone with suanite and an internal one with kotoite (Marincea 1998). Szaibelyite is widely distributed and occurs in all the boron-bearing skarns. Its modal abundance (up to 30% of the rock volume) is highest in the outer zones of the boron-bearing skarn bodies, where the mineral extensively replaces suanite.

Samples for the present study were collected from the Bolfu–Tony, Baia Roşie and Antoniu waste dumps and from a small area opened by the –7 level of the Baia Roşie mine.

ANALYTICAL PROCEDURES

Because of the general lack of chemical data, the chemical composition was established by means of both electron-microprobe and wet-chemical analysis.

Electron-microprobe analyses were performed in wavelength-dispersion mode, using a CAMECA SX–50 apparatus. Analytical procedures and specifications are similar to those reported by Marincea (1999). The beam diameter was conventionally set at 10 μm so as to minimize sample degradation; however, for the analysis of other phases (oxides, silicates, anhydrous borates), a more focused beam was used. The overlap correction and PAP routine programs of Pouchou & Pichoir (1985) were applied. Since the fine needles of szaibelyite were found to be generally too narrow (commonly less than 1 μm in width), bunches of crystals were analyzed. Back-scattered electron images were used for the selection of appropriate areas, as well as for routine checks for compositional inhomogeneity.

Wet-chemical analyses were carried out using a set of standard methods of quantitative analysis (gravim-

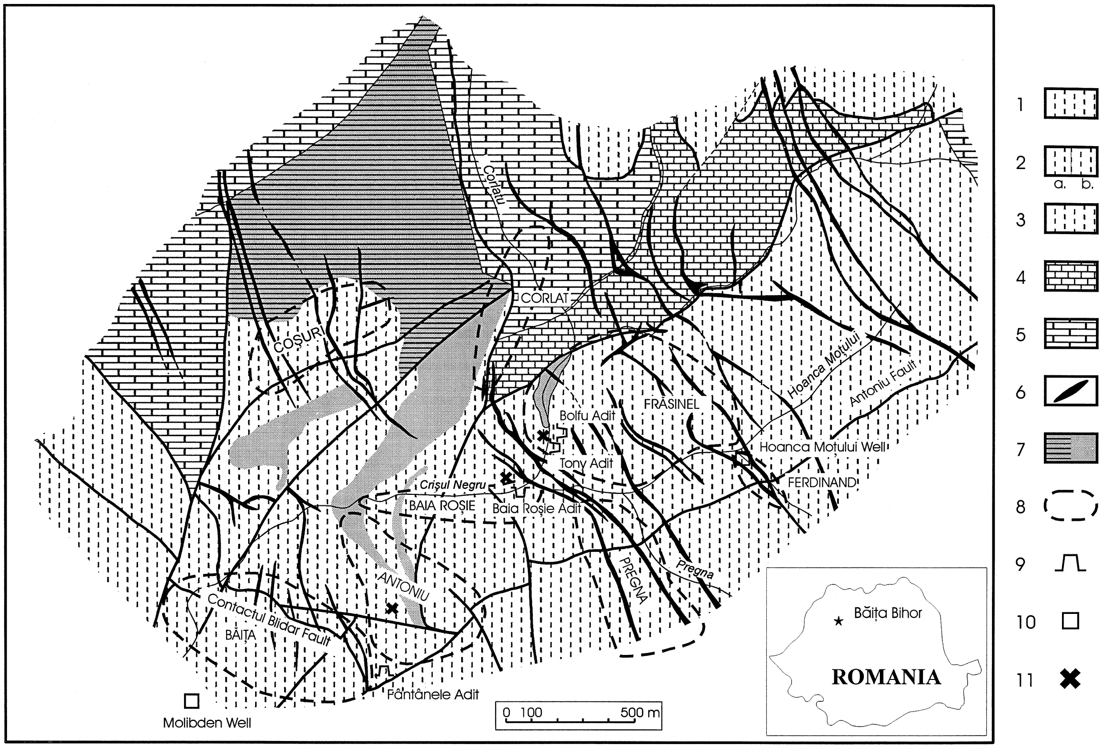

FIG. 1. Geological sketch of Baĭţa Bihor area, redrawn from Stoici (1974) and modified by Ilinca (1998). Symbols in the legend represent: 1–3: the Codru system of nappes; 1 Permian schistose clays and sandstones, 2 Triassic (Anisian–Norian) limestones (a) and dolostones (b), 3 Lower and Middle Jurassic (schistose clays, sandstones and black limestones); 4–5: The Bihor nappe; 4 Upper Jurassic (Oxfordian–Tithonic) limestones, 5 Lower Cretaceous (Barremian) limestones; 6 Upper Cretaceous – Paleogene "banatites", dyke rocks of basaltic or andesitic composition; 7 hornfels and skarns; 8 mining field; 9 adit; 10 mining well; 11 szaibelyite-bearing waste dumps.

etry, colorimetry and absorption spectrometry). These methods are the same as those described by Marincea (1999); however, some of the conditions of dissolution (*i.e.*, the preliminary melting with Na_2CO_3 in platinum crucibles) differ in detail. Boron concentration was determined by inductively coupled plasma – atomic emission spectrometry, F and Cl by hydropyrolysis, and H_2O by the Penfield method. Further details on the methods can be found in Marincea (1998). The mineral separates were prepared using conventional magnetic and heavy-liquid techniques, after carefully hand-picking. Because the impurities (*i.e.*, brucite, calcite, dolomite, serpentines) could not be eliminated entirely using this technique, the concentrates obtained were pulverized to –40 to +80 mesh and then washed with cold 0.5 N hydrochloric acid for one day. The samples separated are 90% pure or better, with the remainder being, as proved by XRD, a serpentine-group mineral.

The scanning-electron microscopy (SEM) study was performed using a JEOL JSM–840 scanning electron microscope, set at 15 kV acceleration voltage and 10 nA beam current.

The transmission electron microscopy (TEM) study was carried out using a Philips CM200 electron microscope operated at 300 kV. Sheaf-like aggregates were etched with hydrochloric acid, then finely crushed in distilled water. The pulverized samples were disaggregated by ultrasonic means and sedimented onto an electron microscope grid that was covered with a supporting film of carbon.

X-ray powder patterns were recorded using an automated Siemens D–5000 Kristalloflex diffractometer, at 0.02°2θ per second, with graphite-monochromatized Cu$K\alpha$ radiation (λ = 1.54056 Å), operated at 40 kV and 30 mA. A step size of 0.04°2θ, a slit system of 1–0.1–1 and a receiving slit of 0.6 mm were used. Samples were run from 10 to 120°2θ. Synthetic silicon (a = 5.4309 Å) was used as an internal standard.

Parallel records of the thermogravimetric (TGA) differential thermogravimetric (DTG) and differential thermal analysis (DTA) of selected samples of szaibelyite were made in static air at a heating rate of 10°C/min, using a MOM 1500 D derivatograph with Pt–PtRh thermocouple. Simultaneous records of thermogravimetric and differential scanning calorimetric (DSC) curves of part of the samples were made using a SETARAM TAG 24 thermobalance coupled with a DSC 111 thermal analyzer, applying a heating rate of 10°C/min, under a constant flow of nitrogen (flow rate 30mL/min). In order to determine the nature of the gases liberated, the outlet of the gas stream was analyzed using a FTS 40 (BIORAD) infrared spectrometer. Prior to analysis, samples were kept for one hour in a vacuum of 10^{-4} torr at 20°C, in order to assure the elimination of the adsorbed water.

The infrared-absorption spectra were obtained with a SPECORD M–80 spectrometer, using a conventional pressed-disk technique. Carefully dried powders were embedded in KBr; a dilution of 2.5 wt.% was used. Spectra were recorded between 250 and 4000 cm^{-1}. To avoid the effect of absorbed water, both szaibelyite and KBr were dehydrated at 150°C for 24 hours prior to analysis.

ASSOCIATED MINERALS

The mineralogy of the Băiţa Bihor boron-bearing skarns is considered in detail elsewhere (Marincea 1998, 2000). At Băiţa Bihor, szaibelyite is closely associated with the following minerals in the outer zones of the magnesian skarn bodies: calcite, dolomite, magnesite, kotoite, suanite, ludwigite, fluoborite, fluorite, chondrodite, norbergite and their alteration products. Secondary parageneses, formed from breakdown of the above minerals, include szaibelyite II, magnetite, brucite, chrysotile, lizardite, clinochlore, lepidocrocite and goethite. Disseminated throughout the boron-bearing skarn is a very minor sulfide assemblage, of which pyrite, galena and sphalerite are perhaps the most notable. Szaibelyite is directly associated with the other borates, calcite, magnetite, chondrodite, chrysotile, lizardite and fluorite. Selected results of the electron-microprobe study are given in Tables 1 and 2 for both Mg silicates and other Mg borates in association.

Although it is not the aim of this paper to discuss in detail the entire borate assemblage in the Băiţa Bihor magnesian skarns, it is important that other borates and some of the closely associated minerals be briefly mentioned here, as they may help one to understand some textural, paragenetic and chemical peculiarities of szaibelyite.

Chondrodite is the most abundant silicate in the szaibelyite-bearing skarn. It occurs as crystals or clusters of crystals dispersed in the carbonate + borate matrix. A thin film of chrysotile ± brucite generally rims the crystals. The mineral shows a narrow range of mg = 100 Mg/(Mg + Fe + Mn) values ($98.53 < mg < 99.40\%$) along with a more extended range of $X_F = F/(F + OH)$ values, from 0.38 to 0.52. Szaibelyite displays no particular spatial association with chondrodite, although it is evident that szaibelyite II crystallizes coevally with chrysotile that replaces this orthosilicate.

Ludwigite from Băiţa Bihor is generally uncommon, although locally abundant (*e.g.*, in part of the samples from Antoniu). Its composition spans a relatively narrow range of $Mg/(Mg + Fe^{2+})$, from 0.057 to 0.143, with a restricted $Al/(Al + Fe^{3+})$ of 0.023 to 0.057.

Suanite generally occurs in the outer zones of the boron-bearing skarn bodies. The mineral is invariably replaced by szaibelyite II (Fig. 2A); nonetheless, up to 5% relict suanite is commonly found in thin section.

Kotoite is very abundant in the boron-bearing skarns from Băiţa Bihor. The mineral occurs as rounded grains up to 0.5 mm across disseminated in the carbonate mass (the "kotoite marble"). Restricted compositional variability in Fe, Mn and Ca contents is characteristic of kotoite at Băiţa Bihor; it is very close to the magnesium end-member. Up to 0.61 mol.% $Fe_3(BO_3)_2$, 0.60 mol.% of the jimboite component, and 0.23 mol.% $Ca_3(BO_3)_2$ are present.

Fluoborite is restricted to some fluorine-rich veins cutting the kotoite-bearing skarn, where it is associated with other F-bearing minerals (*e.g.*, fluorite, chondrodite) and szaibelyite (Fig. 2B). The mineral ranges in X_F value from 0.525 to 0.573. The extent of substitutions of Mn, Fe and Ca for Mg is not significant; it affects up to 0.37% of the octahedral sites (Marincea 2000).

Serpentine-group minerals generally occur as an alteration-related rim on chondrodite and, to a lesser extent, as isolated bunches of fibers intergrown with szaibelyite. X-ray powder patterns reveal the presence of both *chrysotile* and *lizardite*. Both serpentine species are characteristically Fe-, Al- and Mn-poor.

Brucite usually occurs in replacement aggregates on chondrodite, ludwigite or kotoite, and is generally intergrown with szaibelyite or serpentine. A thin crust of brucite invariably surrounds the kotoite grains (Fig. 2C). Brucite may also appear as ragged laths 1–2 mm in length, disseminated in the carbonate mass. On the basis of the textural relationships, part of brucite appears to have formed at the same time as szaibelyite. Brucite pseudomorphs of kotoite or chondrodite are invariably conspicuously enriched in F (up to 7.60% of OH is replaced by F), whereas fluorine is not present in the "primary" brucite and in that pseudomorphic after ludwigite or szaibelyite to any appreciable extent.

Magnetite is very scarce in the boron-bearing magnesian skarns from Băiţa Bihor. It generally forms small clusters of grains (up to 0.1 mm across) or occurs as isolated euhedral crystals in aggregates of szaibelyite + magnetite ± brucite that are presumably pseudomorphic after ludwigite.

TABLE 1. ELECTRON-MICROPROBE ANALYSES OF SELECTED SAMPLES OF MAGNESIAN SILICATES FROM BĂIŢA BIHOR

Sample	1340	1395A	1395B	1397	2187A	2187B	2187C	2191	1795
Mineral(1)	cho	cho	cho	cho	cho	cho	cho	liz	clin
No.(2)	9	8	6	3	6	12	7	3	3
SiO_2	34.57	33.92	34.11	33.53	35.12	34.96	34.70	39.22	30.07
TiO_2	0.08	0.04	0.03	0.79	0.02	0.02	0.05	0.00	0.03
Al_2O_3	0.01	0.01	0.01	0.00	0.00	0.02	0.01	0.22	23.62
B_2O_3	0.00	0.00	0.00	0.74	0.00	0.00	0.00	1.05	0.00
Fe_2O_3(3)	-	-	-	-	-	-	-	-	0.00
FeO(3)	0.74	0.34	0.30	0.39	0.78	0.63	0.61	4.39	0.17
MgO	58.18	57.88	57.88	57.50	57.44	58.12	57.66	39.11	33.66
MnO	0.81	0.43	0.34	0.49	0.41	0.27	0.18	0.10	0.00
CaO	0.04	0.07	0.05	0.05	0.11	0.01	0.05	0.46	0.10
F	5.87	5.20	4.97	4.27	5.63	5.48	5.28	0.00	0.54
H_2O(4)	2.60	2.90	2.95	3.22	2.46	2.64	2.68	-	12.54
F=O	-2.48	-2.19	-2.10	-1.80	-2.37	-2.31	-2.23	-	-0.23
Total	100.42	98.60	98.54	99.18	99.60	99.84	98.99	84.55	100.50
NUMBER OF IONS ON THE BASIS OF N(5) (O,OH,F)									
Si	1.972	1.963	1.973	1.925	2.017	1.999	2.000	3.810	5.550
Ti	0.004	0.002	0.001	0.034	0.001	0.001	0.002	0.000	0.004
Al	0.001	0.001	0.001	0.000	0.000	0.001	0.001	0.025	5.138
B	0.000	0.000	0.000	0.073	0.000	0.000	0.000	0.176	0.000
Fe^{3+}	-	-	-	-	-	-	-	-	
Fe^{2+}	0.035	0.016	0.015	0.019	0.037	0.030	0.029	0.357	0.026
Mg	4.947	4.993	4.991	4.922	4.918	4.955	4.956	5.664	9.262
Mn	0.039	0.021	0.017	0.024	0.020	0.013	0.009	0.008	0.000
Ca	0.002	0.004	0.003	0.003	0.007	0.001	0.003	0.048	0.020
F^-	1.059	0.952	0.909	0.775	1.023	0.991	0.963	-	0.315
OH^-	0.988	1.117	1.140	1.234	0.941	1.008	1.032	-	15.439

(1) signification of symbols: cho = chondrodite; liz = lizardite; clin = clinochlore; (2) number of point analyses; (3) total Fe as FeO for chondrodite and lizardite; for clinochlore, FeO and Fe_2O_3 were deduced from FeO_T, after the adjustment of the ferric/ferrous ratios in order to fulfill the charge balance; (4) H_2O calculated for stoichiometry in chondrodite and clinochlore; (5) N = number of (O,OH,F) atoms [7 cations and 10 (O,OH,F) for chondrodite; 14 (O) in the anhydrous part of the formula for lizardite; 20 cations and 36 (O,OH,F) for clinochlore].

Crystal Morphology and Textural Relationships

Three textural types of szaibelyite have been identified in the boron-bearing skarns from Băiţa Bihor. (1) Sheaf-like aggregates of acicular crystals (Fig. 2D) are intimately intergrown with brucite and locally with magnetite; they suggest pseudomorphism of fluoborite (in the first case) or of ludwigite (in the second). (2) Bundles free of brucite or interwoven aggregates of needle-like crystals of szaibelyite that may contain relics of suanite (Fig. 2A) are considered to result from pseudomorphism accompanying the hydration of suanite. (3) "Spherulitic" aggregates are composed of radial bundles of fibers up to 3 mm across (Fig. 2E). The growth of this material likely involves the pseudomorphic replacement of a precursor other than suanite or kotoite. No relics of this precursor mineral have been found; this textural variety of szaibelyite may have formed by metasomatic replacement of pre-existing brucite or even of periclase in the dolomitic marble. The first two textural varieties (henceforth referred to as szaibelyite II) clearly appear to postdate both chondrodite and fluoborite, whereas the latter variety (henceforth referred to as szaibelyite I) appears to be in equilibrium with fluoborite.

In all cases, szaibelyite occurs as crudely radiating, felted (Fig. 2F) or fan-shaped aggregates of acicular crystals, commonly enclosed by calcite. The morphology of both radiating and felted aggregates of szaibelyite is illustrated by scanning electron micrographs in Figure 2 that reveal parallel and subparallel intergrowths, which explains the fan-shape disposition observed under the optical microscope. Individual crystals are needle-like, up to 3 μm thick, with longest dimensions (up to 0.2 mm) parallel to [001]. Individual faces in the [001] zone are difficult to distinguish (Fig. 2). Neither twinning nor cleavage was observed, and the fracture is conchoidal.

TABLE 2. SELECTED CHEMICAL COMPOSITIONS OF MAGNESIAN BORATES OTHERS THAN SZAIBELYITE, BĂIŢA BIHOR

Sample	1397	2182	2229	1850	2103	1850	2141	1396A	2226B
Mineral(1)	ko	ko	ko	lw	lw	su	su	fb	fb
No.(2)	4	9	10	5	11	3	6	5	5
B_2O_3	36.36	36.06	36.25	17.96	17.93	47.39	46.21	18.80	18.97
TiO_2	-	-	-	0.02	0.06	-	-	-	-
Al_2O_3	0.01	0.01	-	0.56	1.26	0.07	0.01	-	-
Fe_2O_3(3)	-	-	-	39.04	38.12	-	-	-	-
FeO(3)	0.24	0.50	0.66	3.11	3.26	0.57	0.26	0.07	0.02
MgO	62.26	61.13	61.10	38.92	38.92	52.39	52.93	64.05	64.53
MnO	0.09	0.64	0.04	0.39	0.35	0.44	0.34	0.08	0.02
CaO	0.12	0.08	0.05	0.12	0.19	0.85	0.04	0.21	0.07
K_2O	0.01	-	-	-	-	-	-	-	-
H_2O(4)	-	-	-	-	-	-	-	7.46	7.19
F	-	-	-	-	-	-	-	16.02	17.09
F=O	-	-	-	-	-	-	-	6.75	7.20
Total	99.09	98.42	98.10	100.12	100.09	101.71	99.79	99.94	100.69
CATIONS ON THE BASIS OF N(5) (O)									
B	2.010	2.013	2.023	1.015	1.011	2.018	2.003	1.000	1.000
Ti	-	-	-	0.000	0.001	-	-	-	-
Al	0.000	0.000	-	0.023	0.049	0.002	0.000	-	-
Fe^{3+}	-	-	-	0.962	0.937	-	-	-	-
Fe^{2+}	0.006	0.014	0.018	0.085	0.089	0.012	0.005	0.002	0.001
Mg	2.972	2.947	2.945	1.900	1.896	1.927	1.981	2.942	2.938
Mn	0.002	0.018	0.001	0.011	0.010	0.009	0.007	0.002	0.001
Ca	0.004	0.003	0.002	0.004	0.007	0.022	0.001	0.007	0.002
K	0.000	-	-	-	-	-	-	-	-
F^-	-	-	-	-	-	-	-	1.561	1.651
$(OH)^-$	-	-	-	-	-	-	-	1.533	1.465

(1) ko = kotoite; lw = ludwigite; su = suanite, fb = fluoborite; (2) number of point analyses; (3) total Fe as FeO for kotoite, suanite and fluoborite; FeO and Fe_2O_3 deduced from FeO_T after adjustment of the ferric/ferrous ratio in order to fulfill the charge balance in ludwigite; (4) as calculated for fluoborite; (5) N = number of oxygen atoms [6(O) for kotoite; 5(O) and 4 cations for ludwigite; 5(O) for suanite; 6(O,OH,F) and B = 1 *apfu* for fluoborite].

Electron-microprobe and X-ray-diffraction analyses indicate that in several samples, crystals of szaibelyite form parallel intergrowths with chrysotile. The origin of this textural intergrowth is not known, but it is apparently structurally controlled and related to the simultaneous growth of the two minerals during metasomatism. A similar intergrowth between szaibelyite and serpentine at a submicroscopic scale was observed by Peng *et al.* (1963), who considered it to be epitactic.

PHYSICAL PROPERTIES

Szaibelyite from Băiţa Bihor does not fluoresce in short-wave ultraviolet radiation ($\lambda = 256$ nm), but some samples are sensitive to long-wave UV ($\lambda = 366$ nm). In this case, it fluoresces in pale yellow tints, as reported by Robbins (1983). The mineral is cathodoluminescent, with a medium pinkish orange response color, which contrasts with the yellow cathodoluminescence of the surrounding calcite, activated by Mn^{2+} (Marincea 1998).

The small size of the crystals precluded accurate determinations of density using the pycnometer. Consequently, the sink–float method was used to measure the density of carefully hand-picked aggregates of crystals, obtained from sample 1406, after etching with 0.5 N hydrochloric acid and washing with distilled water. The value obtained by immersion in bromoform diluted with toluene is $D_m = 2.73(1)$ g/cm^3, in good agreement with the calculated values in Table 3, obtained on the basis of cell volumes and chemical data, assuming that Z is equal to 4 formula units per cell (Peng *et al.* 1963). This value is, however, slightly larger than that reported by Watanabe (1939) for the szaibelyite from the same occurrence ($D_m = 2.70$ g/cm^3).

Because of the small grain-size, the spindle stage method could not be directly used to determine the directions of vibrations and thence the indices of refraction. Consequently, α was determined as the smallest observed index and γ as the largest one, using carefully hand-picked powders, immersed in temperature-cali-

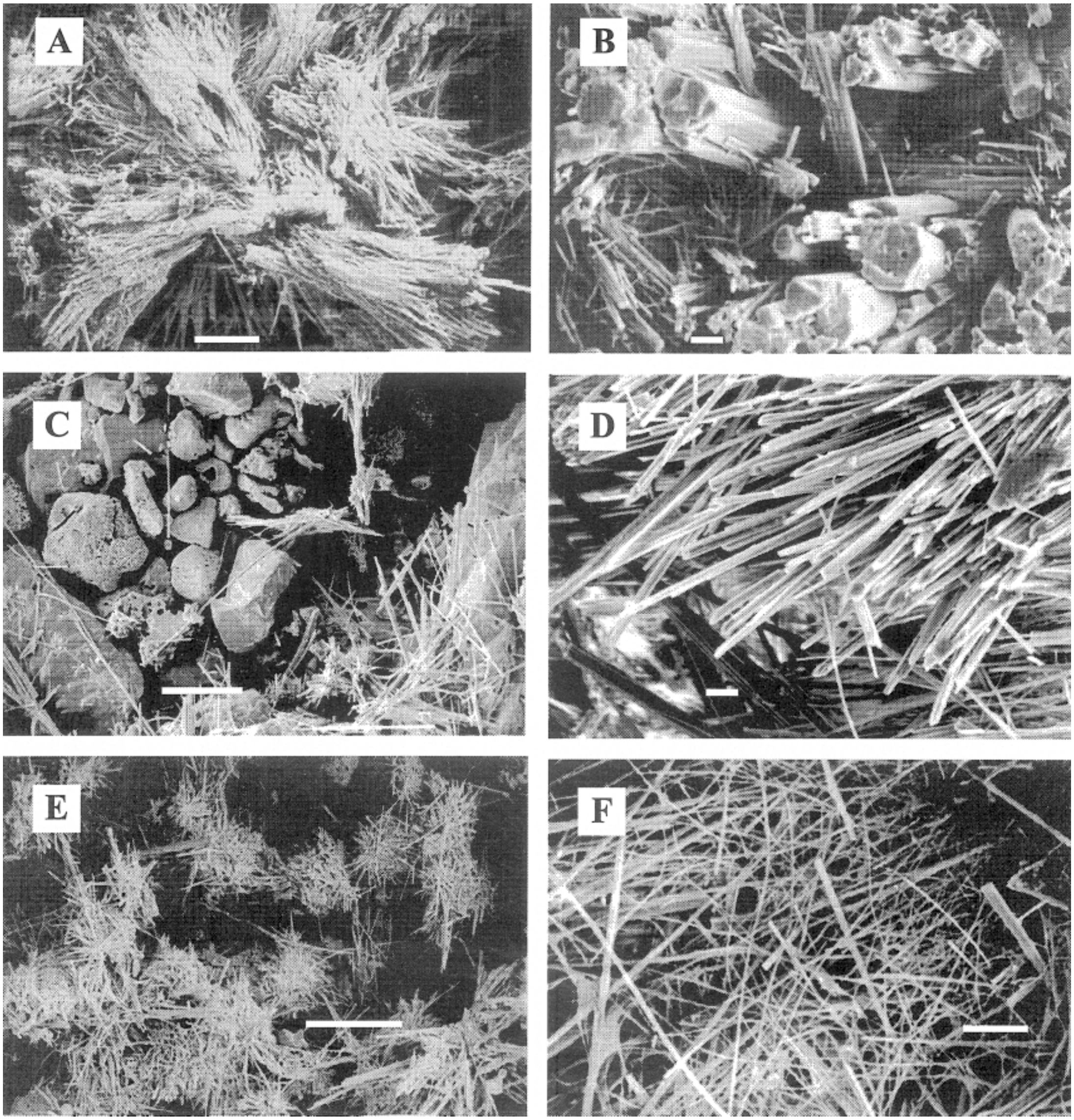

FIG. 2. Representative scanning-electron micrographs of szaibelyite from Baĭţa Bihor. (A) Sheaf-like aggregates of szaibelyite pseudomorph after suanite. Scale bar = 100 μm. (B) Acicular crystals of szaibelyite associated with hexagonal prisms of fluoborite. Scale bar = 10 μm. (C) Tuft of szaibelyite crystals (right) associated with ovoid grains of kotoite partially coated by porous crusts of brucite. Scale bar = 100 μm. (D) Detail of a sheaf-like stacking of acicular crystals of szaibelyite. Scale bar = 10 μm. (E) Radiating aggregates of szaibelyite crystals. Scale bar = 100 μm. (F) Felt-like aggregate of szaibelyite crystals. Scale bar = 10 μm.

brated oils. As a first approximation, one can assume that $\gamma \cong \beta = n_{\max}$ and $\alpha = n_{\min}$ (Palache *et al.* 1951, Shabynin & Mytushina 1964). The indices of refraction, as determined for szaibelyite in sample 1406 using the Becke line method and Na light (λ = 589 nm) and assuming the optical orientation proposed by these authors ($X = \alpha$, $Y = \beta$, $Z = \gamma$, with Z perpendicular to elongation) are: $\gamma \cong \beta$ = 1.652(3) and α = 1.576(2). Nonetheless, if β can be measured, it is found to differ from γ by a quasi-constant value of (–)0.004 (Palache *et al.* 1951, Varlakov 1962, Peng *et al.* 1963). Thus the mean index of refraction of szaibelyite is better approximated

TABLE 3. CALCULATED PHYSICAL PARAMETERS OF SELECTED SAMPLES OF SZAIBELYITE FROM BĂIŢA BIHOR

Sample	$M^{(1)}$	$V^{(2)}$	D_x	K_C	$D'_x{}^{(3)}$	$\bar{n}_x{}^{(4)}$	$K_P{}^{(5)}$	$1-(K_P/K_C)$
1043	165.733*	408.596	2.693	0.2325	2.689	1.626	0.2323	0.0009
1055	168.338$^{\blacklozenge}$	407.233	2.745	0.2322	2.693	1.637	0.2278	0.0189
1394	168.132*	408.663	2.732	0.2324	2.691	1.635	0.2290	0.0146
1394	166.708$^{\blacklozenge}$	408.663	2.709	0.2336	2.677	1.633	0.2308	0.0120
1397	167.532$^{\blacklozenge}$	407.536	2.730	0.2330	2.684	1.636	0.2290	0.0172
1406	168.554*	409.919	2.730	0.2292	2.728	1.626	0.2291	0.0004
1672	168.881*	408.286	2.747	0.2319	2.696	1.637	0.2277	0.0181
1794	167.196$^{\blacklozenge}$	406.124	2.734	0.2326	2.688	1.636	0.2287	0.0168
1795	168.605$^{\blacklozenge}$	406.034	2.757	0.2319	2.696	1.639	0.2268	0.0220
1797	172.267*	408.606	2.799	0.2314	2.702	1.648	0.2235	0.0341
1797	169.244$^{\blacklozenge}$	408.606	2.750	0.2315	2.701	1.634	0.2274	0.0177
1885	167.965$^{\blacklozenge}$	406.197	2.746	0.2322	2.693	1.638	0.2277	0.0194
1886	169.594*	407.333	2.765	0.2319	2.696	1.641	0.2262	0.0246
1886	168.932$^{\blacklozenge}$	407.333	2.754	0.2317	2.699	1.638	0.2271	0.0199
1937	169.711*	408.345	2.760	0.2321	2.694	1.641	0.2266	0.0237
2103	167.003$^{\blacklozenge}$	403.498	2.748	0.2329	2.685	1.640	0.2275	0.0232
2141	168.899$^{\blacklozenge}$	404.088	2.775	0.2317	2.699	1.643	0.2253	0.0276
2185	168.167$^{\blacklozenge}$	408.061	2.736	0.2323	2.692	1.636	0.2285	0.0164

(1) molecular mass: * as calculated on the basis of wet-chemical analyses; $^{\blacklozenge}$ as calculated on the basis of electron-microprobe analyses; (2) unit-cell volume (in Å^3), as deduced from least-squares refinement of X-ray powder data; (3) calculated according to Gladstone-Dale law, by using the mean index of refraction ($\bar{n}$ = 1.6253), and the chemical molar refractivity (K_C); (4) $\bar{n}_x = D_x \cdot K_C + 1$; (5) $K_P = (\bar{n} - 1)/D_x$.

as $\bar{n} = (2\gamma + \alpha - 0.004)/3$. In our case, that leads to a mean index of refraction of 1.6253.

The Gladstone–Dale compatibility indices [$1 - (K_P/K_C)$], as derived using $\bar{n}$, the calculated densities and the Gladstone–Dale constants given by Mandarino (1976) except k_{B2O3} = 0.241 [as calculated by Mandarino (1981) for the boron oxide], are superior on the scale of Mandarino (1981), except for six that are excellent (Table 3).

CHEMICAL DATA

Wet-chemical analysis

Table 4 shows representative data obtained by wet-chemical analysis of separates of szaibelyite from Băiţa Bihor. All the compositions show evidence of admixed serpentine minerals, identified by XRD. Subtracting stoichiometric serpentine in order to eliminate SiO_2, it is possible to propose a normative composition for the analyzed samples and to derive the composition of the szaibelyite itself (Table 4).

Prior to treatment of the separates with hydrochloric acid, analyses have also been made for chlorine, but did not reveal any trace of this element. The presence of 0.20 wt.% Cl in the results of Peters (1863) cannot therefore be accounted for. Neither was fluorine detected in any appreciable quantity (*i.e.*, 0.005–0.010 wt.%, near the limit of detection). Some other elements (*i.e.*, Zn, Ba, Sr), were sought, but lie below the limit of detection of the method used (absorption spectrometry). Inductively coupled plasma – atomic emission spectrometry analysis of sample 1043 indicates in fact low contents of Zn (580 ppm) and very low contents of Ba (4 ppm) and Sr (18 ppm).

The compositions of szaibelyite derived in Table 4 represent mean compositions at the scale of a sample. Their corresponding chemical-structural formulae were calculated assuming that B = 2 atoms per formula unit (*apfu*). The resulting formulae are remarkably close to stoichiometry: the sums of cations (including H) are invariably very close to 6 *apfu*, whereas the cation charge closely approximates the ideal value of 12. In all but two cases, Fe^{2+} predominates over Fe^{3+}. In fact, the very low contents of Fe^{3+} and Al may be due to the admixed serpentine-group minerals, which were subtracted as stoichiometric compounds.

Szaibelyite from Băiţa Bihor has a very narrow compositional range (Table 2, Fig. 3). The sussexite component varies slightly from 0.40 to 0.88 mol.%, and the proportion of $Fe_2(B_2O_4OH)(OH)$ reaches up to 1.06 mol.%, apparently without relation to the spatial position of the samples in the metasomatic bodies. In fact, nothing is known about the extent of solid-solution between $Fe_2(B_2O_4OH)(OH)$ and szaibelyite, nor between this and sussexite. Note that a solid-solution series toward a Fe end-member of the szaibelyite group may be anticipated, as it has been synthesized (*e.g.*, Diman & Nekrasov 1969).

Szaibelyite incorporates only minor amounts of Ca, up to 1.50 wt.% CaO according to data in the literature (*i.e.*, Shabynin & Mytushina 1964, Pertsev 1971,

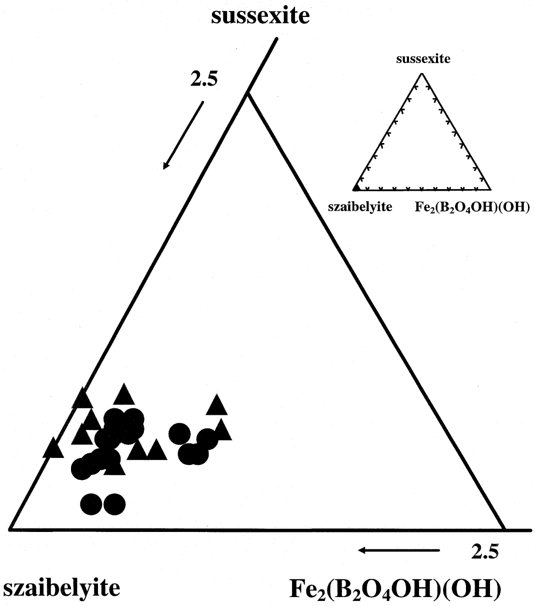

FIG. 3. Diagram showing the solid solution of szaibelyite from Baĭţa Bihor in terms of the szaibelyite – sussexite – $Fe_2(B_2O_4OH)(OH)$ solid-solution series. Plots of compositions obtained by wet-chemical analysis (solid triangles) and by electron-microprobe analysis (solid dots).

TABLE 4. RESULTS OF WET-CHEMICAL ANALYSES OF SELECTED SAMPLES OF SZAIBELYITE FROM BĂIȚA BIHOR⁽¹⁾

Sample	1043	1394	1406	1659	1672	1797	1839	1848	1886	1937
SiO_2	0.43	4.27	1.03	1.03	3.00	1.64	0.24	0.44	2.75	0.32
B_2O_3	40.78	37.18	40.37	39.84	37.48	38.97	40.93	39.88	38.17	40.58
Al_2O_3	0.17	0.17	0.22	0.17	0.29	0.45	0.00	0.46	0.00	0.08
Fe_2O_3	0.11	0.16	0.19	0.03	0.12	0.13	0.37	0.15	0.13	0.25
FeO	0.13	0.00	0.14	0.59	0.44	0.23	0.82	0.35	0.00	0.88
MgO	46.12	46.38	46.73	46.26	45.48	47.37	46.43	46.05	46.89	46.25
MnO	0.51	0.39	0.59	0.41	0.38	0.72	0.69	0.32	0.65	0.53
CaO	0.16	0.07	0.09	0.04	0.05	0.08	0.00	0.00	0.00	0.03
H_2O^+	10.89	11.02	10.80	10.66	10.60	10.60	10.66	10.53	10.71	10.74
H_2O^-	0.31	0.00	0.00	0.31	1.32	0.00	0.00	0.86	0.11	0.00
Total	99.61	99.64	100.16	99.34	99.16	100.18	100.14	99.04	99.41	99.66
PROPOSED NORMATIVE COMPOSITIONS (WT.%)										
serpentine	0.99	9.83	2.38	2.38	6.92	3.78	0.55	1.01	6.34	0.74
szaibelyite	98.31	89.81	97.78	96.65	90.92	96.40	99.59	97.17	92.96	98.92
H_2O^+	0.31	0.00	0.00	0.31	1.32	0.00	0.00	0.86	0.11	0.00
DEDUCED COMPOSITIONS OF SZAIBELYITE (WT.% OXIDES)⁽²⁾										
B_2O_3	41.481	41.393	41.287	41.221	41.223	40.424	41.099	41.042	41.058	41.028
Al_2O_3	0.173	0.194	0.225	0.176	0.319	0.467	0.000	0.473	0.000	0.076
Fe_2O_3	0.112	0.182	0.194	0.031	0.132	0.132	0.374	0.154	0.138	0.254
FeO	0.132	0.000	0.143	0.610	0.484	0.240	0.823	0.360	0.000	0.890
MgO	46.475	46.880	46.728	46.788	46.700	47.423	46.379	46.939	47.461	46.434
MnO	0.519	0.436	0.603	0.424	0.418	0.743	0.688	0.329	0.700	0.534
CaO	0.163	0.073	0.092	0.041	0.055	0.084	0.000	0.000	0.000	0.025
H_2O^+	10.945	10.842	10.728	10.709	10.669	10.487	10.637	10.703	10.643	10.759
NUMBER OF IONS ON THE BASIS OF 2 BORON ATOMS										
B	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Al	0.006	0.006	0.007	0.006	0.011	0.016	0.000	0.016	0.000	0.003
Fe^{3+}	0.002	0.004	0.004	0.001	0.003	0.003	0.008	0.003	0.003	0.005
Fe^{2+}	0.003	0.000	0.003	0.014	0.011	0.006	0.019	0.009	0.000	0.021
Mg	1.935	1.956	1.955	1.961	1.956	2.026	1.949	1.975	1.997	1.955
Mn	0.012	0.010	0.014	0.010	0.010	0.018	0.016	0.008	0.017	0.013
Ca	0.005	0.002	0.003	0.001	0.002	0.003	0.000	0.000	0.000	0.001
H	2.039	2.024	2.008	2.007	2.000	2.005	2.000	2.016	2.003	2.027
Σ cations	6.002	6.002	5.995	6.000	5.993	6.077	5.992	6.027	6.020	6.025
charge	11.973	11.990	11.991	12.000	12.000	12.168	11.992	12.057	12.040	12.031
X_{Mn}⁽³⁾	0.614	0.508	0.709	0.504	0.505	0.877	0.806	0.402	0.844	0.653
X_{Fe}⁽³⁾	0.153	0.000	0.152	0.705	0.556	0.292	0.958	0.452	0.000	1.055
X_{Ca}⁽³⁾	0.256	0.102	0.152	0.050	0.101	0.146	0.000	0.000	0.000	0.050

(1) results expressed in wt.%; (2) totals recalculated to 100%; (3) X_{Mn} = 100·Mn/(Mg+Mn+Fe^{2+}+Ca) (%); X_{Fe} = 100·Fe^{2+}/(Mg+Mn+Fe^{2+}+Ca) (%); X_{Ca} = 100·Ca/(Mg+Mn+Fe^{2+}+Ca) (%).

Lisitsin *et al.* 1985), and the samples from Băiţa Bihor are no exceptions: only up to 0.16% from the octahedral sites normally occupied by Mg (Takéuchi & Kudoh 1975) are filled by Ca, compared to up to 2.5% Ca found by Lisitsin *et al.* (1985) in samples from Tayozhnoye (southern Yakutia). In fact, no Ca analogue of szaibelyite is known; sibirskite (Vasil'kova 1962) has the same composition, with Ca instead of Mg, but its structure is unknown.

Electron-microprobe data

Representative results of the electron-microprobe analyses of szaibelyite from Băiţa Bihor are given in Table 5. Marincea (1998) gave the complete list of reference data used in the diagram in Figure 3. Results of many random-point analyses were averaged to obtain the data in Table 5, which was possible because all the analyzed samples proved to be chemically homogeneous. A 100-s energy-dispersion scan indicated no elements with atomic number greater than 8, other than those reported here; Cl, K, Na and Zn were sought but not detected. As the analysis by wet chemistry indicates that the amount of Fe^{3+} is very low, all iron was considered to be divalent. Chemical-structural formulae were calculated on the basis of 6(O,OH,F) and 2 B cations per formula unit. Hydroxyl groups and the corresponding H_2O in the composition were added in order to fulfill charge balance.

TABLE 5. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF SELECTED SAMPLES OF SZAIBELYITE FROM BĂIŢA BIHOR$^{(1)}$

Location	Antoniu					Baia Roşie					Bolfu - Tony				
Sample	1055	1397	2182	Mean$^{(6)}$	Std$^{(6)}$	1662	1797	2103	Mean$^{(6)}$	Std$^{(6)}$	1394	1850	2185	Mean$^{(6)}$	Std$^{(6)}$
N$^{(2)}$	7	12	4	84		6	6	5	50		9	13	6	28	
B_2O_3	41.53	42.01	40.84	41.55	0.44	41.17	41.09	42.31	41.67	0.59	42.39	40.99	41.86	41.75	0.71
Al_2O_3	0.02	0.07	0.06	0.03	0.03	0.30	0.09	0.01	0.11	0.12	0.03	0.04	0.02	0.03	0.01
MgO	46.89	46.10	46.78	47.06	0.48	46.88	46.87	46.14	46.64	0.41	46.38	47.00	47.25	46.88	0.45
MnO	0.58	0.44	0.36	0.42	0.15	0.54	0.39	0.63	0.46	0.11	0.33	0.49	0.46	0.43	0.09
FeO$^{(3)}$	0.26	0.82	0.78	0.41	0.22	0.37	0.86	0.35	0.50	0.23	0.35	0.68	0.30	0.44	0.21
CaO	0.09	0.05	0.04	0.06	0.05	0.05	0.04	0.09	0.05	0.02	0.05	0.08	0.02	0.05	0.03
$H_2O^{(4)}$	11.00	11.64	10.34	10.94	0.37	10.56	10.57	11.38	11.16	0.58	11.97	10.43	11.10	11.17	0.66
F	0.04	0.04	0.23	0.07	0.07	0.06	0.04	0.05	0.05	0.01	0.01	0.09	0.10	0.07	0.04
F=O	-0.02	-0.02	-0.10	-0.03	0.03	-0.03	-0.02	-0.02	-0.02	0.00	-0.00	-0.04	-0.04	-0.03	0.02
Total	100.39	101.15	99.33	100.51	0.69	99.90	99.93	100.94	100.62	0.48	101.51	99.76	101.07	100.79	0.73
NUMBER OF IONS ON THE BASIS OF 2 B AND 6 (O,OH,F)															
B	2.000	2.000	2.000	2.000	0.000	2.000	2.000	2.000	2.000	0.000	2.000	2.000	2.000	2.000	0.000
Al	0.001	0.002	0.002	0.001	0.001	0.010	0.003	0.000	0.004	0.004	0.001	0.001	0.001	0.001	0.000
Mg	1.950	1.895	1.979	1.956	0.031	1.967	1.970	1.884	1.933	0.043	1.890	1.981	1.950	1.940	0.046
Mn	0.014	0.010	0.009	0.010	0.004	0.013	0.009	0.015	0.011	0.002	0.008	0.012	0.011	0.010	0.002
Fe^{2+}	0.006	0.019	0.019	0.010	0.005	0.009	0.020	0.008	0.012	0.006	0.008	0.016	0.007	0.010	0.005
Ca	0.003	0.001	0.001	0.002	0.001	0.002	0.001	0.003	0.001	0.001	0.001	0.002	0.001	0.001	0.001
$(OH)^-$	2.047	2.141	1.957	2.035	0.057	1.983	1.987	2.176	2.070	0.093	2.182	1.967	2.050	2.069	0.108
F	0.004	0.003	0.021	0.006	0.007	0.005	0.004	0.004	0.004	0.001	0.001	0.008	0.009	0.006	0.004
$X_{Mn}^{(5)}$	0.710	0.519	0.448	0.506	0.183	0.653	0.450	0.785	0.562	0.121	0.420	0.597	0.559	0.510	0.093
$X_{Fe}^{(5)}$	0.304	0.987	0.946	0.506	0.270	0.452	1.000	0.419	0.613	0.270	0.420	0.796	0.356	0.510	0.238
$X_{Ca}^{(5)}$	0.152	0.052	0.050	0.101	0.061	0.100	0.050	0.157	0.051	0.042	0.052	0.099	0.051	0.051	0.027

(1) results expressed in wt.%; (2) number of single spot analyses; (3) total iron as FeO; (4) as calculated in order to fulfill the charge balance; (5) $X_{Mn} = 100 \cdot Mn/(Mg+Mn+Fe^{2+}+Ca)$ (%); $X_{Fe} = 100 \cdot Fe^{2+}/(Mg+Mn+Fe^{2+}+Ca)$ (%); $X_{Ca} = 100 \cdot Ca/(Mg+Mn+Fe^{2+}+Ca)$ (%); (6) Mean = the mean value obtained from all the analyzed samples; Std = standard deviation.

The boron content of several samples is slightly higher than that necessary for stoichiometry. The excess B results in a slight deficiency in divalent octahedrally coordinated cations, but does not affect the proportions of Mg, Mn, Fe and Ca. Electron-microprobe analyses confirm that the composition of szaibelyite from Băiţa Bihor is fairly close to that of the szaibelyite end-member, having $X_{Mn} = 100 \bullet Mn/(Mg + Mn + Fe^{2+} + Ca) \leq 0.73\%$, $X_{Fe} = 100 \bullet Fe^{2+}/(Mg + Mn + Fe^{2+} + Ca) \leq 1.01\%$ and $X_{Ca} = 100 \bullet Ca/(Mg + Mn + Fe^{2+} + Ca) \leq 0.20\%$. Plots of the bulk compositions obtained by electron-microprobe analysis in terms of szaibelyite – $Fe_2(B_2O_4OH)(OH)$ – sussexite (Fig. 3) are very close to those derived from the wet-chemical analyses. Note that the three textural types of szaibelyite described above are virtually indistinguishable in terms of their Mn and Fe contents.

A minor amount of F is present in all the samples (Table 5). The presence of fluorine in some of the powdered separates (*e.g.*, 1397, 1850) was moreover confirmed by specific-ion electrode analysis. An overlap with associated fluoborite cannot explain these F contents, since at Băiţa Bihor fluoborite is scarce (Marincea 2000). Fluorine was consequently included in the chemical-structural formulae in Table 5. It is expected that F substitutes for some of the "free" OH groups (*i.e.*, those not included in the diorthoborate groups). The contents of H_2O necessary for charge balance were calculated taking into account the fluorine contents. Note that 0.06–0.12 wt.% F were mentioned in samples of szaibelyite from Saint Dizier (Tasmania) by Kwak & Nicholson (1988). The slight F content of szaibelyite from Băiţa Bihor (up to 1% of the hydroxyl groups are replaced by F) seems to reflect the fluorine activity in the fluid phase (see below).

TEM AND X-RAY POWDER STUDY

Szaibelyite fibers analyzed by transmission electron microscopy (× 500,000) typically produce selected-area electron diffraction (SAED) patterns indicative of the presence of only one of the three polytypes reported by Takéuchi & Kudoh (1975). In the SAED patterns showing an a^*–c^* section of the reciprocal lattice (not shown), absences of the type h = odd in ($h0l$) indicate the $P2_1/a$ space group. When tilted away from the exact [001] zone axis (about the a^*–b^* section), the SAED patterns indicate that (1) the lattice is primitive, as there are no systematic absences in the (hkl) reflections, and (2) the 2_1 screw is characteristic since absences of the type k = odd in ($0k0$) are invariably present.

Several sets of X-ray powder-diffraction patterns were obtained for selected samples of szaibelyite from Băiţa Bihor. The complete datasets were given by Marincea (1998) and are available upon request.

Results of the refinements of the unit-cell parameters are given in Table 6. They are based on 27 to 38 (corrected) X-ray powder lines between 8.00 and 1.48 Å,

TABLE 6. CRYSTALLOGRAPHIC PARAMETERS OF SZAIBELYITE, BĂIȚA BIHOR*

Sample	*a* (Å)	*b* (Å)	*c* (Å)	β(°)	*V* (Å^3)	n$^{(1)}$	N$^{(2)}$	k$^{(3)}$
1043	12.571(6)	10.430(5)	3.128(3)	94.95(4)	408.6(3)	7	32	0.7214*
1055	12.570(5)	10.411(5)	3.129(2)	96.00(3)	407.2(3)	10	35	0.7213◆
1394	12.565(6)	10.403(4)	3.133(2)	96.02(2)	407.3(2)	4	31	0.7208*
1396	12.555(7)	10.401(7)	3.142(3)	95.10(7)	408.7(3)	3	36	0.7209◆
1397	12.547(5)	10.398(3)	3.137(2)	95.26(4)	406.9(5)	5	29	0.7211◆
1406	12.578(7)	10.413(4)	3.144(3)	95.44(4)	409.9(4)	4	32	0.7207*
1659	12.560(7)	10.396(6)	3.126(3)	95.92(3)	406.0(3)	6	34	0.7210*
1660	12.600(4)	10.423(4)	3.140(3)	95.96(3)	410.1(1)	7	31	0.7211◆
1672	12.569(5)	10.403(4)	3.139(2)	95.87(3)	408.3(3)	7	27	0.7211*
1673	12.564(4)	10.405(3)	3.132(2)	96.00(2)	407.2(2)	7	33	0.7209◆
1794	12.543(7)	10.386(5)	3.132(3)	95.49(5)	406.1(4)	4	32	0.7208◆
1795	12.536(4)	10.397(5)	3.131(2)	95.76(2)	405.2(3)	9	28	0.7210◆
1797	12.575(3)	10.407(2)	3.138(1)	95.76(2)	408.6(2)	5	33	0.7215*
1839	12.531(7)	10.387(5)	3.138(3)	95.60(3)	406.5(3)	4	33	0.7213*
1848	12.543(6)	10.385(5)	3.122(3)	95.89(3)	404.5(3)	4	37	0.7207*
1885	12.561(3)	10.392(3)	3.129(2)	96.03(2)	406.2(2)	9	38	0.7206◆
1886	12.563(4)	10.402(4)	3.134(2)	95.83(4)	407.4(1)	5	33	0.7208*
1937	12.558(9)	10.407(7)	3.138(3)	95.32(6)	408.3(4)	3	32	0.7213*
2103	12.526(7)	10.391(5)	3.113(2)	95.20(3)	403.5(2)	6	31	0.7214◆
2141	12.537(8)	10.387(6)	3.119(3)	95.81(4)	404.1(3)	8	36	0.7207◆
2185	12.579(7)	10.418(4)	3.130(3)	95.84(2)	408.1(2)	7	30	0.7208◆

* samples from Antoniu (1055, 1396, 1406, 1397, 1839, 1885, 1886, 2141), Baia Roşie (1043, 1659, 1794, 1795, 1797, 2103) and Bolfu - Tony (1394, 1660, 1672, 1673, 1848, 1937, 2185); (1) number of least-squares refining cycles; (2) number of reflections in the 2θ range 10 - 65° used for refinement; (3) k = mean cation radius, in Å (see text) *as calculated on the basis of wet-chemical analyses; ◆as calculated on the basis of electron-microprobe analyses.

for which unambiguous indexing was possible. As expected, the best match between calculated and observed patterns was achieved for a monoclinic $P2_1/a$ symmetry, which confirms the presence at Băiţa Bihor of this polytype and agrees perfectly with the results of the TEM study and with the findings of Lovas & Dodony (1997), who studied the type material.

The mean parameters obtained as weighed average of the different values in Table 6 are *a* 12.559(18), *b* 10.402(12), *c* 3.132(8) Å and β 95.77(33)°, where the errors in the brackets correspond to the standard deviations of the mean (2σ) for each set of data in the table. These cell parameters do not differ substantially from those reported by Lovas & Dodony (1997) for the type material [*a* 12.571(1), *b* 10.4025(9), *c* 3.1333(4) Å and β 95.60(1)°]. They are slightly greater than those determined by Brovkin & Nekrasov (1966) for the synthetic szaibelyite of stoichiometric composition (*a* 12.539, *b* 10.390, *c* 3.122 Å and β 94.08°), which may be explained by the limited (Fe^{2+},Mn,Ca)-for-Mg substitutions. Substitution of larger cations ($^{VI}Fe^{2+}$ = 0.77 Å, ^{VI}Mn = 0.82 Å, ^{VI}Ca = 1.00 Å) for the smaller ^{VI}Mg [r = 0.72 Å; all ionic radii values from Shannon (1976)] should cause an increase in the cell dimensions. This is the case for the cell volume, but the cell-parameter changes are very anisotropic. One may use the comprehensive factor k as an expression of the mean cation radius calculated assuming the chemical compositions. The values of k, calculated as $k = 0.01 \bullet (X_{Mg} \bullet r\,^{VI}Mg + X_{Mn} \bullet r\,^{VI}Mn + X_{Fe} \bullet r\,^{VI}Fe^{2+} + X_{Ca} \bullet r\,^{VI}Ca)$, are given in Table 6. The data show that, in spite of an important spread of the values, the correlation between k and *b* is positive (correlation coefficient $k_b = 0.31$), whereas the correlation between k and β is negative (correlation coefficient $k_\beta = -0.39$). On the contrary, the cell parameters *a* and *c* remain practically constant within the standard errors.

THERMAL BEHAVIOR

Many authors (*e.g.*, Watanabe 1953, Shabynin 1955, Lee 1958, Grigoriev *et al.* 1966, Melnik *et al.* 1984, Lisitsin *et al.* 1985) have previously studied the thermal behavior of szaibelyite. All recognized on the DTA curve a single major endothermic effect, corresponding to dehydration. This effect was recorded at 640°C by Melnik *et al.* (1984), at 670°C by Watanabe (1953) and Lisitsin *et al.* (1985), at 680°C by Lee (1958) and at 690°C by Shabynin (1955). The discrepancy between the quoted temperatures may be due to differences in grain size, heating rate or composition among the analyzed samples.

Figure 4 shows DTA, DTG and TGA curves of a selected sample of szaibelyite from Băiţa Bihor, whereas Table 7 gives the temperatures and weight losses corresponding to the main effect, as recorded for five samples.

Prior to analysis, the samples were desiccated for 12 hours at 110°C. Consequently, no losses in H_2O were recorded between 20 and 110°C. Instead there is a slight loss in weight between ~150°C and ~600°C, the temperature of the beginning of the endothermic effect recorded on the DTG curves. This weight loss is evidently due to the loss of H_2O, identified by infrared spectrometry of the evolved gases. Between ~600 and 700°C, hydroxyl is abruptly expelled as H_2O. Lines of szaibelyite may be recognized in the XRD patterns until 650°C. After 300°C, however, there is a progressive decline in the intensities of the szaibelyite reflections, accompanied by line broadening, and the pattern changes visibly at 700°C (Marincea 1998). Although all hydroxyl is lost at 650–680°C, remnants of the original unit-cell volume persist at least to 700°C. Possibly this pattern is attributable to a slow accommodation to the structure of the anhydrous pyroborate that results by dehydration.

TABLE 7. THERMAL BEHAVIOR OF SELECTED SAMPLES OF SZAIBELYITE FROM BĂIȚA BIHOR

Sample	Temperature of the main endothermic effect on various curves (°C)			Cumulative loss in weight on TGA$^{(1)}$ curve (wt.%)		Loss on ignition (wt.%)		Enthalpy, based on the DSC curve (mJ)
	DTA$^{(1)}$	DTG$^{(1)}$	DSC$^{(2)}$	600°C	700°C	600°C	700°C	
1043	670	655	662	3.39	12.58	3.05	12.82	-7117.93
1406	660	655	-	0.55	11.25	0.50	11.20	-
1659	655	635	-	1.90	12.50	1.75	12.36	-
1672	660	640	-	1.30	12.00	1.25	12.04	-
1848	660	635	659	1.78	10.26	1.54	11.08	-7654.98

(1) recorded in air, at a heating rate of 10°C/min.
(2) recorded in nitrogen, at a heating rate of 20°C/min.

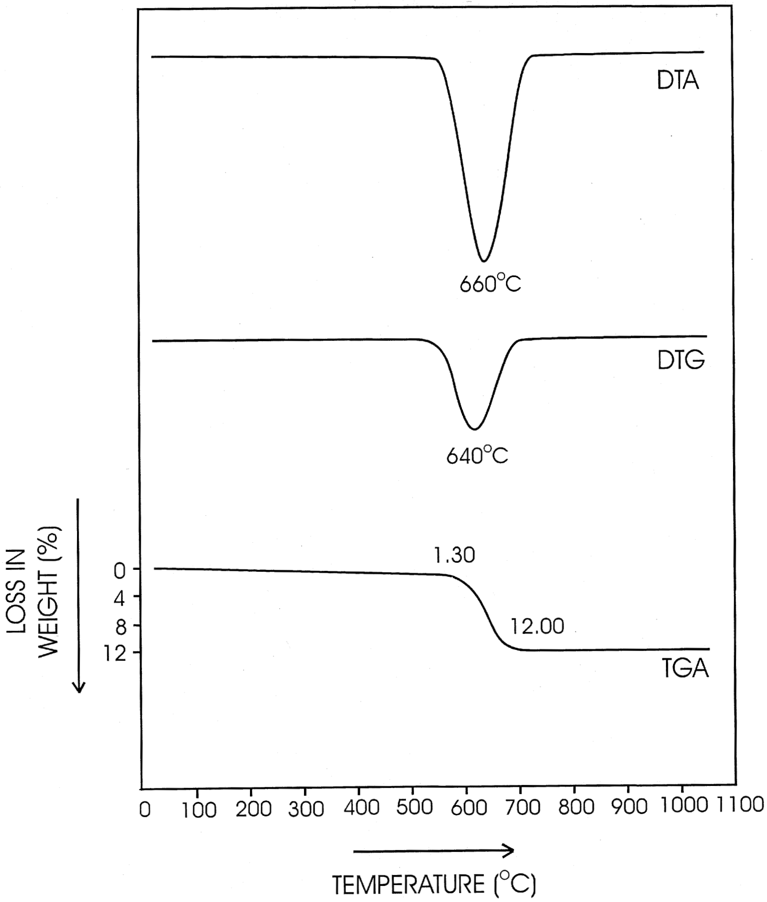

FIG. 4. Thermal curves recorded for a selected sample of szaibelyite from Baĭţa Bihor (sample 1672): differential thermal analysis (top), differential thermogravimetric analysis (middle), and thermogravimetric analysis (bottom).

The pronounced DTA peak centered at about 650°C marks the complete dehydration of the samples. Analysis of the evolved gas by IR indicates that the weight loss should be entirely attributed to the loss of H_2O. Note, however, that fluorine is in all cases below the detection limit (~0.1 wt.%) of the infrared gas chromatograph used here. The endothermic effect at ~650°C corresponds to weight losses of 9.19–10.70 wt.% (Table 7), lower than the ideal value of 10.71 wt.% H_2O in szaibelyite, but also lower than the total weight losses. The thermal decomposition of szaibelyite starts in reality at approximately 150°C and is complete at 650–680°C. Up to 30 wt.% of the H_2O in the "free" hydroxyl groups (*i.e.,* those not included in pyroborate anions) is expelled before 650°C. In disagreement with data reported by Grigoriev *et al.* (1966) for "hydroxylascharite", no endothermic effect in the range between 150°C and 200°C was detected on the DTA curves.

X-ray powder-diffraction data for the breakdown product can be indexed on the basis of the unit cell of the monoclinic ($P2_1/a$) polymorph of $Mg_2B_2O_5$, which yields the unit-cell parameters in Table 8.

INFRARED-ABSORPTION DATA

A representative infrared-absorption spectrum of selected samples of szaibelyite from Băiţa Bihor is given in Figure 5, whereas band positions and intensities obtained for three representative samples, whose location is given in Table 6, are listed in Table 9, together with data taken from the literature.

All the infrared spectra show, in the principal OH-stretching region, a prominent absorption band at ~3560 cm^{-1} and a broad, poorly resolved one centered at ~2510 cm^{-1}. A broad hump centered at ~3410 cm^{-1} also occurs in some cases, but it is always associated with ab-

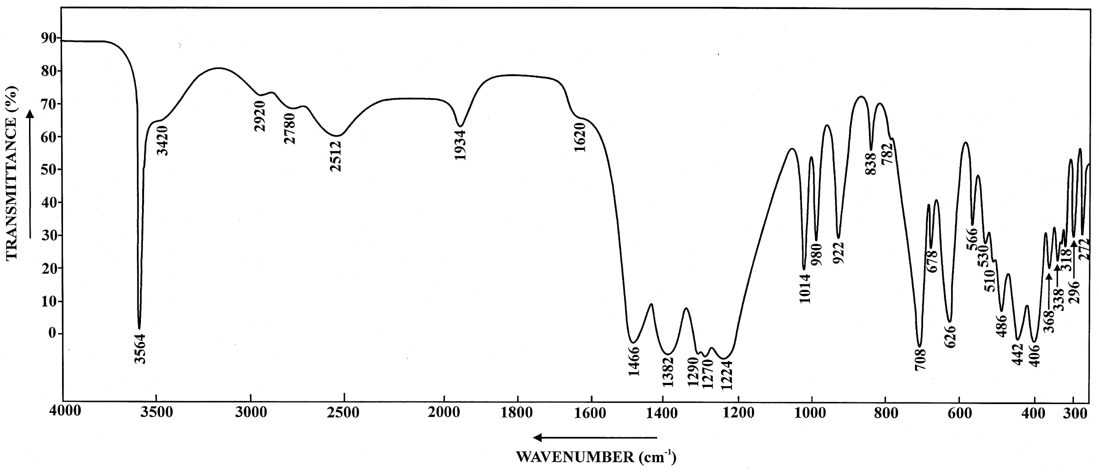

FIG. 5. Infrared spectrum of a selected sample of szaibelyite from Baĭţa Bihor.

TABLE 8. CRYSTALLOGRAPHIC DATA FOR $Mg_2B_2O_5$ OBTAINED AS BREAKDOWN PRODUCT OF SZAIBELYITE

Sample	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
1043	12.302(2)	3.126(1)	9.177(3)	104.53(2)	341.558
1406	12.295(5)	3.122(1)	9.201(6)	104.38(3)	342.148
1672	12.308(11)	3.126(6)	9.211(6)	104.40(4)	343.263
1848	12.311(5)	3.126(1)	9.203(5)	104.05(3)	343.541

sorption at 1620–1640 cm^{-1}, suggesting that these samples contain adsorbed (molecular) water.

Inspection of the structure proposed for szaibelyite by Takéuchi & Kudoh (1975) indicates the O(2) and O(3) anions as hydrogen-bond acceptors, the two hydrogen bonds being O(4)–H...O(2) and O(6)–H...O(3), respectively. There are consequently two distinct hydrogen positions in the structure. Two OH-stretching bands are thus expected to occur. All the authors who have previously presented infrared spectra of szaibelyite in the fundamental-stretching region (*e.g.,* Moenke 1962, Akhmanova 1962, Plyusnina & Kharitonov 1963, Weir 1966, Suknev & Brovkin 1970, Lisitsin *et al.* 1985) have already identified the high-wavenumber band. Some of them (*i.e.*, Plyusnina & Kharitonov 1963, Suknev & Brovkin 1970, Lisitsin *et al.* 1985) also reported at least one low-wavenumber OH-stretching band; however, many of their samples are suspected to contain adsorbed H_2O or other (hydrous) impurities, and the spectral range between 1700 and 3000 cm^{-1} was generally ignored (Table 9).

The band at ~2510 cm^{-1} is of particular interest, because it was ignored in all but two of the cited works (Table 9). Its lower frequency and broadness indicate stronger hydrogen bonding (Nakamoto *et al.* 1955). Taking into account the structure resolved by Takéuchi & Kudoh (1975), the high-wavenumber band at ~3560 cm^{-1} may be assigned to the weak hydrogen bond involving O(6)–H...O(3), whereas that at ~2510 cm^{-1} corresponds to the stronger one, involving O(4)–H...O(2). Using the equation proposed by Libowitzky (1999) in order to correlate the O–H...O bond lengths with the O–H stretching frequency [$\nu_{O-H} = 3592 - 304 \bullet 10^9 \bullet \exp(-d/0.1321)$], it is possible to calculate the positions of the two OH-stretching bands. They must occur at 3419 and 2461 cm^{-1}, for O–O distances of 2.812 and 2.564 Å, respectively (Takéuchi & Kudoh 1975). Small displacements toward wavenumbers higher than those theoretically predicted occur in the case of both bands; the origin of these displacements must be sought in the non-linearity of the O–H...O bond (Nakamoto *et al.* 1955). Three other absorption bands, ignored by most of the previous authors (Table 9) occur at ~1930, ~2780 and ~2920 cm^{-1}, respectively. Since they are reduced to a single absorption maximum by deuteration (Suknev & Brovkin 1970), the absorption maxima at ~2780 and ~2920 cm^{-1} must represent a single band, split by resonance interactions. As in most of the acid salts with asymmetric hydrogen bridges (Ryskin 1974), these bands must represent overtones of the OH-bending modes. Judging by their spectral position and shape, the medium-to-strong absorption bands at ~1270 and ~925 cm^{-1} could be assigned to the bending motions δ (OH) (in plane) and γ (OH) (out of plane) of the B–OH bond. The three γ (OH) and two γ (OH) overtones must consequently occur near the values recorded for the bands at ~2780–2920 cm^{-1} and ~1930 cm^{-1}, respectively, whereas the two δ (OH) band must be superposed on the OH-stretching band at ~2510 cm^{-1}.

The spectral region between 1600 and 600 cm^{-1} hosts bands that may be essentially assigned to the vibrational motions of the (B_2O_4OH) structural group (Takéuchi 1958). It is possible to assign most of the

TABLE 9. INFRARED FREQUENCIES (cm^{-1}) RECORDED IN THE SPECTRA OF SZAIBELYITE FROM BĂIȚA BIHOR, AS COMPARED WITH SIMILAR DATA FROM LITERATURE

Takéuchi (1958)	Moenke (1962)	Akhmanova (1962)	Plyusnina & Kharitonov (1963)	Weir (1966)	Suknev & Brovkin (1970)	Sample 1043	Sample 1394	Sample 1406	Character, intensity(1)
3552	3568	3560	3534	3555	3570	3564	3560	3560	s, sh
-	-	-	3096	-	2930	2920	2918	2922	w, b
-	-	-	2688	-	2780	2780	2780	2780	w, b
-	-	-	2475	-	2520	2512	2520	2508	m, b
1900	-	-	1953	-	1940	1934	1932	1932	m-w, b
-	1640(2)	1640-1500	-	-	-	1620(2)	-	-	w, b
-	1482	-	1452	1425	1470	1466	1470	1460	vs, sh
-	1385	1380	1399	-	1400	1382	1400	1400	vs, sh
1270	1280	1290	1276	1270	1280	1290	1290	1285	s, b (shd)
-	1254	-	1242	1245	1250	1270	1270	1265	m-s, sh
1230	1225	1220	1224	1230	1230	1224	1232	1228	m-s, b
1075	-	1090	-	1085	-	-	1090	1085	w, shd
1010	1014	1020	1015	1010	1018	1014	1014	1014	m, sh
979	982	980	982	977	983	980	980	980	m, sh
921	928	925	920	922	927	922	924	924	m, sh
830	840	840	840	835	843	838	840	840	w, b
775	790	790	789	785	790	782	785	780	w, b
-	707	710	706	700	710	708	706	708	vs, sh
690	682	-	680	-	683	678	680	680	m-s, sh
-	626	620	628	625	626	626	628	626	vs, sh
-	568	565	565	570	568	566	566	568	m, sh
-	539	535	-	538	535	530	532	532	m, sh
-	512	505	-	-	510	510	510	512	w, sh
-	496	-	-	486	490	486	484	482	m, b
-	445	430-415	-	432	447	442	440	442	m, b
-	408	-	-	395	407	406	404	406	m, sh
-	-	-	-	330	-	368	364	364	m, sh
-	-		-	310	-	338	338	336	m, sh
-	-		-	-	-	318	318	318	m, sh
-	-		-	-	-	296	296	296	m, sh
-	-		-	-	-	272	272	270	m, sh

(1) intensities and character of the bands accorded with those reported by Takéuchi (1958), Weir (1966), Suknev & Brovkin (1970) and Gadsden (1975): s = strong; m = medium; w = weak; vs = very strong; sh = sharp; b = broad; shd = shoulder. For the bands not reported by these authors, as observed. (2) band due to the adsorbed water (see text). Samples located as in Table 6.

bands in this region by analogy with data on $Mg_2B_2O_5$ (Weir & Schroeder 1964, Suknev 1970). The bands around 1460, 1400, 1290 and 1230 cm^{-1} are probably due to the quadruply degenerate antisymmetric stretching of the BO_3 group. A supplementary band at ~1090 cm^{-1} may be due to the tilting motions of the O–O bases of the BO_3 triangles. The bands at ~1015 and ~840 cm^{-1} are probably due to symmetric B–O–B stretching vibrations, whereas the doublet at ~780 and ~705 cm^{-1} can be attributed to the out-of-plane bending of [BO_3]. Bands corresponding to the in-plane bending vibrations of this group must be those at ~680 and (probably) ~625 cm^{-1}.

The structure of szaibelyite was solved by Peng *et al.* (1963) and refined by Takéuchi & Kudoh (1975). Both studies showed that the dominant structural units are chains of edge-sharing distorted $Mg(O,OH)_6$ octahedra, two octahedra in width, running parallel to the *c* axis. Two non-equivalent chains share their O corners to form a sheet parallel to (100). The sheets are cross-linked by (B_2O_4OH) structural groups in which a BO_3 and a BO_2OH triangle polymerize by sharing an "O" corner. Taking into account the structure, the interpretation of infrared spectra at lower wavenumbers (less than 600 cm^{-1}) is more difficult, because several effects overlap (*e.g.*, rocking and torsion of the BO_2 "lateral" units in the [B_2O_4OH] structural group, hydroxyl librations, internal vibrations of the [$Mg(O,OH)_6$] octahedra), but lattice vibrations must predominate in this region. In the broad hump centered around 400 cm^{-1}, several bands overlap, generated by *M*–O stretching motions in octahedra and by B–O bending vibrations. The band at ~485 cm^{-1} has been tentatively assigned to an in-plane B–O motion by Weir & Schroeder (1964), but this assignment is uncertain as a similar band is observed at 490 cm^{-1} in the spectrum of periclase (Farmer 1974). A low-intensity band observed at ~405 cm^{-1} may be tentatively assigned to a bending motion of the hydroxyl groups, as in the case of brucite, where a such band occurs at ~415 cm^{-1} (Ryskin 1974).

DISCUSSION AND CONCLUSIONS

From textural and paragenetic relationships, szaibelyite at the type locality may have formed not only during retrograde metamorphism, but also as a primary phase. Szaibelyite II, formed by replacement of suanite, ludwigite, fluoborite or kotoite, generally encloses relics of these minerals and maintains diagnostic textural signs of pseudomorphism, for example bunches of crystals or radiating aggregates. The randomly oriented, felt-like fibers of szaibelyite, the sheaf-like or radiating aggregates free of relics or the crystals isolated in the carbonate matrix may be interpreted as a product of the direct metasomatism of dolomite at a higher activity of H_2O and boron. On the basis of reciprocal textural relationships (*e.g.*, szaybelyite I rimming fluoborite veins that cross-cut chondrodite crystals), the primary szaibelyite may have formed nearly simultaneously with fluoborite, but later than the discrete grains of chondrodite.

The well-constrained paragenesis and the intimate relationship between szaibelyite II and serpentine, on the one hand, and between szaibelyite and the surrounding calcite, on the other hand, can provide important constraints concerning the physicochemical conditions of crystallization. The temperatures resulting from the application of the calcite–magnesite geothermometer of Rice (1977) on calcite coating szaibelyite I are 311–465°C for magnesite contents of 0.80–3.20 mol.% (Marincea 1998). Assuming that calcite in the rim cocrystallized with szaibelyite, this range of temperature may be presumed to define the upper temperature-limit for the crystallization of szaibelyite by boron metasomatism of the pre-existing dolomite. On the other hand, the textural features described above suggest that the crystallization span of szaibelyite II is defined by the coeval alteration of chondrodite to serpentine. A minimum temperature for szaibelyite crystallization could thus be estimated from the stability field of serpentine. Stable isotope data from chrysotile and lizardite associated with magnetite in serpentinites suggest that these serpentine species can form at temperatures between 130 and 260°C (Wenner & Taylor 1971, 1974). At Băiţa Bihor, these species are invariably associated with szaibelyite II. Accepting that the isotopic equilibria in the two situations are practically the same, the lower boundary of the temperature range for the replacement parageneses can therefore be estimated at less than 260°C, as defined by the simultaneous development of serpentine. A compilation of experimental data presented by Barsukov & Kurilshikova (1957), Grigoriev & Nekrasov (1966) and Nekrasov & Malinko (1973) indicates that, at low pressures, szaibelyite may indeed crystallize between 160° and 260°C.

Brucite is rarely associated with secondary szaibelyite, which indicates that in most cases the borate in replacement aggregates was formed according to the reaction suanite + H_2O = szaibelyite (*e.g.*, Aleksandrov 1982). According to the experiments of Grigoriev & Nekrasov (1966), szaibelyite may form by this reaction below 250°C. Experimental investigations of Grigoriev & Nekrasov (1966) and Aleksandrov (1974) showed that, at low pressures (up to 1 kbar), szaibelyite is a stable phase in the system $MgO – B_2O_3 – H_2O \pm CO_2$ below 450°C; above this temperature, it breaks down to suanite. There is, however, no evidence that the conditions of these experiments are close to those expected during the period of szaibelyite crystallization. None of the experiments cited above took into consideration the presence of fluorine in the system, whereas the magnesian skarns from Băiţa Bihor are extremely rich in F-bearing minerals, such as chondrodite, norbergite, fluoborite, phlogopite and fluorite. This overall paragenesis indicates a much higher activity of fluorine than in other boron-bearing magnesian skarns in Romania, which explains the fluorine content of szaibelyite. Fluorine undoubtedly affected the equilibria among (F–OH)-bearing phases, but the reasonable agreement between the experimental temperatures and those estimated from carbonate geothermometry or suggested by the association chrysotile (lizardite) – szaibelyite indicates a relatively low influence of the fluorine activity on the temperatures of crystallization.

Constituents other than fluorine probably did not influence the phase equilibria. Low potentials of iron and manganese are clearly indicated by the low contents in these elements of all minerals occurring in the szaibelyite-bearing skarns. In fact, the boron-bearing skarn from Băiţa Bihor is characteristically iron-poor and clearly differs from other similar deposits in Romania (*i.e.*, Ocna de Fier, Cacova Ierii or Maşca–Baişoara), where ludwigite is the main rock-forming mineral and magnetite is abundant.

As for the pressure of formation, the stability of the association suanite + spinel indicates a maximum value of 3 kbar, whereas the absence of calcium borates shows that at Băiţa Bihor, pressure exceeded 0.6 kbar (Pertsev 1977).

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