NEW AXINITE OCCURRENCE FROM BÜKK MTS., NE HUNGARY

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Abstract: The ‘Y-adit’ (Lillafüred, Bükk Mts.) was known for years as the only axinite (Ca-Al-borosilicate mineral group) occurrence from Hungary. Here the axinite is the component of hydrothermal quartz – albite – chlorite – calcite veins, in Triassic metabasalts. We report a new, recently discovered axinite occurrence from the Bükk Mts., at Létrás-tető Hill. This new occurrence is in the vicinity of the Y-adit, but the two axinite-bearing parageneses are completely different from each other. The newly discovered axinite is the rock-forming component in Triassic metabasalts of the Szentistvánhegy Metavolcanic Formation. The rock body suffered potassic metasomatism, which overprinted the axinite formation. The source of the boron and the relationship with other borosilicates from the Bükk Mts. has not been clarified yet.

Keywords: axinite-(Fe), Bükk Mts., boron, potassic metasomatism, metavolcanics

1. INTRODUCTION

Axinite group comprises triclinic, boron-bearing sorosilicate minerals. The word “axinite” originates from the Greek word αξίνα (“axina”, meaning axe) and refers to the characteristic habit of the euhedral crystals. The end-members of the axinite group are axinite-(Fe) [Ca2FeAl2BO3Si2O12(OH)], axinite-(Mg) [Ca2MgAl2BO3Si2O12(OH)], axinite-(Mn) [Ca2MnAl2BO3Si2O12(OH)] and tinzenite [(Ca,Mn,Fe)3Al2BO3Si2O12(OH)]. A miscibility gap exists between axinite-(Fe) and axinite-(Mn), and between axinite-(Mn) and tinzenite at low temperature. As the temperature is increasing, the Mn content of axinite-(Fe) and the Fe content of axinite-(Mn) is typically increasing [1]. The crystal structure of axinite is composed of tetrahedrally and octahedrally coordinated cations. The tetrahedra are built by B2SiO10 planar clusters (six-membered ring from two disilicate groups, connected by two BO4 tetrahedra), while the octahedra form Fe(Mn,Mg) – Al – Al – Al – Al- Fe(Mn,Mg) finite chains, connected by CaO6 octahedra [2].

In the Carpathian region axinite is known from two types of environments: (1) in hydrothermal veins of metamorphic rocks; and (2) in the contact zones of granitoids and sedimentary or volcanic rocks [3]. The occurrence known from the Bükk Mts. [4, 5], where axinite-(Fe) occurs as the constituent of alpine-type hydrothermal
quartz – albite – chlorite – calcite veins in the Triassic Szinva Metabasalt Formation (Y-adit, Lillafüredi), fits into the first genetic type. Here the axinite is homogeneous or slightly zoned and has two distinguishable generations, due to two hydrothermal events. Accessory minerals are titanite, apatite-(F), magnetite, hematite, and Fe-Ti-oxides.

Besides axinite, other borosilicate minerals are also known from the Bükk Mts. The schörler variety of tourmaline \((NaFe^{2+}_6Al_4(BO_3)_3Si_6O_{18}(OH)_3)\) was described from the Bagolyhegy Metarhyolite Formation, both as a constituent of quartz – albite (+/- epidote – chlorite – Fe-oxide) veins and within the cement of brecciated quartz – orthoclase veins. A less significant tourmaline (dravite variety) occurrence is known in the Szentistvánhegy Metavolcanics, at Felsőhámor [6, 7].

The newly found axinite occurrence is in a completely different paragenesis than the known one. It is a rock-forming constituent of Szentistvánhegy Metavolcanics, at Létrás-tető, Bükk Mts. We have investigated the chemical and mineralogical composition of the axinite-bearing rock body, the wall rock shale, and related metavolcanics from the vicinity (from Szinva Metabasalt). The composition of some further metavolcanics samples from the Szentistvánhegy Metavolcanics are also used for comparison [8].

2. GEOLOGICAL BACKGROUND

The age of the outcropping rocks of the Bükk Mts. extends from the late Carboniferous to the Jurassic. In the area of “Bükk Paraautochthonous” (i.e., Pre-Cenozoic Bükk without the Szarvaskő unit), the Permian-Triassic marine succession starts with continuous coastal and shallow water sedimentation from the Late Permian to the Early Triassic. It was interrupted by extended volcanism in the Ladinian, then carbonate platforms, and basin facies sedimentation followed in the Middle and Late Triassic. After a sedimentary gap, this succession is overlain by Jurassic deep-sea siliciclastic-carbonate sediment [9]. In the Late Cretaceous, the Paleozoic-Mesozoic rocks of the Bükk underwent dynamothermal anchizonal regional metamorphism, however, the degree of metamorphism is not uniform [10].

The Triassic succession of Bükk Mts. contains three metavolcanics formations. The Bagolyhegy Metarhyolite has a within-plate character, and probably is the proximal product of a single volcanic center. The Szentistvánhegy Metavolcanics forms a Ladinian horizon composed of calc-alkaline rocks and originated from a chain of several volcanic centers. Szinva Metabasalt bodies are embedded in Carnian limestone, generated due to local submarine alkali basalt flows. The formations can be separated from each other based on their trace element signature \((Zr/TiO_2, Nb/Y, Nb/Ta ratios)\) [8]. From these three formations, the Szentistvánhegy Metavolcanics is the most diverse both in terms of geochemistry and mineralogy, and also this is the one to which the investigated axinite-bearing rock body belongs.

The site of the studied axinite-bearing body is characterized by the outcrops of several fragmented metavolcanic bodies originating from all three formations at a major tectonic boundary zone (Figure 1). The axinite bearing body is a fault block,
at several tens of meters scale, embedded in a shale matrix, without dynamic metamorphic features.

**Figure 1**
Schematic geological map of the wider zone of the studied rock bodies (a) and its location within the Carpathian Basin (b) and the Bükk Mts. (c). On the geological map yellow signs indicate the sites of axinite-bearing bodies. The SE locality was studied by [4, 5], and the NW is described in this study.

3. **APPLIED METHODS**

The chemical compositions of the samples were determined by the laboratory of ALS Global for major, minor, and trace elements as well. The major and minor elements were measured by a ME-ICP06 analysis based on aqua regia dissolution and the ICP-AES method. ME-MS81 analyses have been carried out to determine trace elements (Li-borate digestion, four acid dissolution, and ICP-MS technique). On the axinite-bearing sample ME-ICP82b analyses (Na2O2 dissolution and ICP-AES) were used to measure the boron and lithium content. In the case of some samples, the X-ray fluorescence spectrometry (XRF) method was also carried out, with a Rigaku Supermini 200 WDXRF instrument (200 W Pd X-ray tube, 50 kV accelerating voltage, 4 mA current, LiF200 / PET / XR25 crystals, 4 g pellets with CEREOX) to determine the chemical composition at the Institute of Exploration Geosciences, University of Miskolc.

The qualitative and quantitative mineralogical composition was determined by X-ray powder diffraction (XRD). For the measurement, a Bruker D8 Advance (40 kV, 40 mA Cu Kα radiation) instrument with a Vantec-1 position sensitive detector, in parallel beam geometry using a Göbel mirror. The phase identification was carried
out using Diffra

\textit{c} Plus EVA software, based on the ICDD PDF2 2005 database, while the quantitative evaluation was carried out in Topas4 software with Rietveld refinement method (NIST SRM 640b Si calibration standard, crystal structure information from AMCSD [11]).

Electron-microprobe studies on carbon-coated polished slabs were used to measure the chemical composition of individual grains (energy dispersive X-ray spectrometry, EDX point measurements, and X-ray maps) and to observe the distribution of the different minerals on back-scattered electron (BSE) images. For the electron microprobe studies, we used a SamX-controlled JEOL JXA 8600 Superprobe (20 kV accelerator voltage, 20 nA beam current), equipped with an SDD-EDX detector.

Textural characteristics and mineralogy were investigated also by optical microscopy on 30 μm thin sections in transmitted light (Zeiss Imager A2m AXIO polarization microscope, Zeiss AxioCam MRc5 camera). All measurements described above except the bulk chemical analyses were performed at the University of Miskolc.

4. RESULTS

4.1. Chemical composition

Within the occurrences of Szentistvánhegy Metavolcanics, the axinite-bearing body belongs to the Bükkszentlászló block [8]. Table 1 summarizes the major and minor element composition, while Figure 2 shows the trace element composition of some selected samples from this block (sample IDs with letter B), together with some others from Szentistvánhegy horizon and Kis-fennsik area (A) from [8], where the trace element composition refers to andesitic or basaltic composition. Heterogeneity of the chemical composition originates partly from initial magmatic composition but also reflects metasomatic alteration. The axinite bearing body (sample B2/1 and B2/2) has relatively high K-, Ba- and Rb-content, which indicates potassic metasomatism.

![Figure 2](image)

*Figure 2*

Trace element concentration plot of selected Szentistvánhegy Metavolcanics samples. The axinite bearing sample (B2/1) is shown with the red line.
The Sr displays characteristic negative anomaly – compared to the upper continental crust [12] – similar to the other occurrences lacking axinite. Linking REE and P to mineral phases is done by electron microprobe investigations. Contrasting major element characteristics are high K content, associated with low Ti content among the studied samples.

Table 1

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<th>Al$_2$O$_3$</th>
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<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>TiO$_2$</th>
<th>P$_2$O$_5$</th>
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<td></td>
<td></td>
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<td>3.0</td>
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<td>0.20</td>
<td>1.14</td>
<td>0.02</td>
<td>6.44</td>
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</tbody>
</table>

In addition to the usual chemical tests, boron content was also measured in sample B2/1, after sodium peroxide fusion. This test was not performed on the other samples. Based on the results, the axinite-containing rock bodyit contains 1770 ppm boron, meaning a net enrichment of 104 times compared to the upper crust.
Li-concentration of the body is approximately corresponding to the crustal average (19 ppm).

4.2. Mineralogical composition analysis of the axinite-bearing body

Based on the XRD analysis (Table 2), more than 60 wt% of the axinite-bearing sample consists of feldspars (mainly potassic feldspars, less albite). Other important constituents are phyllosilicates (chlorite, biotite), diopside, actinolite, and titanite. The axinite constitutes 6 wt% of the whole sample (Figure 3). This composition differs significantly from the previously known body with axinite-bearing veins [4, 5] as this rock contains no calcite and quartz and only a low amount of albite.

![XRD diffractogram of the axinite-containing rock body](image)

**Figure 3**

XRD diffractogram of the axinite-containing rock body

Generally, metavolcanics from the Bükk Mts. were the subject of several rock alteration processes, which resulted in various chemical and mineralogical compositions, and only trace element geochemistry is suitable to identify the common protolith. The mineralogical compositions of rock bodies from Szentistvánhegy Metavolcanics are diverse (Table 2), but even so, sample B2 is considered unusual in many ways. The highest potassic feldspar content is coupled with the lack of quartz. Ca-Al silicates are generally present in the metavolcanics, as the products of the metamorphism, like (allanitised) epidote, clinozoisite, pumpellyite, prehnite, and titanite; the axinite-bearing samples contain no more of these than titanite in a quantity high enough to be detectable with XRD. Furthermore, this is the only rock body of the Szentistvánhegy Metavolcanics which contains pyroxene and actinolite in higher amounts.
New axinite occurrence from Bükk Mts., NE Hungary

Table 2

Mineralogical composition of selected Szentistvánhegy Metavolcanics samples, based on XRD analyses. B2 represents the axinite-bearing body (data from [8])

<table>
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<tr>
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<th>B7</th>
<th>B17</th>
<th>A12</th>
<th>A3</th>
<th>A4</th>
<th>A7</th>
<th>A8</th>
<th>B9</th>
<th>B10</th>
<th>B30</th>
<th>B4</th>
<th>B18</th>
<th>B31</th>
<th>B29</th>
<th>B2</th>
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<tbody>
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<td>Quartz</td>
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<td>37.9</td>
<td>28.7</td>
<td>27.3</td>
<td>30.0</td>
<td>19.3</td>
<td>51.5</td>
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<td>26.6</td>
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<td>34.8</td>
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Based on the electron microprobe analyses, the Fe-dominant member of the axinite group occurs in the studied rock body, just like in the case of the earlier known occurrence (Figure 4). Axinite appears as tabular, euhedral, whitish, some 100 µm or even mm-sized crystals, which are well observable with optical microscopy (Figures 5, 6). It occurs as a rock-forming constituent and not as a vein-filling mineral, which is a unique phenomenon in global terms. Rock-forming axinite was described before only from New Zealand [13, 14], but the reliability of this information can be questioned.

Axinite crystals are partly decomposed and substituted by potassic feldspars, and in a lesser amount albite (Figure 7) in the typical K-feldspar and chlorite-dominated matrix. Rare earth elements can be detected in the axinite as micrometric inclusions in rare cases. Axinites are surrounded by unoriented, few tens of micrometers long actinolite laths (Figure 8). The matrix is composed of potassic feldspar and chlorite, with minor albite. The potassic feldspars are euhedral in some cases. The albite crystals are often nested, surrounded by more intensively chloritized areas, from where the axinite is usually absent. Sporadically allanite-(Ce), and as its weathering product cerianite-(Ce) can occur, as well as euhedral zircon. Apatite and resorbed titanite are also typical.
Figure 4

Crystal chemical classification of axinite from the investigated and the previously known occurrence [5]. Note that the crystal chemistry was measured with a different tool and technique (EDX in this study and WDX previous study).

Further, typical accessories are Fe-oxide patches hosting a wide range of elements such as Al, Si, P, Pb, V, Cu, Zn, and As (Figure 9), yet the Fe-oxide phases (amorphous or crystalline) and the relation of hosted elements (ionic replacement or nanoinclusions) are undefined. The presence of the first three elements is usual in Fe-oxides from the Bükk Mts, but the others are not typical in other rock bodies. Pb-V-Zn-As-bearing mineral phases occur individually also as nests of micrometric grains, in albitic–chloritic domains (Figure 10). Chemical compositions measured by EDX are not precise enough to identify these minerals, due to their small grain size, but most probably they are the members of the brackebuschite supergroup. It cannot be excluded that the appearance of the Pb-V-Zn-Cu-As-bearing phases is connected to the axinite, as many examples are described in the literature, where axinite and Pb–Zn mineralization are coupled [15–18].

It is possible, that not the axinite is the only B-bearing mineral phase in the rock body, as B concentration calculated based on the axinite content (6 wt% axinite, with 1.9% boron meaning 1146 ppm boron) is less than B concentration measured with ICP-AES (1770 ppm). From the identified minerals, feldspars can incorporate B, as well as the amorphous material, which according to the balanced XRD and major element content is a Fe-rich aluminosilicate material, also hydrated based on the L.O.I data.
New axinite occurrence from Bükk Mts., NE Hungary

Figure 5
Axinite-(Fe) with polarizing microscope (1N)

Figure 6
Axinite-(Fe) with polarizing microscope (XN)

Figure 7
X-ray map of an axinite-(Fe) crystal partly replaced by potassic K-feldspar (Kfs) and albite (Ab). (Ap = apatite, Ax = axinite, Chl = chlorite)

Figure 8
BSE image showing the unoriented actinolite (Act) laths around the axinite (Ax) crystal (Ab = albite, Kfs = K-feldspar, Tn = titanite)

Figure 9
BSE image showing Fe-oxide rich in Si, Al, P, Pb, Cu, Zn, and As (left) and its EDX spectrum (right). One of the pores of the Fe-oxide mineral contains axinite-(Fe). (Ab = albite, Ax = axinite, Fe-ox = Fe-oxide, Kfs = K-feldspar)
4.3. Mineralogy of neighboring rocks

The shale wall rock (sample B2/3) is composed mainly of albite with minor sericite and potassic feldspar, calcite nests are abundant in the highly foliated texture. Typical accessory minerals are slightly decomposed titanites, and micrometric allanites (often connected to apatite), sometimes monazite and barite.

Metavolcanics from two small bodies in the close vicinity (samples 1812 and 1819) have a different composition than the axinite bearing body, corresponding to the doleritic variety of Szinva Metabasalt. Their matrix is composed of albite and chlorite, with subordinate potassic feldspar while diopside is common in both bodies. Apatite usually occurs as some μm-long, often fractured needles (Figure 11). The low-grade
metamorphism led to the generation of Ca-Al-silicates, such as epidote and pumpellyite. Resorbed titanites (sometimes with ilmenite) and relict zircons may occur. The two samples are very similar with some differences. Biotite is abundant in sample 1819. Sample 1812 is characterized by smaller grain size, a lesser amount of pyroxenes, more chlorite, and significantly less biotite. In sample 1819 biotite plates are often partly replaced by a Ca-Al-silicate mineral along the cleavage planes (Figure 12). The chemical composition is closest to the grossular-andradite series (“gran-dite”) which can be characteristic for low-grade metamorphic facies [19, 20]. This phase was not described from the Bükk Mts. earlier, but even in our samples, it requires further investigations.

5. Discussion

The chemical and mineralogical composition of the samples can be interpreted as the axinite-hosting rock is metabasalt from the Szentistvánhegy Metavolcanics, which was subjected to a boron-bearing and a later stage potassic metasomatism. For the axinite formation, the chemical elements are abundant in any basaltic and andesitic rock, except for boron. Boron is an incompatible element, which means it is characteristic mainly for felsic melts, but the B content of the rocks usually decreases with H2O content. Micas can incorporate a significant amount of B, so shale-type sedimentary rocks and volcanics originating from the melting of this type of sediment can be rich in B. Smectites in the oceanic crust can absorb B from the seawater. Metamorphism, on the other hand, can lead to the depletion of B due to devolatilization [21].

The most common borosilicate minerals are tourmalines. In contrast to tourmalines, axinite usually develops in calcic-basic, Al-poor environments, at low CO2 fugacity, furthermore, it is usually generated at relatively low temperature and low pressure [1, 2, 13, 22], although the appropriate p–T range is wider than allowing any reliable conclusion for the original geological environment [22]. No experimental data are available regarding the pH conditions, but based on the characteristic paragenesis axinite is generated probably at elevated pH [23]. This is consistent with the observation of Hayes et al [24], who states that the amount of axinite is decreasing due to pH decrease. Although generally, the formation environment of axinite and tourmaline is not the same, there are examples where these two minerals occur together [1, 25, 26].

Fehér [7] assumes that tourmalines of the Bükk Mts. draw the B from the host metavolcanics, mostly metarhyolite. In his opinion, originally the boron content of the rock was hosted by phyllosilicates, but later it escaped due to metasomatism, leading to the currently measurable low boron content of the rock. Similar processes have often been described for the formation of axinite [13, 27, 28]. Other authors originated B through fault zones and fractures [22, 29], or rarely it is described as a primary magmatic compound [22]. It is also possible in our case that boron originated from metasomatized felsic metavolcanics of the magmatic suite.
Axinite can replace earlier mineral grains like epidote, amphibole, garnet, pyroxene, and feldspar [1]. Epidote and axinite can replace plagioclase [25]. Axinite can weather to secondary Fe-oxide – oxyhydroxide minerals, which are capable to incorporate metals into their structure [24], which might be a possible process in the Bükk Mts.

Usually, the axinite-bearing parageneses contain quartz, calcite, epidote, actinolite, and albite (e.g., [25]), although for the occurrence introduced in this study, only actinolite and albite are significant from these. The absence of calcite from the paragenesis is caused by Ca incorporation into other Ca-minerals, like pyroxene, amphibole, epidote, actinolite, or hornblende [22], however here only the amount of actinolite is significant. Furthermore, compared to the neighboring metavolcanics, the axinite-bearing body is relatively Ca-depleted. This may be the result of the potassic metasomatism, replacing a significant part of the Ca-bearing silicates, including the axinite grains partly, with potassic feldspars.

In the axinite-(Fe) bearing rock body the REE are incorporated into the allanite observed by electron microprobe, while P appears as apatite and Ti is contained in titanite. These phases are below the detection limit of XRD analysis.

6. SUMMARY AND CONCLUSIONS

A new axinite-(Fe) occurrence was found at Létrás-tető, Bükk Mts., NE Hungary, near another occurrence (Y-adit) known for years. While the formerly known axinite occurs in quartz–albite–chlorite–calcite veins of metabasalt, the axinite in the newly found occurrence is the rock-forming component of a B-K-metasomatized metabasalt in a fault block. The axinite formation precedes the potassic metasomatism, as axinite is partly replaced by potassic feldspars. The surrounding sedimentary rocks and metavolcanics do not contain axinite, meaning that boron metasomatism is a localized phenomenon. Based on the current result it is not obvious whether a genetic relationship between the two axinite occurrences, or between the axinite and the tourmaline occurrences of the Bükk Mts. exists.

ACKNOWLEDGEMENT

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REFERENCES

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