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First record of zinc-bearing spinel and staurolite from the metamorphic basement of the Transdanubian Midmountains Unit, W Hungary

Zn-tartalmú spinell és staurolit a Dunántúli-Középhegység metamorf aljzatából

Kálmán TÖRÖK[1]

(3 figures, 1 table and 1 plate)

Abstract

Breakdown of Zn-bearing staurolite to Zn-bearing spinel and andalusite is described from the Garabonc-1 borehole in the polymetamorphic basement of the Transdanubian Midmountains Unit, south of the Lake Balaton. This is a first record of the Zn-bearing spinel from the polymetamorphic crystalline basement in Hungary. Zn-bearing spinels formed under contact metamorphic conditions (P=100-200 Mpa and T= about 600 °C).

As revealed by the microprobe measurements, staurolites have quite uniform composition with ZnO content ranging between 1.18 and 2.37 wt%. In contrast with this the ZnO content of spinels varies within a much wider range (8.54-20.34 wt%).

Összefoglalás

A Garabonc-1 mélyfúrásban feltárt polimetamorf cordierites-andaluzitos csillámpalában Zn-tartalmú spinellt és Zn-tartalmú staurolitot azonosítottunk. A Zn-tartalmú staurolit szétesése Zn-tartalmú spinellé és andaluzittá kontakt metamorf körülmények között ment végbe kb. 100-200 MPa nyomáson és 600 °C hőmérsékleten.

A mikroszondás elemzések szerint a staurolit ZnO tartalma viszonylag szűk tartományban mozog (1,18-2,37%). Ezzel szemben a spinellekben mért ZnO mennyisége jóval tágabb határok között változik (8,45-20,34%).

Key words: spinel, staurolite, micaschist, polymetamorphism, contact metamorphism, Hungary

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[1] Department of Petrology and Geochemistry, Eötvös University, H-1088 Budapest, Múzeum krt. 4/a, Hungary

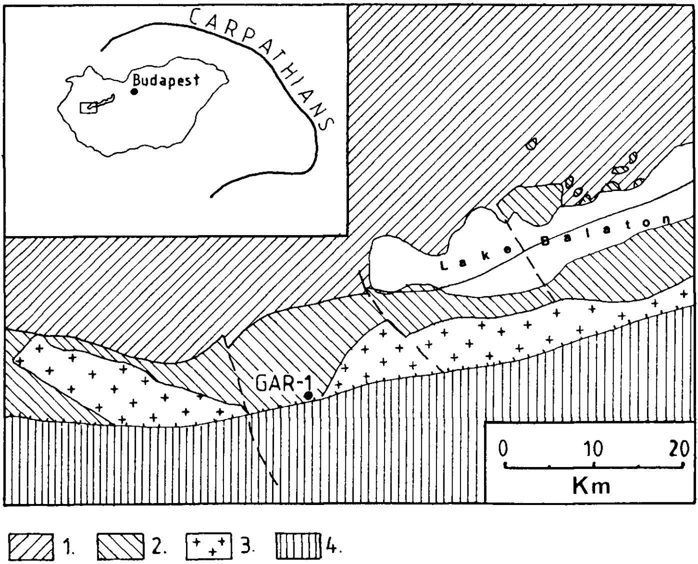

Fig. 1. Simplified geological map of the surroundings of the Garabonc-1 borehole (excluding Tertiary formations). **1.** Non metamorphic Upper Palaeozoic–Mesozoic of the Transdanubian Midmountains Unit. **2.** Lower Palaeozoic rocks of the Transdanubian Midmountains Unit, affected by very-low to low-grade Hercynian metamorphism. **3.** Hercynian granitoids of the Transdanubian Midmountains Unit. **4.** Unmetamorphosed or very-low to low-grade Alpine metamorphosed rocks of the Igal-Bükk Unit (Palaeozoic-Mesozoic). **barbed line** - Balaton-line; **solid** and **dashed** lines- other tectonic lines.

Introduction

This paper is devoted to the first description of zinc-bearing staurolite and zinc-bearing spinel from the metamorphic rocks of Hungary. Breakdown of staurolite to andalusite ± biotite have already been reported from the crystalline basement of southwest Hungary (ÁRKAI, 1984; TÖRÖK, 1990), but spinel was not involved in those reactions.

Formation of zincian spinel as a result of dehydration of zinc-bearing staurolite has been previously studied by ATKIN (1978), STODDARD (1979), and SCHUMACHER (1985). The P–T conditions usually reflect low-pressures and upper-amphibolite to lower-granulite facies conditions, though formation of zincian spinels in greenschist facies conditions has been reported (KRAMM, 1977) as well. The other common formation of zincian spinel is the desulfidation reaction of sphalerite (SPRY & SCOTT, 1986; MOORE & REID, 1988). A less common formation of Zn-bearing spinel is attributed to both retrograde and prograde breakdown reactions of biotite containing up to 0.24 wt% ZnO (DIETVORST, 1980).

Zinc-bearing spinel and staurolite have been found in a polymetamorphic cordierite andalusite-bearing micaschist penetrated in a depth range of 1962–1980 m in the borehole Garabonc–1. Location and a sketch geologic map is presented in Fig 1.

The micaschist has been affected by three metamorphic episodes (ÁRKAI, 1987; TÖRÖK, 1992).

Medium-pressure (800–900 MPa), medium-grade (500–550 °C) Barrovian-type metamorphism occurred first, defined by the appearance of staurolite and kyanite. The second metamorphic episode was low-pressure/medium-grade in character (200–300 MPa and 560–580 °C) marked by the formation of andalusite. Finally, contact metamorphism (100–200 MPa and 600–640 °C) was caused by an intruding granitoid body. The characteristic minerals are andalusite, cordierite, fibrolite and spinel.

The micaschist is composed mainly of quartz, biotite, muscovite, oligoclase, andalusite, with a minor amount of cordierite, staurolite, sillimanite (fibrolite), garnet, spinel, chlorite, tourmaline, sphene, ilmenite, rutile, zircon, monazite, xenotime, calcite, clay minerals, and ore minerals such as sphalerite, galenite and chalcopyrite. For more detailed petrographic and locality description refer to ÁRKAI (1987) and TÖRÖK (1992).

Staurolite-spinel relations

Staurolite is found exclusively as xenoblastic, ragged relics mantled by andalusite in association with biotite, pale green xenoblastic spinel and ilmenite (Plate 1, fig. 1). Biotite is sometimes missing from the assemblage. Spinel grains are found around the staurolites and are mostly in direct contact with them. Both minerals are wrapped around by the andalusite. Spinel is sometimes missing from the mineral paragenesis though staurolites in such places have the same composition as those in association with spinel.

There is no evidence on the zinc source of the staurolite which formed during the first, Barrovian-type metamorphic stage at pressures of about 800–900 MPa and temperatures over 550 °C as it was revealed by TÖRÖK (1992) using plagioclase-garnet-muscovite-biotite geothermo-barometry of GHENT and STOUT (1981). When the pressure dropped, the staurolite became unstable and transformed together with muscovite and quartz to andalusite and biotite during the second, low-pressure metamorphic stage. This reaction is marked by andalusites enclosing biotite and relict staurolite without spinel. Some of the staurolites have survived this reaction and partly broke down in the reaction:

$$\text{staurolite} + \text{muscovite} + \text{quartz} = \text{andalusite} + \text{spinel} \pm \text{biotite} \pm \text{ilmenite} \quad (1)$$

during the third, contact metamorphism. Various stages of completion of the reaction (1) can be observed in the thin sections from the complete lack of spinel to the almost total disappearance of staurolite (Plate 1, fig. 2).

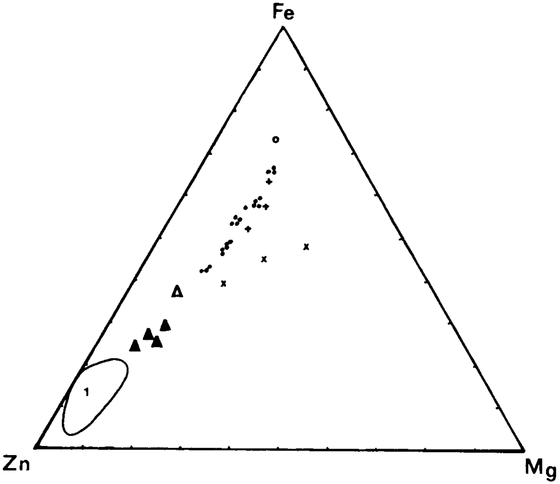

Fig. 2. Fe(II)-Mg-Zn triangular plot for the comparison of the chemical compositions of metamorphic Zn-spinels of different origin. Analyses marked by dots were conducted by the author, the sources of the others are:

1.	SPRY and SCOTT (1986)
solid triangles	MOORE and REID (1989)
open triangle	FROST (1973)
pluses	SCHUMACHER (1985)
open circle	ATKIN (1978)
crosses	STODDARD (1979)

A reaction similar to reaction (1) was proposed by SCHUMACHER (1985) in the contact aureole of the Glenn Doll diorite within the stability field of the andalusite under oxidative conditions:

$$\begin{aligned}&\text{zincian staurolite} + \text{muscovite} + \text{quartz} + O_2 = \\ &= \text{andalusite} + \text{Zn-rich spinel} + \text{magnetite} + \text{biotite} + H_2O\end{aligned} \tag{2}$$

In the Garabonc aureole there is ilmenite instead of magnetite which may reflect lower O_2 fugacity than at Glenn Doll.

The maximum P–T conditions for the reaction (1) are probably very close to the upper boundary of the stability field of andalusite. Though fibrolite is also present in the rock, but it is quite rare and cannot be found in association with the spinel and staurolite.

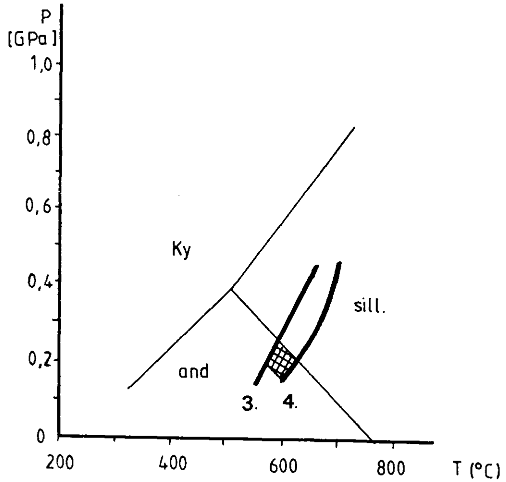

Fig. 3. P–T relations of reactions (3) and (4) and the stability field of the Al_2SiO_5 species after HOLDAWAY (1971). The box represents the P–T estimation for the breakdown of the Zn-bearing staurolite to Zn-bearing spinel and andalusite.

Mineral chemistry and discussion

Zn-bearing staurolites and spinels were analysed using an AMRAY 1830 I scanning electron microscope equipped with EDAX PV 9800 EDS detector. A 20 KV acceleration potential was used with 1–2 nA beam current and a beam diameter of about 3 micrometres. Synthetic and natural minerals were used as standards.

ZnO content is highly variable in the measured spinels (see Table 1), it ranges between 8.54 and 20.34 wt%. The variation in Zn content is balanced by the Fe while the Mg content of the spinels does not vary significantly (Fig. 2). These changes are possibly due to changes in Zn/Fe ratio in the former staurolites. The high variability in Zn/Fe ratios seem to be a common feature with spinels in the series $(Fe,Zn,Mg)Al_2O_4$ related to different metamorphic environments (see Fig. 2). It may depend on the zinc content of staurolite from which spinels have crystallized and on the further possible zinc contributions, mainly from desulfidation reaction of sphalerite. If sphalerite is involved in the reaction, spinel compositions close to pure gahnite can be measured (FROST, 1973; SPRY & SCOTT, 1986; MOORE & REID, 1989). In the case of spinels produced by staurolite breakdown, more hercynite and spinel ($MgAl_2O$) component can be expected as it seems to be evident from the spinel compositions (ATKIN, 1978; STODDARD, 1979; SCHUMACHER, 1985, and this study), plotted in the Zn-Fe-Mg triangular plot (see Fig. 2). Almost pure hercynite with only 0.42 wt% ZnO content was reported by KWAK (1974) in spite of the observed breakdown of staurolite containing 2.48 wt% ZnO.

According to measurements of HICKS et al. (1985) Zn content of zincian spinels is also influenced by the metamorphic grade. Spinels become richer in gahnite component as metamorphic grade decreases.

In contrast with the measured spinels, staurolites have quite uniform composition with ZnO content ranging between 1.18 and 2.37 wt% (Table 1), which corresponds well with data reported from similar environments (ATKIN, 1978; SCHUMACHER, 1985).

Higher Zn content in staurolite as well as in spinel is usually related to Zn ore formation or to sphalerite desulfidation reactions (SPRY & SCOTT, 1986; MOORE & REID, 1989). Though sphalerite is present in the rock in minor amount, but it crystallized during the third, contact metamorphism and was not present in the rock during the first metamorphic stage, which gave rise to the staurolite formation.

There is no evidence on the possible contribution of sphalerite to the Zn content of spinels either. Both the Zn-bearing spinels and sphalerites have crystallized during the third metamorphic event, but observations on microscope and microprobe (by the help of backscattered electron image) contradict the idea of contribution of sphalerite to the Zn content of spinels. The first observation is that these two minerals cannot be found in the same paragenesis. Spinels are always mantled by andalusite which probably protected the spinel grains from the effects from outside. The second observation is that there is no sign of sphalerite decomposition in the investigated samples.

Peak P–T conditions established on the basis of mineral equilibria (TÖRÖK, 1992) for the third, contact metamorphic stage may mark the upper pressure-temperature limits of the breakdown of Zn-bearing staurolite to Zn-bearing spinel and andalusite. Timing of the Zn-bearing spinel producing reaction can be approached first by the production of andalusite along with the spinel. Since spinel inclusions occur only in the second generation of andalusite which preceeded the formation of fibrolite, therefore spinel may have formed close to the peak contact metamorphic conditions. As fibrolite formed only in very small quantity it is assumed that the peak P–T conditions were close to the andalusite/sillimanite boundary.

Two well known reactions can be used as lower and upper temperature boundaries:

$$\text{staurolite} + \text{muscovite} + \text{quartz} = \text{andalusite} + \text{biotite} + H^2O \qquad (3)$$

from the lower temperature side which is 575 ± 15 °C at 200 MPa pressure (HOSCHEK, 1969). The

$$\text{muscovite} + \text{quartz} = Al_2SiO_5 + \text{potash-feldspar} \qquad (4)$$

reaction gives the upper temperature limit (Fig. 3, reaction curve of ALTHAUS et al., 1970). This limit was not reached because the samples contain primary muscovite in association with quartz.

Taking into consideration the P–T conditions limited by reactions (3) and (4) and the stability field of andalusite, the breakdown of Zn-bearing staurolite to Zn-bearing spinel and andalusite is estimated to have been about 600 °C at pressure of about 200 MPa (Fig. 3).

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Table 1. Representative analyses and mean compositions of spinels and staurolites.

1. A representative Zn-bearing spinel analysis. Numbers in the next column are mean compositions and range for 20 analyses. Cation numbers are on the basis of 4 oxygens.

2. A representative Zn-bearing staurolite analysis. Numbers in the next column are mean staurolite compositions and range for 22 analyses. Cation numbers are on the basis of 23 oxygens.

FeO* total iron as FeO

b.d. below detection limit

	1.		2.	
SiO_2	b.d.		26.50	26.38; 24.87-27.26
TiO_2	b.d.		0.50	0.53; 0.42-0.62
Al_2O_3	55.44	55.52; 54.28-56.73	52.65	53.30; 52.25-54.83
FeO	22.53	25.88; 19.92-32.54	12.80	13.27; 11.51-15.21
MnO	0.34	0.37; 0.22-0.61	0.37	0.44; 0.33-0.54
MgO	3.55	3.48; 3.12-3.90	2.32	2.19; 1.83-2.52
ZnO	17.63	14.64; 8.54-20.34	2.13	1.84; 1.18-2.37
total	99.91		97.27	
Si	0.000		3.742	
Ti	0.000		0.053	
Al	1.908		8.762	
Fe(III)	0.092		0.000	
Fe(II)	0.457		1.511	
Mn	0.008		0.044	
Mg	0.154		0.488	
Zn	0.380		0.222	
total	2.999		14.822	

Plate 1.

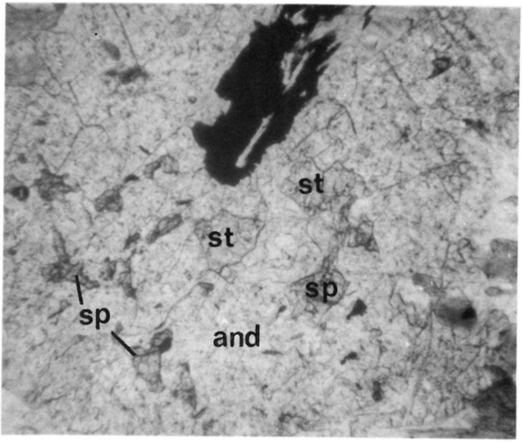

Fig. 1. Ragged staurolite (st) and spinel (sp) enclosed in andalusite (and).

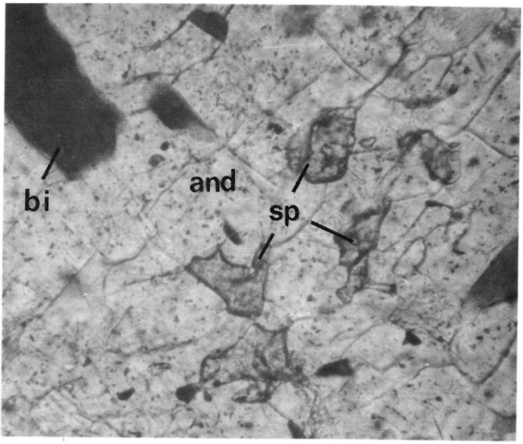

Fig. 2. Spinel (sp) and biotite (bi) mantled by andalusite (and).