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Apophyllite from the Upper Pliocene Grad volcaniclastics, NE Slovenia

Apofilit iz zgornjepliocenskih vulkanoklastitov Grada v severovzhodni Sloveniji

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Abstract

In some lava fragments from the Grad volcaniclastics, apophyllite occurs as a reaction product of quartzite accidentals and still molten alkali basaltic lava, and also, as a hydrothermal mineral in vesicles and veinlets. Apophyllite can be encountered only in the lava fragments, while in the host volcaniclastic only zeolites occur.

During the rise of alkali basaltic magma to the surface, it assimilated some of the Tertiary sediments. Consequently, the residual and deuteric liquids probably became slightly enriched with silica and enabled crystallisation of apophyllite. Under zeolite facies conditions, apophyllite became unstable and got replaced by zeolites.

Kratka vsebina

V nekaterih odlomkih lave v vulkanoklastitih iz okolice Grada se pojavlja apofilit kot reakcijski produkt vključkov kvarcita in alkalne bazaltne lave, pa tudi kot hidrotermalni mineral v votlinicah plinskih mehurčkov in drobnih žilicah. Apofilit najdemo le v odlomkih lave, medtem ko se v vulkanoklastitu, ki te odlomke vsebuje, pojavljajo le zeoliti.

Alkalna bazaltna magma je med dvigovanjem na Zemljino površje asimilirala nekaj sedimentov terciarne starosti. Zato so postali rezidualni in deuterični fluidi nekoliko bogatejši s kremenico, kar je omogočilo kristalizacijo apofilita. V pogojih zeolitnega faciesa je postal apofilit neobstojen, in pričeli so ga nadomeščati zeoliti.

Introduction

Alkali basaltic volcanic rocks from Grad, northeastern Slovenia (Fig. 1), are closely related to the Upper Pliocene - Romanian volcanic activity in the Styrian basin (Winkler, 1926; 1927; Balogh et al. 1990), which produced extrusions of basanite and nepheline basanites at Klöch and Kindsberg and nephelinites at Stradner Kogel, and volcaniclastic occurrences in the form of maars or tuff cones at Kapfenstein and Fehring (Poschl, 1991; Poulditis, 1981).

Volcanics, extruded at Grad were deposited on the surface of an alluvial fan which produced thick deposits of sands and gravels (Kralj, 1995). In the early stage of volcanic activity, a small cinder cone developed, composed of scoria and welded tuff deposits. Some minor lava flows were rapidly autobrecciated in the contact with wet alluvial sediments. Under the influence of external moisture, many secondary minerals formed in still hot autobrecciated lavas.

In the late stage of volcanic activity, hydrovolcanic explosions predominated, producing cross-stratified hydrovolcanic tuffs and voluminous lahars which destroyed the formerly developed cinder cone. All settled volcaniclastics were rapidly eroded by, and redistributed with fluvial currents forming mixed volcaniclastic - terrigenous deposits which also infilled the crater. Overlying sediments were deposited in a meandering river environment.

In some lava blocks, apophyllite amounts to 20 % of the bulk rock, replacing groundmass, infilling vesicles and occurring as a reaction aureole around accidental quartzite grains. The paper deals with the apophyllite formation and its instability under geochemically modified and lower-temperature hydrothermal conditions.

Alkali basalts from Grad

In the Grad area, no coherent lavas are preserved. For this reason, lava blocks, scattered in lahars and debris flows have been gathered to study their petrological and chemical characteristics. Over 50 samples were analysed for abundances of the

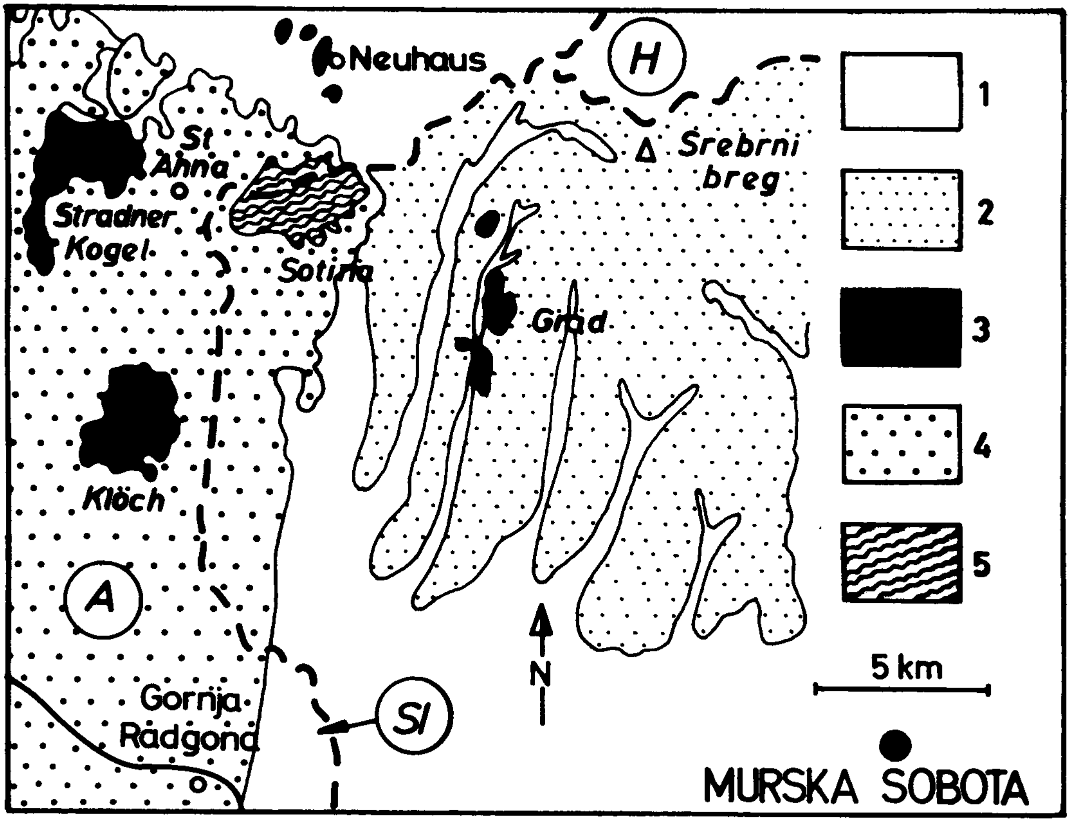

Fig. 1. Simplified geological map of the Grad area and a part the neighbouring regions in Austrian Styria (modified after Winkler, 1926, and Oberhauser, 1980).

Sl. 1. Poenostavljena geološka karta področja Grada in dela sosednjih regij Avstrije in Madžarske (prirejeno po Winklerju, 1926 in Oberhauserju, 1980)

1 - Quarternary, kvartar; 2 - Pliocene, pliocen; 3 - Upper Pliocene basaltic volcanics, zgornjepliocenske bazaltne predornine; 4 - Sarmatian, sarmatij; 5 - Pre-Tertiary basement, predterciarna podlaga

following major oxides and trace elements :

SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, Fe_2O_3, FeO, MnO, TiO_2, P_2O_5, H_2O^+, H_2O^-, CO_2; Ag, As, Au, B, Ba, Be, Br, Cd, Co, Cr, Cs, Cu, Ge, Hf, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Se, Sr, Ta, Th, U, V, W, Y, Zn, Zr, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Ir, Hg; in some of the samples Bi, Cl, Ga, Li, In, S, Tl, Pr, Gd, Dy, Ho, Er, Tm, Pd and Pt were also deteremined.

Lavas are characterised by porfiritic texture. Altered volcanic glass and augite microlites are dominant consituents. Volcanic glass is extensively replaced by Ca-montmorillonite, illite, chlorite, quartz, zeolites and iron oxides. Augite is the most common phenocryst. Olivine is rare in occurrence, and it may be altered into iddingsite. Phenocrysts of nepheline and sanidine are very rare, too. Xenoliths are composed of peridotite - lherzolite (Hinterlechner-Ravnik & Mišič, 1986). Accidental constituents are quartz grains and mudstone fragments.

The original chemical composition of rocks is probably basanitic (Hinterlechner-Ravnik & Mišič, 1986) although extensive alteration of volcanic glass unables reliable classification of rocks. Crystallisation of clay minerals caused appreciable depletion in alkaline and alkaline-earth elements and the composition shifts from basanites towards picrobasalts. The formation of zeolites increased the content of alkali and alkali-earth elements, as well as strontium, rubidium and barium. On the other hand, the presence of accidental quartzite grains in lava fragments increases the overall silica content and makes the rock composition basaltic instead of basanitic. Table 1 shows the avearge chemical composition of fragments of lavas and welded scoria lapilli tuffs from debrite and gravelly sediments.

A great part of accidentals has been admixed to the lavas when moving on the surface. Some of them, however, could have been admixed to magma when rising towards the surface. Consequently, some accidentals show no corrosion reactions with lava, but some of them are strongly corroded or even totally resorbed.

Very common accidentals are quartzite or quartz grains owing to their abundance in sediments of alluvial fan. The reaction aureole, surrounding quartzite or quartz grains may consist of stubby green amphiboles or apophyllite.

Apophyllite occurrence

Apophyllite formed only in the lava clasts which occur in volcaniclastic sediments and never infills the interstitial space of volcaniclastic rocks, oposite to zeolites chabasite, phillipsite and analcime which are commonly encountered as pore cement and veinlet filling. For this reason, apophyllite must have crystallised prior to the lava desintegration and the following settling in volcaniclastic sediments.

Volcaniclastic sediments containing apophyllite-bearing lava clasts are dominantly lahars and debris flow deposits. Volcaniclastic material commonly ranges from 20-50 wt.% of the bulk rock. Matrix contains silt, sand and gravel of non-volcanic terrigenous origin (Table 1).

In some of the studied lava fragments, apophyllite amounts up to 20 wt.% of the crystalline rock constituents (Table 2). It replaces groundmass, infills vesicles and tiny fractures, and occurs as a reaction aureole surrounding quartz and quartzite grains. The most common accompanying authigenic minerals are analcime, chabasite and phillipsite, whereas laumontite, wairakite, Ca-montmorillonite and illite occur in subordinate amounts. Apophyllite may subsequently be replaced by zeolites, mainly phillipsite and chabasite.

Apophyllite surrounding some quartz grains seems to form as a reaction product of molten lava and detritial quartz (Plate 1 - Fig. 1). Yet, another samples (Plate 1 - Fig. 2) contain quartzite grains with the apophylite aureole and also, apophyllite veinlets serving as a conduit for reacting hydrothermal solutions. Apophyllite also infills vesicles and replaces groundmass, and very rarely, even augite crystals.

Zeolites - chabasite and phillipsite - commonly infill vesicles in the sediment which bears the lava clasts with apophyllite. Zeolites partially or completely replace apophyllite (Plate 1 - Fig. 3, Plate 1 - Fig 4).

Table 1. Petrographic composition of debris flow deposits at Grad. The contents are in vol.%, and determined under the microscope

Tabela 1. Petrografska sestava debritov iz Grada. Vsebnosti so v volumskih odstotkih in so določene z mikroskopsko raziskavo

Sample	VRF1	VRF2	VRF3	Q	F	N	T	I	P	C	Ma	SVRF
Gr1		22.0	5.7	5.2				1.1			64.2	27.7
Gr1/2		31.9	4.0	13.0			1.7	1.1		12.0	22.9	47.8
Gr1/8		45.7	2.1	14.7	+		0.3	0.4		4.2	46.0	35.9
Pi22		40.4	3.1	7.1			0.2	21.0	0.9	26.6	0.3	43.5
Pi25		32.5	2.3	14.7		+				10.1	37.0	37.5
Pi36	5.6	21.8	2.8	18.2			+	4.6		10.4	35.6	30.2

VRF1 - weakly altered fragments of coherent basaltic rocks with low vesicularity (< 7 vol.%); **VRF2** - altered fragments of coherent basaltic rocks with vesicularity between 7-20 vol.%; **VRF3** - altered fragments of coherent basaltic rocks with high vesicularity (> 20 vol.%); **Q** - quartz and quartzite grains; **F** - plagioclase grains; **N** - nepheline grains; **T** - heavy minerals (augite, garnets, rutile, staurolite); **I** - fragments of siltstones; **C** - cement; **Ma** - fine-grained matrix; **SVRF** - sum of the coherent basaltic rock fragments

VRF1 - mlo spremenjeni klasti bazaltne lave z majhnim številom votlinic (< 7 vol.%); **VRF2** - spremenjeni klasti bazaltne lave z votliničavostjo med 7-20 vol.%; **VRF3** - spremenjeni klasti bazaltne lave, ki so močno votliničasti (> 20 vol.%); **Q** - zrna kremena in kvarcita; **F** - zrna plagioklazov; **N** - zrna nefelina; **T** - težki minerali (avgit, granati, rutil, stavrolit); **I** - odlomki meljevcev; **C** - cement; **Ma** - drobnozrnata osnova; **SVRF** - vsota vseh klastov bazaltne lave

Table 2. Mineral composition of the apophyllite-bearing lava fragments, determined by X-ray diffraction method. Estimated content is in wt.%

Tabela 2. Mineralna sestava odlomkov lave, ki vsebujejo apofilit, določena z rentgensko difrakcijsko metodo. Ocenjene vsebnosti so v masnih odstotkih

	Mf	O	N	Ap	A	W	Ch	Ly	La	Ph	M/I	Ca-M	Q
PgB7	20	10	10	2	10	15	10	10	10		10		
PiK1	40	10		20						25	3		2
PiK2	25	8	10	5	15		15	10			5		5
PiK4	20	5		15	15		10		15		10	5	5

Mf - augite, avgit, O - olivine, olivin, N - nepheline, nefelin, Ap - apophyllite, apofilit, A - analcime, analcim, W - wairakite, wairakit, Ch - chabasite, habazit, Ly - levynite, levyint, La - laumontite, laumontit, Ph - phillipsite, phillipsit, M/I - muskovite/illite, muskovit/illit, Ca-M - calcic montmorillonite, kalcijski montmorillonit, Q - quartz, kremen

Discussion

Apophyllite is a Ca-K hydrous silicate which contains no alumina. It commonly occurs in high-temperature hydrothermally altered basalts (Kristmannsdottir & Tomasson) as a secondary mineral, along with various zeolite species.

Petrological evidence indicates that in the Grad volcanics, apophyllite formed prior to desintegration of coherent lavas and deposition of fragments in mixed volcaniclastic - terrigenous sediments. Many of the apophyllite bearing lava clasts that occur in lahars and debris flows also contain zeolites, although neither apophyllite, nor zeolites can be found as interstitial cements. The reaction aureole, surrounding some quartzite accidentals indicates that apophyllite developed at relatively high temperatures when the lavas were still in a molten condition. At lower temperatures wairakite, analcime and finally chabasite and phillipsite formed. Under lower temperature conditions apophyllite became unstable and got replaced by zeolites.

Table 3. Chemical composition of an apophyllite bearing lava fragment - PiK1
Tabela 3. Kemična sestava odlomka lave, ki vsebuje apofilit - PiK1

Major elements (wt.%)	Basalt (18)*	PiK1
SiO_2	43.8	44.6
TiO_2	1.88	1.29
Al_2O_3	13.6	9.58
Fe_2O_3	5.0	4.20
FeO	4.4	2.5
MnO	0.21	0.14
MgO	5.88	4.72
CaO	10.8	14.6
Na2O	3.22	1.07
K2O	1.91	2.94
P2O5	0.98	0.69
H2O+	4.6	10.1
H2O-	2.9	2.6
CO2	0.48	0.47
l.o.i.	5.88	13.3

*average value of 18 samples of lava fragments from the same lithofacies which do not contain apophyllite

Trace elements (ppb)	Basalt (18)*	PiK1
B	10	50
Be	4.5	2
Sc	11.8	8.3
V	190	300
Cr	96	69
Co	36	34
Ni	82	92
Cu	24.5	19.1
Zn	120	84
As	2	<2
Se	3	<3
Rb	56	90
Sr	1510	500
Y	22	<10
Zr	297	84
Nb	118	90
Mo	5	<5
Cd	2	<1
Sb	0.4	0.4
Cs	4	1
Ba	1046	1000
La	76.8	49.6
Ce	138	87
Nd	56	34
Sm	9.3	5.6
Eu	2.8	1.8
Tb	1.0	0.8
Yb	2.1	1.4
Lu	0.26	0.18
Hf	6	4
Ta	6	4
W	57	44
Pb	2	<2
Th	10	6.8
U	3.9	2.0

Chemical analyses of the apophyllite-bearing lava have shown (Table 3) that the apophyllite bearing lava clasts contain more silica and less alumina than the average. The altered rocks are also depleted in sodium and magnesium and many trace elements including Sr, Ba, and rare earth elements, and is enriched with calcium and boron. Apophyllite formation is most likely related to the existence of an external source of silica, which was most probably molten or partially molten sedimentary material incorporated in lavas near or at the surface. Apophyllite surrounding quartz accidentals indicates a direct reaction of quartz and molten lava. Apophyllite could also crystallise from deuteric fluids, which became enriched with silica due to assimilation of the silica-rich sediments by lavas when they rised near or at the surface. On the other hand, zeolitisation increases the abundances of sodium, potassium, strontium, barium and rubidium in the overall chemical composition. It can be related to the action of hydrothermal fluids or percolating ground water as is described in Oahu, Hawaii (Iijima & Harada, 1968). The conditions that favoured crystallisation of zeolites caused instability of apophyllite, and consequently, it became partially or completely replaced by phillipsite or chabasite.

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References

B a l o g h, K., L o b i t z e r, H., P e c s k a y, Z., R a v a s z, C s., S o l t i, G. 1990: Kelet- Stajerorszagi es Burgenlandi tercier vulkanitok K/Ar kora. - Foldt. Int. Evi. Jel. 1988, 451-468, Budapest

H i n t e r l e c h n e r - R a v n i k, A., M i š i č, M. 1986: Peridotitne nodule v bazaltnem tufu pri Gradu v Prekmurju. - Geologija 28/29, 205-218, Ljubljana

I i j i m a, A., H a r a d a, S. 1968: Authigenic zeolites in zeolitic palagonite tuffs on Oahu, Hawaii. - Amer. Mineral. 54, 182 -197, Washington

K r a l j, P. 1995: Gornjepliocenski fluvialni i vulkanoklastični sedimenti područja Grada u sjevernoistočnoj Sloveniji. - Ph. D. Thesis, University of Zagreb, 128p., Zagreb

K r i s t m a n n s d o t t i r, H., T o m a s s o n, J. 1978: zeolite zones in geothermal areas in Iceland. In: Sand, L.B. & Mumpton, F.A. (eds.), Natural zeolites, 277-284, Pergamon, Oxford

O b e r h a u s e r, R. (ed.) 1980: Der geologische Aufbau (sterreichs. - Springer, 700p., Wien

P l e n i č a r, M. 1968: Osnovna geološka karta SFRJ 1:100000, list Goričko. Zvezni geološki zavod, Beograd

Pl e n i č a r, M. 1970: Osnovna geološka karta SFRJ 1:100000. Tolmač za list Goričko in Leibnitz, 1-40. Zvezni geološki zavod, Beograd

P o s c h l, I. 1991: A model for the depositional evolution of the volcaniclastic successions of a Pliocene maar volcano in the Styrian basin (Austria). - Jb. Geol. B.-A. 134/4, 809-843, Wien

P o u l d i t i s, Ch. 1981: Petrologie und Geochimie basaltischer Gesteine des steirischen Vulkanbogens in der Steiermark und im Burgenland. - Diss. Univ. Wien, 146p., Wien

W i n k l e r, A. 1926: Geologische Spezialkarte der Republik (sterreich 1:75000, Blatt Gleichenberg, Zone 18, Kol XIV, Nr. 5256. Geologische Bundesanstalt, Wien

W i n k l e r, A. 1927: Erlauterungen zur geologischen Spezialkarte der Republik Österreich, Blatt Gleichenberg. Geologische Bundesanstalt, 1-164, Wien

Plate 1 - Tabla 1

Fig.1. Apophyllite formed as a reaction product between alkali basaltic magma and the quartzite accidental

Sl. 1. Apofilit, ki je nastal kot reakcijski produkt med alkalno bazaltno magmo in vključkom kvarcita

Fig. 2. Apophyllite veinlets cutting a quartzite grain

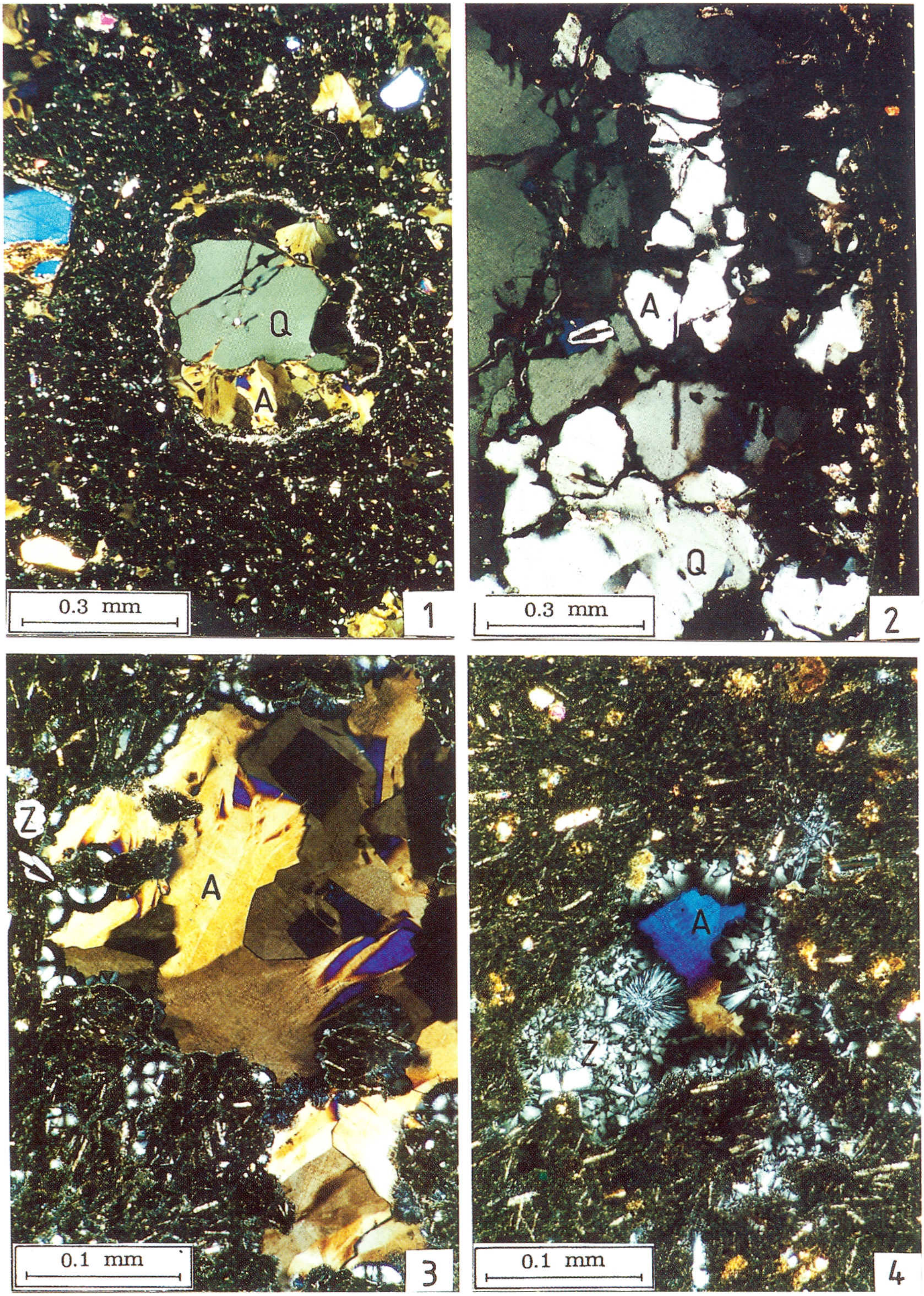
Sl.2. Apofilitne žilice, ki sekajo zrno kvarcita

Fig. 3. Phillipsite replacing apophyllite

Sl. 3. Phillipsit, ki nadomešča apofilit

Fig. 4. Phillipsite replacing apophyllite

Sl. 4. Filipsit, ki nadomešča apofilit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