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Flowstone-like calcite in the andesite of Jarmuta Mt. – dating the Holocene tectonic activity in the vicinity of Szczawnica (Magura Nappe, Outer Carpathians, Poland)

EDYTA JUREWICZ[1], HELENA HERCMAN[2] AND KRZYSZTOF NEJBERT[3]

[1,3]*Warsaw University, Faculty of Geology, al. Żwirki i Wigury 93, PL-02-089 Warsaw, Poland.*
[1]*E-mail: edyta.jurewicz@uw.edu.pl*; [3]*E-mail: knejbert@uw.edu.pl*
[2]*Polish Academy of Sciences, Institute of Geological Sciences, ul. Twarda 51/55, PL-00-818 Warsaw, Poland. E-mail: hhercman@twarda.pan.pl*

ABSTRACT:

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Extensional fractures partly filled with calcite showing the characteristics of flowstone have been observed in the andesite from Jarmuta Mt. The isotopic composition of this calcite indicates low-temperature crystallization conditions and its vadose origin. U-Th dating of the flowstone-like calcite indicates ages of ~2.5-6.5 ka. The calcite grew on a rough and fresh andesite surface, and hence its age may correspond to the age of the extensional fractures. Rhythmically distributed intergrowths of clay minerals present in the calcite may reflect annual climatic oscillations and show that the calcite grew for at least 500 years. The calcite filling the extensional fractures, like the calcite cementing the loosened cataclastic zones cutting the andesite, does not show any features indicating younger deformations. The origin and geometric features of the fractures show that they could have formed in response to increased strike-slip activity within the deep fault zone known as the Dunajec Fault, which may coincide with the fracture zone between the Upper Silesian and Małopolska blocks.

Key words: Flowstone-like calcite, Geochronology, Extensional fractures, Deep fault zone, Andesite, Pieniny Klippen Belt (PKB).

INTRODUCTION

During field studies on the andesite from the Malinowa Quarry on Jarmuta Mt. (Text-fig. 1A), tectonic surfaces covered with calcite that resembled flowstone rather than hydrothermal mineralization were observed. The flowstones were relatively thick, up to several to over a dozen centimetres, and had a macroscopically distinct growth pattern, separated by several dissolution stages. The presence of such calcite was also observed in loose, crumbly cataclastics, in which there were no macroscopic signs of later, post-mineralization deformation indicating a relatively young age.

At the beginning of our investigations we did not preclude a hydrothermal origin of the flowstone-like calcite. A hydrothermal origin is quite plausible because of the presence in the study area of exploited ore veins associated with andesite dykes (e.g. MAŁKOWSKI 1918, 1923; WOJCIECHOWSKI 1955; BIRKENMAJER 1958, 1979). Andesitic volcanism and associated hydrothermal

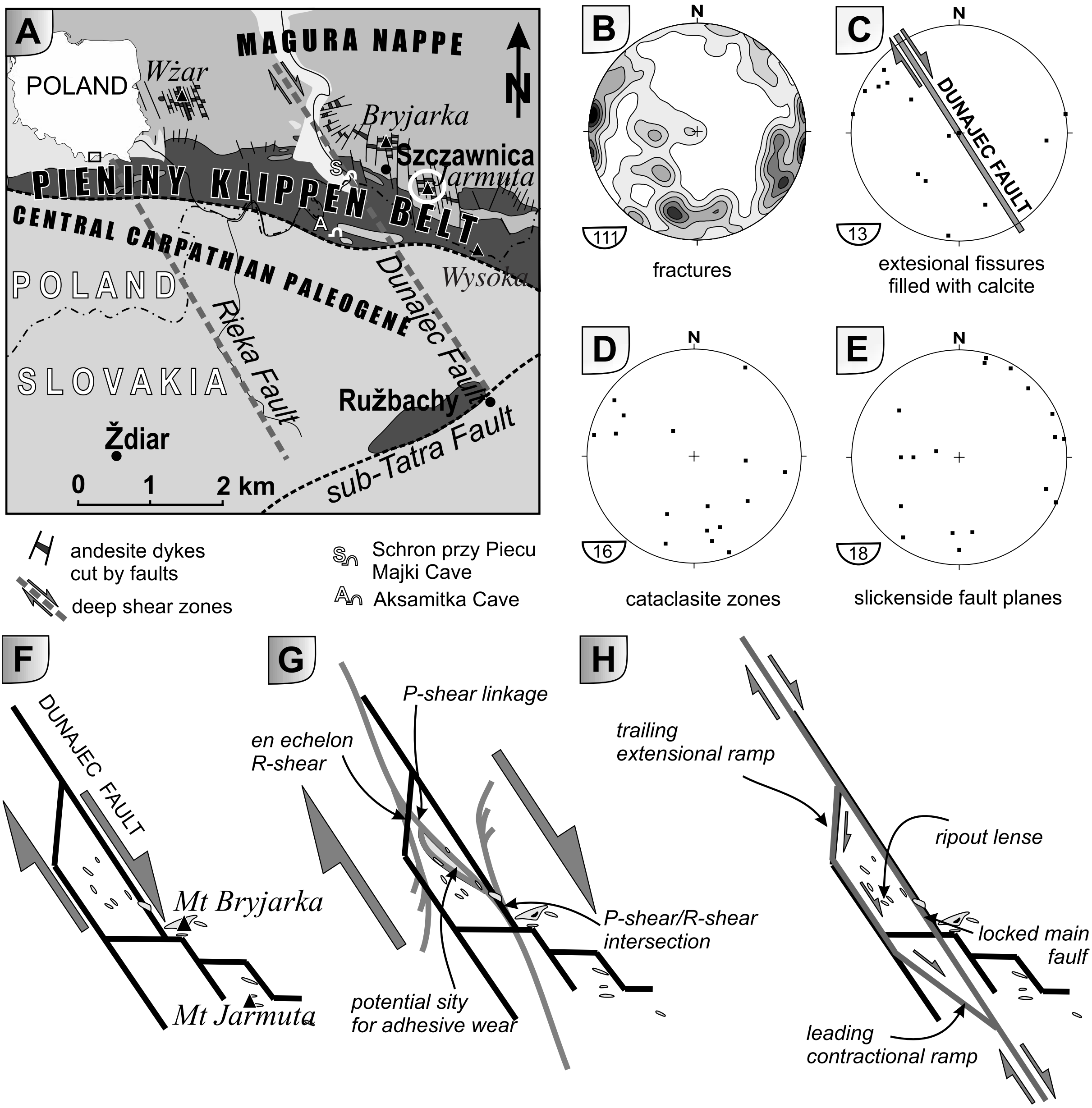

Fig. 1. Structural data of investigated area. A – study area (white ring) in relation to the main structural units (after BIRKENMAJER 1979, modified by JUREWICZ 2005). B-D – stereoplot of tectonic patterns within the andesite, projection on the lower hemisphere; B – contour plot of the fractures; C – pole to the extensional fissures filled with calcite; D – pole to the shear zones; E – pole to the slickenside fault planes; F – Dunajec Fault and related faults after BIRKENMAJER (1979) and new field data; interpretation of andesite dykes occurrences (in grey) by UHLIG (1905); G-H – two interpretations of the Dunajec Fault and related andesite dykes on the basis of the SWANSON (2005) model: G – restraining steps in *en echelon* R-shear/P-shear arrays, forming an irregular fault with a distinctive restraining bend geometry as a potential site for adhesive wear; H – double *en echelon* system with the development of extensional ramps at the trailing edges and contractional ramps at the leading edge of the ripout slab

activity could be connected with the subduction zone postulated in this region e.g. by TOKARSKI (1978) and BIRKENMAJER (1986, 2003). The age of hydrothermal activity in the Jarmuta Mt. area was determined as almost synchronous with the intrusion of the andesite, i.e. 11.35 (±0.45) Ma (SZELIGA & MICHALIK 2003; SZELIGA & *al.* 2005). The rise in CO_2 emission – like in the Northern Apennines – could be an aftermath of increased seismic activity (MILLER & *al.* 2004). This origin of carbon dioxide could be expected because of risen content of mantle helium postulated by LEŚNIAK & *al.* (1997). According to LEŚNIAK & *al.* (1997), the strong mantle helium signal could be connected with dyke formation episodes resulting from subduction and post-collision volcanism (see TOKARSKI 1978; BIRKENMAJER 2003). However, OSZCZYPKO & ZUBER (2002) provided geological and isotopic evidence that CO_2-rich chloride waters in the Polish Flysch Carpathians were of diagenetic origin, and that the CO_2 content was unrelated to the andesitic volcanism.

The main aim of this paper has been to determine the age and origin of the flowstone-like calcite, which could then be used to recognise events linked with the youngest tectonic activity in the study area. U-series dating, stable isotope analyses, chemical analyses (ICP MS, XRF, EPMA), and XRD methods were applied.

Geotectonic position of the so-called "Pieniny Mts. andesite"

Due to its location, the andesite volcanism occurring in the vicinity of Szczawnica has been related to the northern boundary of the Pieniny Klippen Belt (PKB) with the Magura Nappe. Within the PKB the occurrence of andesite dykes was linked with the so-called Grajcarek Unit distinguished by BIRKENMAJER (1979, 1986). Deposits of the Grajcarek Unit were formed in the sub-Pieniny part of the Magura Basin to the north of the Czorsztyn Basin and were subject during the Laramide phase to retro-arc thrusting on the autochthonous Czorsztyn Unit (BIRKENMAJER 1979). According to this concept, the Klippen units should be located below the Grajcarek Unit and the boundary between the PKB and the Outer Western Carpathians would be located at the stratigraphic boundary between the Jarmuta and Szczawnica formations within the Magura Nappe. However, the structural analysis of JUREWICZ (1994, 1997) in the Małe Pieniny Mts. showed that, on the contrary, the Klippen Units were overthrusted onto the Magura Nappe. There is no evidence for distinguishing a separate Grajcarek Unit among the deposits of the Magura Unit, because its northern margin is of stratigraphic character (between the Jarmuta and Szczawnica formations) and is difficult to recognise in the field as a boundary between two main structural units (PKB and Outer Carpathians). As a result, the Grajcarek Unit should be incorporated in the Magura Unit and the northern boundary of the PKB should be moved to the south, towards the contact with the Klippen units. Andesite from the Grajcarek Unit, assigned by BIRKENMAJER (1979) to the PKB, thus belongs solely to the Magura Unit (Text-fig. 1A).

BIRKENMAJER & *al.* (1987) and BIRKENMAJER (2003) linked andesite volcanism in the vicinity of Szczawnica with the so-called Pieniny Andesite Line (PAL), which runs WNW-ESE, sub-parallel to the PKB and is connected with the Odra Fault. According to BIRKENMAJER (2003) and TRUA & *al.* (2006), andesitic rocks in the PKB are products of hybridisation of mantle-derived magma during its ascent along tension fissures that opened over the subducted slab of the North European Plate. The most recent isotopic K-Ar dating of BIRKENMAJER & PÉCSKAY (1999, 2000) indicates two phases of volcanic activity, both within the interval 12.5–10.8 Ma (~Sarmatian). Petrologically, the dykes and sills are represented by basaltic andesite and andesite according to the TAS classification; on the diagram of PECCERILLO & TAYLOR (1976) most of the andesites plot in the medium-K field, but some of them are also located close to the medium-K/ high-K boundary (MICHALIK & *al.* 2004, TRUA & *al.* 2006).

Field investigations and analysis of geophysical data indicate that the andesitic dykes can be connected with a deep fault zone called the Dunajec Fault. A section of this fault was described by BIRKENMAJER (1979) as a dextral strike-slip fault shifting the northern margin of the PKB on the eastern side by ca. 700 m south-eastwards (Text-fig. 1A). The south-east continuation of this deep fault zone could be recognized in the vicinity of Ružbachy where it is marked by the presence of travertine. To the north of the PKB, this fault could be responsible for the disturbance in the course of the isobaths of the Magura Nappe overthrust which is clearly visible on the map of OSZCZYPKO-CLOWES & OSZCZYPKO (2004). To the east of the Dunajec Fault, the Magura Nappe is thicker (*op. cit.*), whereas as to the west an elevation of some older structures can be observed in the Szczawa tectonic window (the Grybów Unit from beneath the Magura Nappe). A similar situation occurs in the southern prolongation of the Dunajec Fault, where the Ružbachy slice emerges from beneath the Central Carpathian Palaeogene. This fault coincides with the repeatedly activated NW-SE Kraków–Myszków strike-slip zone (JUREWICZ 2005; JUREWICZ & NEJBERT 2005), which separates the Małopolska and Upper Silesian blocks and which could be a part of a larger zone – the Szczecin–Kraków–Prešov fault zone (ŻABA 1996; BUŁA & *al.* 1997). For this reason, the occurrence of andesite dykes could be connected with zones of adhesion originating as a result of shearing processes (Text-fig. 1F), like in the models proposed by SWANSON (2005) (Text-fig. 1G-H). The strike-slip fault activity resulted initially in the formation of the andesite dykes, followed in a later phase by the formation of ripout lenses with flowstone-like calcite.

Andesite on Jarmuta Mt.

On Jarmuta Mt. 23 andesite dykes have been noted with strikes parallel to the orientation of the PKB; they range in thickness from 10 to ca. 100 m and dip steeply southwards (MAŁOSZEWSKI 1958, 1962). MAŁKOWSKI (1923) described them as volcanic dykes linked with two intrusion stages. The andesite occurs within the reddish shales of the Malinowa Shale Formation and sandstone of the Jarmuta Formation (BIRKENMAJER 1979). The complex dyke structure (chonolite form) is the effect of magma penetration of tectonically disturbed beds, accompanied by metamorphism of the surrounding rocks and propylitization of andesite (MAŁKOWSKI 1923). The dykes are composed of amphibole and amphibole-augite andesite (MAŁKOWSKI 1921; MICHALIK & *al.* 2004, 2005). In the fine-grained variety with macroscopically visible biotite, the amphiboles underwent almost complete transformation. BIRKENMAJER (2003) pointed out that the andesites of Jarmuta Mt. "are often strongly carbonatized/calcitized". These processes accompanied the longitudinal and transverse joint systems and could be linked with the breakdown of plagioclases and amphiboles by carbon dioxide of magmatic origin, which emanated through the fractures, or with post-magmatic hydrothermal activity. The K-Ar age of the andesite dykes on Jarmuta Mt. is ~11.1-11.6 Ma (BIRKENMAJER & PÉCSKAY 1999, 2000).

The occurrence of andesite on Jarmuta Mt. is accompanied by ore mineralization, which was exploited from 1732 to 1740 (BIRKENMAJER 1979; BIRKENMAJER & *al.* 2004). The mineral composition of the ore vein and description of the surrounding rocks was presented by MAŁKOWSKI (1918), who noted that bulk of the vein was composed of limonite, with subordinate galena, pyrite, pyrrhotite, quartz, apatite, gypsum and calcite. Analysis of another 1-4 cm thick vein (WOJCIECHOWSKI 1950, 1955) showed the presence of chalcopyrite, bornite, covellite, malachite, azurite, cerussite, arsenopyrite, sphalerite and magnetite, as well as native metals (Au, Ag, Cu, Hg). Dispersed sulphide mineralization, with rare bismuth tellurides, was also described from hydrothermally altered sedimentary rocks on Jarmuta Mt. (BANAŚ & *al.* 1993). The K-Ar age of the hydrothermal processes which produced the ore-bearing vein on Jarmuta Mt. was determined as 11.35±0.45 Ma (BIRKENMAJER & *al.* 2004; SZELIGA & *al.* 2005).

METHODS OF STUDY

Mineralogical and petrographical study

Minerals were identified by means of conventional optical microscopy and XRD studies. Polished thin sections were examined using a petrographic microscope working in transmitted and reflected mode. The study was performed at the Institute of Geochemistry, Mineralogy and Petrology, while the photographical documentation was completed on an ECLIPSE E600W POL microscope at the Scanning Electron Microscopy and Microanalysis Laboratory in Warsaw University.

XRD analyses were accomplished on a DRON-1 diffractometer at the Institute of Geochemistry, Mineralogy and Petrology. Powdered calcite samples were mounted on a glassy plate and irradiated with CoK$_\alpha$ radiation. Data were collected over the range 5° to 70° 2Q, in the step-scan mode employing 0.04° 2Q step-size, and counting time 8 s per step.

Chemistry of whole rock samples (ICP ES, ICP MS)

The chemical composition of the calcite within the extensional fractures in the andesite was determined by analyses of whole rock samples, carried out in the ACME Laboratory in Canada. Major elements, including Ca, Mg, Mn, Fe, Si, were analysed using the ICP ES method. Samples for the analysis were prepared by fusion of 0.2 g of the sample with $LiBO_2$. The calibration standard No. SO-18/CSB was applied. Trace elements, including Ba, Sr, Th, U, and REE, were analysed by ICP MS, after fusion of 0.2 g of the powdered calcite with $LiBO_2$. The calibration standard No. SO-18 was used. Standard procedures commonly applied during determination of the chemical composition by means of these methods were applied.

EPMA

The microprobe study of the calcite was carried out by means of the CAMECA SX100 at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances in Warsaw University. These analyses were done under the following instrumental conditions: accelerating voltage 15 keV, beam current 10 nA, and beam diameter from 20 μm to 40 μm, depending on the size of the calcite grains analyzed. Analyses of the mineral grains stable under the electron beam, as well as BSE images were performed using a focused electron beam. Natural and synthetic materials distributed by CAMECA and SPI Supplies were used as the calibration standards.

U-series dating

U-series dating was performed at the Institute of Geological Sciences, Polish Academy of Sciences in Warsaw. Typically, 10-20 g of clean calcite with no visible traces of detrital admixtures were separated from each layer studied. Standard chemical procedures for uranium and thorium separation from carbonate samples were applied (IVANOVICH & HARMON 1992). The samples were dissolved in ca. 6 M HNO_3 and the ^{228}Th-^{232}U spike (UDP10030 code from Isotrak, AEA Technology) mixture was added as an indicator of the chemical procedure efficiency. After oxidation of the organic matter using H_2O_2, a preliminary U and Th concentration was made using co-precipitation with iron hydroxides. After iron removal using ether extraction, U and Th were separated by ion exchange using DOWEX 1x8 resin. After final purification, U and Th were electro-deposited on steel disks. The energetic spectra of the alpha particles were collected using the OCTETE PC spectrometer made by EG&G ORTEC. Spectra analyses and age calculations were done using "URANOTHOR 2.6" software, which is the standard software developed in the U-Series Laboratory of the Polish Academy of Sciences in Warsaw (GORKA & HERCMAN 2002). Half-lives of uranium and thorium isotopes are based on CHENG & *al.* (2000). The quoted errors are 1σ. U concentration in all the samples, as well as the efficiency of chemical separation of U and Th (>50%) were sufficiently high for α-spectrometry analyses.

Stable isotope analyses of calcite

Stable isotope analyses were performed in the Institute of Geological Sciences, Polish Academy of Sciences in Warsaw. Standard procedures for carbonate samples were applied (orthophosphoric acid at 25° C, for more details see MCCREA 1950). About 10 mg of calcite were drilled from 2-3 layers of each studied sample of the flowstone-like calcite (marked as a, b...). Carbon and oxygen isotopic composition in CO_2 was measured using the Finnigan Mat Delta Plus mass spectrometer. The results are given relative to the VPDB standard. The uncertainty for $\delta^{13}C$ is 0.05‰ and for $\delta^{18}O$ is 0.1‰.

CALCITE IN ANDESITE FROM JARMUTA MT.

Calcite occurs commonly in the andesite on Jarmuta Mt. The presence of calcite as intergrowths in amphibole-augite andesite was noted by MAŁOSZEWSKI (1958, 1962). He suggested the numerous limestone fragments in the conglomeratic members of the Jarmuta Formation as the possible source of carbonates. A large amount of calcite may also have resulted from the breakdown of feldspars during hydrothermal water-rock interaction that took place after crystallisation of the andesite. These calcites occur as replacements along the growth zones and fractures within the pla-

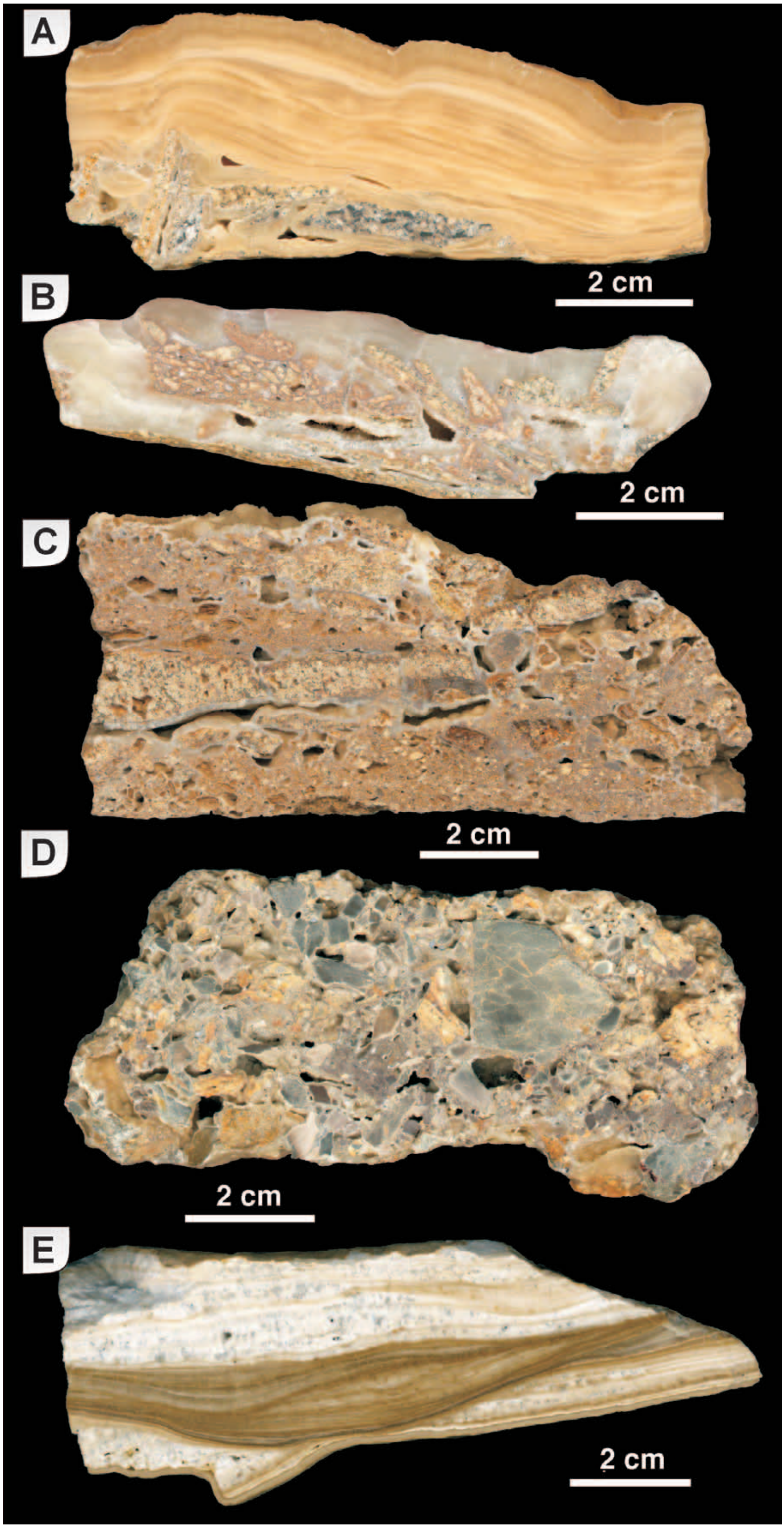

Fig. 2. Textural varieties of calcites at the Jarmuta Mt. (A-D). A – thick vein of yellowish flowstone-like calcite from the extensionally opened fractures (220/60); B, C – transparent calcite from the shear zone comprising cataclased andesite, split along textures; note spaces partly filled with calcite; D – tectonic breccia composed of fragments of andesite, mylonitized andesite and marls cemented with post-tectonic calcite; note that spaces between clasts are not completely filled with calcite; E – flowstone calcite from the Aksamitka Cave

gioclases. Calcite also occurs in the form of several centimetre-thick veins of twinned milky calcite completely filling fracture fissures with even smooth walls. The thin veins mineralising the irregular fractures are filled with blocky calcite crystals.

Field studies have shown the presence of calcite resembling flowstone (Text-fig. 2A, compare 2E) along fractures oriented at ~220/55 and ~300/80 (Text-fig. 1C). The fractures in which this calcite occurs are from several- to over a dozen centimetres wide indicating their extensional character. The rough wall surfaces and angular slivers of wall-rock wedged in the fracture also support the extensional character of these fractures. The flowstone-like calcite occurring along these planes is typically about 2-7 cm thick. Polished surfaces show growth lines in the form of laminae composed of streaks of honey-coloured transparent calcite and milky calcite (Text-fig. 2A). The bottom surface of the dipping fracture planes with flowstone-like calcite shows features indicative of water flowing under gravity, such as gentle carving and polishing of the calcite-coated surface. On some part of the wall-rock, typically on the upper surface of the fracture, the flowstone-like calcite is coated with 2-3 mm euhedral grains of calcite. Such crystals also occur in thin, extensionally opened fractures, in which the flowstone-like calcite is not present.

The flowstone-type calcite was formed in extensional fractures with orientations (Text-fig. 1C) close to the prevailing orientation of fractures measured in the andesite dykes on Jarmuta Mt. (Text-fig. 1B). They are also concordant with the orientation of the cataclastic zones (Text-fig. 1D), but they does not similar course to the slickesides (Text-fig. 1E). The open fractures usually have strikes parallel or *en échelon* to the Dunajec strike-slip fault (Text-fig. 1C).

In the cataclastic zones, the orientation of which is close to the strike of fractures within the entire

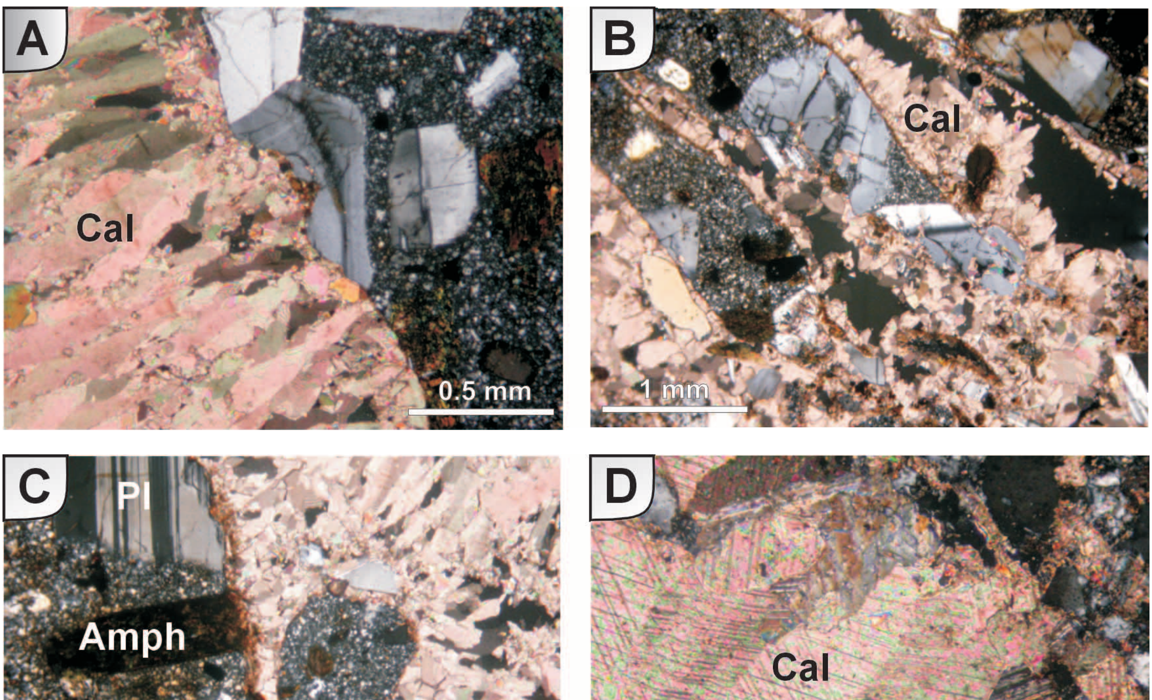

Fig. 3. Flowstone-like calcite from andesite (A-C) and palisade calcite vein from sandstone of the Jarmuta Formation, Magura Nappe (D). A – sharp contact between andesite and flowstone-like calcite growth within the irregular extensional fracture; note the lack of twins in elongated calcite grains; B – druses of calcite between extensionally broken andesite; note sharp-edged fragments of andesite; C – angular fragment of andesite within calcite; note poorly distinguishable zones of calcite growth (see Text-fig. 4 for details); D – dense twins in palisade calcite from vein within the sandstone of the Magura Nappe; Amph – amphibole, Cal – calcite, Pl – plagioclase; transmitted light, crossed polars.

dyke (Text-fig. 1B-D), a textural arrangement can be observed. These zones are thus zones of tectonic loosening. Fractures are parallel to the elongation textures and partly filled with calcite in the form of druses or flowstones (Text-fig. 2B). The calcite also cements tectonic breccias (Text-fig. 2D) composed of fragments of andesite and marly shale, which occur in the neighbourhood of andesite dykes (Malinowa Shale Formation – BIRKENMAJER 1979).

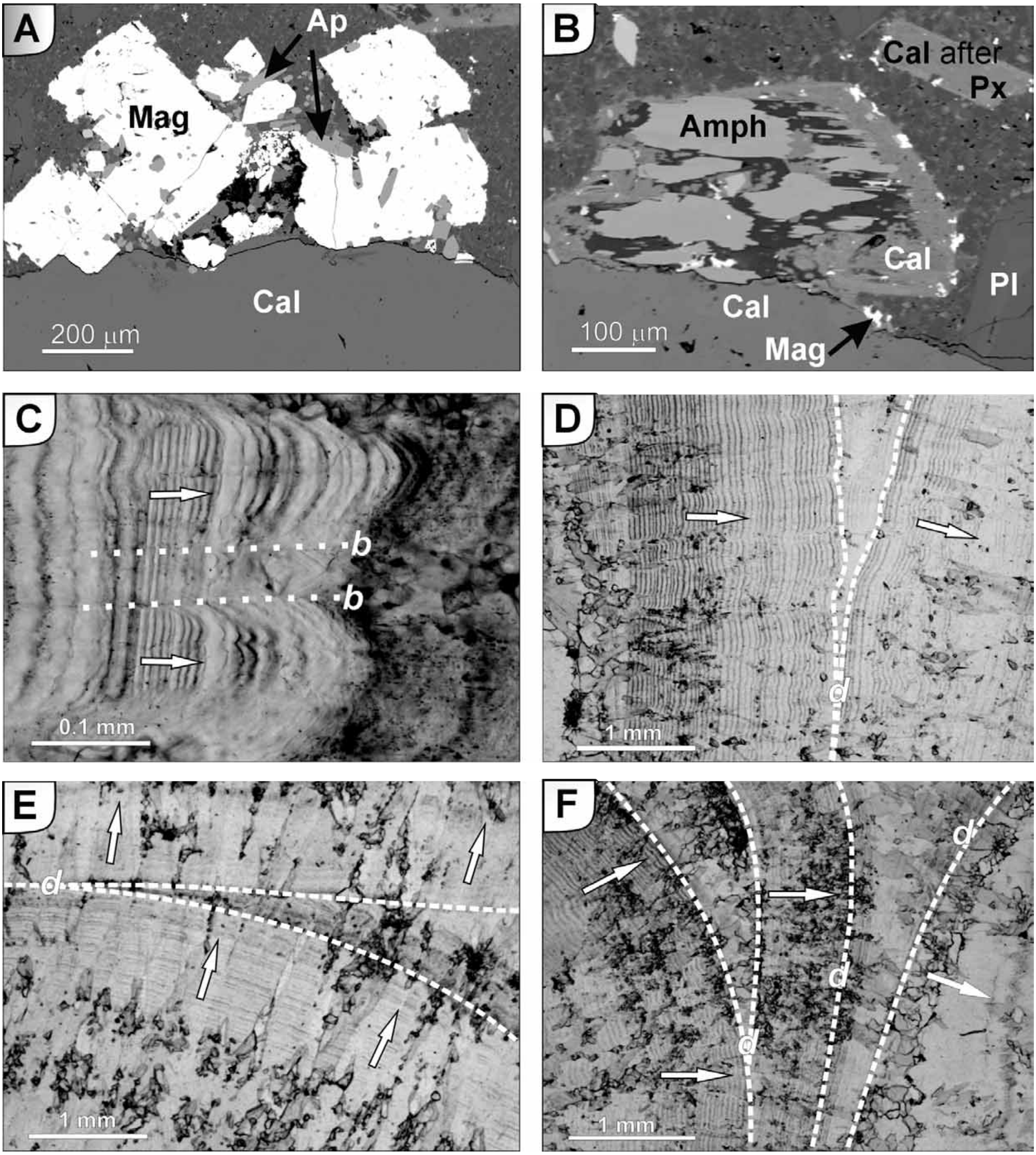

Fig. 4. Petrography of the flowstone-like calcite at Jarmuta Mt. A-B – Back scattered electron (BSE) images illustrating the contact between flowstone-like calcite and andesite. The andesite contains phenocrysts of amphibole and pyroxene, partly or completely replaced by calcite; C-F – internal texture of flowstone-like calcite visible under transmitted polarised light, parallel nicols. Thin growth zones of calcite are emphasised by a small admixture of clay minerals (dark grey); compromise boundary (b – dotted line) and dissolution surfaces (d – dashed lines on fig. D-F); arrows indicate the crystal growth direction; Cal – calcite, Mag – magnetite, Pl – plagioclase, Px – pyroxene

Petrography of the flowstone-like calcite veins

The flowstone-like calcite filling the extensional fractures in the andesite exploited in the quarry on Jarmuta Mt. is composed of radial-fibrous calcite (Text-fig. 3A). Within the flowstone-like calcite angular andesite fragments of different sizes (Text-fig. 2A-B) occur commonly and can also be observed in thin sections (Text-fig. 3B-C). The contact between the calcite and andesite is sharp, without traces of thermal or chemical influence (Text-fig. 4A-B). No clastic material from the sandstone and shale building the Magura Nappe surrounding the andesite has been observed in the calcite veins.

The calcite veins is composed of elongated crystals; individual grains are up to 2-3 mm long (Text-fig. 3A, C). The flow-stone like calcite are characterised by the absence of twinning (Text-fig. 3A), which distinguishes them from the calcite that fills fractures in the sandstones (Jarmuta Formation) of the Magura Nappe (Text-fig. 3D). Individual crystals lie parallel to each other and perpendicular to the planes of the extensional fractures (surfaces with incipient crystals). Microscopic images show growth zones on which the subsequent flowstone-like calcite accretes (Text-fig. 4C-D). Compromise boundaries along which the simultaneously growing calcite crystals adapt to each other, as well as zones documenting episodes of multiple dissolution of earlier-formed calcite can also be observed (Text-fig. 4D-F). The individual growth zones of the flowstone-like calcite are clearly distinguishable due to the presence of small amounts of dust-like clay minerals (Text-fig. 4C-F). The admixture of these minerals is clearly visible in the microscopic images (Text-fig. 4C) and was documented by XRD analyses (Text-fig. 5).

Other textural varieties of calcite

Besides the flowstone-like calcite within the extensional fractures, several other types of calcite mineralization have been recognised. These calcites occur as veins (in the andesite and in the Jarmuta Formation of the Magura Nappe), as pseudomorphs after pyroxene, amphibole and plagioclase phenocrysts, as well as in the form of irregular concentrations replacing the fine-grained groundmass.

In the andesite occur thin veins, up to several millimetres wide, filled with blocky calcite (Text-fig. 6E). Within the veins there are small fragments of andesite; one of them, composed of amphibole, is surrounded by thin contact zone of a mixture of fine-crystalline clay minerals and iron hydroxides (Text-fig. 6F). The calcite veins from the Magura

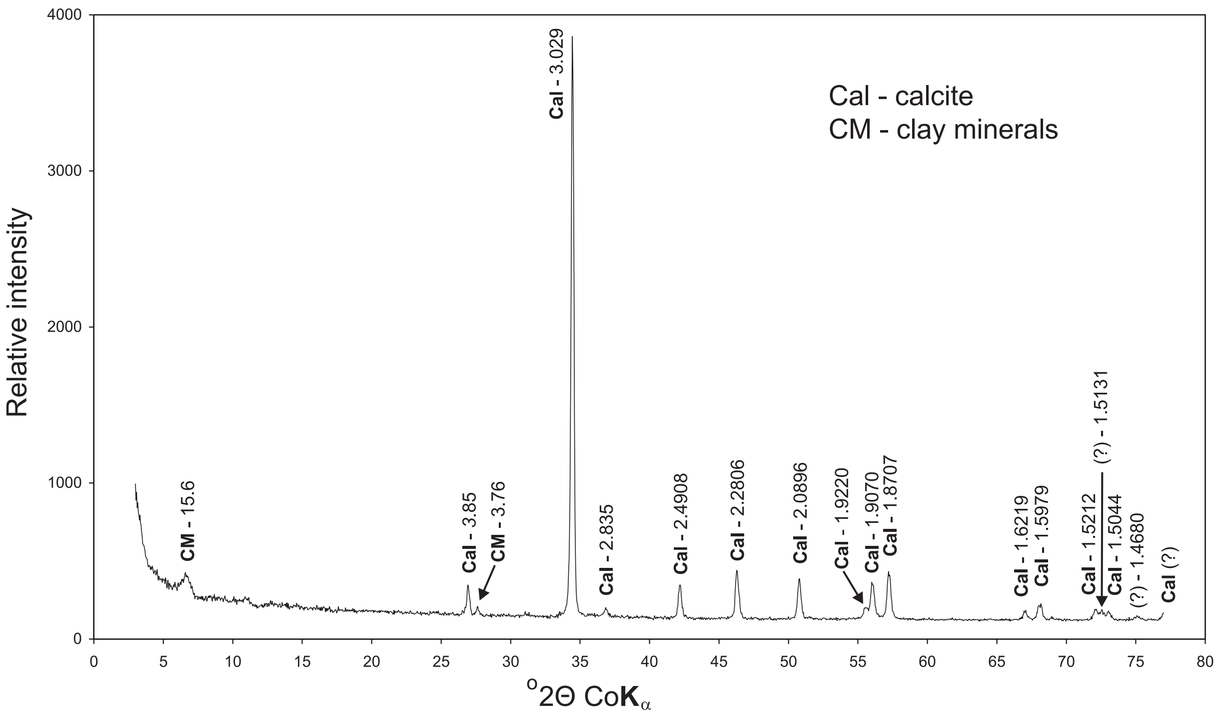

Fig. 5. XRD pattern of the flowstone-like calcite from extensional vein in andesite at Jarmuta Mt.; sample P-1

Nappe sandstones (Jarmuta Formation) are from several mm to over ten cm wide. The veins have a blocky calcite structure of large euhedral crystals (ca. 2-3 cm) with a well-developed network of twinning lamellae, with local deformation zones which, according to PASSCHIER & TROUW (1997), may indicate temperatures above 200°C.

The pyroxene, amphibole and feldspar phenocrysts, as well as the groundmass in between them, are commonly replaced by calcite (Text-fig. 6A-D). These calcite replacements have been observed at different stages of their development, from the initial stages, i.e. areoles of calcite around the phenocrysts (Text-fig. 4B), to calcite pseudo-

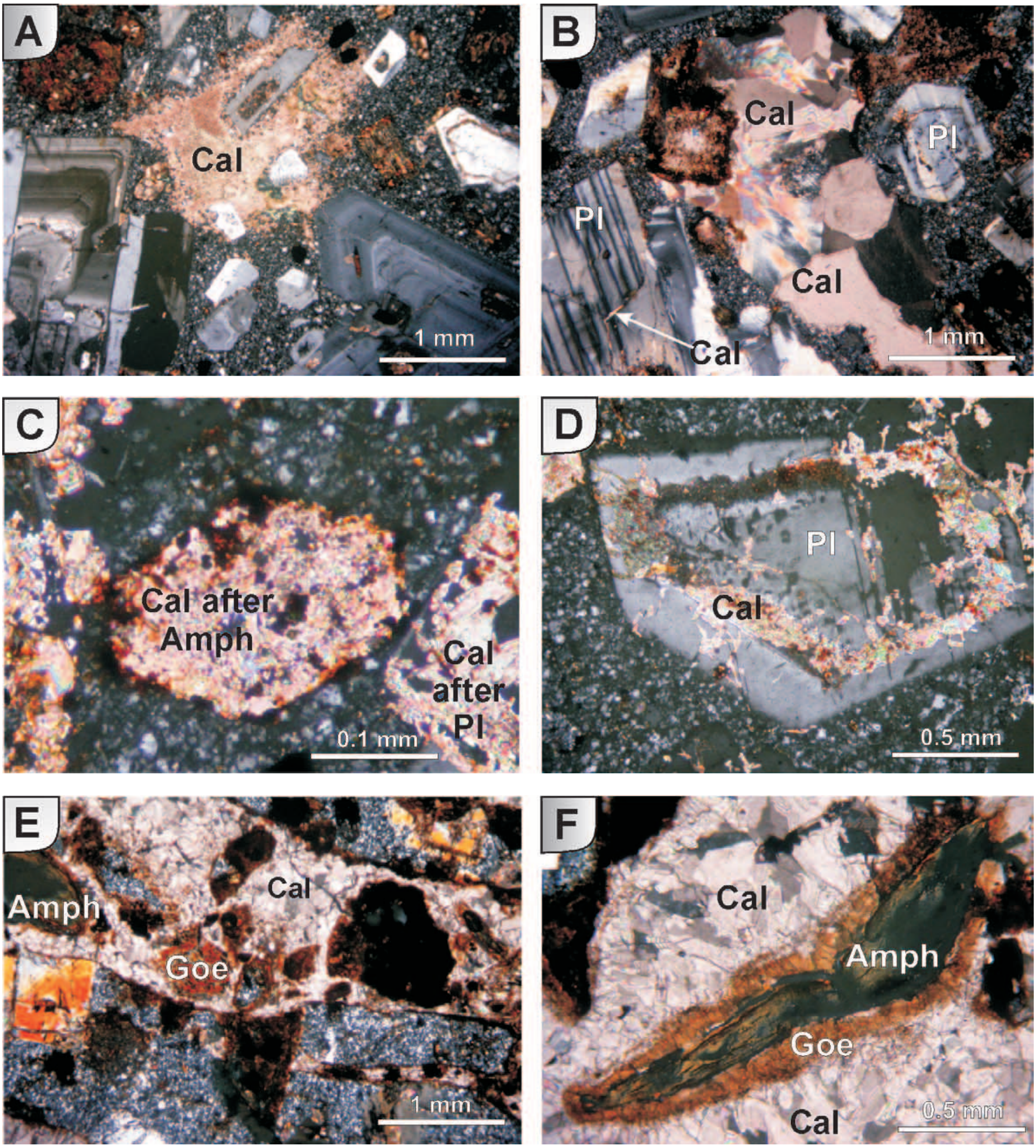

Fig. 6. Calcite mineralization in andesite from the Jarmuta Mt. A – fine grained calcite within the andesite groundmass; B – irregular calcite aggregate within andesite and micro-vein of calcite within fractured crystal of plagioclase (arrowed); C – calcite pseudomorph after pyroxene and plagioclase phenocrysts; D – fine-grained calcite replacements along growth zone of plagioclase; E – thin veins of calcite within cataclased andesite; F – vein of calcite with fragments of altered amphibole, rimmed by goethite; Amph – amphibole, Cal – calcite, Goe – goethite, Pl – plagioclase, Px – pyroxene; transmitted light, crossed polars

morphs after pyroxene and amphibole crystals (Text-figs 4B, 6C). It is not precluded that Ca-rich growth zones in plagioclase phenocrysts were selectively replaced by calcite (Text-fig. 6D).

Chemical composition of the calcite

The chemical composition of the calcite within the extensional fractures in the andesite was determined by analyses of whole rock samples and EPMA.

ICP ES and ICP MS determinations of the chemical composition of the flowstone-like calcite carried out in ACME show very low concentrations of trace elements (Table 1). The flowstone-like calcite is composed almost entirely of stoichiometric calcite containing only minor quantities of MgO (up to 0.7 wt. %). The presence of such elements as Ba, Sr, U and Y, at concentration which exceeded the detection level of the ICP MS method used at ACME, was also noted. In contrast to the flowstone-like calcite, the calcite veins from the Jarmuta Formation revealed higher concentrations of Sr (1234.1 ppm) and Ba (6089.6 ppm), as well as ICP MS-measurable concentrations of REE (Table 1). Their REE pattern, normalised to the North American Shale Composition standard (NASC) (Gromet & *al.* 1984) gave a flat REE pattern with a distinct positive Eu anomaly (Text-fig. 7).

The chemical composition of the flowstone-like calcite was also determined by EPMA analyses and compared with determinations of other forms of calcite occurrences in the andesite and in deposits of the Magura Nappe (Text-fig. 8). Microprobe analyses were carried out on calcites occurring as flowstone-like calcite, thin veins in andesite, calcite intergrowths in pseudomorphs after pyroxene and amphibole phenocrysts, and in palisade calcite from veins in the Magura Nappe.

Flowstone-like calcite. The chemical composition of calcite filling the extensional fractures in andesite is close to that of stoichiometric calcite. The only significant admixture of this calcite generation is magnesium, the MgO content varying from 0.6 to 1.08 wt. %. The total content of Mn, Fe and Sr oxides did not exceed 0.17 wt. %.

Thin calcite veins in andesite. The chemical composition of the calcite veins is distinctly different from that of the flowstone-like calcite. This calcite is characterised by a very high content of MnO, between 3.5 and 4.35 wt. %, and increased concentrations of FeO (between 1.39 to 2.02 wt. %) and MgO (between 0.28 and 0.43 wt. %). The content of strontium in this calcite generation is very low and does not exceed 0.07 wt. %.

Calcite pseudomorphs after pyroxene phenocrysts. The chemical composition of calcite occurring with layered silicates in pseudomorphs after pyroxene is

Sample	P-16	M-15	Aver_AJm
		wt. %	
Fe2O3	0.04	0.96	5.56
MnO	0.01	0.14	0.14
MgO	0.75	0.26	1.74
CaO	55.76	54.62	7.79
LOI	43.4	43	3.43
TOT/C	12.29	12.09	n.a.
TOT/S	0.01	0.12	n.a.
Total	99.92	98.98	99.72
		ppm	
Pb	23	1.1	4.55
Sr	201.9	1234.1	863.18
Ba	107.5	6089.6	702.48
Th	*< 0.1*	*< 0.1*	6.55
U	0.3	*< 0.1*	2.28
Y	0.5	4.2	19.35
La	*< 0.5*	0.8	31.02
Ce	*< 0.5*	1.8	58.58
Pr	0.03	0.28	6.44
Nd	*< 0.4*	1.4	24.38
Sm	*< 0.1*	0.3	4.65
Eu	*< 0.05*	0.41	1.42
Gd	*< 0.05*	0.6	3.70
Tb	0.02	0.09	0.58
Dy	0.06	0.76	3.19
Ho	*< 0.05*	0.13	0.63
Er	*< 0.05*	0.32	1.78
Tm	*< 0.05*	*< 0.05*	0.28
Yb	*< 0.05*	0.19	1.76
Lu	*< 0.01*	0.03	0.27

Table 1. Chemical composition of the calcite veins. Sample P-16 represents flowstone-like calcite from the andesite at Jarmuta Mt., sample M-15 – the calcite vein with typical palisade texture from the Jarmuta Formation (Magura Nappe), Aver_AJm average chemistry of the andesite from Jarmuta Mt. calculated on the basis of 6 analysed samples

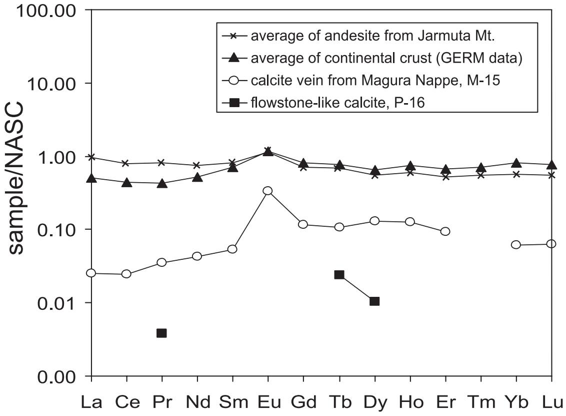

Fig. 7. REE pattern of the calcite veins from Jarmuta Mt. Chemical data for North American Shell Composition standard (NASC) after GROMET & *al.* (1984); average chemical composition of continental crust from GERM database (http:\\ earth-ref.org) containing modified data of TAYLOR & MCLENNAN (1985)

characterised by a high content of FeO and MgO, from 11.27 to 18.53 wt. % and from 7.49 wt. % to 9.31 wt. %, respectively. The MnO content lies between 0.90 and 1.98 wt. %. The content of SrO in this calcite, as in the previous two generations, is low and does not exceed 0.05 wt. %.

Calcite pseudomorphs after amphibole phenocrysts. The chemical composition of this calcite is close to the composition of calcite developed as thin veins in the andesitic cataclastic rock. It is characterised by a higher content of Mn, between 2.20 to 3.26 wt. %, and of FeO, from 0.43 to 1.21 wt. %. Concentrations of MgO typically lie within 0.28 to 0.82 wt. %; sporadically higher concentrations up to 1.21 wt. % have been noted. The content of SrO in this calcite generation very rarely exceeds 0.10 wt. %.

Calcite veins in the Magura Nappe. Calcite occurring in the form of veins of palisade calcite in the Magura Nappe is characterised by a high content of SrO, reaching 0.28 wt. %. The concentrations of FeO and MnO typically do not exceed 1 wt. %: FeO (0.42 to 1.02 wt. %); MnO (0.23 to 0.51 wt. %). MgO concentrations in this calcite generation were typically below detection level; single analyses indicated up to 0.2 wt. % of MgO.

RESULTS OF ISOTOPIC ANALYSES

Three samples of flowstone-like calcite from the total of 18 samples were selected for U-series dating and stable isotope study. All the samples studied were composed of non-porous, dense, well-crystallised calcite with no traces of re-crystallisation or secondary dissolution and cementation. Sample Jarmuta-1 was divided into two parts that were dated separately. The results of the geochronological investigations of the three samples of the flowstone-like calcite in the extensional fractures on Jarmuta Mt., compiled in Table 2, yielded ages falling in the range 2.48 ± 0.54 to 6.39 ± 0.72 ka. The results of stable isotope composition (oxygen and carbon) of the calcite samples from Jarmuta

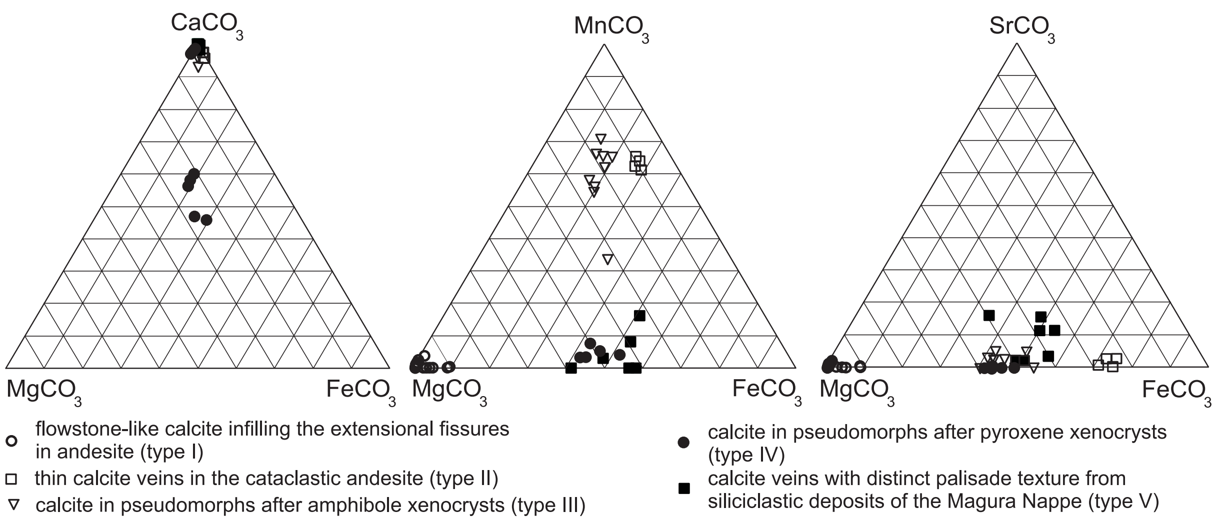

Fig. 8. Chemistry of the different generations of the calcite from andesite at Jarmuta Mt. determined by means of EPMA

Sample	Lab. No.	U [ppm]	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{230}Th/^{232}Th$	Age [ka]
Jarmuta 1/1	W 1453	0.2604±0.0084	1.8056±0.0626	0.0432±0.0044	46	4.78 ± 0.51
Jarmuta 1/2	W 1454	0.2643±0.0011	1.8671±0.0800	0.0574±0.0063	28	6.39 ± 0.72
Jarmuta 2	W 1455	0.1665±0.0094	2.0064±0.1093	0.0348±0.0060	137	3.83 ± 0.67
Jarmuta 3	W 1456	0.2459±0.0133	1.9236±0.1042	0.0226±0.0049	33	2.48 ± 0.54

Table 2. U-series dating of flowstone-like calcite from andesite on Jarmuta Mt.

Sample	Age [ka]	$\delta^{18}O$ [‰]	$\delta^{13}C$ [‰]
Jarmuta			
Jarmuta 1 a	ca. 6.4 – 4.8	-7.945	-7.472
Jarmuta 1 b		-7.714	-7.818
Jarmuta 1 c		-7.434	-8.567
Jarmuta 2 a	ca. 3.8	-7.616	-8.722
Jarmuta 2 b		-7.238	-9.288
		-7.246	-9.297
Jarmuta 3 a	ca. 2.5	-7.266	-8.288
		-7.264	-8.257
Jarmuta 3 b		-7.320	-8.356
Aksamitka Cave			
Aksamitka 1	ca. 120	-7.440	-5.368
Aksamitka 2	ca. 100	-7.215	-3.599
Aksamitka 3	ca. 60	-7.441	-3.619
Schron przy Piecu Majki Cave			
PM 2/1	ca. 5.7	-6.720	-9.469
		-6.712	-9.491
PM 2/2	ca. 3.7	-6.534	-9.101

Table 3. Oxygen and carbon isotope composition of flowstone-like calcite from Jarmuta Mt. and speleothems from Aksamitka and Schron przy Piecu Majki Caves

Mt. are summarised in Table 3. For the purpose of comparison of the stable isotope composition, speleothems from the Aksamitka Cave and the Schron przy Piecu Majki Cave were also investigated (Table 3). These caves are located in the vicinity of the study area (see Text-fig. 1A for location).

DISCUSSION

The chemical composition of flowstone-like calcite filling the extensional fractures in the andesite on Jarmuta Mt. differs from the composition of calcites of other origin that are also recognised in the andesite (Text-figs 7-8). The calcite occurring in the form of thin veins in the andesite, and as pseudomorphs after pyroxene and amphibole phenocrysts, are characterised by a high contents of Fe, Mg and Mn, showing the influence of the chemical composition of the surrounding rocks on the concentration of these elements in the calcite (Text-fig. 8). The low content of Fe and Mn in the calcite filling the extensional fractures indicates that its origin was not linked with the evolution of the hydrothermal solutions.

The higher content of SrO determined in the calcite veins from the Magura Nappe (Jarmuta Formation) may be a result of relict sea-water influencing the composition of the formation water. On the other hand, the very low content of SrO in the flowstone-like calcite points to the lack of a genetic link with the formation water from the Magura Nappe. The composition of the water responsible for the growth of the flowstone-like calcite in the andesite was probably controlled solely by meteoric water. Higher concentrations of MgO reflect a small admixture of clay minerals (Text-fig. 4C-F), probably trioctahedral smectites, as evidenced by the position *(00l)* of reflections at 15.6 Å and 3.76 Å. (Text-fig. 5). The insignificant influence of formation water from the Magura Nappe deposits may point to the formation of the flowstone-like calcite in the andesite after the uplift of the study area, which resulted in the runoff of formation water with an increased content of SrO. The absence of a genetic link between the flowstone-like calcite and the calcite veins of palisade texture from the Jarmuta Formation (Magura Nappe) is also supported by REE data (Text-fig. 7).

The flowstone-like calcite filling the extensional fractures in the andesite on Jarmuta Mt. is similar with regard to its growth, chemical composition and conditions of origin to cave flowstones, e.g. in the Aksamitka Cave, from which it differs in its younger age. The oxygen isotope composition of the Jarmuta calcite is similar to that of the Aksamitka stalagmite (Table 3). The heavier carbon in the Aksamitka stalagmite suggests a lower proportion of biogenic carbon – the rock overburden above the cave was thicker. The heavier oxygen in the flowstone from the Schron przy Piecu Majki Cave is probably a result of deposition in a shallow cave and partial evaporation. In effect, microcrystalline, white, porous calcite was deposited.

Investigations of the isotopic composition of common occurrences of CO_2-rich and CO_2-free water in the Polish Outer Carpathians indicate their complex genesis, i.e. mixing between meteoric and diagenetic waters released during burial diagenesis, and show no relation to the andesite volcanism (OSZCZYPKO & ZUBER 2002). The chemical and isotopic compositions of the flowstone-like calcite indicate that the waters from which the calcite crystallised in the extensional fractures were also not related to the andesite (Text-figs 7-8). This calcite could have crystallised from surface waters, e.g. the stream waters presently flowing from the Siodło pass on Jarmuta Mt., which disappear in the vicinity of the northern boundary of the andesite dyke, close to the flowstone-like calcite veins (perhaps in analogous extensional fractures). This interpretation is evidenced by the similar isotopic composition of $\delta^{18}O$ in the flowstone-like calcite (Table 3) to that of other spelean deposits occurring in the vicinity of Krościenko (Aksamitka and Schron przy piecu Majki caves), which evidently precipitated from meteoric water (Text-fig. 9). Additionally, the $\delta^{18}O$ signature of the calcite studied falls into the range of the spelean deposits precipitated from mineral water in the vicinity of Krynica (Text-fig. 9),

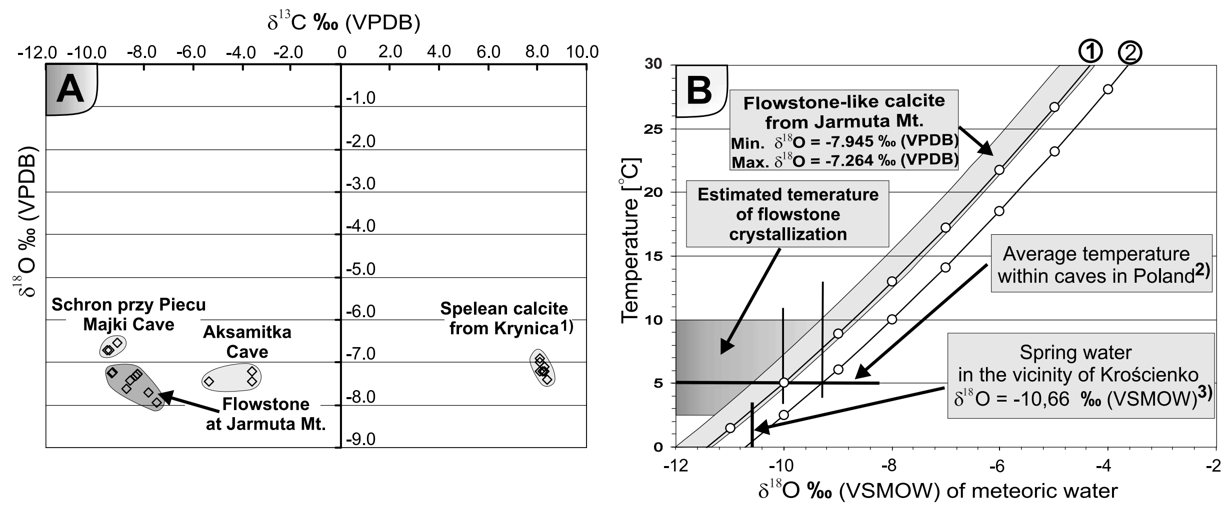

Fig. 9. Stable isotopic composition of the studied flowstone-like calcite; A) Plot of $\delta^{13}C$ vs. $\delta^{18}O$ of the flowstone-like calcite at Jarmuta Mt. in comparison to the data for spelean calcite located in the vicinity of the study area; $\delta^{18}O$ vs temperature plot for studied flowstone-like calcite. The grey zone represent the $\delta^{18}O$ calcite composition of the flowstone-like calcite from Jarmuta Mt. expressed as a function of temperature and istotopic composition of the meteoric water, calculated using the equation of HAYS & GROSSMAN (1991); 1 – calcite from Aksamitka Cave, 2 – calcite from Schron przy Piecu Majki Cave. 1)DULIŃSKI & *al.* (1995); 2)SIARZEWSKI 1996; 3)HUMNICKI (2006)

in which the oxygen isotopic composition was controlled by shallow groundwater of meteoric origin (DULIŃSKI & *al.* 1995). The scattered $\delta^{13}C$ values in the calcite samples studied (Text-fig. 9) may reflect the interaction of meteoric water with host rocks, input of organic carbon derived from soil-gas CO_2 or the influence of CO_2 of deep origin, as was suggested for spelean calcites from the vicinity of Krynica (DULIŃSKI & *al.* 1995). Taking into account the composition of spring water in the vicinity of Szczawnica (^{18}O (VSMOW) from -10.9 ‰ to -10.42‰; according to HUMNICKI 2006), average annual temperature within Carpathian caves (SIARZEWSKI 1996), as well as $\delta^{18}O$ values of the calcite in the range -7.945 ‰ (VPDB) to -7.238 ‰ (VPDB), we postulate a low temperature of crystallisation of the flowstone-like calcite, probably not exceeding 10°C (Text-fig. 9).

U-series dating results indicate a young, Holocene age of the flowstone-like calcite. The stable isotope composition of the calcite is in the range typical of calcites precipitating from meteoric water (Text-fig. 9). There are no isotopic indicators of a hydrothermal origin. The probable mechanism of formation of the flowstone-like calcite was crystallisation from meteoric water under conditions similar to those in caves. Likewise, observation of fluid inclusions (one-phase, small and usually located at the contact of mineral grains) indicates their low-temperature origin. In southern Poland, the date of about 6.5 ka can be correlated with the late Atlantic period (when the climate was slightly warmer and more oceanic than today), which later passed into the subboreal phase (LINDNER 1992). The vadose origin of the calcite suggests that the rhythmically distributed clay mineral intergrowths (Text-figs 4C-F) may reflect annual growth zones (see FAIRCHILD & *al*. 2001; BETENCOURT & *al.* 2002). Calculation of the number of growth zones in the 2.5-cm flowstone-like calcite (Text-fig. 2A), on the assumption that each growth zone was produced during one year, shows that the calcite grew for at least 500 years. Numerous traces of dissolution indicate that this phenomenon was probably even longer (see Text-fig. 4D-F).

The Holocene age of the flowstone-like calcite filling the extensional fractures does not automatically point to the age of the fractures themselves. Observations of fracture walls in the field, as well as under a polarising microscope and electron microscope, show that the andesite did not undergo earlier weathering, as the fracture walls are rough, with numerous angular fragments of andesite (Text-figs 2-4). It can be assumed that the filling by calcite took place directly after the formation of the fractures, which is evidenced by the lack of clastic material (e.g. detrital quartz) in the calcite.

The open character of fractures not completely filled with calcite, as well as the morphology of the wall surfaces indicates their extensional origin. The same tectonic regime was also responsible for the formation of fractures parallel to the elongated textures within catactastic zones. The spatial orientation of the fractures with the flowstone-like calcite shows geometric correspondence with the course of the andesite dykes and orientation of fractures and cataclastic zones within the dykes (Text-fig. 1). Analysis of the chemical composition of the andesite from the Szczawnica region (PIN & *al*. 2004; JUREWICZ & NEJBERT 2005) indicates that its composition is not typical of andesite from subduction zones, and that its formation may be linked with a deep dextral fault zone – the Dunajec Fault. The dyke array has an *en échelon* position to the Dunajec Fault, which can be correlated with the tectonic contact between the Małopolska and Upper Silesian blocks.

Dextral strike-slip activity in this zone might have been responsible for the formation of adhesion zones utilised by the andesite magma in the Miocene as well as for the extensional fractures filled with flowstone-like calcites in the Holocene. The extensional fractures probably formed as ripout lenses due to the increasing strike-slip movement along the Dunajec Fault (see SWANSON 2005). The fact that extensional fractures filled with flowstone-like calcite occur only within the andesite dykes may be attributable to the heterogeneity and steep dips of the rocks of the Magura Nappe: the extensional stresses were probably released on the bed surfaces so that extensional fractures were not able to form.

The tectonic character of the boundary between the Upper Silesian and Małopolska blocks has been discussed e.g. by: BOGACZ (1980), BROCHWICZ-LEWIŃSKI & *al*. (1983), OBERC (1994), BUŁA & *al*. (1997) and MALINOWSKI & *al*. (2005). The most complex structural study of this contact zone, its kinematic and dynamic analysis based on both field studies and core data, was presented by ŻABA (1999). Several intervals of increased strike-slip tectonic activity have been distinguished within this zone. The first interval was linked with sinistral transpression at the Silurian/Devonian boundary, when the Małopolska Block underwent relative uplift, accompanied by the formation of flower structures and small-scale volcanic activity. The second interval took place in the Late Carboniferous and was linked with two stages of dextral transpression, accompanied by intense granite formation. A later stage of tectonic activity in this zone is evidenced by the Miocene andesite dykes around this zone in the vicinity of Szczawnica. Finally, calcite from the extensional fractures with flowstone-like calcite dates the youngest tectonic activity in this zone to the Holocene (see Table 2).

The Dunajec Fault is not the only fault of this type in the PKB area; a similar, parallel deep-fault zone most probably occurs to the east of it, along the Poprad River valley. Its activity is evidenced e.g. by small seismic shocks noted in historical times (WIEJACZ 1994). Such zones may also occur to the west of the Dunajec Fault, e.g. the Rieka Fault, Białka Fault and Czarny Dunajec Fault (JUREWICZ 2005). Movement on the last fault might have been responsible for the earthquake in December 2004 (magnitude 4.7 on the Richter scale), the epicentre of which was in the Czarny Dunajec region.

CONCLUSIONS

1. Fractures cutting the andesite dykes, in which flowstone-like calcite was noted, are of extensional origin, which is evidenced e.g. by the rough walls of the fractures, fracture widths in the range of over ten centimetres and their incomplete filling.
2. The U-Th age of the flowstone-like calcite is ~2.5–6.5 ka, which points to the fact that it was formed under climatic conditions similar to those of modern times and at a similar relief. The calcite grew on a rough and unweathered andesite surface and its age can therefore be attributed to the age of the fractures.
3. The isotopic composition of the calcite filling the fractures indicates its low-temperature crystallisation conditions and vadose origin. The growth pattern is similar to that of cave flowstones.
4. The presence of zones rich in clay minerals may reflect annual climatic oscillations, suggesting that the calcite formed over an interval of at least 500 years.
5. Neither the calcite filling the extensional fractures nor the calcite cementing the loosened cataclastic zones bears evidences of later deformation (lack of twinning, fractures, and displacements).
6. The extensional origin and geometrical features indicate that the formation of the fractures could be linked with increased strike-slip activity within the deep fracture zone known as the Dunajec Fault. The latter fault could be correlated with a southern prolongation of the boundary between the Upper Silesian and Małopolska blocks. The spatial distribution of the fractures shows that they display an *en échelon* pattern around this zone.

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