

ORIGIN OF CALCITE-CEMENTED HOLOCENE SLOPE BRECCIAS FROM THE DŁUGA VALLEY (THE WESTERN TATRA MOUNTAINS)

Michał GRADZIŃSKI¹, Renata JACH¹ & Ewa STWORZEWICZ²

¹ *Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2a, 30-063 Kraków, Poland, M.G. e-mail: gradzinm@ing.uj.edu.pl, R.J. e-mail: jach@ing.uj.edu.pl*

² *Institute of Systematics and Evolution of Animals, Polish Academy of Sciences, ul. Sławkowska 17, 31-016 Kraków, Poland, e-mail: stworzewicz@isez.pan.krakow.pl*

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Abstract: New locality of slope breccias was found in the Western Tatra Mts. It occurs in the Długa Valley on a steep slope of ravine beneath the belt of Jurassic radiolarite cliffs. The breccia consists of angular clasts of radiolarite bound with calcite cements. Void spaces between the clasts contain shells of Holocene snails. The cements are built of columnar crystals composed of acicular subcrystals and of skeletal crystals. The crystals grew rapidly from supersaturated solution due to CO₂ degassing. Cementation occurred in vadose conditions in the Atlantic Phase soon after the scree formation.

Key words: slope breccias, calcite cements, radiocarbon dating, Holocene, Tatra Mts.

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INTRODUCTION

Distinctive Quaternary deposits, known as slope breccias, occur in the Western Tatra Mountains. They consist of clasts of local carbonate rocks bound with calcite cements. Such breccias were found in a few small outcrops. They were first reported by Rabowski (1930) from the Miętusia and Mała Łąka Valleys (see also Zawidzka, 1967). Kotański (1954, 1958) found and described other occurrences of slope breccias – in the lower part of the Tomanowa Valley, near the Iwaniacka Pass and near the Beskid Pass, among others. Similar deposits have been reported by Głazek (1965) from the Lejowa Valley. The hitherto described slope breccias did not include any faunal remains, which precluded their precise dating. Some of the breccias have been considered to be Pleistocene in age, on the grounds of superposition or their present form and location (Kotański, 1958; Zawidzka, 1967). Other ones are Holocene in age, and some of these are possibly still growing (Głazek, 1965; Kotański, 1979).

Similar breccias, known from the Northern Calcareous Alps (Ampferer, 1907), and from the Central Carpathians in Slovakia (Ložek, 1960; Ložek & Zaruba, 1965; Šavrnich, 1984), are accepted, also on the base of malacofauna, to be interglacial Pleistocene deposits. By analogy, the slope breccias from the Tatra were referred to Holocene or warm phases of Pleistocene (Kotański, 1958; Zawidzka, 1967). It

should be stressed, however, that the age of any of the breccias in the Tatra has been not firmly determined, neither palaeontologically nor radiometrically. No studies have been also done into the petrography of their cements or conditions and mechanism of their cementation.

This paper presents the result of a study on the age and formation conditions of the slope breccias found at a new locality, in the Długa Valley (Fig. 1, cf. Gradziński *et al.*, 2000). The locality, found in summer 2000, has not been earlier reported in literature.

LOCATION OF THE BRECCIAS

The Długa Valley is a left-side tributary valley of the Chochołowska Valley. It extends from the state boundary on the west to the Huciska glade in east and is ca. 1700 m long. It begins at a junction of several steep ravines. The whole drainage basin of the Długa valley is incised into carbonate and siliceous rocks of the Križna Nappe, monoclinally dipping to the north (Guzik & Guzik, 1958; Guzik, 1959). Cliffs and steps built of layered Jurassic radiolarites of the Sokolica Radiolarite Formation occur near the mentioned junction of the ravines (Lefeld *et al.*, 1985).

The breccias were found in the southernmost ravine, at an altitude of ca. 1250 m about 1500 m from the mouth of the Długa Valley (Fig. 1). The breccias occur as cemented

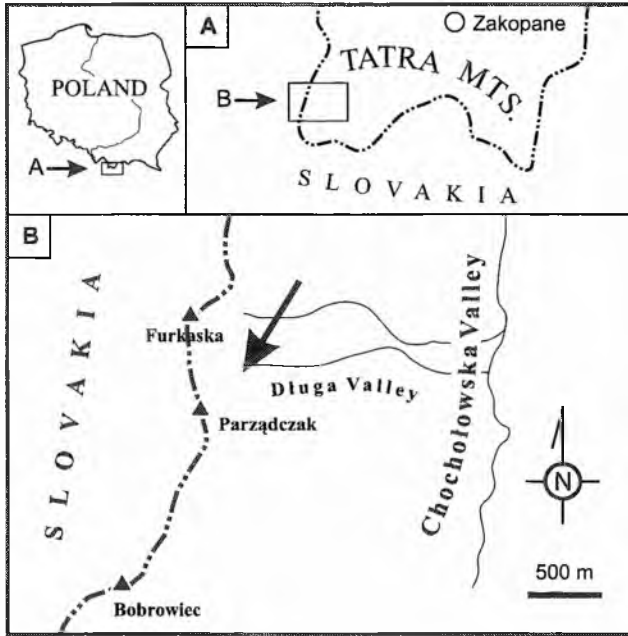


Fig. 1. Location of studied breccia outcrop

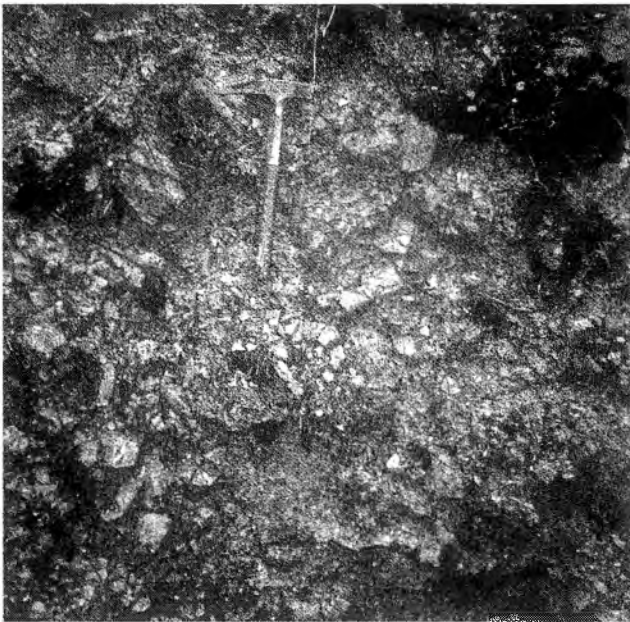


Fig. 2. A part of rock-cliff built of breccia

rubble, covered with vegetation. The rubble covers the steep left slope of the ravine, directly beneath a belt of Jurassic radiolarite cliffs. The breccias are now being eroded and form small cliffs that locally exceed two metres in height (Fig. 2). Breccia fragments of various size can be found on the bottom of the ravine.

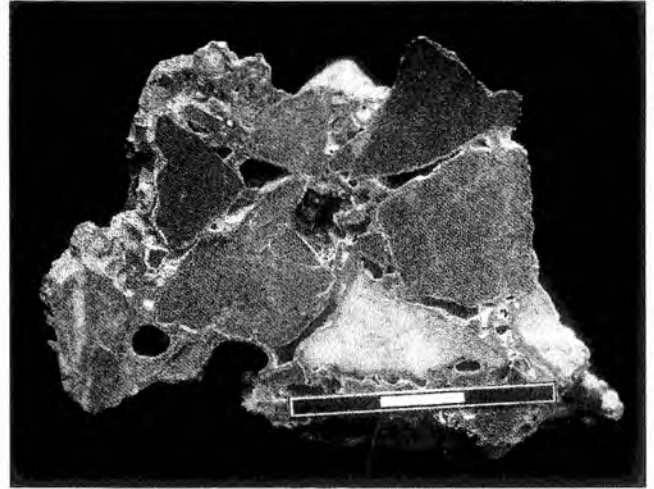


Fig. 3. Detailed view of breccia, polished section, note cavities between clasts, scale bar 3 cm

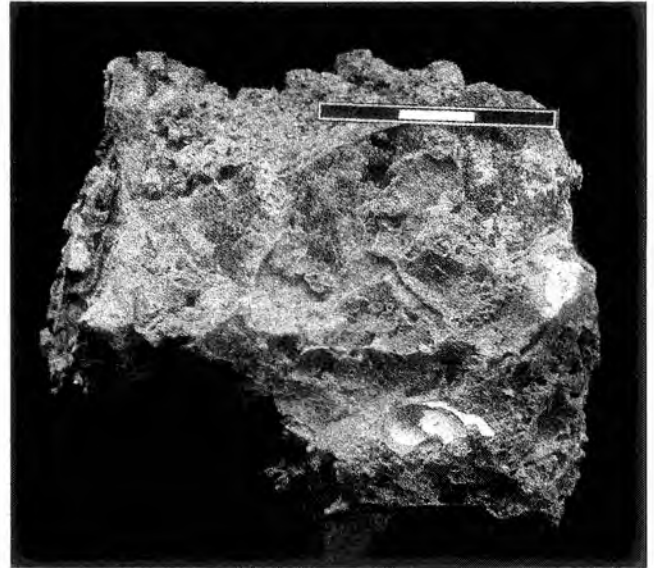


Fig. 4. Detailed view of breccia, note a broken snail shell, scale bar 3 cm

PETROGRAPHY OF THE BRECCIAS

Results

The breccia consists of angular clasts of radiolarites, and subordinate amount of red nodular limestones and light Upper Jurassic limestones. The angular clasts are usually from a few millimetres up to a dozen centimetres in size; exceptionally up to several tens of centimetres. The breccia is clast-supported and lacks fine-grained matrix (Figs 3, 4). Void spaces among the clasts contain snail shells debris. The distribution of the clasts is random and no sedimentary structures were seen in the outcrops.

The cement of the breccias occurs in the form of calcitic crusts on clast surfaces, usually coating the clasts completely. In general, the crusts reduce the void space between

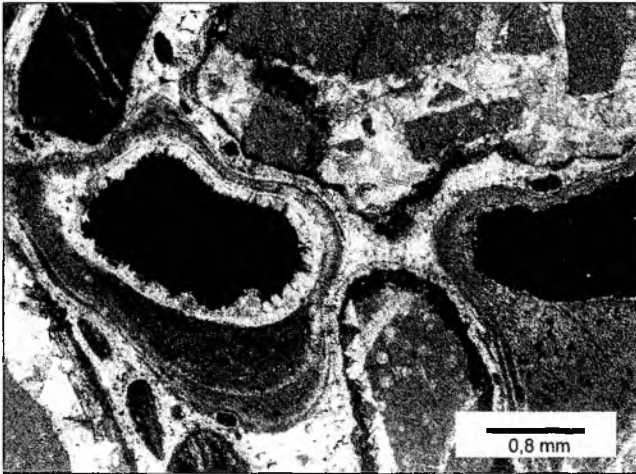


Fig. 5. Internal structure of breccia, meniscus cement joining adjacent clasts and voids filled with silt are visible, thin section, II nicols

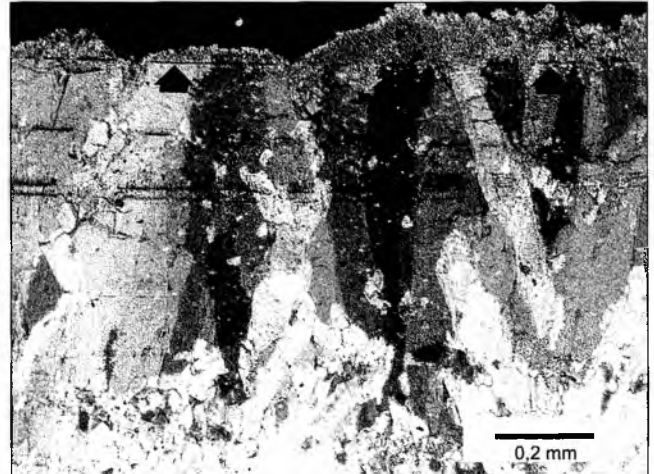


Fig. 6. Columnar calcite crystals, note competitive crystal growth pattern and flat crystal terminations (arrows), thin sections, X nicols

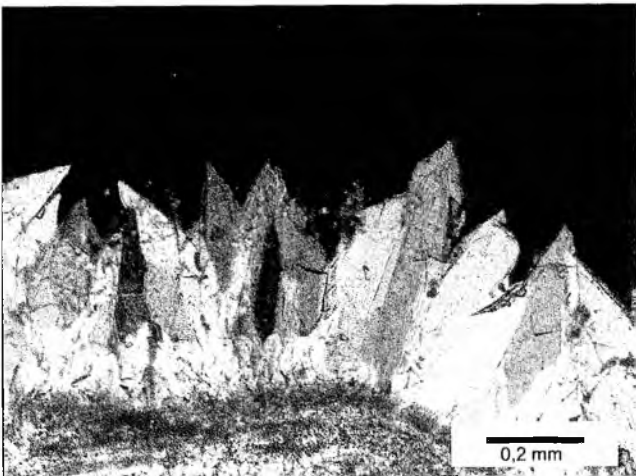


Fig. 7. Columnar calcite crystals growing inside snail shell, note competitive crystal growth pattern and acute crystal terminations, thin section, X nicols

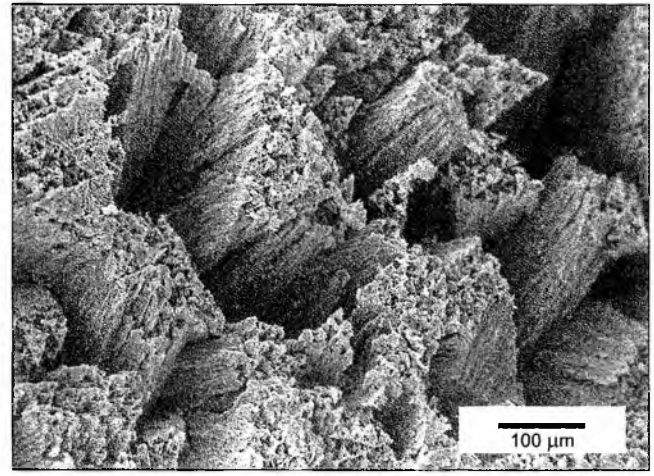


Fig. 8. Columnar crystals built of needle shaped subcrystals. SEM image

the clasts and constrict the throats between the voids. The crusts range in thickness from a millimetre to more than 4 mm. Most surfaces of the crusts are smooth, but acicular terminations of calcite crystals are sometimes visible with a naked eye.

The calcitic crusts are devoid of macroscopic voids, though they are fairly laminated. The lamination is marked by alternation of dark and light laminae, the latter being usually thicker. The laminae are subparallel to the surfaces of the encrusted clasts. Near the contacts between adjacent clasts the laminae are usually bent, and the crust forms bridges of meniscus cements (Fig. 5; cf. Dunham, 1971). Locally, the laminae on undersides of clasts are thicker and form microstalactites, characteristic of gravitational cements (cf. Müller, 1971). No structures characteristic for pedogenic conditions have been observed, such as rhizoids, rhizocretions or alveolar septal structures (cf. Tucker & Wright, 1990, p. 344).

Examination under transmitted-light microscope and

scanning electron microscope (SEM) has shown that the cements in the crusts consist of: (i) columnar calcite crystals, (ii) micritic calcite, (iii) non-carbonate admixture. It should be noted that no structures of organic origin have been found.

The columnar calcite crystals form compact laminae. Individual crystals are up to 1 mm in high and are triangular in sections perpendicular to their *c* axes (Figs 6, 7). The number of crystals often decreases with increasing distance from the nucleation surface, which means that they competed for free growth space (Bathurst, 1975, p. 422). Their terminations are often flat (Fig. 6), but at some places acute terminations are visible (Fig. 7). The terminations are often uniform within one cavity, that is all crystals in one cavity have acute terminations and flat in another. No traces of crystal corrosion have been found.

Observations in SEM indicate that many columnar calcite crystals consist of strongly elongated, acicular subcrystals, twinned along the *c* axis (Fig. 8). The SEM observa-

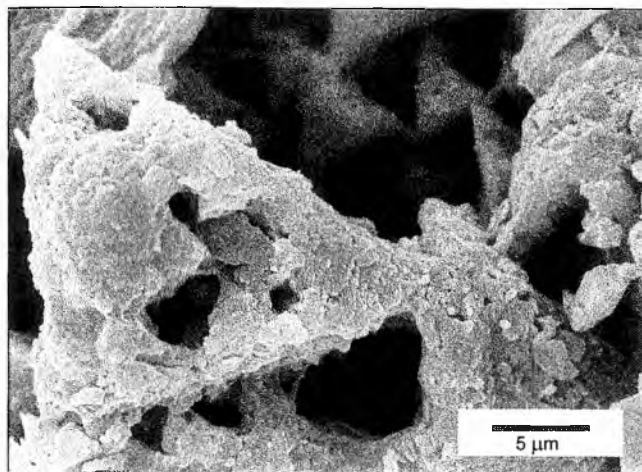


Fig. 9. Skeletal calcite crystal, SEM view

tions revealed also the presence of skeletal crystals of calcite (Fig. 9). They have only outer faces developed and grow successively from the faces inwards. Such crystals originate when outer faces grow faster than cores (Jones & Renault, 1996).

Calcite micrite often occurs in the described crusts as laminae of variable thickness, covering the columnar calcite crystals. Alternation of micrite laminae and laminae built of acicular calcite crystals imparts the distinctive, macroscopic lamination to the crusts. Calcite micrite is also lining the lower parts of many cavities. It forms then characteristic concentrations, crescentic in cross-section. Calcite micrite has not been found within snail shells.

The described crusts include sporadic fine quartz grains and homogenous dark peloidal aggregates. The agglomerates consist of clustered and bound silicate and iron oxide grains. Both the agglomerates and the quartz grains are detritic admixtures, incorporated into the calcitic cements.

Interpretation

The habits and fabrics of calcite in the cements of the breccias are comparable to those in various freshwater carbonate cements, including spelean calcites. The competitive growth of columnar calcite crystals proves that the crystals are primary, not transformed by diagenetic processes (Bathurst, 1975; González *et al.*, 1992). The columnar crystals, composed of distinct acicular subcrystals, and the skeletal crystals are a result of rapid crystal growth from highly supersaturated solution (Given & Wilkinson, 1985; González *et al.*, 1992; Jones & Renault, 1996).

The crystals with flat terminations grew in solution film of limited thickness. Such crystals originate at the air-water interface when lateral growth is forced, which results in flat termination, while acute termination can not form (*cf.* Broughton, 1983; Kostecka, 1993; Gradziński *et al.*, 1997). Microstalactitic cement present in the breccias, is also related to vadose conditions.

Calcite micrite was most probably brought in by percolating water, deposited in the cavities and then incorporated

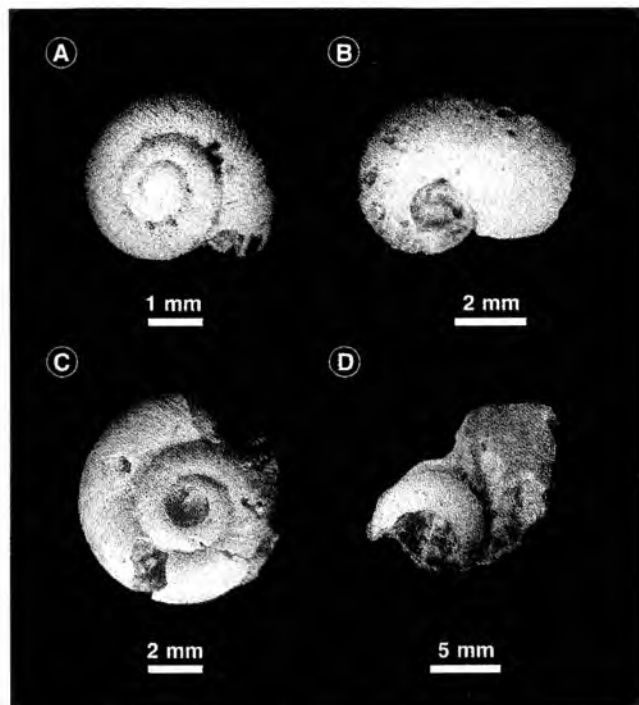


Fig. 10. Chosen snails found within breccia: A. *Discus rudertus*, B. *Eucobresia nivalis*, C. *Chilostoma cf. faustinum*, D. *Bradybaena fruticum*

into the calcite crusts. This micrite is hence a specific kind of internal sediment, similar to crystal silt, defined by Dunham (1969) and typical of vadose diagenetic environments. Such micrite may come from destruction of older carbonate rocks that built the breccias or from cements that crystallised earlier, though its genetic relation to biogenic processes can not be ruled out (*cf.* Jones & Kahle, 1995).

The described features indicate vadose cementation of the breccias. Phreatic conditions existed locally within the breccias, as prove the crystals with acute terminations. Such crystals grow from water films thicker than those from which grow the crystals with flat terminations (Kostecka, 1993; Gradziński *et al.*, 1997). The occurrence of these crystals on roofs of cavities is evidence of complete filling of the cavities with water, that is of local occurrence of perching phreatic conditions. The onset of phreatic conditions was probably related to episodes of intense water supply and possibly resulted from systematic decrease in permeability of the breccias, related to the decrease in size of cavities and constricting of the throats by progress in cementation.

MALACOFAUNA

The breccia includes sporadic snail shells. Most of them occur as small broken fragments. The shells are cemented together with the limestone rubble and, as the least mechanically resistant component, break during sampling. A few relatively well preserved specimens could be identified as *Bradybaena fruticum* (Müller), *Chilostoma cf. faustinum*

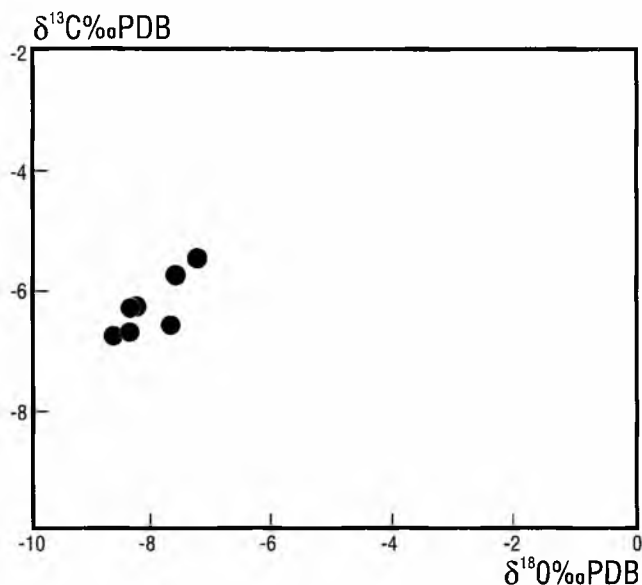


Fig. 11. Cross plot diagram showing stable isotope composition of calcite cements

(Rossmäslar), *Discus ruderatus* (Ferrusac) and *Eucobresia nivalis* (Draparnaud) (Fig. 10).

All these species occur recently in the Tatra (Dyduch-Falniowska, 1988, 1991) and are also known from Holocene deposits, including calcareous tufas from Podhale (Alexandrowicz, 1997). *Ch. faustinum* was also reported from a Holocene tufa fan in the Kraków cleft in the Tatra (Alexandrowicz, 1988). It should be noted that *D. ruderatus* was especially common in Podhale in the Preboreal and Boreal Phases, and is known also from the Alleröd Phase. The snails found in the breccia could be supplied to their present location in the scree together with the rubble, could be washed by water, but they could also dwell cavities within the surficial layer of scree. *D. ruderatus* is now reported from such settings (Dyduch-Falniowska, 1991).

STABLE ISOTOPE COMPOSITION IN THE CEMENTS

A sample of ca. 20 mg of calcitic cements was separated under binocular microscope. Values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of carbonates were determined using measurements made with mass spectrometer SUMY, at the Institute of Geological Sciences, Academy of Sciences of Belarus at Minsk. The carbonate samples were treated with 100% orthophosphoric acid. Carbon dioxide was then collected in a trap with liquid nitrogen and purified in vacuum. Measurement error (single standard deviation, $\pm 1\sigma$) was $\pm 0.2\text{‰}$. Stable isotope ratios in carbonate samples are presented in this paper in reference to the PDB standard. The $\delta^{13}\text{C}$ values of the studied cements fall within the range -6.8 to -5.4, and the values of $\delta^{18}\text{O}$ within the range -8.6 to -7.2 (Fig. 11). The obtained stable isotope ratios for oxygen are similar to the ratios from various freshwater carbonates.

The stable isotope ratio in calcite depends on the ratio

of these isotopes in water and temperature of crystallisation. This relation is described by the formula presented by O'Neil *et al.* (1969) and modified by Friedman and O'Neil (1977). Using this formula and the $\delta^{18}\text{O}$ values of modern waters of the Tatra, given by Rozanski and Dulinski (1988), it may be demonstrated that cements with this isotope composition could form in the Tatra under the present climatic conditions. They could also form in other temperature range if the crystals grew in non-equilibrium conditions, for example because of the high crystallisation rate (cf. Chafetz & Lawrence, 1994).

The $\delta^{13}\text{C}$ values in the studied breccias indicate a marked enrichment in the light carbon isotope (^{12}C), indicative of vegetation during crystallisation of the cement (cf. Cerling, 1984; Baker *et al.*, 1997). These values generally fall within the range typical of carbonates precipitated from solutions rich in CO_2 , related to metabolism of C3 plants, characteristic of the temperate climatic zone. A slight shift in the analysed samples towards the heavier isotope compositions may be due to: kinetic fractionation effects during crystallisation of the cements, CO_2 degassing preceding crystallisation or a significant admixture of atmospheric CO_2 (cf. Cerling, 1984; Dulinski & Rozanski, 1990; Baker *et al.*, 1997). The elevated $\delta^{13}\text{C}$ values may be also due to admixture of carbonate detritus from the substrate rocks, incorporated into the cements. The detritus would have the $\delta^{13}\text{C}$ value of ca. -1‰ , so measured together with the cement precipitated from water would shift the $\delta^{13}\text{C}$ value towards the higher values.

AGE OF THE BRECCIAS

A sample of cements, of ca. 50 g, was separated under binocular microscope. It was then cleaned, ground and baked in 450°C . Measurements of radiocarbon activity were made using liquid scintillation counter LKB 1211 PACK BETA at the Institute of Geological Sciences, Academy of Sciences of Belarus at Minsk (sample IGSB 737). The radiocarbon date was calculated following the recommendations by Stuiver and Polach (1977). The obtained date is 5430 ± 130 BP. The cement sample was also dated using the Th/U method. The obtained date is $<19\ 000$ BP (Dr Helena Hercman, personal information, 2000). This age is open due to a significant admixture of detritic thorium.

The obtained radiocarbon age of the cement should be considered as approximate only. The studied sample included the whole thickness of the calcitic crusts, so the age is averaged over all laminae. The true age of every lamina may markedly depart from the obtained average value (cf. Pustovoytov, 1998). The date may be also too old because of incorporation of "dead" carbon in older, detritic calcite material. Moreover, the precision of the obtained date could be influenced by variable concentration of $^{14}\text{CO}_2$ in soil (Wang *et al.*, 1994).

MECHANISM OF BRECCIA CEMENTATION

Mechanisms that may lead to near-surface cementation of coarse-grained Quaternary sediments include: increase in ion concentrations during freezing of water (Vogt & Corte, 1996), evaporation (Bunting & Christensen, 1980), diffusion of carbon dioxide from solution due to equilibration of concentrations (Pentecost & Viles, 1994) and biological activity (Jones & Kahle, 1985).

Some features of the described cements, such as alternation of laminae composed of micrite and those of columnar calcite crystals, resemble cements forming in cryogenic environments (Vogt & Corte, 1996). Cements in cryogenic environments usually form only beneath large clasts, as pendants or cutans (Courty *et al.*, 1994; Vogt & Corte, 1996; Pustovoytov, 1998) or as calcite crusts below active glaciers (Souchez & Lemmens, 1985). Distribution of cements in the described breccia and its general setting distinguish it definitely from the deposits listed above. Also the stable isotope ratios in the studied cements differ from those known from cryogenic calcites. The latter are enriched in the light oxygen isotope due to strong kinetic fractionation of oxygen isotopes upon freezing of water (Jouzel & Souchez, 1982), which results in enrichment in the lighter isotope of the remaining water and, consequently, of the crystallising calcite (e.g., Sharp *et al.*, 1990; Fairchild *et al.*, 1993). Also stable isotopes of carbon are fractionated during crystallisation of cryogenic calcites (Clark & Lauriol, 1992). Calcite formed in such conditions has extremely high values of $\delta^{13}\text{C}$, up to +17.0‰. However, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the studied cements are typical of freshwater carbonates and do not display the anomalies described above. This excludes freezing phenomenon as a factor controlling crystallisation of the studied cements. The above conclusion agrees well with the radiocarbon age of the cements, which relates their formation to the Holocene warm phase. It may be supposed, however, that despite of this, the influence of evaporation on precipitation of the cement was negligible, as the oxygen isotope ratios do not display features indicative of evaporation, that is they are not shifted towards the higher values (Epstein & Mayeda, 1953).

Another mechanism that could cause precipitation of the calcium carbonate cements of the studied breccias could be equilibration of CO_2 concentrations between the solution and atmosphere. This process is important in calcareous tufas, especially near springs and at high-gradient rapids of streams, where increased flow turbulence favours increased degassing of water (e.g., Szulc, 1983; Mertz-Preiß & Riding, 1999). The topography of the studied breccia locality excludes the second possibility. It seems likely that the scree whose cementation led to the formation of the described breccia, was supplied with water from nearby seepages. It may be accepted that water was flowing as a thin film over the clast surfaces, outgassing the dissolved carbon dioxide through diffusion due to the gradient of temperature or pressure. Calcitic cement was precipitated in a consequence. Petrographic similarity of the studied cements to spelean calcites, which form mainly by equilibrating of CO_2 pressure between water and cave atmosphere, corroborates this

interpretation.

The last mechanism to be discussed is the biogenic consumption of CO_2 . This mechanism is considered one of the main factors in the growth of calcareous tufas (e.g., Julia, 1983; Szulc, 1983; Pedley, 1992). In contrary to many calcareous tufas, the carbonate crusts cementing the described breccias lack any biogenic structures. This suggests a negligible role of organisms in precipitation of the calcium carbonate cements. It should be noted, however, that growth of calcium carbonate crystals around biocalcified microbial cells is a known phenomenon (Guo & Riding, 1994; Szulc & Smyk, 1994). When this is the case, cementation results in obliteration of primary biogenic features of the sediment. Such situation could occur during cementation of the studied breccias, especially as the cementation was taking place in conditions of low energy of flow, which favours growth of various microbial structures (cf. Pedley, 1992). Moreover, the calcified moss, debris of higher plants or algal encrustations, typical of calcareous tufas, could form only at the outer surface of the breccias and this could be removed by erosion.

CONDITIONS OF BRECCIA CEMENTATION

The presented facts and interpretations provide basis for a reconstruction of the conditions of the breccia cementation. The distribution of the breccia indicates that it formed by cementation of rubble composed of rocks that are cropping out around the place. The scree cover was supplied with water from small seepages situated higher on the slope. The seeping water was rich in Ca^{2+} and HCO_3^- ions. The calcium ions might come from dissolution of both, Jurassic limestones and radiolarites, as the latter include up to 30% of calcium carbonate (Krajewski & Myszka, 1958, p. 223). The $\delta^{13}\text{C}$ values found in the carbonate cements are indicative of rich vegetation cover during the rubble cementation (cf. Cerling, 1984). The vegetation controlled the amount of CO_2 in water and, in consequence, the possibility of water to dissolve calcium carbonate. Thus, the water became oversaturated with respect to calcite. When such a water infiltrated the porous scree, it lost dissolved carbon dioxide. This in turn, resulted in precipitation of calcite cements and formation of the breccia.

Though the lack of structures typical of pedogenic environments in the studied breccias testifies to the lack of permanent plant cover on the scree surface, the stable isotope ratios in the cements suggest that relatively rich vegetation was present nearby (see above). This indicates that processes of cementation preceded the succession of plants encroaching on the freshly formed scree cover, that is they occurred rather shortly after the scree formation.

Precipitation of the calcite cements was not limited to specific horizons, which is in contrast with other cemented Quaternary sediments described from the temperate climate zone (Jørgensen, 1974; Aber, 1979; Strong *et al.*, 1992). The closest analogue are the surface-cemented rudites noted by Pentecost (1993) and Pentecost and Viles (1994). Most deposits described from the Central Carpathians, which are

Pleistocene cemented scree covers (Ložek & Zaruba, 1965), differ from breccia described here with the presence of greater amount of cement derived from erosion of *terra rosa*. This fact was interpreted as indicative of climate and, by implication, of the time of the breccia formation (Ložek & Záruba, 1965), but it seems that this may also depend on local setting. Other slope breccias in the Tatra, and some of the breccias from Slovakia (see e.g., Šavrnich, 1984) are similar to the one described here, but a comparison of their detailed petrographical and geochemical characteristics would be helpful.

The radiocarbon age of cements in the studied breccia indicates that its cementation has taken place in the Atlantic Phase of the Holocene, that is during the intensified growth of calcareous tufas in Poland (Pazdur *et al.*, 1988) and in Europe (Goudie *et al.*, 1993). The subsequent increase in climate humidity at the break of the Atlantic and Subboreal Phases, recorded in peatbogs and other sediments in the Podhale region (Obidowicz, 1990; Alexandrowicz, 1997) resulted probably in intense fluvial erosion and destruction of the earlier cemented breccias.

CONCLUSIONS

1. The breccias found in the Długa Valley are deposits of cemented scree cover composed of locally derived clasts. Cementation occurred soon after the scree formation.
2. The main mechanism of cementation was CO₂ degassing due to pressure contrast; the role of biogenic consumption of CO₂ seems negligible.
3. The cementation of the breccias has taken place in vadose conditions, in a way similar to that of spelean calcite formation.
4. Cementation of the breccias took place in the Atlantic Phase of the Holocene.

Acknowledgements

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REFERENCES

- Aber, J. S., 1979. Glacial conglomerates of the Appalachian Plateau, New York. *Quaternary Research*, 11: 185–196.
- Alexandrowicz, S. W., 1988. Cones of calcareous tufas in national parks of Tatra Mts. and Pieniny Mts. (In Polish, English summary). *Ochrona Przyrody*, 46: 362–382.
- Alexandrowicz, W. P., 1997. Malacofauna of Quaternary deposits and environmental changes of the Podhale Basin during the Late Vistulian and Holocene. (In Polish, English summary). *Folia Quaternaria*, 68: 7–132.
- Ampferer, O., 1907. Über Gehängebreccien der nördlichen Kalkalpen. *Jahrbuch der Kaiserlich-Königlichen Geologischen Reichsanstalt*, 57: 727–752.
- Baker, A., Ito, E., Smart, P. L. & McEwan, R. F., 1997. Elevated and variable values of ¹³C in speleothems in a British cave system. *Chemical Geology*, 136: 263–270.
- Bathurst, R. G. C., 1975. *Carbonate Sediments and their Diagenesis. Developments in Sedimentology*, 12. Elsevier, Amsterdam, 658 pp.
- Broughton, P. L., 1983. Secondary origin of the radial fabric in stalactitic carbonates. *International Journal of Speleology*, 13: 43–66.
- Bunting, B. T. & Christensen, L., 1980. Micromorphology of calcareous crusts from the Canadian High Arctic. *Geologiska Föreningens i Stockholm Förhandlingar*, 100 [for 1978]: 361–67.
- Cerling, T. E., 1984. The stable isotope composition of modern soil carbonate and its relationship to climate. *Earth Planetary Science Letters*, 71: 229–240.
- Clark, I. D. & Lauriol, B., 1992. Kinetic enrichment of stable isotopes in cryogenic calcites. *Chemical Geology*, 102: 217–228.
- Courty, M.-A., Marlin, C., Dever, L., Tremblay, P. & Vachier, P., 1994. The properties, genesis and environmental significance of calcitic pendants from High Arctic (Spitsbergen). *Geoderma*, 61: 71–102.
- Chafetz, H. S. & Lawrance, J. R., 1994. Stable isotopic variability within modern travertines. *Géographie Physique et Quaternaire*, 48: 257–273.
- Dunham, R. J., 1969. Early vadose silt in Townsend mound (reef), New Mexico. In: Friedman, G. M. (ed.), *Depositional Environment in Carbonate Rocks. Society Economic Paleontologists and Mineralogists, Special Publication*, 14: 139–182.
- Dunham, R. J., 1971. Meniscus cement. In: Bricker, O. P. (ed.), *Carbonate Cements*. Johns Hopkins Press, Baltimore, pp. 297–300.
- Dulinski, M. & Rozanski, K., 1990. Formation of ¹³C/¹²C isotope ratios in speleothems: a semi-dynamic model. *Radiocarbon*, 32: 7–16.
- Dyduch-Falniowska, A., 1988. Similarity, diversity and equitability of snail communities in lower mountain zone in the Tatra Mountains. *Zeszyty Naukowe Akademii Górniczo-Hutniczej*, 1112, *Folia Malacologica*, 2: 7–28.
- Dyduch-Falniowska, A., 1991. *The gastropods of the Polish Tatra Mountains*. Polska Akademia Nauk, Zakład Ochrony Przyrody i Zasobów Naturalnych, Kraków, 111 pp.
- Epstein, S. & Mayeda, T., 1953. Variation of O¹⁸ content of waters from natural sources. *Geochimica et Cosmochimica Acta*, 4: 213–224.
- Fairchild, I. J., Bradby, L. & Spiro, B., 1993. Carbonate diagenesis in ice. *Geology*, 21: 901–904.
- Friedman, I. & O'Neil, J. R., 1977. Compilation of stable isotope fractionation factors of geochemical interest. In: Fleischer, M. (ed.), *Data of Geochemistry. US Geological Survey Professional Paper*, 440-KK: 1–12.
- Given, R. K. & Wilkinson, B. H., 1985. Kinetic control of morphology, composition, and mineralogy of abiotic sedimentary carbonates. *Journal of Sedimentary Petrology*, 55: 109–119.
- Głazek, J., 1965. Recent oncolites in streams of North Vietnam and of the Polish Tatra Mts. (In Polish, English summary). *Rocznik Polskiego Towarzystwa Geologicznego*, 35: 221–242.
- González, L. A., Carpenter, S. J. & Lohmann, K. C., 1992. Inorganic calcite morphology: roles of fluid chemistry and fluid flow. *Journal of Sedimentary Petrology*, 62: 382–399.

- Goudie, A. S., Viles, H. A. & Pentecost, A., 1993. The late-Holocene tufa decline in Europe. *Holocene*, 3: 181–186.
- Gradziński, M., Jach, R. & Stworzewicz, E., 2000. Nowe stanowisko czwartorzędowych brekcji zboczowych w Tatrach. (In Polish only). In: *Materiały 34. Sympozjum Speleologicznego, Kościelisko, 20-22.10.2000*. Sekcja Speleologiczna Polskiego Towarzystwa Przyrodników, Kraków, pp. 36.
- Gradziński, M., Rospondek, M. & Szulc, J., 1997. Paleoenvironmental controls and microfacies variability of the flowstone cover from Zvonivá Cave in the Slovakian Karst. *Slovak Geological Magazine*, 3: 299–313.
- Guo, L. & Riding, R., 1994. Origin and diagenesis of Quaternary shrub facies, Rapolane Terme, central Italy. *Sedimentology*, 41: 499–520.
- Guzik, K., 1959. Mapa geologiczna Tatr Polskich. B1. Bobrowiec. (In Polish only). Wydawnictwa Geologiczne, Warszawa.
- Guzik, K. & Guzik, S., 1958. Mapa geologiczna Tatr Polskich. A1. Furkaska. (In Polish only). Wydawnictwa Geologiczne, Warszawa.
- Jones, B. & Kahle, C. F., 1985. Lichen and algae agents of biogenesis in karst breccia from Grand Cayman Island. *Bulletin of the Canadian Petroleum Geology*, 33: 446–461.
- Jones, B. & Kahle, C. F., 1995. Origin of endogenetic micrite in karst terrains: a case study from the Cayman Islands. *Journal of Sedimentary Research*, A65: 283–293.
- Jones, B. & Renaut, C. F., 1996. Skeletal crystals of calcite and trona from hot-spring deposits in Kenya and New Zealand. *Journal of Sedimentary Research*, 66: 265–274.
- Jouzel, J. & Souchez, R. A., 1982. Melting-refreezing at the glacier sole and the isotopic composition of water. *Journal of Glaciology*, 28: 35–42.
- Jørgensen, N. O., 1974. Carbonat-silica cementation of Pleistocene fluvio-glacial gravels from Denmark. *Bulletin of the Geological Society of Denmark*, 23: 293–301.
- Julia, R., 1983. Travertines. In: Scholle, P. A., Bebout, D. G. & Moore, C. H. (eds), *Carbonate Depositional Environments*. American Association of Petroleum Geologists, Memoir, 33: 1–54.
- Kostecka, A., 1993. Calcite from the Quaternary spring waters at Tylicz, Krynica, Polish Carpathians. *Sedimentology*, 40: 27–39.
- Kotański, Z., 1954. Tentative genetical classification of breccias on the basis of studies concerning the High-Tatric Trias in the Tatra Mountains. (In Polish, English summary). *Rocznik Polskiego Towarzystwa Geologicznego*, 24: 63–116.
- Kotański, Z., 1958. Preglacial and interglacial deposits in the Tatra Mts. (In Polish, English summary). *Acta Geologica Polonica*, 8: 275–301.
- Kotański, Z., 1979. Trasa A5. (In Polish only). In: Lefeld, J. (ed.), *Przewodnik LI Zjazdu Polskiego Towarzystwa Geologicznego, Zakopane 13-15 września 1979*. Wydawnictwa Geologiczne, Warszawa, pp. 96–107.
- Krajewski, R. & Myszka, J., 1958. Manganiferous limestones in the Tatra Mts. between the Chochołowska and Lejowa Valleys. (In Polish, English summary). *Instytut Geologiczny, Biuletyn*, 126: 209–300.
- Lefeld, J., Gaździcki, A., Iwanow, A., Krajewski, K. & Wójcik, K., 1985. Jurassic and Cretaceous lithostratigraphic units of the Tatra Mountains. *Studia Geologica Polonica*, 84: 3–93.
- Ložek, V., 1960. Breccie von Muráň. (In Czech, German summary). *Věstník Ústředního Ústavu Geologického*, 35: 469–471.
- Ložek & Záruba, 1965. Pleistocene detrital breccias in karst areas in Slovakia. (In Czech, English summary). *Československý Kras*, 16 [for 1964]: 67–76.
- Merz-Preiß, M. & Riding, R., 1999. Cyanobacterial tufa calcification in two freshwater streams: ambient environment, chemical thresholds and biological processes. *Sedimentary Geology*, 126: 103–124.
- Müller, G., 1971. "Gravitational" cement: An indicator for the vadose zone of the subaerial diagenetic environment. In: Bricker, O. P. (ed.), *Carbonate Cements*. Johns Hopkins Press, Baltimore, pp. 301–302.
- Obidowicz, A., 1990. Eine Pollenanalytische und Moorkundliche Studie zur Vegetationsgeschichte des Podhale-Gebietes (West-Karpaten). *Acta Palaeobotanica*, 30: 147–219.
- O'Neil, J. R., Clayton, R. N. & Mayeda, T. K., 1969. Oxygen isotope fractionation in divalent metal carbonates. *Journal of Chemical Physics*, 51: 5547–5558.
- Pazdur, A., Pazdur, M. F., Starkel, L. & Szulc, J., 1988. Stable isotopes of Holocene tufa in southern Poland as paleoclimatic indicators. *Quaternary Research*, 30: 177–189.
- Pedley, M., 1992. Freshwater (phytoherm) reefs: the role of biofilms and their bearing on marine reef cementation. *Sedimentary Geology*, 79: 255–274.
- Pentecost, A., 1993. British travertines: a review. *Proceedings of the Geologists' Association*, 100: 23–39.
- Pentecost, A. & Viles, H. A., 1994. A review and reassessment of travertine classification. *Geographie Physique et Quaternaire*, 48: 305–314.
- Pustovoytov, K., 1998. Pedogenic carbonate cutans as a record of the Holocene history of relic tundra-steppes of the Upper Kolyma Valley (North-Eastern Asia). *Catena*, 34: 185–195.
- Rabowski, F., 1930. Dyluwialne martwice wapienne w Tatrach. (In Polish only). *Państwowy Instytut Geologiczny, Posiedzenia Naukowe*, 27: 45.
- Rozanski, K. & Dulinski, M., 1988. A reconnaissance isotope study of waters in the karst in the Western Tatra mountains. *Catena*, 15: 289–301.
- Sharp, M., Tison, J.-L. & Fiernes, G., 1990. Geochemistry of subglacial calcites: implication for the hydrology of the basal water film. *Arctic and Alpine Research*, 22: 141–152.
- Souchez, R. A. & Lemmens, M., 1985. Subglacial carbonate deposition: An isotopic study of a present-day case. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 51: 357–364.
- Strong, G. E., Giles, J. R. A. & Wright, V. P., 1992. A Holocene calcrete from North Yorkshire, England: implications for interpreting palaeoclimates using calcrites. *Sedimentology*, 39: 333–347.
- Stuiver, M. & Polach, H. A., 1977. Discussion. Reporting of ^{14}C data. *Radiocarbon*, 19: 355–363.
- Szulc, J., 1983. Genesis and classification of calcareous sinter deposits. (In Polish, English summary). *Przegląd Geologiczny*, 31: 231–237.
- Szulc, J. & Smyk, B., 1994. Bacterially controlled calcification of freshwater *Schizotrix*-stromatolites: an example from the Pieniny Mts., Southern Poland. In: Bertrand-Sarfati, J. & Monty, C. (eds), *Phanerozoic Stromatolites II*. Kluwer Academic Publishers, Dordrecht, pp. 31–51.
- Šavrnok, J., 1984. Sutínové brekcie Kameňanského krasu. (In Slovak only). *Slovenský kras*, 22: 143–150.
- Tucker, M. E. & Wright, V. P., 1990. *Carbonate Sedimentology*. Blackwell, Oxford, 482 pp.
- Vogt, T. & Corte, A., 1996. Secondary precipitates in Pleistocene and present cryogenic environments (Mendoza Precordillera, Argentina, Transdanubia, Siberia, and Seymour Island, Antarctica). *Sedimentology*, 43: 53–64.
- Wang, Y., Amundson, R. & Trumbore, S., 1994. A model of $^{14}\text{CO}_2$ and its implications for using ^{14}C to date pedogenic carbonate. *Geochemica et Cosmochemica Acta*, 58: 393–399.

Zawidzka, K., 1967. On the geology of the region of the Przełęcz Sywarowa pass in the Western Tatras. (In Polish, English summary). *Acta Geologica Polonica*, 17: 623–651.

Streszczenie

GENEZA HOLOCENSKICH BREKCJI ZBOCZOWYCH Z DOLINY DŁUGIEJ (TATRY ZACHODNIE)

Michał Gradziński, Renata Jach & Ewa Stworzewicz

W Tatrach Zachodnich występują specyficzne czwartorzędowe utwory zwane brekcjami zboczowymi lub stokowymi (Kotowski, 1958). Są one zbudowane z klastów lokalnych skał węglanowych i spojone kalcytowymi cementami. Jak dotychczas nie został precyzyjnie określony wiek tych osadów, nie były też prowadzone badania dotyczące petrograficznych cech cementów spajających te brekcje, jak i warunków i mechanizmów zachodzenia procesów cementacji.

Nowe stanowisko brekcji zboczowych zostało zlokalizowane w górnej części Doliny Długiej na wysokości ok. 1250 m n.p.m. (Fig. 1). Brekcje są obecnie erodowane i tworzą niewielkie skałki o wysokości miejscami przekraczającej 2 m (Fig. 2). Są one zbudowane z ostrokrawędzistych klastów radiolarytów, czyli pochodzących z materiału lokalnego. Klasty tworzą zwarte szkielet ziarnowy brekcji, a pomiędzy nimi znajdują się puste przestrzenie (Fig. 3, 4). Rozmieszczenie klastów jest chaotyczne. Klasty są spojone kalcytowymi cementami.

Badania w mikroskopie petrograficznym i w skaningowym mikroskopie elektronowym wykazały, że cementsy są zbudowane z: kolumnowych kryształów kalcytu, mikrytu kalcytowego i domieszek niewęglanowych (Fig. 5–7). Kolumnowe kryształy wzrastały z różnej grubości filmu wodnego pokrywającego klasty, natomiast mikryt kalcytowy i domieszki detrytyczne były nanoszone przez wodę perkolacyjną i inkorporowane w obręb wzrastających cementów.

Pokrój i więźba kalcytowych cementów spajających dyskutowane brekcje jest analogiczna jak różnorodnych węglanowych cementów słodkowodnych jak np. *spelean calcites*. Wzrost kolumnowych kryształów kalcytu w sposób konkurencyjny dowodzi, że kryształy te są pierwotnymi, a nie przekształconymi przez procesy diagenetyczne (Bathurst, 1975; González *et al.*, 1992). Budowa kryształów kolumnowych z wyraźnych subkryształów o igłowym pokroju dowodzi ich krystalizacji w warunkach znacznego przesylenia roztworu (Fig. 8; Given & Wilkinson, 1985; González *et al.* 1992). O takich warunkach świadczą również kryształy szkieletowe (Fig. 9; Jones & Renaut, 1996). Powyższe fakty wskazują na szybki wzrost kryształów kalcytu. Cechy części cementów jak: płaskie zakończenia kryształów, obecność cementu meniskowego i stalaktytowego świadczą, że cementacja brekcji zachodziła w warunkach wadycznych ponad zwierciadłem wód gruntowych. Podkreślić trzeba, że nie zostały stwierdzone jakiegokolwiek struktury pochodzenia organicznego, ani struktury związane z cementacją w warunkach pedogenicznych.

W obrębie brekcji występują sporadycznie skorupy ślimaków (Fig. 4). Większość z nich to jedynie niewielkie, pokruszone fragmenty. Skorupy są scementowane wraz z gruzem i, jako najmniej odporny mechanicznie element, pękają podczas pobierania prób. Kilka lepiej zachowanych okazów udało się zidentyfikować jako: *Bradybaena fruticum*, *Chilostoma cf. faustum*, *Discus ruderatus* i *Euobresia nivalis* (Fig. 10). Wszystkie powyższe gatunki współcześnie występują w Tatrach. *Ch. faustum* był notowany również

z holocenijskiego stożka martwicowego w Wąwozie Kraków (Alexandrowicz, 1988). Natomiast wszystkie stwierdzone w dyskutowanych brekcjach gatunki zostały opisane z holocenijskich osadów, w tym martwic wapiennych Podhala (Alexandrowicz, 1997). Stwierdzone w brekcji ślimaki mogły być наносzone na piarg razem z gruzem skalnym, namywane przez wodę, a *D. ruderatus* mógł także zasiedlać pustki pomiędzy klastami w przypowierzchniowej części piargu budującego brekcję. W takich miejscach jest on stwierdzany współcześnie w Tatrach (Dyduch-Falniowska, 1991).

Wartości $\delta^{13}\text{C}$ badanych cementów mieszczą się w przedziale od -6.8 do -5.4, a wartości $\delta^{18}\text{O}$ w przedziale -8.6 do -7.2 (wartości podane vs PDB; Fig. 11). Otrzymane stosunki izotopów trwałych tlenu z badanych cementów są zbliżone do analogicznych wartości z różnorodnych słodkowodnych węglanów. Analogiczne wartości cechowałyby współcześnie powstające węglany w Tatrach, przy założeniu równowagowego frakcjonowania izotopów tlenu w trakcie krystalizacji. Natomiast stosunki izotopów trwałych węgla wskazują na znaczną domieszkę lżejszego izotopu węgla – ^{12}C pochodzącego z glebowego CO_2 związanego z roślinnością typu C3 (cf. Cerling, 1984; Baker *et al.*, 1997). Pomierzony wiek radiowęglowy (nr lab. IGSB - 737) cementów wynosi 5430 ± 130 lat BP.

Cechy petrograficzne cementów i sytuacja przestrzenna brekcji świadczą, że są to osady scementowanego piargu złożonego z klastów lokalnego materiału. Mechanizmem powodującym cementację było przede wszystkim odgazowanie CO_2 na skutek różnicy ciśnień; rola biogenicznej konsumpcji CO_2 i parowania wody wydaje się być znikoma. Cementacja brekcji przebiegała w warunkach wadycznych w sposób analogiczny do powstania *spelean calcites* i zachodziła w okresie atlantyckim.