Springs with active calcium carbonate precipitation in the Polish part of the Tatra Mountains

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ABSTRACT
During the field work carried out in the years 2002-2006 over the floral composition in 340 water-springs in the Tatra National Park (TNP) eight springs with calcium carbonate precipitation were detected. Eight springs drain water away from carbonate rocks in three areas generally: Kopieniec slope of Olczyska Valley, lower parts of Lejowa Valley and in Kościeliska Valley. Two types of spring CaCO₃ accumulation were identified relatively to intensity of the process and stability of the precipitation products. The calcifying springs represent the highest Ca²⁺, and HCO₃⁻ ions concentrations among all investigated springs. In comparison with typical tufa depositing springs, the values appear to be rather low.

KEY WORDS: carbonate precipitation, spring, the Polish Tatra Mountains, tufa

Introduction

Calcareous tufas are, apart from cave speleothems, the main sediments resulting from decalcification of karstic water. Porous tufa deposits form at or near the groundwater outflow via the overall reaction:

\[ \text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow \]

Intensity of carbonate precipitation and deposition reveals close relationship with the local environment, and depends especially on humidity and temperature conditions (Andrews, 2006). The optimal climatic conditions for tufa deposition in the Carpathian Mountains and its foreland prevailed during Holocene Atlantic Phase when due to intense denudation significant amount of calcium carbonate was released (Pulina, 1974). A decline of active tufa formation has been observed in all Europe over the last three thousand years, probably due to the climatic change (Goudie et al., 1993).

In the Polish Tatra Mountains fossil tufa from the Kraków Gorge was described, where plants encrusted by calcium carbonate accumulated as a fan at the foot of a rock wall. In this site the precipitation ceased probably soon after the 13 – 14 century AD climatic optimum (Alexandrowicz, 1988). Another type of freshwater calcium carbonate accumulations found in the Tatra Mts comprise slope breccias formed in Holocene or in the warm phases of Pleistocene. They are composed of locally derived carbonate rock fragments bound with calcite cement. The calcite cement forms a laminated crust on the rock clasts (Kotański 1958; Gradziński et al., 2001). Their formation in recent times is limited probably to one occurrence recorded by Kotański (1971).

Recent calcareous tufa-forming springs are rare in the Polish Tatra Mts, although actively forming tufa deposits are known from many sites in Southern Poland (Mastella, 2001; Alexandrowicz, 2004). Alexandrowicz (1988) suggested that the present climatic conditions prevailing in the Tatra Mts are too severe for tufa accumulation. As to our knowledge, the only known springs actively accumulating calcite, were described in Lejowa Valley
(Głazek, 1965). Głazek (1965) found thin calcareous layers on rubbles, rocks and irregular oncolites of algae origin in three small springs situated on the western slope of this Valley. Another tufa forming spring located in the northern part of the Tatra Mts was reported from Bobrowiecka Valley in Slovakia and was characterized by relatively high temperatures of 14-16 °C (Kowalski, 1920).

From the ecological point of view the calcareous crenal habitats with active calcium carbonate precipitation are very rare and vulnerable phenomena with numerous rare and endangered taxa (Wołejko 2004). “Petrifying springs with tufa formation” (Natura 2000 kode: 7220) are priority habitat types designated by European Union as particularly deserving intensive conservation care (Council Directive 92/43/EEC). Their value is also accented in the Polish list of natural habitats coming under protection (Dz.U. Nr 92, poz, 1029).

In this work we present sites of active precipitation of \( \text{CaCO}_3 \) found in the Tatra National Park (TNP) during a field work carried out over vegetation in spring areas in the years 2002-2006. A spring area is defined here as a special habitat in and around the place where the groundwater comes to the surface, which is developed directly under the water influence.

**Methods**

The water temperature and pH were measured for each site in situ. Water was collected for laboratory measurements in selected springs in May and October 2006 and analyzed within three days of sampling. Calcium and magnesium were analyzed by atomic absorption spectroscopy (SOLAAR M6). Alkalinity was determined by titration. Saturation indices (log IAP/\( \text{K}_{eq} \)) of the water were calculated using a computer program, PHREEQC (Parkhurst, 1995).

**Results and discussion**

**Site description**

340 spring areas were investigated in relation to floral composition as a main topic of the study carried out during the four years. 240 of the studied springs emerge from carbonate rocks. Calcium carbonate precipitates were detected in eight springs (Fig. 1) which drain away water from carbonate rocks generally in three areas: Kopieniec slopes in Olczyska Valley (Dolina Olczyska), lower parts of Lejowa Valley (Dolina Lejowa) and in Kościeliska Valley (Dolina Kościeliska), all located within the lowest climatic-vegetation zone (lower montane belt). The calcifying springs can be roughly divided into two types.
relating to intensity of the process and stability of the precipitation products.

**Table 1.** Synthesis of the most important ecological features of carbonate precipitating springs

<table>
<thead>
<tr>
<th>*</th>
<th>Locality</th>
<th>Coordinates</th>
<th>Altitude (m a.s.l.)</th>
<th>Water temp. (°C)</th>
<th>Spring discharge (l/s)</th>
<th>Slope (°)</th>
<th>Spring area (m²)</th>
<th>Vegetation cover in the spring area (%)</th>
<th>Geological basement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lejowa Valley</td>
<td>N49 16 10.7 E19 50 30.6</td>
<td>990</td>
<td>6.1</td>
<td>0.1-1</td>
<td>35</td>
<td>128</td>
<td>94</td>
<td>limestone</td>
</tr>
<tr>
<td>2</td>
<td>Lejowa Valley</td>
<td>N49 15 49.9 E19 50 12.0</td>
<td>1120</td>
<td>6.3</td>
<td>0.1-1</td>
<td>40</td>
<td>11</td>
<td>53</td>
<td>limestone</td>
</tr>
<tr>
<td>3</td>
<td>Lejowa Valley</td>
<td>N49 15 32.6 E19 50 30.4</td>
<td>1110</td>
<td>5.3</td>
<td>0.1-1</td>
<td>35</td>
<td>107</td>
<td>70</td>
<td>shale</td>
</tr>
<tr>
<td>4</td>
<td>Staników Gully</td>
<td>N49 16 00.5 E19 53 00.4</td>
<td>1210</td>
<td>8</td>
<td>0.1-1</td>
<td>10</td>
<td>94</td>
<td>90</td>
<td>limestone</td>
</tr>
<tr>
<td>5</td>
<td>Miętusia Valley,</td>
<td>N49 15 50.1 E19 52 51.2</td>
<td>1185</td>
<td>9.4</td>
<td>0.1-1</td>
<td>25</td>
<td>27</td>
<td>50</td>
<td>limestone</td>
</tr>
<tr>
<td>6</td>
<td>Kościeliska Valley</td>
<td>N49 15 20.7 E19 52 37.5</td>
<td>1124</td>
<td>5.2</td>
<td>0.1-10</td>
<td>30</td>
<td>56</td>
<td>62</td>
<td>clay, limestone</td>
</tr>
<tr>
<td>7</td>
<td>Olczyska Valley</td>
<td>N49 16 27.2 E20 00 04.5</td>
<td>980</td>
<td>7.5</td>
<td>0.1-1</td>
<td>70</td>
<td>33</td>
<td>48</td>
<td>limestone</td>
</tr>
<tr>
<td>8</td>
<td>Olczyska Valley</td>
<td>N49 16 31.3 E20 00 25.6</td>
<td>1080</td>
<td>9</td>
<td>0-0.1</td>
<td>30</td>
<td>15</td>
<td>79</td>
<td>clay, limestone</td>
</tr>
</tbody>
</table>

* - numbers in the table correspond with numbers used in the map

The first type is represented by two springs with evidently long term accumulation of calcium carbonate. They detailed characteristic are given below. The main ecological features are summarized in Table 1.

![Fig. 2. A general view on an intensively calcifying spring in Olczyska Valley (no 7).](image)

The first spring area is localized at the bottom of Olczyska Valley on the right side of Olczyski Stream (number 7 in Table 1). It is developed on a steep (about 70°), rocky surface with the water emergence about seven meters above the level of the Olczyski Stream (Fig. 2). Discharge of water from the contact of a limestone and weathered rock ranges from 0.1 to 1 l/s. The upper part of the spring area is completely covered by dense carpet of moss.

![Fig. 3. Intensive CaCO₃ precipitation of *Palustriella commuta* mats (spring no 7).](image)

*Palustriella commutata* (species typical for springs on carbonate bedrock). Because of the high slope inclination in the lower part of the spring area, the bryophytes carpet is developed to lesser extend and does not cover more than
30% of the spring area. The outflowing water seeps slowly through the moss carpet and then trickles down the rock. 5-10 cm thick porous moss-tufa deposit (Fig. 3) is forming under the moss which is growing upward while its lower parts become calcified. Due to the steep slope, fist-size fragments of the highly porous moss-tufa peel off and fall directly to the stream where they are washed away at higher water levels, limiting tufa accumulation at this site. The limestone bedrock is covered by a laminated tufa-crust up to 0.5 cm thick (Fig. 4) in the lower part of the spring area.

Calcite precipitation of similar intensity as the one described above was detected within a spring area localized on Adamica slope in Kościeliska Valley (number 6). The substrate of this site is unstable, composed of a loam together with small stones. Palustriella commutata dominates in the upper part of the area forming a dense carpet and higher plants like Festuca carpatica and Viola biflora inhabit the lower part. In the upper part, the calcite encrusted the lower, water soaked parts of the moss. The higher plants grow in separate clusters within the lower part of the spring area and thin calcite crust develops there not only on living plants but also on all available surfaces present within the spring area like pebbles, dead leaves, twigs, etc. Loose fragments of moss-tufa were also seen.

After about 10 meters the spring waters flow down to a nearby periodic stream.

In the second, more often observed, type of springs the calcification is less intensive and was observed only on lower, water soaked
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parts of bryophyte layer. The lower parts of the mosses are tightly covered by a thin (maximum 1 mm) carbonate crust (Fig. 5) not seen on the surface of the moss carpets. Under SEM, the CaCO$_3$ consists of micritic and sparry calcite crystals that grow directly upon the mosses. Euhedral crystals of different morphology were observed (Fig. 6, 7). Springs of this group are very similar in ecomorphology. All are typical helocrenes (seepage springs).

Table 2. Chemical analyses of water (average values from two measurements done in May and October) from selected springs.

<table>
<thead>
<tr>
<th>*</th>
<th>Locality</th>
<th>pH</th>
<th>Ca$^{2+}$ (mg/l)</th>
<th>Mg$^{2+}$ (mg/l)</th>
<th>HCO$_3^-$ (mg/l)</th>
<th>SI$_{calcite}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lejowa Valley</td>
<td>8.3</td>
<td>62.69</td>
<td>4.16</td>
<td>180.01</td>
<td>0.72</td>
</tr>
<tr>
<td>4</td>
<td>Staników Gully</td>
<td>7.8</td>
<td>80.00</td>
<td>12.16</td>
<td>311.30</td>
<td>0.57</td>
</tr>
<tr>
<td>6</td>
<td>Kościeliska Valley</td>
<td>7.72</td>
<td>61.80</td>
<td>1.78</td>
<td>186.87</td>
<td>0.15</td>
</tr>
<tr>
<td>7</td>
<td>Olszyska Valley</td>
<td>7.6</td>
<td>54.47</td>
<td>14.05</td>
<td>218.37</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* - numbers in the table correspond with numbers used in the map

A good example of this type of springs is provided by a spring area located on the left side of Lejowy Stream near the entrance to the valley (number 1). This site is irrigated along the whole spring area and it represents a non-concentrated source of groundwater. The substrate is composed of limestone pebbles and flattened boulders. Water in the upper part is invisible on the surface and slowly seeps through dense moss carpets appearing at the end of the spring area, where it forms small trickles. The whole spring area is covered by moss layer predominated by *Palustriella commutata*. Other species of bryophyte, e.g. *Bryum pseudotriquetrum* and *Philonotis calcarea* are also present, but in much lower abundance. In the herb layer *Petasites albus*, *Viola biflora* and *Heliosperma quadridentatum* were noted.

A different situation occurs in the spring area (number 4) in Staników Gully. The water emerges on a weak inclination slope and forms a small stream. On its both sites a swampy zone with the same vegetation composition as in the helocrene described above has developed. There are only small tufts of *P. commutata* growing directly in the stream. A weak calcite encrustation is visible only on the bedrock and on the mosses tufts along the main stream.

**Factors controlling calcium carbonate precipitation**

The concentrations of Ca$^{2+}$, Mg$^{2+}$ and HCO$_3^-$ ions in the calcite precipitating springs are among the highest values when taking into account all springs in the Tatra Mts, for which the data were available (Fig. 8). Other ions are present in very low concentrations. Ion concentrations in the springs are relatively stable over time (Oleksynowa, Komornicki, 1996).

![Fig. 8. Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$ concentrations in springs on carbonate substrate (● - data compiled from Oleksynowa, Komornicki, 1956, 1957, 1958, 1960, 1964, 1989, 1990 and ○, - authors' data)](image-url)
Although the calcite precipitating springs represent the highest ion concentrations within the Tatra Mts, when compared with typical tufa depositing springs, the values appear to be rather low. Hajek et al. (2002) found the minimum calcium concentration needed for occasional calcite precipitation to be about 90 mg/l and for forming reinforcement tufa deposits to be about 250 mg/l in spring fens in the Western Flysch Carpathians. In the investigated springs the highest calcium concentration was found in water emerging from Staników Gully (no 4) and it was 80 mg/l (Tab. 2). The calcium concentration in the two visually most intensively calcifying springs (no 6, 7) was 50-60 mg/l and the values are distinctly below the value estimated by Hajek et al. (2002) for the ephemeral calcite precipitation (90 mg/l Ca).

The basic condition for calcite precipitation is that the solution becomes supersaturated, i.e. that saturation index (SI) exceeds zero. Results of chemical modeling using PHREEQC (Parkhurst, 1995) show that all the described springs are slightly supersaturated with respect to calcite, with the SI value being within the range of 0.08 – 0.72 SI (Table 2). However it is a well known phenomenon that kinetic constraints permit substantial supersaturation to occur without resulting in calcite precipitation (House, 1984).

Calcium carbonate precipitation in streams becomes conspicuous when average annual SI values exceed 0.75, and significant tufa deposition occurs above SI 0.85 (Merz-Preiβ, Riding, 1999). Lower calcium concentrations and SI values between -0.1 and 0.5 were also noted in sites with calcite precipitation (Boyer, Wheeler, 1989).

The visual inspection of the springs in relation to the water chemistry leads to the conclusion that the ions saturation is not a definitive factor controlling the calcite precipitation in the investigated springs. The most intensively calcifying springs have the lowest SI values and the Ca\[^{2+}\] concentrations are also among the lowest (Table 2). Common for all the precipitating springs are very low water efficiency within the range of 0.1-1 l/s (Table 1) and a moss cover which is particularly dense immediately to the water emergence. The dense carpet of bryophyte slows down the water flow and serves as a nucleation site for the carbonates. Apart from the passive control of mosses on carbonate precipitation, induction of supersaturation by photosynthetic uptake of CO\(_2\) and water evaporation can play an important role in this environment. It should be noted however that mosses are not generally considered to play an active role in the carbonate precipitation as in the case of cyanobacteria and algae (Merz-Preiβ, Riding, 1999). Pentecost (1980) attributed the encrustation of *Palustrriella commutata* to the presence of epiphytic cyanobacteria which trap calcite particles. Our SEM investigations do not confirm any significant moss colonization by microorganisms; the calcite is deposited directly on moss tissues but without preference of any particular moss part (Fig. 6, 7).

The case of the spring in the Staników Gully is consistent with the observations conducted by Hajek et al. (2002). The calcium concentration in the Staników spring waters is near the value needed for occasional calcite precipitation and therefore the observed weak encrustation of the spring bed resulted probably directly from water chemistry at this site.

More research is needed to explain the mechanism of calcite precipitation in the Tatra springs and to evaluate the role of bryophytes in the process. As pointed out by Janssen *et al.* (1999) active tufas can be regarded as natural laboratories where carbonate precipitation can be studied in situ and because they are always associated with micro-organisms and higher plants, these sites form suitable research objects for answering the question about the possible biological influence on carbonate precipitation. The presented tufas from the northern part of the Tatra Mountains, though very ephemeral, provide an ideal site for studying biogenic processes. The inorganic factors alone do not seem to provide favorable conditions for calcite precipitation in the investigated springs.
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Conclusions

1. Active calcite precipitation was found in the Polish part of the Tatra Mts. in eight springs located in Olczyska Valley (Dolina Olczyska), lower parts of Lejowa Valley (Dolina Lejowa) and in Kościeliska Valley (Dolina Kościeliska).

2. The highest amount of Ca$^{2+}$ and HCO$_3^-$ ions in water relative to other springs localized in Tatra Mts., localization at relatively low attitudes (up to ~1200m) as well as low water efficiency are probably the three main abiotic factors that meet together in these springs, resulted in calcite precipitation. The calcium precipitation is enhanced by dense moss carpets growing in the spring areas.

3. Two types of calcite precipitating springs were distinguished. Two springs (at the bottom of Olczyska Valley and on Adamica slope in Kościeliska Valley) represent long term accumulation of calcium carbonate, forming tufa deposits. In the other springs occasional calcite precipitation occur resulting in calcite encrustation of lower, water soaked parts of the moss.

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