# CALCITE CONCRETIONS IN TURONIAN MARLY SILICITES, CENTRAL BOHEMIA

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#### ABSTRACT

Calcite concretions from both Přední Kopanina (Prague suburb) and Hředle quarries were the subject of the reported study, or more exactly, insoluble residues from concretions occurring in totally decalcified lower Turonian "marly" silicites (opuka in Czech and Plänerkalk in German languages). Both localities belong stratigraphically to Bílá hora formation - member of the Bohemian Cretaceous Basin.

Mutual comparison of chemical analyses recalculated to "normative" minerals reveals that in the course of diagenesis initial compositions of sediments have been changed remarkably. The original content of normative feldspars preserved in concretions and nodular beds ranges between 9.4 and 18.5 %, remarkably decreases to 4.3 - 10.6 % in host rocks affected by diagenesis. At the same time the content of clay and mica minerals (kaolinite, chlorite, illite or glauconite) in host sediments increases two or three times (from 7.3 - 11.2 % to 18.1 - 22.7 %).

Comparison of concretions insoluble residues (I.R.) with decalcified host sediments from two quarries near village Hředle showed a different picture. The I.R. of concretions contain 10.2 - 25.3 % of feldspars comparing with 6.2 - 7.9 % in host sediments. However, the content of clay and mica minerals, which in I.R. of concretions forms about 28.8 - 33.9 %, decreases three up to five times (to 6.8 - 7.3 % content) in host rocks.

Reasons for this irregularity are supposed to be attributed to the late diagenesis and epigenesis, which not only completely remove calcite, but also dissolute feldspars and clay and mica minerals in host sediments. Microsparitic calcite concretions, which are much denser and less porous than the host rocks, preserve the original composition of the sediment, because the removal of calcite from them passed very slowly.

KEYWORDS: calcite concretions, Přední Kopanina, Turonian, diagenesis, clay and mica minerals, marly silicite

#### 1. INTRODUCTION

Calcite concretions preserving a composition of original sediments have become very popular in studies of diagenetic processes. Concretions, nodules and nodular layers occur in siliceous limestones of Lower Turonian age in many localities (i.e. Hředle, Džbán, Zeměchy, Přední Kopanina, Bílá Hora, Přibylov, Skuteč, Choceň (Vorlova skála), Jezbina near Jaroměř, Kuks, Boskovice, Čížovka, Letovice, Tatenice and elsewhere). The host marly silicites (opuky in Czech, or Plänerkalk in German) (a part of Bílá hora formation) represent a very important building and sculptural stone (Čech et al., 1980). They consist mainly of microsparitic calcite, badly crystallized quartz (opal CT, chalcedony), allothigenic as well as authigenic clay and mica minerals: namely kaolinite, smectite, illite (muscovite), glauconite; Kfeldspars, plagioclase and pyrite are subordinate.

According to Zahálka (1926, 1935) Turonian marly silicites represent typical epicontinental marine facies, which originated in maximum depth of 200 m. Due to diagenetic dissolution of opal spicules of sea sponges and their transformation into minute lepispheres of opal CT (which is mixed with clayeysilt, sandy particles with carbonate mud and shells or rests of microorganisms) the rock looks very fine.

A decomposition of organic remnants and matter shortly after sedimentation caused changes of pH and redox-potential resulting in formation of spherical concretions or later of ellipsoidal nodules and in following coalescence of nodular layers and beds. Pores in original sediments were quickly cemented by microsparitic calcite and thus they can preserve the original mineral composition of the sediment. On the other hand, not cemented clastic particles in porous sediment were affected with epigenetic processes including significant impressions of meteoritic pore solutions. Besides. dissolution. а mineral transformations and neo-formations are supposed to be most important diagenetic processes.

### 2. PŘEDNÍ KOPANINA QUARRY

The marly silicite quarry located at Prague suburb represents an important source of building stone used for construction and reconstruction of historic buildings in Prague and its vicinity since second half of 14<sup>th</sup> century. The locality was subject of many researches (Zahálka, 1926, 1935; Šrámek et al., 1991). About 10 m high quarry wall exposes the beds containing in the lower and middle part of the profile ellipsoidal, spherical concretions and nodules (see Fig.1). In the upper part there are beds of nodular



Fig. 1 Schematic profile through Lower-Turonian marly silicites at Přední Kopanina Quarry with selected data of porosimetric analysis and of total porosity, values of calcite content and compressive strength data.

A – "soap-like" silicite ("mydlák") – light yellow in colour, liefly disintegrating silicite of poor quality; B – "white", tabular silicite with plentiful foraminiferas; C – "gold opoka", beige coloured, tabular silicite; D – "big quartz" – yellowish to rusty coloured, smudgy silicites with large limestone concretions of greyish-blue colour; E – "small red quartz" – beige to rusty coloured, smudgy, slab-like jointed silicites with limestone concretions of greyish-blue colour; F – "makovka - zelenáč" – slab-like jointed silicites of poor quality with lenses of calcite concretions; G – "šlupky" - yellow-grey, thin bedded silicite; H – "huňáč" – siliceous marlstone to limestone, grey, hard with slab-like jointing, massive, hardly workable; I – "šlupky" - yellow, thin bedded silicite; J – yellowish plastic clays; L – "quartz" – limestone slab, hard, massive; L' – overlying siliceous marlstone, slab-like jointed or peel-like disintegrated silicites of poor quality.

Numbers 10 –18 show samples taken: 10 - overburden, 11 - "huňáč", 13 - green, 14 - small quartz, 15 - big quartz, 16 - "šlupky" on red., 17 - gold/ red, 18 - calcareous concretion

silicified limestone called "small quartz" (beds marked as E, F and K). Bluish to greyish massive carbonate concretions up to 0.4 - 0.8 m in size are very dense and hard. Schematic quarry profile with a brief characterization of particular layers is shown in Fig. 1, chemical analyses in Table 1. Recalculations of chemical analyses into "normative" minerals are shown in Table 2 and those based on non-carbonate basis in Table 3.

Both recalculations have proven differences in mineral composition between concretions or nodules

and host rock. There is a higher calcite content seen in concretion or nodules in comparison with its amount in host sediments. Furthermore, concretions and nodules are also enriched in feldspars. On the other hand host rocks are seen to have higher content of clay and mica minerals with regard to concretions (Table 2). The differences have appeared also in the results recalculated on non-carbonate basis (Table 3), but they are less apparent. One third or a half of composing minerals is represented by SiO<sub>2</sub> modifications.

 Table 1
 Chemical analyses of one concretion, three nodular layers and three host sediments from Přední Kopanina quarry (Chemical analyses were made in ČUP laboratory, Stráž p. Ralskem in 1989. Nos. of analyses are in accordance with Fig.1)

| Oxide             | 18         | 15/2    | 14/1    | 11        | 16      | 15/3       | 10/*   |
|-------------------|------------|---------|---------|-----------|---------|------------|--------|
|                   | Concretion | "Big    | "Small  | Thick     | Shells  | Shells     | Over-  |
|                   |            | quartz" | quartz" | limestone | above   | above "big | burden |
|                   |            |         |         |           | "golden | quartz"    |        |
|                   |            |         |         |           | opoka"  | -1         |        |
| SiO <sub>2</sub>  | 19.52      | 51.00   | 61.04   | 59.63     | 65.85   | 75.76      | 71.47  |
| TiO <sub>2</sub>  | 0.08       | 0.17    | 0.15    | 0.13      | 0.23    | 0.52       | 0.22   |
| $Al_2O_3$         | 1.27       | 4.25    | 4.16    | 3.25      | 7.12    | 7.63       | 5.97   |
| $Fe_2O_3$         | 0.28       | 1.73    | 1.19    | 0.69      | 1.26    | 1.12       | 1,34   |
| FeO               | 0.37       | 0.26    | 0.12    | 0.20      | 0.08    | 0          | 0.08   |
| MnO               | 0.04       | 0.05    | 0.03    | 0.25      | 0.03    | 0.02       | 0.01   |
| MgO               | 0.10       | 0.27    | 0.27    | 0.22      | 0.32    | 0.32       | 0.35   |
| CaO               | 42.88      | 22.71   | 16.49   | 18.28     | 11.88   | 14.13      | 8.99   |
| Na <sub>2</sub> O | 0.10       | 0.57    | 0.43    | 0.40      | 0.78    | 0.46       | 0.39   |
| $K_2O$            | 0.35       | 0.90    | 1.30    | 0.84      | 1.30    | 0.65       | 1.26   |
| $SO_3$            | 0          | 0       | 0       | 0         | 0       | 0.31       | 0      |
| $CO_2$            | 33.91      | 17.18   | 13.54   | 14.82     | 8.41    | 0          | 7.58   |
| $P_2O_5$          | 0.05       | 0.07    | 0.05    | 0.07      | 0.09    | 0          | 0.09   |
| $H_2O^+$          | 1.25       | 1.34    | 1.10    | 0.98      | 2.01    | 0          | 1.93   |
| $H_2O^-$          | 0.27       | 0       | 0       | 0         | 0       | 0          | 0      |
| S                 | 0.02       | 0.02    | 0.03    | 0.03      | 0.02    | 0          | 0.04   |
| С                 | 0          | 0       | 0       | 0         | 0       | 0          | 0.01   |
| Sum               | 100.49     | 100.52  | 99.90   | 99.79     | 99.38   | 100.92     | 99.73  |

| Table 2 | Přední | Kopanina | quarry - | - recalculation | of | chemical | analyses | into | normative | minera | ls |
|---------|--------|----------|----------|-----------------|----|----------|----------|------|-----------|--------|----|
|---------|--------|----------|----------|-----------------|----|----------|----------|------|-----------|--------|----|

| Sample Nos.             | 18<br>Concre-<br>tion | 15/2<br>"Big<br>quartz" | 14/1<br>"Small<br>quartz" | 11<br>Thick<br>limestone | 16<br>Shells<br>above | 15/3<br>Shells<br>above "big | 10/*<br>Over-<br>burden |
|-------------------------|-----------------------|-------------------------|---------------------------|--------------------------|-----------------------|------------------------------|-------------------------|
| Normative minerals      |                       | 1                       | Ĩ                         |                          | "golden<br>opoka"     | quartz"                      |                         |
| Calcite                 | 77.0                  | 39.2                    | 30.2                      | 33.3                     | 21.7                  | 21.9                         | 16.8                    |
| Modif. SiO <sub>2</sub> | 16.0                  | 43.3                    | 51.6                      | 52.6                     | 51.3                  | 54.8                         | 60.6                    |
| Goethite                | 0.3                   | 1.9                     | 1.3                       | 0.7                      | 1.4                   | 1.4                          | 1.5                     |
| K-feldspar              | 1.7                   | 4.3                     | 5.0                       | 2.9                      | 1.7                   | 0.0                          | 2.1                     |
| Albite                  | 2.5                   | 4.8                     | 3.7                       | 3.4                      | 6.6                   | 3.4                          | 3.3                     |
| Clay+ Mica min.         | 1.9                   | 4.3                     | 7.8                       | 6.7                      | 16.6                  | 17.8                         | 15.1                    |
| Others                  | 0.3                   | 0.4                     | 0.4                       | 1.0                      | 0.6                   | 1.0                          | 0.7                     |
| Sum                     | <b>99.</b> 7          | 98.2                    | 100.0                     | 100.6                    | 99.9                  | 100.3                        | 100.3                   |

\*overburden beds are partly decalcified

Table 3 Přední Kopanina quarry - recalculation of chemical analyses on non-carbonate basis

| Sample Nos.             | 18      | 15/2        | 14/1    | 11        | 16      | 15/3    | 10/*   |
|-------------------------|---------|-------------|---------|-----------|---------|---------|--------|
| Normativo               | Concre- | "Big        | "Small  | Thick     | Shells  | Shells  | Over-  |
| Normative               | tion    | quartz"     | quartz" | limestone | above   | above   | burden |
| minerals                |         |             |         |           | "golden | "big    |        |
|                         |         |             |         |           | opoka"  | quartz" |        |
| Modif. SiO <sub>2</sub> | 70.5    | 73.2        | 73.8    | 78.2      | 65.5    | 69.9    | 72.6   |
| Goethite                | 1.3     | 3.2         | 1.9     | 1.0       | 1.7     | 1.8     | 1.8    |
| K-feldspar              | 7.5     | 7.3         | 7.2     | 4.3       | 2.2     | 0.0     | 2.5    |
| Albite                  | 11.0    | 8.1         | 5.3     | 5.1       | 8.4     | 4.3     | 4.0    |
| Clay+Mica min.          | 8.4     | 7.3         | 11.2    | 10.0      | 21.2    | 22.7    | 18.1   |
| Others                  | 1.3     | 0.7         | 0.6     | 1.5       | 0.8     | 1.3     | 0.8    |
| Sum                     | 100.0   | <b>99.8</b> | 100.0   | 100.1     | 99.8    | 100.0   | 99.8   |

**Table 4** Chemical analyses of I.R. from two<br/>concretions and of host rocks from "White"<br/>and "Yellow" quarries near Hředle, Džbán<br/>plateau

| Oxides                         | I.R. of  | "White" | I.R. of  | "Yellow"  |
|--------------------------------|----------|---------|----------|-----------|
|                                | A concr. | quarry  | B concr. | quarry    |
|                                | "White"  | host    | "Yellow" | host rock |
|                                | quarry   | rock    | quarry   |           |
| SiO <sub>2</sub>               | 60.20    | 89.32   | 65.19    | 89.33     |
| TiO <sub>2</sub>               | 0.20     | 0       | 0.56     | 0         |
| $Al_2O_3$                      | 14.11    | 3.70    | 14.88    | 3.26      |
| Fe <sub>2</sub> O <sub>3</sub> | 10.78    | 1.15    | 12.85    | 1.93      |
| FeO                            | 0.23     | 0       | 0        | 0         |
| MnO                            | 0.01     | 0       | 0.14     | 0         |
| MgO                            | 2.02     | 0.32    | 1.51     | 0.26      |
| CaO                            | 1.47     | 0.50    | 1.03     | 0.57      |
| Na <sub>2</sub> O              | 0.43     | 0.07    | 0.03     | 0.07      |
| K <sub>2</sub> O               | 3.73     | 1.60    | 2.30     | 1.30      |
| $SO_3$                         | 0        | 0       | 0.34     | 0         |
| $P_2O_5$                       | 0.07     | 0       | 0.19     | 0         |
| $CO_2$                         | 0.10     | 0       | 0        | 0         |
| $H_2O^+$                       | 5.91     | 1.92    | 0        | 2.24      |
| Sum                            | 99.26    | 98.58   | 99.02    | 98.96     |

 Table 5 Normative composition of I.R. – A and B concretions

| No.              | Concr. | Rock    | Concr. | Rock     |
|------------------|--------|---------|--------|----------|
| Normat.          | Α      | "White" | В      | "Yellow" |
| minerals         |        | quarry  |        | quarry   |
| SiO <sub>2</sub> |        |         |        |          |
| modif.           | 30.0   | 82.5    | 39.7   | 83.7     |
| Goethite         | 12.5   | 1.3     | 13.8   | 2.2      |
| K-Feldsp.        | 14.6   | 7.3     | 10.0   | 5.6      |
| Albite           | 10.7   | 0.6     | 0.2    | 0.6      |
| Clay and         |        |         |        |          |
| Mica min.        | 28.8   | 7.3     | 33.9   | 6.8      |
| Others           | 0.5    | 2.2     | 2.2    | 1.0      |
| Sum              | 97.1   | 101.2   | 99.8   | 99.9     |
|                  |        |         |        |          |

#### 3. DECALCIFIED CONCRETIONS AND SILICITES FROM HŘEDLE QUARRIES

Massive, whitish, yellowish, homogenous completely decalcified silicites, near Hředle village (Džbán plateau), contain abundant obscure ellipsoidal voids ensued by dissolution of coalescending nodules being 20 - 40 cm in size. At the bottom of plenty caverns there are loose clayey-silty residual depositions. These sediments in empty voids are easily accessible in two quarries, called "White" and "Yellow" according to the colour of the rocks. Both silicites were used as a good building material for houses and farm constructions in wide vicinity.

### 4. INSOLUBLE RESIDUES (I.R.)

Insoluble residues (I.R.) from two concretions were analysed in the laboratory of the Czech police and compared with host rocks studied earlier by Woller (1975), see Table 4.

X-ray diffraction made in Geological Institute has identified quartz/SiO<sub>2</sub> mineral modifications, Kand Na-feldspars, pyrite, 7Å kaolinite, 10 Å illite/mica mineral and 14 Å smectite; no mineral with mixed layer structure was found.

Roughly one third of concretions is composed of  $SiO_2$ -modifications. Both analysed concretions are enriched in goethite (originally pyrite), feldspars but also clay and mica minerals (!). Comparing with concretions, the host rocks are enriched in quartz/silica modifications (2 - 2.5 times), but depleted in feldspars as well as clay and mica minerals, what is seen to be quite strange.

Explanation of this irregularities can be clarified with mechanism of gradual dissolution: at first of calcite, later on of feldspars, clay and mica minerals. As calcite concretions originated in early diagenesis stage were much denser than ordinary host sediments, their dissolution was slower and prolonged. During this period already about 1/2-2/3 of feldspars and 1/3-3/5 clay and mica minerals were dissolved from the host sediments.

#### 5. CONCLUSIONS

A study of calcite concretions from Lower Turonian of Bílá hora formation has confirmed that these are suggested to be a very good instrument to ascertain the initial composition of sediments. The examination of calcite concretions and nodular beds done in locality Přední Kopanina has proved that their formation proceeds in a sediment with 30 - 80 % of porosity. The original sediment, rich in calcite, opal, also detritic forms of SiO<sub>2</sub>, quartz, feldspars or clay and mica minerals, was due to formation of concretions isolated from the post-diagenetic and epigenetic changes. Host sediments are depleted to about 1/2 of feldspars and at the same time two or three times enriched in mica and clay minerals.

Analyses of the insoluble residues from concretions and host rocks at Hředle locality have proved the different trend in the content of Na- and K feldspars. The feldspar content in concretions is higher than in the host rock (10.2 - 25.3 % compared with 6.2 - 7.9 % in the host rock). But the content of clay and mica minerals is remarkably higher in the

concretions (28.8 - 33.9 % compared with 6.8 - 7.3 % in the host rocks). Such irregularity is supposed to be attributed to the dissolution of calcite being slower in case of dense concretions than in highly porous silicites during diagenesis, epigenesis and weathering.

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