

# MINERAL FORMS AND SILICA DIAGENESIS IN WEATHERING SILCRETES OF VOLCANIC ROCKS IN SLOVAKIA

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**Abstract:** The sequences of diagenetic changes of polymorphic silica modifications in weathering silcretes from volcanic rocks of Central and Eastern Slovakia was studied by comprehensive methods. It was found that these changes follow a similar way to that described for the diagenesis of biogenic opals, that is from opal (opal-A) through opal-CT-chalcedony-secondary quartz with gradual changes of silica crystallinity.

In the formation of the different weathering silcrete types direct silica precipitation participated together with processes of alternate dissolution-reprecipitation and recrystallization and gravity transport.

Direct precipitation of silica from colloidal solutions through a gel stage is documented by the presence of colloidal fabric and features. "Pseudo-brecciated" textures of silcrete is evidence of gravity transport of the (aged) gel fragments. The progressive change in the crystallinity of secondary silica forms is usually a complex process which is connected with changes in the degree of saturation of weathering solution to the individual polymorphic silica phases and with the presence of some other components which may accelerate these changes. The weathering silcreted in the studied volcanic rocks are relict in nature. They originated in conditions characteristic of intensive (hydrolytic) weathering. Silcreted are juxtaposed (superimposed) on iron-rich illuviated kaolinitic clays or secondary Fe-, Mn- and Ti-oxides. They are preserved in the fissures and cavities of weathered rocks as erosion remnants of the paleoweathering crusts. Therefore these silcreted can serve as paleoweathering indicators.

**Key words:** paleoenvironment, weathering, diagenesis, silica, silcrete, opal, chalcedony, quartz.

## Introduction

Secondary forms of silica are often found as coatings and infillings in the fissures of weathered volcanic rocks (Neogene) in Central and Eastern Slovakia. Although these secondary forms of silica were sporadically described, in our literature, their genesis was most frequently linked with hydro-thermal or exhalation processes in volcanic rocks (Forgáč 1963; Marková 1977). Opal from the weathering conditions was only mentioned by Spišiak & Hovorka (1979).

Their colloidal features and in places juxtaposition on illuviated clay, Fe-, Mn- and Ti-oxides show that they belong to the group of weathering or "pedogenic" silcreted, or quartzose duricrusts (duricrete) (Thiry & Milnes 1991).

Many authors in the world have devoted themselves to the study of silcreted from the points of view of typology, genesis and stratigraphic importance (Arbey 1980; Summerfield 1983; Thiry & Millot 1987; Arakel et al. 1989; Hesse 1989; Thiry & Milnes 1991; Milnes & Thiry 1992).

In this paper we deal with mineralogical and geochemical study of the weathering silcreted from several volcanic regions in Slovakia. Our aim is to recognize the diagenetic changes in weathering (pedogenic) silcreted which follow a similar way to that recognized for biogenic silica, identify the resulting silica products and delineate the processes involved. We treated them as paleoweathering features which may indicate paleoenviron-

mental conditions (relief, climate). This provided the framework in which we examined these polymorphic changes.

## Methods of study

The weathering silcreted were studied with comprehensive methods. Micromorphological methods of study of thin sections of undisturbed samples impregnated with artificial resin (CHS Polyester) in a vacuum, enabled the study of various cross sections from infillings and coatings, and so revealed the character of mineral assemblage and the degree of changes. These thin sections were studied with the help of a polarizing and scanning electron microscope.

X-ray diffractometric analyses were carried out using  $\text{CuK}\alpha$  radiation, (Ni-filter, 30 kw, 20 mA) in the range 4-55°2 $\theta$ . The samples were prepared by settling a suspension of finely ground material onto slides.

Chemical analyses were carried out by classic way (wet analysis) at the Faculty of Sciences of Comenius University in Bratislava (analyst: Polakovičová). Trace elements were determined by OES at the same laboratory (analyst: Vančo). Electron microprobe analyses were done from polished thin sections (analyst: Caňo, D. Štúr Institute of Geology, Bratislava).

The sampling sites of individual silcreted in Central and Eastern Slovakia are presented on the schematic map (Fig. 1). The

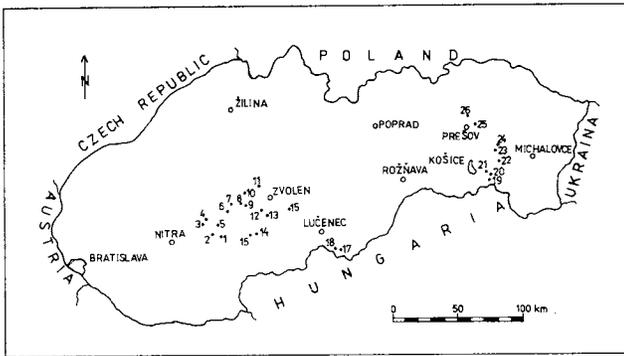


Fig. 1. Location of the studied silcretes in Slovakia. 1 — Tlmače, (andesite), 2 — Kozárovce, (andesite), 3 — Obyce, (andesite), 4 — Bátorovce, (andesite), 5 — Orovnica, (andesite), 6 — Nová Baňa, (rhyolite), 7 — Žarnovica, (andesite), 8 — Hliník, (andesite), 9 — Sklené Teplice, (andesite), 10 — Stará Kremnička (rhyolite), 12 — Jastrabá, (andesite), 13 — Babina-Sása, (andesite), 14 — Tepličky, (andesite), 15 — Sitnianska Lehôtka, (andesite), 16 — Viglaš-Javorie, (andesite), 17 — Šiatorošská Bukovinka, (basalt), 18 — Šiatoroš, (andesite), 19 — Kaľša, (andesite), 20 — Slanec, (andesite), 21 — Ruskov, (andesite), 22 — Dargov, (andesite), 23 — Banské, (andesite), 24 — Vehec, (andesite), 25 — Maglovec, (andesite), 26 — Fintice, (andesite).

greatest part of them form silcretes in fissures of weathered andesites, less frequently rhyolites, and most rarely basalts.

### Diagenesis of SiO<sub>2</sub>

The term "diagenesis of SiO<sub>2</sub>" relates to various phenomena. According to Hesse (1988), this term is often used for changes of phase transformations of individual polymorphic silica modifications, for designation of silicification processes of formerly non-siliceous rocks, but sometimes also for the process of formation of siliceous cement in rocks such as in sandstones. Silicification as a diagenetic phenomenon may have various degrees of expression, from insignificant to dominant, depending on sources. The source of silica may be organic or inorganic.

Silicification is observed as a local phenomenon in cavities, and in pores on the surface of sediments of arid regions, in the form of fine layers and laminae, and also as a regional phenomenon in individual strata, or in the framework of a whole formation. It was described from pedogenic (weathering) environments (Thiry & Ben Brahim 1990; Milnes et al. 1991; Milnes & Thiry 1992), from sedimentary and groundwater environments (Mizutani 1970; Arakel et al. 1989; Noble & Stempwort 1989; Summerfield 1983; Thiry & Milnes 1991).

Silicification of fossil woods (Forgáč et al. 1990), the origin of cherts in carbonates and carbonate sandstones (Wilson 1966) the origin of silcretes of a weathering (pedogenic) nature, evaporitic silcretes and groundwater silcretes (Smale 1973; Hatfield 1975; Arbey 1980; Summerfield 1983; Khalaf 1988; Thiry & Milnes 1991) may be examples of partial silicification.

Williams & Crerar (1985), Williams et al. (1985), Hesse (1988) and some other authors were concerned with the study of the silica diagenesis derived from organic sources of silica. It was shown that this transformation goes in the direction opal-(A)-opal-CT-chalcedony-quartz, with progressive raising of the degree of crystallinity.

Silcretes from weathering (pedogenic) or evaporitic environments, and groundwater silcretes have inorganic sources. The mineralogical assemblage and sequence of the formation of polymorphic phases of silica in such silcretes were also studied by various authors (Meyer 1984; Thiry & Millot 1986; Hesse 1989; Thiry & Milnes 1991).

These changes were also confirmed by our study of weathering silcretes in the volcanic rocks of Central and Eastern Slovakia. In agreement with the above mentioned ideas, we will use the term *silica diagenesis* to designate polymorphic transformations of secondary forms of silica.

### Mineral forms of silica in silcretes

The mineral forms of SiO<sub>2</sub> in individual coatings and infillings of fissures are simple formed by opal-(A) and opal-CT, and also complex with variable polymorphous modification of SiO<sub>2</sub> (opal-opal-CT-chalcedony-quartz). The extensive sample material, which we have available from various volcanic areas of Slovakia, enabled us to demonstrate a significant temporal and spatial variability in silica forms.

The weathering silcretes are mainly formed of *amorphous* to *crypto-crystallitic* (opal-(A), opal-CT, lussatite), *fibrous types of quartz* (quartzine, chalcedony) and *equant or elongated quartz* (microquartz, megaquartz).

a) Amorphous to crypto-crystalline types of SiO<sub>2</sub> are represented by *opal (opal-A-amorphous)* and *opal-CT*.

*Opal (opal-A)* is the primary form of silica, which is formed by direct translocation and precipitation of polymer forms of silica. Multigeneration infillings or coatings have often originated by transition through the stage of gels (Fig. 2). In cases where, together with SiO<sub>2</sub>, colloidal particles of suspended clay or Ti-oxides are illuviated, typical colloform features are formed. This testifies to the descending transfer of siliceous gels.

The colour of opals is very varied. Opals are sometimes completely transparent (hyalite), sometimes milky brown, red or green. Red, brown or green colouring is caused by an admixture of illuviated clays, oxides of Fe and Mn (Fig. 3). The transparent form (hyalite) has a low content of impurities and a water content of up to 6 %.

Some opals have certain features of anisotropy manifesting itself by weak birefringence under the microscope. This points to a crypto-crystalline nature caused by a certain arrangement of polymer particles of silica and the formation of crystallites.

The isotropic character of opals is preserved especially if they are superimposed on illuviated clays, the presence of which, evidently prevents a better arrangement of polymerized forms of silica.

*Opal-CT* is the transitional member from amorphous to crystalline forms of SiO<sub>2</sub>. Its X-ray diffractograms contain one to three peaks of cristobalite and one peak of tridymite (from which the name "opal-CT — that is opal-cristobalite-tridymite" is derived). A "fibrous texture" is characteristic of opal-CT. Petrographic study under the microscope showed that these fibrous forms have the optical properties of *lussatite* ("length-slow" chalcedony, Siedlecka 1976; Arbey 1980) which, like opal, has multigeneration pattern of accumulation in micro-laminae. It is characterized by the fact that individual fibres are oriented parallel to the crystallographic axis-c. It forms specific spheritic forms in pore spaces.

In the clay fraction, which forms the coatings in the interior

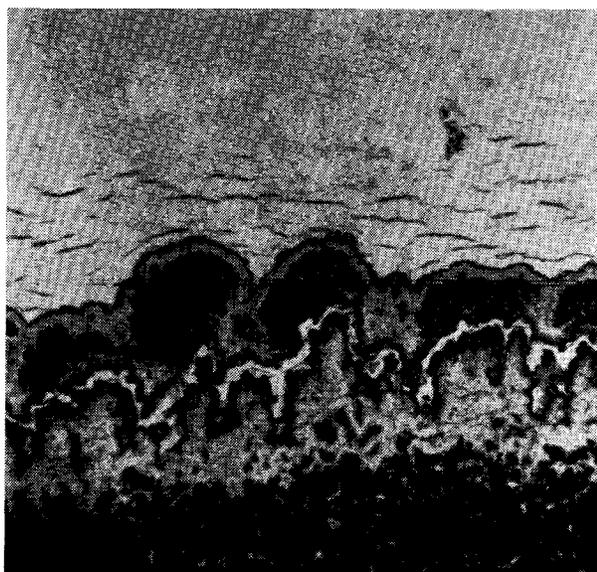


Fig. 2. Micro-fissures in opal as a result of the dehydration of gels. Opal silcretes are deposited on colomorphic incrustation formed by an admixture of oxides of Mn, clay and opal. The original surface of the fissure was formed by carbonates, which were dissolved and replaced by silcretes. Their forms indicate to this. Non-crossed polarizers (PPL), Magn. 30 $\times$ . Loc. Slanec.

of pores, the crypto-crystalline form of low temperature — *cristobalite*, or as it is sometimes called opal-C (Arbey 1980), is also often found. It is typical by the presence of a sharp peak at 0.404 nm (Fig. 4).

b) *Fibrous types of quartz* are represented in weathering silcretes by various modifications of *chalcedony* and *quartzine*.

The most frequent variety is *chalcedony*, or as it often called "chalcedony quartz" or "chalcedony sensu strictu" (length-fast chalcedony). The lengthening of fibres of chalcedony is perpendicular to the crystallographic *c*-axis (Fig. 5). The fibres have a spherulitic character as if growing from one point of the substratum (Fig. 6). This type of chalcedony most frequently occurs in pore infillings. Paralelly arranged fibres of chalcedony which alternate with quartzine, form borders on opal silcretes (Fig. 7).

*Zebraic chalcedony* is characterized by a very pretty extinction pattern in the form of broken ribbons ("zebraic") with crossed polarisers (Fig. 5). According to McBride & Folk (1977), this is a result of systematic snail-like twisting of crystallographic *c*-axes around the axes of fibres. It is evident from microscopic study that zebraic chalcedony is found as quartzine rime in which individually growing segments typical for quartzine are also preserved (Fig. 8). Zebraic chalcedony is peripherally often replaced, by mega-quartz (Fig. 9).

*Quartzine* (length-slow chalcedony) has, as already stated, lengthening of individual fibres parallel with the axis-*c* (Fig. 10), (Folk & Pitman 1971; Siedlecka 1972, 1976). Although according to optical criteria, many forms show this polymorphic modification, we did not succeed in precisely distinguishing which individual types belong to opal-CT and which to quartz, in this phase of study, especially because we did not succeed in separating pure phase samples for X-ray study. The studied samples showed the presence of quartz together with opal-CT.

A modification, which is transitional between the equant and fibrous types is found most frequently. It is called "flamboy-



Fig. 3. Alternation of individual laminae of opal (white), with laminae of oxides of Mn (black) and illuviated clays (grey). PPL, Magn. 22 $\times$ . Loc. Machulince.

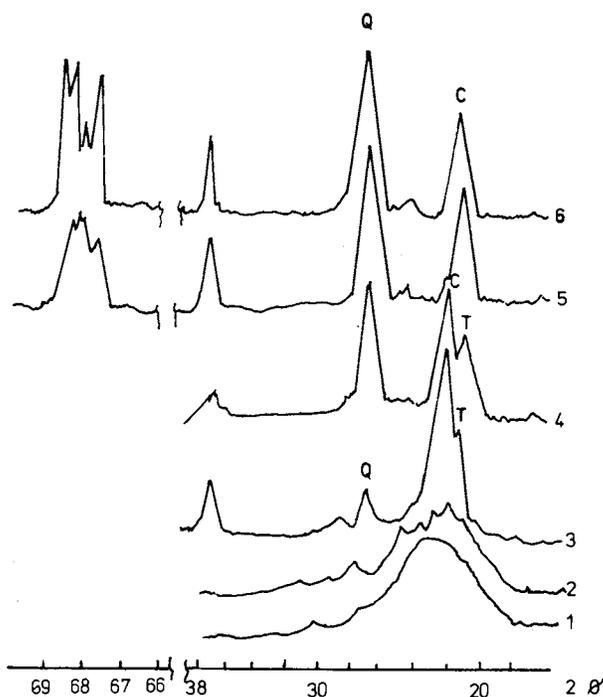


Fig. 4. X-ray diffractograms representing the progress of diagenetic polymorphic changes of  $\text{SiO}_2$ . 1 — Opal which is characterized by a diffuse peak between 19 and 25° (2 $\theta$ ). Loc. Machulince. 2 — Opal with weak features of recrystallization and with features of transition to opal-CT, is shown by the presence of little peaks in the range 19–25° (2 $\theta$ ). Loc. Slanec. 3 — Opal-CT with a peak around 0.409 nm, with a little differentiated peak of tridymite. Loc. Slanec. 4 — Opal-CT with a higher degree of crystallinity, with a differentiated peak of tridymite, and a lower peak *d*(001) at 0.401 nm. 5 — X-ray diffractogram of quartz with a lower degree of crystallinity. Loc. Kozárovce. 6 — X-ray diffractogram of quartz with a better arranged structure, which is shown by a characteristic differentiation of four peaks around 68° (2 $\theta$ ). Loc. Slanec.

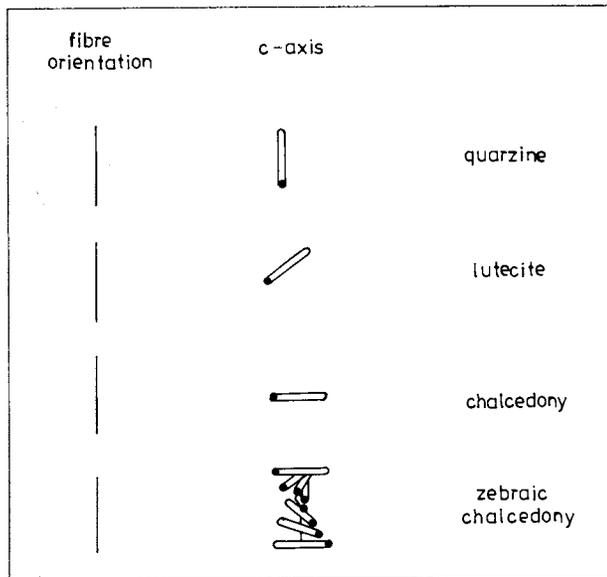


Fig. 5. Orientation of crystallographic c-axes in the fibre-like types of quartz (Milliken 1979, with modification according to Hesse 1989).

ant chalcedony" (Arbey 1980) or "flamboyant extinguishing quartz". It is shown by typical extinction caused by the presence of composite fanning and sheaf-like crystals, the boundaries of which may not be clearly distinguishable (Fig. 10). According to Hesse (1985), flame extinction is more the result of growth of crystal domains than of deformation processes.

c) *Equant or elongated forms of quartz* are, as already mentioned, the result of complex changes of  $\text{SiO}_2$ , and are connected with progressive dissolution and reprecipitation, and with a falling concentration of  $\text{SiO}_2$  in solutions. They are represented by *microcrystalline quartz* and *megaquartz*.

*Microcrystalline quartz* (micro-quartz — Folk & Pitman 1971) is composed of small crystals of quartz (5–20  $\mu\text{m}$ ), which usually have a uniform granular structure (Fig. 11). If the size of crystals

is smaller than the resolution power of the microscope, one can also name it *crypto-crystalline quartz* (Hesse 1988).

*Megaquartz* with the size of individual crystals over 20  $\mu\text{m}$ , usually have a mosaic texture but often show progressive increase in crystal size from the substratum to the periphery (*petaloid*), that is to the centre of pores and fissures. It usually fills pore spaces (Fig. 11). The size of these individuals hardly ever reaches several mm so we do not consider the name "mega-quartz" to be entirely accurate. It is used to distinguish the size of crystal forms. Its representation in silcretes is not substantial, and usually it only forms the domains in the interior of silcretes.

### The mechanisms of formation of weathering silcretes

Petrographic study in the field and under the microscope convincingly indicates that weathering silcretes arise as a result of the downward migration of  $\text{SiO}_2$ . Their distribution and textures in individual profiles and in zones accessible to observation are the result of progressive multigeneration translocation of silica in *solutions* or under gravity. More detailed study enabled the identification of two types of origin of silcretes in the coatings/infillings of fissures and cavities by *gravitational translocation* of silica and some more *complex* processes.

Weathering systems are open and unbalanced. All components in this system are mobile and may be added to — or subtracted from the system depending on weathering conditions. During hydrolysis (pH 5–9.6) most basic cations and  $\text{SiO}_2$  are mobile (Pedro 1979). During intensive weathering of volcanic rocks (complete hydrolysis — monosialitization) silica is leached, since this is only partly bound in the secondary products of weathering. Reduction of the proportion of water (dehydration), or a change of some parameters (pH, temperature) may lead to the saturation of solutions in relation to amorphous silica. In super-saturated solutions,  $\text{SiO}_2$  polymerizes, and polymer particles of colloidal dimensions are gradually



Fig. 6. Typical chalcedony (lenght-fast chalcedony) in the middle part of the infilling of a fissure. Crossed polarizers (XPL), Magn. 35 $\times$ . Loc. Kozárovce.

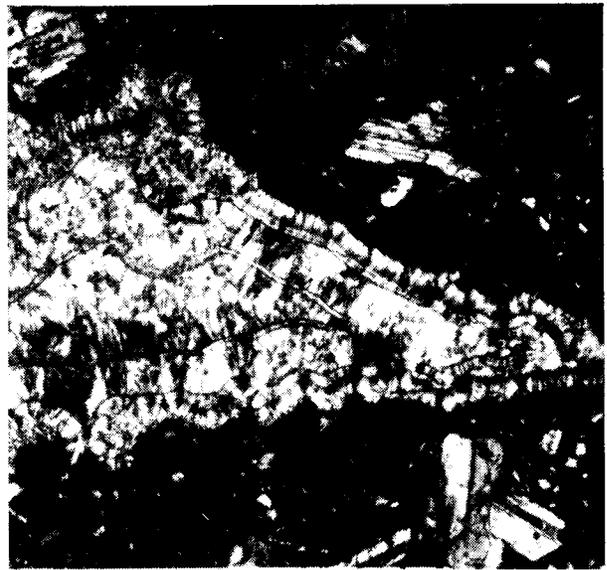


Fig. 7. Chalcedony with subparallel oriented fibres perpendicular to the wall of a cavity alternates with fan-like type chalcedony in the laminar type of silcretes. XPL, Magn. 30 $\times$ . Loc. Slanec.



Fig. 8. Zebraic chalcedony formed on the laminar type of quartzine. An interpenetration of flame-like chalcedony is separated by the sharp boundary in the upper corner. XPL, Magn. 48 $\times$ . Loc. Slanec.

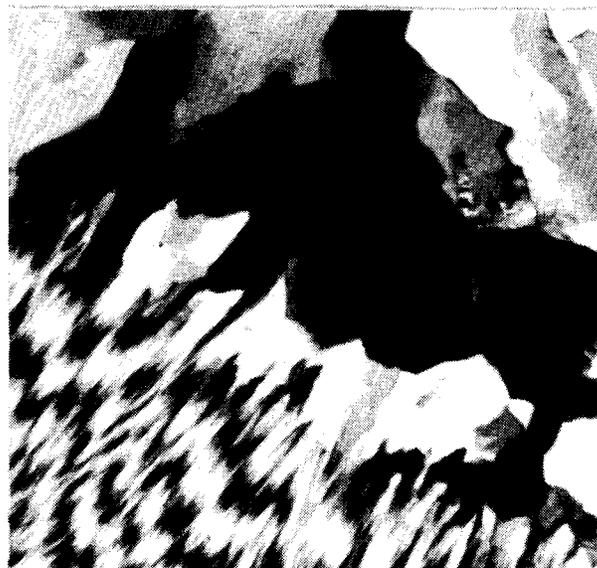


Fig. 9. Zebraic chalcedony peripherally replaced by mega-quartz, with progressive change in the size of crystals. This change is observed on the boundary of two laminae. XPL, Magn. 48 $\times$ . Loc. Slanec.

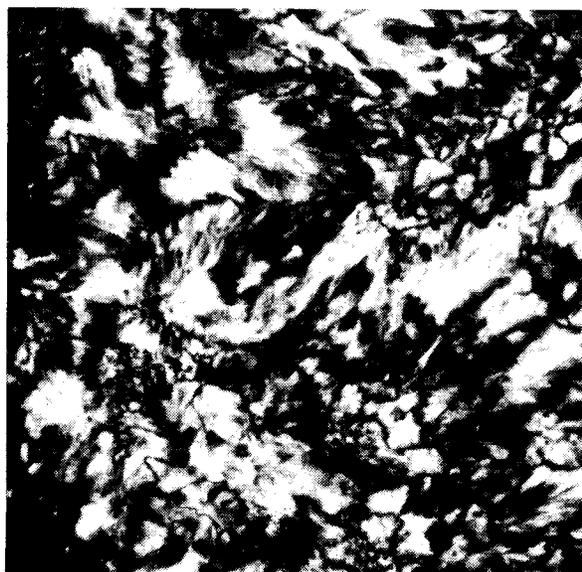


Fig. 10. Flamboyant chalcedony with characteristic forms of extinction conditioned by the presence of complex fan-like crystals of lutecite, the individual boundaries of which are not distinguishable. XPL, Magn. 95 $\times$ . Loc. Slanec.

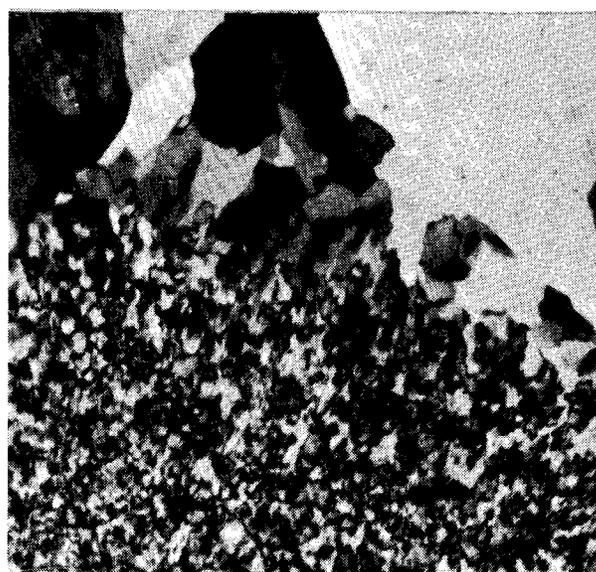


Fig. 11. Gradual transition of micro-quartz to mega-quartz on the contact with carbonates (calcretes). XPL, Magn. 48 $\times$ . Loc. Slanec.

formed. These remain suspended as sol in alkaline solutions, or gradually coagulate as gels in highly saline solutions or in a more dilute acidic environment (Williams & Crerar 1985).

Silica polymers have a high negative surface charge density, born by the peripheral silanol groups (Williams & Crerar 1985). These may be neutralized (and flocculated) by positively charged ions.

Although these ions are leached in conditions of hydrolysis, they may be relatively concentrated at the head of the weathering front. With gradual increase in the content of basic cations, the gels are immobilized and deposited in the form of opals. (The formation of calcretes — calcite, aragonite in fissures also points

to this). Processes of adsorption at phase boundaries are another mechanism affecting their accumulation.

This origin of silcretes can be identified under the microscope, from the laminar texture and mutual juxtaposition on illuvial clays (Fig. 12). In some cases, it is also possible to determine the direction of clay illuviation.

Dehydration of silica gels is connected with the origin of contraction fissures. When these dry out individual particles are freed and are then by gravity transported to empty spaces in the underlying sites (Fig. 13). These particles rarely stay individualized. Usually they are consolidated by a new portion of silica. Thus the very varied "pseudobrecciated" textures of weathering silcretes are formed (Fig. 14).

As it was said in the preceding section, silcretes of a sim-

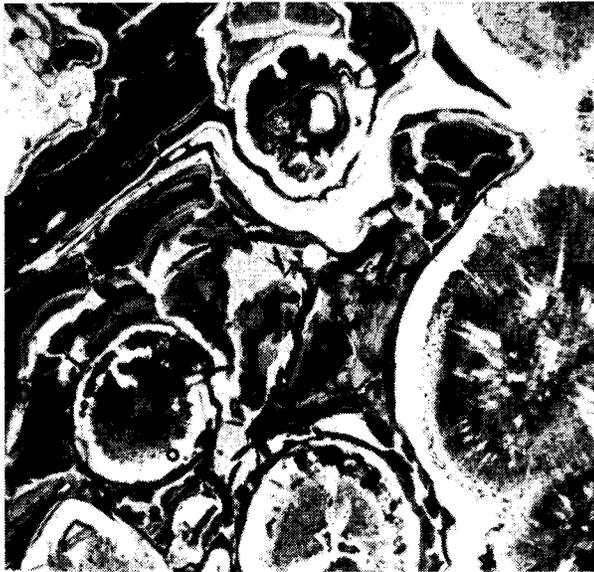


Fig. 12. Nodular forms of silcretes with borders of chalcedony alternating with laminae of opals and illuviated clay (grey laminae). PPL, Magn. 22 $\times$ . Loc. Machulince.

ple nature are rare. Usually illuvial processes alternate with gravitational processes, so that silcretes, calcretes and clay coatings (infillings) accumulate together. They therefore have a complex character, since part of them also recrystallize by ageing or recrystallize after dissolution.

The morphology of weathering silcretes is a reflection of the conditions of their formations. Most frequently they are *laminar*, and *multi-generation*. These occur especially in coatings on the walls of fissures. *Pseudo-brecciated* types are found in the infillings of fissures and cavities. Finally *nodular* silcretes are most frequently the result of gradual replacement of nodular forms of calcretes (aragonite), which occurred together with silcretes. These "pseudomorphic" silcretes may also acquire other rarer forms (Figs. 15, 16).

#### Processes of dissolution-precipitation of secondary forms of silica in weathering silcretes

Polymorphic modifications of silica, which are juxtaposed on one coating or infilling in weathering silcretes, point to the fact that they are not only the result of simple deposition from the solutions. In silcretes, we see a large number of interpenetrations with colloform fabric which indicate some postdepositional changes. More detailed microscopic study shows that some polyforms of silica are selectively dissolved (partly or completely), and are replaced by new ones with a better organized structure (Figs. 17-20). It is possible to conclude from this that processes of dissolution-precipitation in microscale also play a very important role in the silica redistribution of silcretes. During these processes, the degree of saturation in relation to individual polymorphic phases changes.

On the basis of this observation, it is possible to express the assumption that the generalized progression of diagenetic changes in the direction opal-(A)-opal-CT-chalcedony (quartzine)-crypto-crystalline quartz or chalcedony-quartz, follows complex routes of transformation in a sequence of dissolution

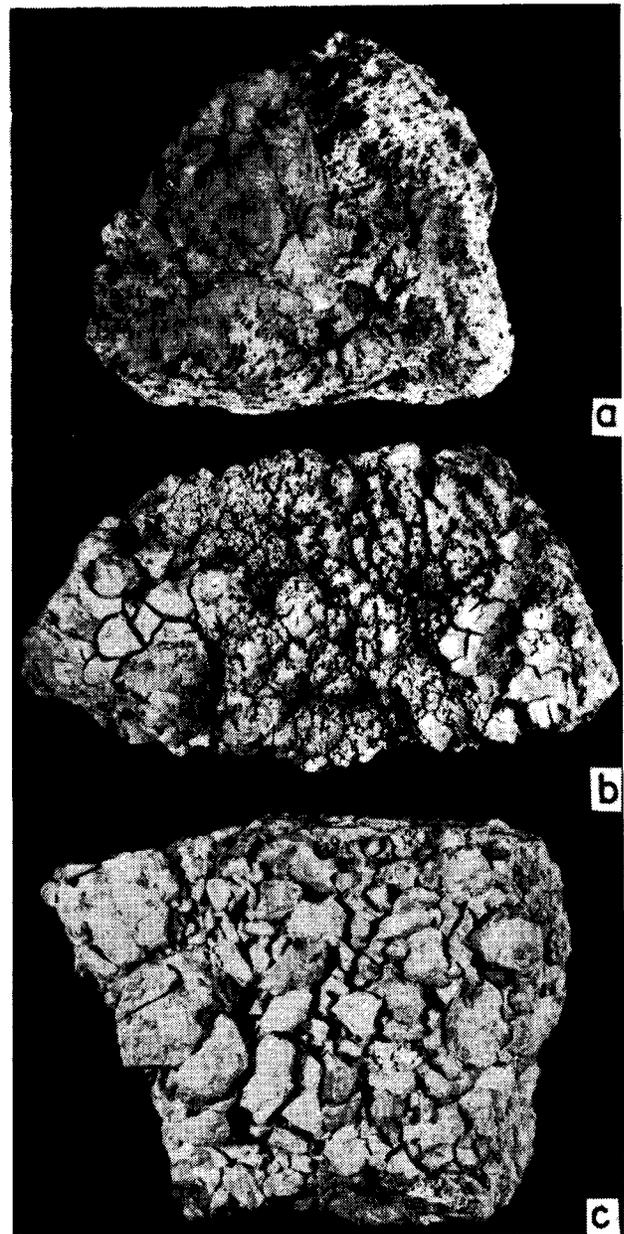


Fig. 13. Sequence of pictures illustrating the origin of silcretes by gravitational translocation. a-b show the origin of fissures as a result of dehydration. After individualization of individual intraclasts along fissures, they penetrate by gravitation into fissures in the underlying rock, to form "pseudo-brecciated structure" of silcretes (c) (about 1/3 of original size). Loc. N.Baña, (silcretes in rhyolites).

and precipitation or reprecipitation, as various authors say (Williams et al. 1985; Williams & Crerar 1985; Hesse 1988).

Observations under the microscope also show that, at the contact zone of the silcretes and calcretes, recrystallization in favour of more organized phases often occurs (Fig. 23). This is in accordance with published data (Williams & Crerar 1985).

Therefore other modifications may progressively precipitate in certain parts of the fissure infillings. In this way it is possible to explain the changes of individual polymorphic modifications in various laminae, which are also distinctly preserved during more advanced phase changes (Fig. 21), and

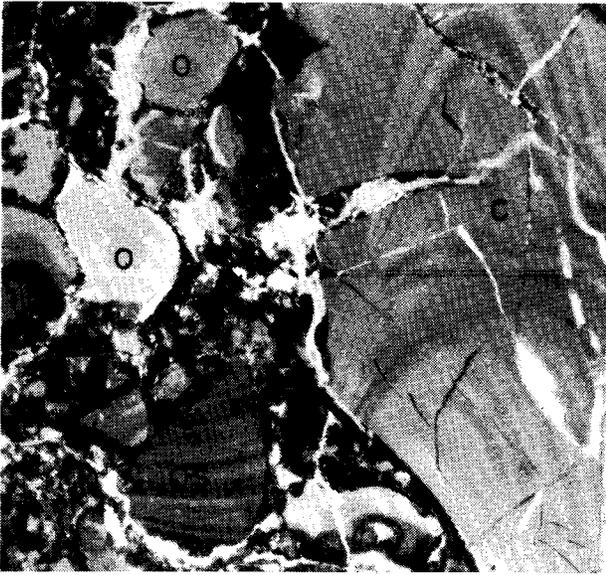


Fig. 14. "Pseudo-brecciated" structure of silcretes in a fissure with laminar features, originally formed by illuviation, and later intraclasts transferred by gravity into infilling of fissures. The intraclasts are of a heterogeneous nature: clay (c), opal (o) and opal with laminae of Fe oxides (os). PPL, Magn. 48 $\times$ . Loc. Šiatorošská Bukovinka.



Fig. 16. Borders of palisade-type chalcedony on the surface of nodular forms of opal (the same as Fig. 12, but XPL), Magn. 22 $\times$ . Loc. Machulince.



Fig. 15. Nodular forms of opal silcretes which apparently originated by replacement of oolitic forms of aragonite at the head of the weathering front. PPL, Magn. 28 $\times$ . Loc. Machulince.

lead to misinterpretation of possible changes of silica modification in the solid state.

### Geochemistry

The geochemical study of silcrete is based on the results of chemical analyses, obtained by the classical method (wet analysis) and by electron microprobe analysis. These results, which were directed towards the study of the major elements

in the silcretes are presented in Tab. 1. The trace elements are presented in Tabs. 2, 3.

It is clear from the study of the major elements, that the chemical composition of individual silcretes is variable and is primarily determined by the association of secondary products in coatings or in infillings. The chemical purity of the silcretes corresponds to the extent to which the pure fraction of secondary forms of  $\text{SiO}_2$  is separated. The highest contents of  $\text{SiO}_2$  are in hyalite-transparent opals and reach up to 99 %, in calculation without water content. In other silcretes the content of  $\text{SiO}_2$  varies, depending on the admixture of clay, secondary oxides of Fe, Mn (Ti), and the presence of other mineral phases (e.g. calcretes).

The water content in silcretes is variable, and clearly dependent not only on the gradual change of polymorphic modifications in the direction of better crystallized forms of quartz, but also on the content of illuvial clays. In pure silcretes of an opal nature, it also reaches several percent (3–5 %).

Red coloured silcretes contain a higher proportion of iron and clay. The contents of clay minerals manifest themselves in raised proportions of Al, K, Mg and Na. Our study identified cases of very weak impregnation of illuvial clays by silica, to opposite cases where hyalitic silcretes were superimposed on illuviated clay coatings. It is probable, and various authors indicate this (Smale 1973; Williams et al. 1985), that the clays play a very important role in the immobilization of  $\text{SiO}_2$ , together with secondary oxides of Fe and Mn, or with calcretes, which sometimes occur in one assemblage as has already been mentioned.

Different coloured varieties of opals contain clays with varying contents of trivalent and bivalent iron. This is evident from the extinction (birefringence) of the illuviated clays. The red clays originated in acidic oxidizing conditions, and were illuviated into fissures without any geochemical changes. The green or white colour of clay was gained due to reduction and leaching of iron in some part of weathered profiles (in micro-reducing conditions).

**Table 1:** Chemical composition of silcretes, mass %.

	1	2	3	4	5	6	7	8	9
SiO <sub>2</sub>	97.15	94.42	94.97	95.24	81.88	43.36	91.21	64.01	63.16
TiO <sub>2</sub>	0.03	0.02	0.02	0.07	0.07	0.45	-	-	-
Al <sub>2</sub> O <sub>3</sub>	0.06	0.10	0.10	0.49	6.55	28.66	0.94	9.93	11.65
Fe <sub>2</sub> O <sub>3</sub>	0.07	0.01	0.01	0.09	1.82	7.98	7.22	0.07	0.14
FeO	0.19	0.26	0.10	0.12	0.15	0.09	-	-	-
MnO	0.00	0.01	0.01	0.01	0.05	0.01	-	-	-
MgO	0.01	0.03	0.01	0.01	0.12	0.28	-	1.11	1.07
CaO	0.04	0.26	0.10	0.17	0.35	0.59	0.64	3.51	4.14
Na <sub>2</sub> O	0.02	0.01	0.01	0.10	0.11	0.21	-	0.01	0.14
K <sub>2</sub> O	0.03	0.01	0.04	0.08	0.04	0.52	-	0.20	0.61
P <sub>2</sub> O <sub>5</sub>	0.01	0.02	0.04	0.01	0.05	0.12	-	-	-
H <sub>2</sub> O <sup>-</sup>	0.75	2.11	1.17	0.73	2.34	4.19	-	-	-
H <sub>2</sub> O <sup>+</sup>	1.40	2.30	3.04	2.28	5.82	13.13	-	-	-
Total	99.74	99.95	99.37	99.33	99.35	99.59			

**Explanations**

1 — Silcrete, Slanec quarry, north west of Slanec railway station. 2 — Silcrete, Machulince, quarry, 4th stage, east of the village of Machulince. 3 — Silcrete, Machulince, quarry, 4th stage, east of the village of Machulince. 4 — Silcrete, Machulince, quarry, 4th stage, east of the village of Machulince. 5 — Silcrete, Tlmače, quarry, east of the village of Tlmače. 6 — Red gel, Machulince, quarry, east of the village of Machulince. 7 — Silcrete, Tlmače, quarry, east of the village of Tlmače. 8 — Silcrete with admixture of clayey material, Slanec, quarry, north-west of Slanec railway station. 9 — Silcrete with admixture of clayey material, Slanec, quarry, north-west of Slanec railway station.

**Table 2:** Trace elements in silcretes, ppm.

	1	2	3	4	5	6	7	8
B	440	<30	<30	51	<30	330	168	<30
Ba	<3	7	7	11	193	<3	6	250
Co	6	6	7	9	17	6	6	14
Cr	1	1	2	1	10	<1	3	9
Cu	55	4	7	14	16	15	37	25
Ga	2	2	4	4	5	2	1	28
Mo	<3	<3	<3	<3	20	<3	<3	<3
Ni	<3	3	3	5	6	3	4	5
Pb	3	3	3	4	8	10	9	20
Sr	12	10	10	15	25	18	20	50
V	16	15	15	20	15	15	16	35
Ag	<3	<3	<3	<3	<3	<3	<3	<3

**Explanations:**

1 — Silcrete, Slanec quarry, north-west of Slanec railway station. 2 — Silcrete, Machulince quarry, 4th stage, east of the village of Machulince. 3 — Silcrete, Machulince quarry, 4th stage, east of the village of Machulince. 4 — Silcrete, quarry west of Kozárovce railway station. 5 — Silcrete, Machulince quarry, 4th stage, east of the village of Machulince. 6 — Silcrete with admixture of clayey material, Slanec quarry, north-west of Slanec railway station. 7 — Silcrete with admixture of clayey material, Slanec quarry, north-west of Slanec railway station. 8 — Red gel, Machulince quarry, 4th stage, east of the village of Machulince.

The frequently mentioned higher contents of TiO<sub>2</sub> in silcretes were not proved. Locally raised proportions of Ti were found in independent laminae (leucoxene?). It is possible to

conclude from this, that Ti, which is partially mobile in an acidic complexing environment, is deposited during a change of conditions, clearly at the head of the weathering front, but most frequently in the form of independent microlaminae. The content of trivalent iron is sometimes very high, and reaches 10 %. It gives a noticeably red colouring. The iron is dispersed in the clay matrix or in independent Fe coatings — "ferrans". The locally raised content of Mn is, like that for Fe in Mn coatings — "mangans". It is clear from these results that the creation of silcretes is the result of eluvial processes in conditions of *hydrolysis*.

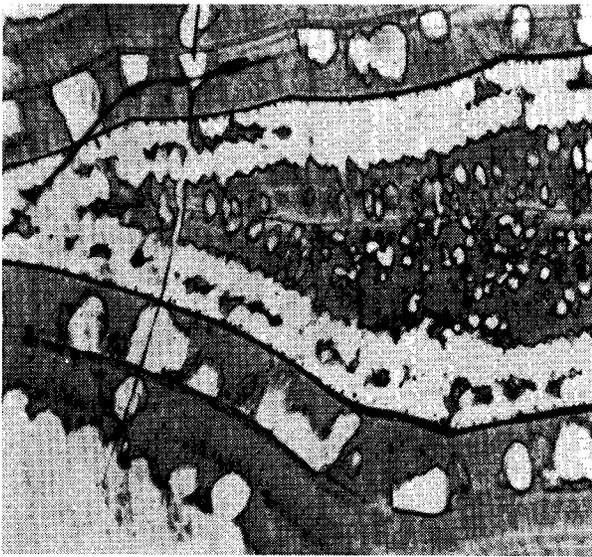
The variable contents of trace elements reflect the local conditions of origin and the varying contents of the admixtures, which occur in the silcretes. Locally high contents of Ba are associated with the clay proportion in the silcretes which was proved by microscopic study. It is not excluded that in some cases, secondary barites could also be present. A relatively higher proportion of Ba may also be found in secondary Mn oxides, which is known from the literature.

The contents of other elements are relatively low to locally raised proportions of Cu and B which were found at the locality of Slanec. We explain their higher concentration due to leaching from the overlying Neogene sediments which covered the volcanites in this area. Of course it is impossible to exclude the possibility that alkaline thermal waters and their percolation in the weathered layers of andesites played some role during the creation of silcretes at this locality. But some features in the field, especially the significantly reduced quantity of silcretes with increasing depth (in the wall of the quarry) and the illuvial features, testify to a weathering (descending) origin.

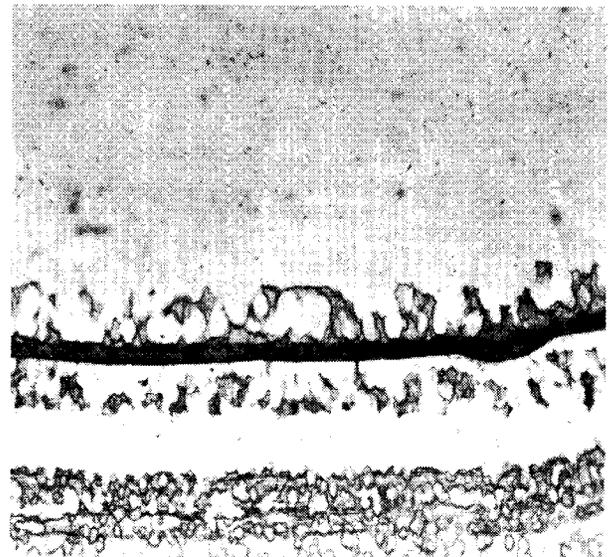
A raised proportion of strontium was recorded in places where weathering calcretes were found together with the silcretes (Sr in carbonates). Vanadium, which might be present in secondary forms of Fe, does not show especially high concentrations.

**Table 3:** Au contents in silcretes and matrix rocks, ppm.

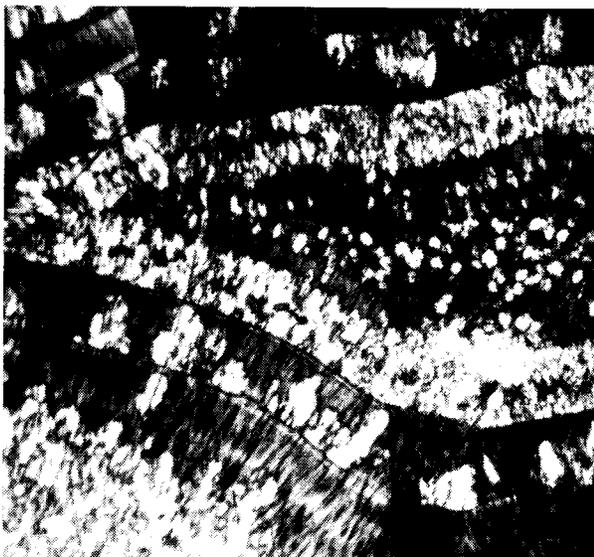
Sample No.	Au	Explanations
1	0.008	Andesite, Slanec quarry, north-west of Slanec railway station
2	0.004	Andesite, Machulince quarry, 4th stage, east of village of Machulince
3	0.004	Andesite, Kozárovce quarry, west of railway station
4	0.004	Silcrete, (hyalite) Machulince quarry, east of village Machulince
5	0.007	Silcrete, Slanec quarry, north-west of Slanec railway station
6	0.008	Silcrete (hyalite), Machulince quarry, 4th stage, east of village of Machulince
7	0.004	Silcrete (milky), Machulince quarry, 4th stage, east of village of Machulince
8	0.002	Silcrete, Kozárovce quarry, west of railway station
9	0.004	Red illuviated material (clay) above east of village of Machulince
10	0.015	Silcrete with admixture of Fe oxides Machulince quarry, east of village of Machulince



**Fig. 17.** Features of selective dissolution of quartzine, and its gradual replacement by flamboyant chalcedony with a periphery of laminae and micro-quartz in the middle of the infilling. PPL, Magn. 30x. Loc. Slanec.



**Fig. 19.** Selective dissolution of quartzine and lutecite in individual laminae, and its replacement with micro-quartz. The dark laminae of lussatite (in the centre) do not bear traces of dissolution, which is clearly connected with the fact that during the elimination of the same phases, other forms of crystals (other specific surface) are formed, which may influence their solubility. PPL, Magn. 48x. Loc. Slanec.



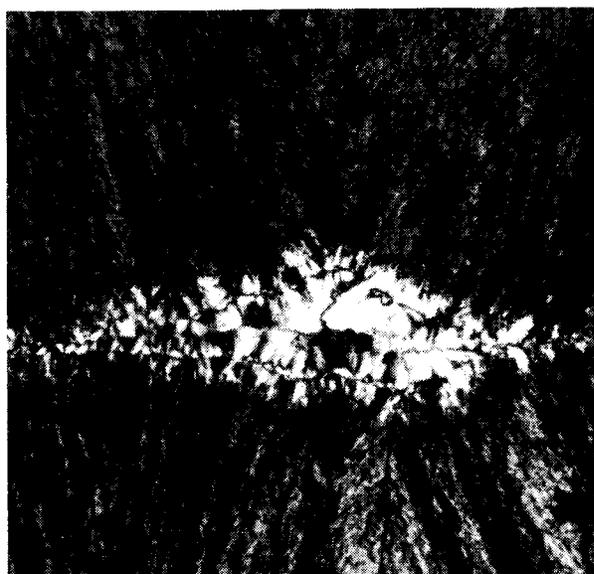
**Fig. 18.** Same as Fig. 17, but with XPL.



**Fig. 20.** Same as Fig. 19, but with XPL, Magn. 48x. Loc. Slanec.



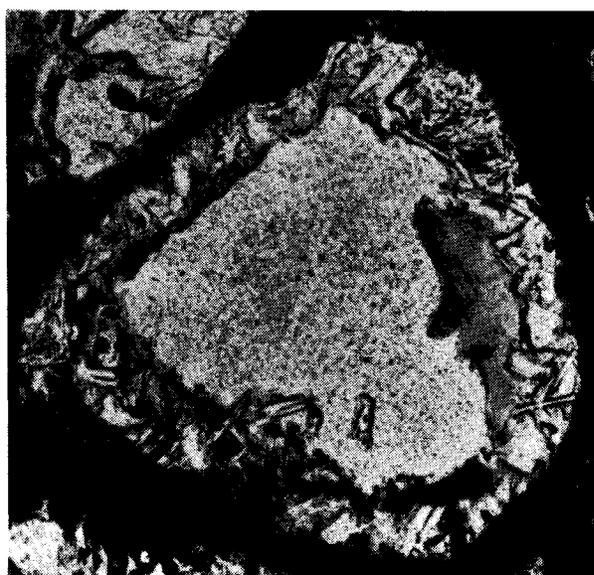
**Fig. 21.** Alternation of laminae with various polymorphic modifications of silica with sharp boundaries between individual laminae. From the margin to the centre: **k** — quartzine, **mg** — micro-quartz, **ch** — chalcedony, **f** — flamboyant chalcedony. XPL, Magn. 30×. Loc. Slanec.



**Fig. 22.** Replacement of quartzine with micro-quartz, at places with crossing of two micro-fissures is clearly the result of selective dissolution and subsequent reprecipitation. XPL, Magn. 95×. Loc. Slanec.



**Fig. 23.** At contact with calcretes, progressive replacement by a polymorphic modification with a higher degree of crystallinity often occurs. The picture shows the replacement of quartzine by mega-quartz (calcretes — white spots with signs of rhombohedra). XPL, Magn. 95×. Loc. Babina-Sása.



**Fig. 24.** On the inner side of a deposit of silcretes in a cavity in rhyolite, an illuviated incrustation of clay is found. According to the results of electron microanalysis, it is formed by gibbsite. Tiny fillets in the silcretes — cristobalite. PPL, Magn. 48×. Loc. Stará Kremnička.

In this context some analyses for gold content in the silcretes and some of the parent rocks (andesites) were carried out. The results showed (Tab. 3) that the concentrations of Au in the silcretes are roughly equal to those in the rocks. From this it is possible to conclude that some portion is associated with the colloidal forms of silica, but their concentration function is not important. However it would also be necessary to compare the contents of gold in mineralized layers of the andesites with higher contents of gold, with the contents in silcretes of this area.

Thus geochemical study, associated with micro-morphological

and petrographic study, confirms that the weathering silcretes originate as a result of the downward migration of silica.

### Paleoenvironmental interpretation

Illuvial features which are found in the coatings and infillings of pores and fissures, birefringent streaks of clay in the silcretes and multigenerational accumulation patterns of the coatings/infillings point out clearly that silicification has de-

veloped near the surface. The illuviated clays mostly have a red colouring, are of a kaolinitic and very occasionally gibbsitic nature (in fissures of rhyolite at Stará Kremnička — proved by X-ray and microprobe analysis, Fig. 24). Fe- and Mn-oxides (ferrans, mangans), Ti-oxides as it is clear from the microscopic study are also juxtaposed on clay coatings. Some silcretes replace the carbonates of calcretes, or form one assemblage in infilling (Figs. 15 and 16). This testifies to the fact that the conditions of origin varied, and the silcretes were deposited mainly at the weathering front, where such elements as Mg, Ca, Sr, Na, Fe and Mn are relatively concentrated (alkaline front). As various works have said (Williams et al. 1985; Hesse 1989) it is probably that the presence of these ions assisted the deposition of silica. The weathering regime during their formation was quite different from that in present day soils which are more illitic-smectitic ( $\pm$ chloritic) in nature. Kaolinitic soils are present only on some sites in which relict (fossil) weathering products are preserved (Čurlík 1977). Fragments of secondary silica and illuviated clays with the features of former coatings were observed in some present day soils developed on mixed material (colluviated).

The illuvial features (coatings, quasiccoatings, infillings) from which it is sometime possible to deduce the direction of illuviation confirm the downward translocation of the substances. Kaolinitic clays were translocated from the higher located zones, but clearly at the time of the silcretes formation. Both features are then genetically bound and relict. Alternate dry and wet periods controlled silica movement in the profiles which lead to multistage accumulation patterns in silcretes. The heterogeneity in polymorphic modification of silica in individual silcretes points to the long-term repetition of the events and thus long-term development of these features. Their preservation is connected with the protective function of the rocks, in the fissures of which they occur. Downwards, in the quarry-walls, where they are observed, they gradually disappear.

Therefore from the paleoenvironmental point of view it is important to state that weathering silcretes and illuviated kaolinitic clays can serve as indicators of paleoweathering conditions (climate and relief). They originated very close to the surface, in warmer, more humid conditions, which prevailed in the Western Carpathians, on the basis of climatic and sedimentological study, during the Late Neogene period (Kraus & Kužvart 1987).

### Conclusions

Comprehensive mineralogical, microscopic and geochemical study of the silcretes in the fissure of weathered volcanic rocks in Slovakia points out clearly that silicification has developed near the surface, in environments where water percolation led to silica and clay illuviation. These are soil environments and silcretes have to be called pedogenic.

The sequence of crystallization of the different silica phases in the voids follows the progression that is also known for the biogenic opals transformations that is from opal through opal-CT, chalcedony to secondary quartz.

Silcrete originated primarily from mobile colloidal solutions (sols). Of course the identified features of dissolution and reprecipitation also testify to the gradual local remobilization of silica in successive stages of weathering crust development. A certain transfer of solidified silcretes was also associated with gravity action.

Petrographic and mineralogical study shows significant spatial and temporal variations of the forms and distribution patterns in individual zones accessible to observation. It is evident that diagenetic changes of polymorphic modifications of silica depend on many factors (pH, temperature, solution concentration, presence of foreign ions and minerals). Pedogenic (weathering) silcretes developed on a paleolandscape and under a hot paleoclimate. This is proved by the presence of illuviated iron-rich kaolinitic (gibbsitic) clay which often alternates with, or is juxtaposed (superimposed) on silcretes. They are relict (fossil) products preserved in the fissures and cavities of weathered rocks. They can be used as an indicator of paleoweathering conditions (climate and paleorelief).

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