OPAL — A NEW HYDROMORPHIC PRECIPITATE TYPE FROM GRAVEL DEPOSITS IN SOUTHERN FINLAND

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Opal precipitates have been found from eleven localities in eskers and ice-marginal formations in southern Finland. The precipitates occur above the present groundwater table in porous gravel layers near the surface. The depth is commonly around 1—2 m. The precipitates build thin (up to 0.3 mm), very light grey, colloform coatings on pebbles, cobbles and boulders. The coatings are composed of fine opal microlayers (mean thickness 0.5 µm). Optical and X-ray determinations show that the coatings are composed of opal of type-A (hyalite). Refractivity index is 1.446 (sodium light). The heated material gives X-ray diffraction lines of low-cristobalite. Optical spectroscopic observations show that traces of uranium cause the bright green fluorescence of these opals (under short-wave ultraviolet radiation). The coatings contain detrital minerals as inclusions and silicified organic remains: thin roots of plants and fungal hyphae.

The model proposed for the formation of the opal coatings is hydromorphic precipitation from vadose water in the soil water zone. In the contacts of boulders and pebbles water evaporated episodically. This lead to supersaturation of silica in the water film. During each evaporation cycle silica coagulated from the water film and precipitated as one microlayer of opal. In the gravel deposits, the prerequisite for the opal formation was a porous texture with large empty voids.

Key words: precipitation, gravel, optical properties, fluorescence, petrography, southern Finland.

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Introduction

In June 1976, pebbles with bright green fluorescent coatings were discovered, by one of us (K.A.K.), in gravel pits at Hakunila, Vantaa, southern Finland. Preliminary microscopic examination showed that the coatings are composed of an amorphous silica or opal and, therefore, represent an unknown type of precipitate in glaciofluvial material. Other hydromorphic precipitates (mainly Fe and Mn oxidate accumalations) have been intensively studied in Finland (see references in Carlson 1982). In the 1980's we made additional observations on the silica precipitates occurring in gravel and sand pits. The silica precipitates were shown to be notably common in certain gravel layers in eskers and ice-marginal formations in southern Finland. Therefore, we considered them as worthy of detailed documentation.

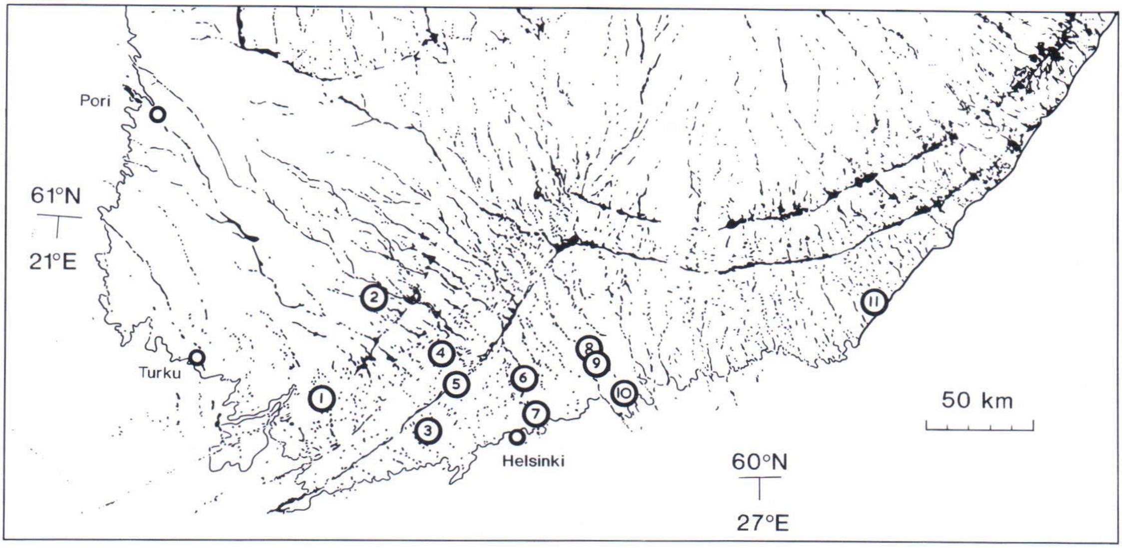

Fig. 1. The gravel and sand pits containing hydromorphic opal in southern Finland. The numbers on the verified opal finds refer to Table 1. The base map gives the distribution of eskers and ice-marginal formations in southern Finland. It is simplified from the map of Quaternary deposits in Finland, 1 : 1 000 000, edited by Kujansuu and Niemelä (1984).

Previous studies

Hyalite (opal of type-A) coatings that occur on rock outcrops have been known for a long time as Müller's Glass. Kunz (1892, p. 145) described fluorescent opal coatings upon gneiss in Frankford, Pa., USA, and Frondel (1962) described examples from several localities worldwide. In Finland, Saarnisto (1969) and Taavitsainen and Kinnunen (1979) have described silica coatings on prehistoric rock paintings situated on steep, vertical outcrop surfaces. These coatings do not usually show greenish fluorescence under shortwave ultraviolet radiation but, instead they show a faint bluish-violet fluorescence under long-wave radiation. These thin coatings act as a natural glaze that protects the pigments of the paintings. This is one of the reasons for their preservation for several thousand years (Taavitsainen and Kinnunen 1979). The coatings distinguish genuine prehistoric rock paintings from fakes and from natural red colorations common on some rock outcrops.

Silica coating is one type of surface texture (turtle-skin type) on sand grains depicted by Krinsley and Doornkamp (1973) from localities worldwide. Kowalkowski (1982) has also observed silica coatings also on Finnish sand grains. To our knowledge, only one earlier observation exist of silica coatings on boulders. This unpublished note, cited by Folk (1978, p. 621), describes opal found in a gravel deposit in Texas. An introductory classification of other surface texture types (striae, crescentic marks, dissolutional cavities etc.) has been given earlier (Kinnunen et al. 1985). These surface textures were observed on Finnish pebbles and boulders in till and glaciofluvial material.

To contrast: various rock varnishes, also called as »desert varnish,» composed of Fe, Mn, Al, Si layers on boulder and rock outcrop surfaces have been studied extensively (Whalley 1983, Hale *et al.* 1983).

Areal distribution

All opal finds are from gravel layers in eskers or in ice-marginal formations. Till sections in-

Table 1. The locations of the gravel pits with observed precipitate layers and pebbles and boulders with coatings of opal. The locality number refers to the map in Fig. 1.

Locality	Base map	Coordinates	Type of glaciofluvial formation	Depth	Type of precipitate
1. Muurla, Kaukola	2023 01	6690.2/2460.7	esker	—	b
2. Tammela, Torronsuo	2024 09	6736.8/2485.3	esker	—	c
3. Siuntio, Suitia	2032 06	6676.6/2510.7	esker	1—2 m	a
4. Karkkila, Ahmoo	2042 04	6712.6/2516.7	proximal part of delta	1—2 m	a
5. Vihti, Ojakkala	2041 08	6697.9/2523.8	distal part of I Salpausselkä (ice-marginal formation)	0.2 m	a
6. Tuusula, Rusutjärvi	2043 06	6702.2/2554.8	esker	2—3 m	a
7. Vantaa, Hakunila	2043 07	6683.5/2561.5	esker	—	c
8. Askola, Nalkkila	3022 01	6716.3/3422.8	esker	0.5 m	a
9. Askola, Nietoo	3022 01	6711.3/3423.8	esker	—	c
10. Porvoo mlk, Epoo	3021 05	6694.5/3437.4	esker	1 m	a
11. Ylämaa, Husu	3044 06	6736.1/3554.7	esker	—	c

Explanations to the type of precipitate:
a — opal occurring *in situ* precipitate in gravel layers. Depth is given from the surface.
b — opal coatings observed on boulders in gravel pits.
c — opal coatings observed on pebbles in gravel pits.

spected at several locations in southern Finland gave negative results. No opal precipitates were found at the few sites investigated in central and northern Finland.

Figure 1 shows the areal distribution of opal in gravel pits. In six localities opal precipitates were discovered in situ (Table 1). In addition, five observations of opal coated pebbles, cobbles and boulders have been made from gravel pits, although the stratigraphic position of these finds is uncertain (Table 1).

Field occurrence

The opal precipitate, found *in situ* in five gravel pits, occurs in gravel layers near surface, usually in depth of about 1—2 m (Fig. 2). The precipi-

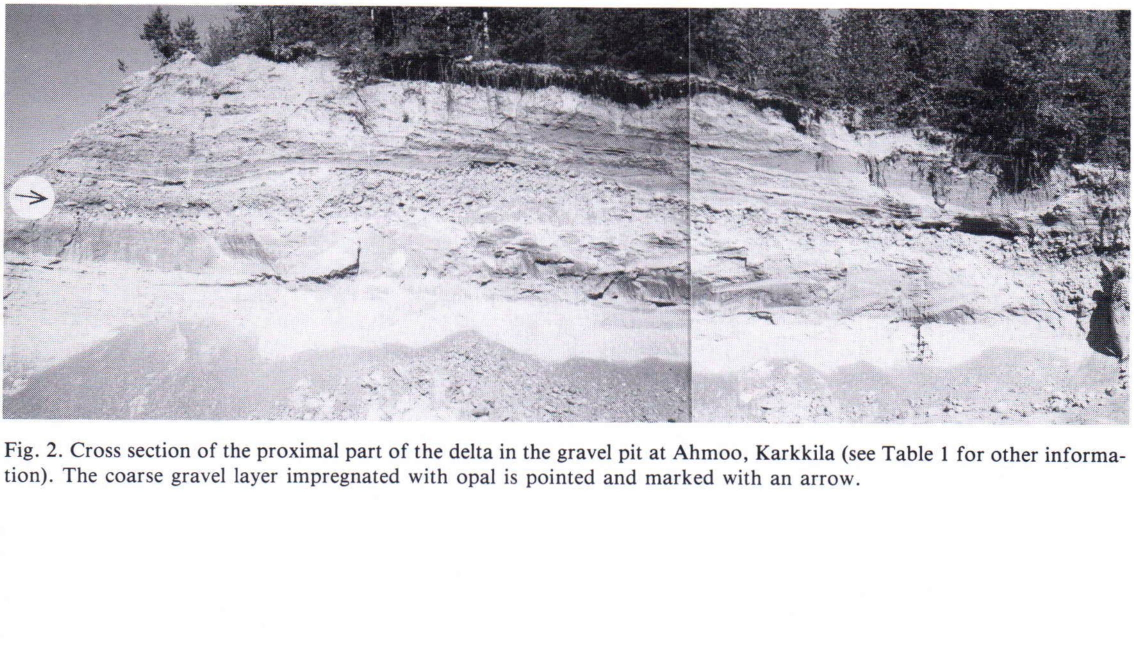

Fig. 2. Cross section of the proximal part of the delta in the gravel pit at Ahmoo, Karkkila (see Table 1 for other information). The coarse gravel layer impregnated with opal is pointed and marked with an arrow.

tate is built up as coatings, preferentially on the under side of boulders. In these gravel layers a grain-supported type of texture is typical; with empty voids below the pebbles and boulders. These voids characterize all the gravel layers with opal precipitates and are thought to be a prerequisite for their formation. The voids probably formed by so-called stone lifting processes associated with freezing and thawing of the soil.

Iron-manganese precipitates were sometimes observed in the same gravel pits, but always in deeper levels than the opal precipitates. This is important because the iron and manganese precipitates in glaciofluvial sediments mark the previous ground-water levels (Koljonen et al. 1976). Usually the iron-manganese precipitates are observed in places where sand and silt compose the matrix, while the voids are empty in the opal containing parts. The type of occurrence of the precipitates on the bottom of clasts and the unabraded surface of the coatings show that the coatings are not recycled. Therefore they formed *in situ*.

Macroscopic description

The color of the opal precipitate varies from very pale orange (Munsell color: 10YR8/2) to very light gray (Munsell lightness value: 8) and sometimes it exhibits iridescent colors. The presence of coatings is independent of the rock type of the clast. The diameter of the individual patches of the precipitate range from 3 to 6 mm and their thickness up to 0.3 mm, on average about 0.1 mm. The opal patches form cellular networks that sometimes coat the entire bottom of the clasts. These cellular networks are formed by the pebble/boulder and boulder/boulder contacts (Fig. 3), which inhibited the formation of the opal precipitate on those contact areas. This micromorphology can be termed meniscus cement according to the terminology used for the authigenic carbonate cements (see Gardner 1983, p. 279). Spherules and a larger thickness of the opal coating is observed on the rims of the patches.

Fig. 3. Opal coating occurring as a whitish network on a plagioclase porphyrite cobble from the Ahmoo locality in Karkkila. Dimensions of the cobble are 93 × 59 × 40 mm.

The thickness of the precipitate varies in some degree from one locality to another. The thickest opal layers (up to 0.3 mm) and largest spherules were observed in the gravel pits of Hakunila, Vantaa. The mineralogical composition and petrographic properties are, however, remarkably similar at different localities. The following detailed mineralogical determinations are from the samples collected from the localities of Ahmoo, Karkkila and Hakunila, Vantaa (see Table 1).

Mineralogy

Optical, physical and X-ray data

Optically the coating is isotropic. Faint strain anisotropy is observed around the spherules. The hardness varies from 5 to 6 on the Mohs scale. The fracture is conchoidal on thicker rim parts. The lustre is pearly on colloform surfaces and vitreous on fracture surfaces. The refractivity index, when measured with the immersion method (sodium light interference filter), varies from 1.44 to 1.45 (mean = 1.446). This corresponds to a water content of about 9 wt.% in opals (see

Phillips and Griffen 1981). The refractivity index of heated samples increased to 1.47. This is explained by water release during the heating.

X-ray studies with a Debye-Scherrer camera showed that the coating is almost completely amorphous. Only at prolonged exposure times do the X-ray photographs reveal one diffuse 6 Å line. It can be interpreted as melanophlogite or as clay minerals. The heated coatings (up to red heat) show one diffuse 2.5 Å line. It is interpreted as low-cristobalite. All lines obtained are too weak for more accurate measurement. Similarly, the wax (vaseline) used on the glass rod of the Debye-Scherrer camera as glue produces its own diffraction lines during prolonged exposure times. This complicates the interpretation.

The optical, physical and X-ray data all confirm that the coatings are composed of opal. It is of type-A (network-type, glass-like hyalite) according to the classification and diagnostic properties given in Yariv and Cross (1979, p. 262—263), Kastner (1979) and Jones and Segnit (1981). The presence of low cristobalite was indicated by the heating experiments of the opal coatings. Cristobalite is the typical crystallization product of type-A opal. It forms in heating from the originally completely amorphous opal.

Reason for the green fluorescence

The green fluorescence of the opal coatings is observable only under short-wave (254 nm) ultraviolet radiation. The ultraviolet lamp used was Raytech model PP1-LS. The intensity of the green fluorescence varies. Usually it is strongest in the rim areas of the opal coating patches. Under long-wave ultraviolet radiation (355 nm) the fluorescence is bluish-violet and weak. The green and yellow-green fluorescence is typical for opals in many localities worldwide (Robbins 1983). It has been attributed to traces of uranium in the opal (Zielinski 1980).

The fluorescence spectra of the opal coatings (short-wave UV-light) from the localities in Ahmoo and in Hakunila were inspected with an OPL diffraction grating spectroscope. The areas of intense fluorescence in the patches were analyzed. A group of four emission lines was detected. This group is diagnostic for the uranyl complex (Gleason 1960, Marfunin 1979). Zielinski (1980) has estimated from detailed chemical analyses (North American material) that the yellow-green fluorescence in secondary silica materials is induced by high uranium content. This content is in the range from 10 to 100 ppm. Accordingly, this range is taken as an estimate for the uranium content for the fluorescent Finnish opal precipitates.

Petrographic description

Microstructures and surface features

The micromorphology of the opal coating (Fig. 4) is colloformic (see Lebedev 1967). Silica spherules are common with diameter up to 0.1 mm. Microstalactites and spherule-coated tubes were also observed. In cross-section the silica coating contains microlayers with individual layers of about 0.5 μm in thickness (Fig. 5). The presence of microlayers suggests rhytmical and periodical deposition of silica. The typical total thickness of the silica coating (0.1 mm) consists correspondingly of about 200 microlayers. The »chickenwire» texture is typical of the upper surface of the opal coating. It is interpreted as dehydration cracks.

The iridescent colors seen on some opal coatings are interpreted to have been caused by this microlayer texture via interference. In Australian precious opals the noticed play of color is caused by diffraction of light from regularly arranged silica spherules about 0.1—0.3 μm in diameter (Darragh et al. 1976).

Inclusions

The opal coating contains several types of impurity as inclusions. The most common are detri-

Fig. 4. A flake of the opal coating detached from the cobble surface, Ahmoo locality, Karkkila. The microstructure is composed of silica globules (a), »chicken-wire» dehydration cracks (b), detrital mineral inclusions (c) and silicified plant remains (d). Thin roots of plants are to be seen as delicate wire-like forms (e) in the photomicrograph. Immersion grain sample with highly collimated, transmitted light.

tal grains of quartz, feldspars, micas and amphiboles; mainly silt in grain size. Fragments loosened from the pebble or boulder surface and their limonitic (cutane) coatings are occasionally found. Fluid inclusions are present but small (below 1 μm). They are monophasic of the liquid-type (water). They form tubular cavities on the pearly surface layer of the coating. Most probably they have been trapped by water release connected with the dehydration of the silica gel. No relicts or molds of saline minerals were detected in the opal coatings.

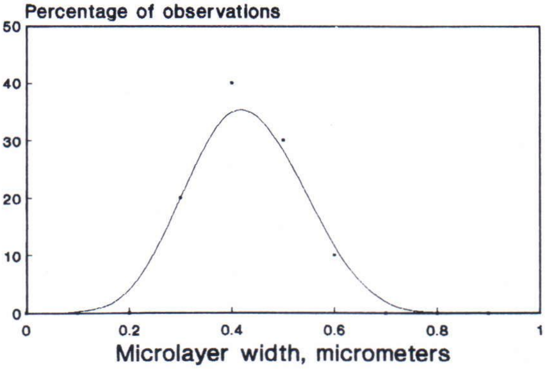

Fig. 5. The distribution of the microlayer widths composing the 0.3 mm thick opal layer on pebbles in Hakunila locality in Vantaa. The layer widths were measured using deep violet light.

Silicified plant remains

Organic remains are common as inclusions in the opal coatings. Most of them are hollow casts partially surrounded by silica. They are observable only with immersion grain samples using highly collimated transmitted light (Fig. 4). The plant remains include thin roots of plants, fungal hyphae, and bacteria.

The silicification of plant remains has been intensively studied (see Hesse, 1989, for a review). In laboratory conditions, silica gel has been observed to replace organic material (Oehler and Schopf 1971). It is concluded, however, that the process of silicification is not a direct replacement. It may be a permeation or void-filling process (Hesse 1989). This agrees with the nature of the plant remains also in the Finnish opal coating, which mainly are casts, or only partially filled with opal.

Mechanism for opal precipitation

Sources of silica

Weathering of the rock-forming silicate minerals is the main source for silica in soil and ground waters. In some Finnish podzol horizons (see Räisänen 1989), silica, together with iron and aluminium, is one of the main elements leached from surface soil layers. It is transported to deeper soil horizons in solution.

Dissolved silica reaches chemical equilibrium in soil solutions in a few hours or days. The typical equilibrium content of the dissolved silica in ground waters lies between the solubility values of quartz and that of the amorphous silica. The equilibrium concentration depends mainly on the temperature in ordinary soil microenvironments (Krauskopf 1959). The concentration line for amorphous silica is shown in Fig. 6. These values (from 60 to 70 ppm when temperature is below 10°C) are higher than the silica contents reported from the groundwaters in southern Finland by Lahermo et al. (1990): from 6 to 30 ppm silica, mean about 15 ppm.

Geochemical considerations

Part of the leached elements are precipitated at specific soil layers in the vadose zone or on the groundwater table. These precipitates are commonly impure amorphous materials composed of Fe, Al, Mn and Si. The resulting precipitates are allophane, iron and manganese oxide accumulations and cutane layers (Ojanperä and Ritari 1984). Biotic action of bacteria and fungi in aerobic conditions may be an important aspect in precipitation of iron and manganese on groundwater table in eskers (Vasari *et al.* 1972).

Krauskopf (1959) has summarized the geochemical behaviour of silica at low temperatures. In soil solutions silica is mostly in true solution as monomeric silicic acid H_4SiO_4. The silica in excess polymerizes to colloidal particles, which form gelatinous silica with coagulation. In acid solution the coagulation is slow. It leads to setting of the gel as hard opal. This is in comparison to the gelatinous porous masses which form in basic solutions.

Precipitation

The field observations and petrographic details, that are important in the interpretation of the hydromorphic opal precipitation in Finland, are as follows:

1. Occurrence of opal as coatings on the ceiling of cavities in gravel layers and on grain contacts. This suggests water/air interaction (Fig. 7).

2. The silica content of the precipitate is high according to its monomineralic hyalite (opal of type-A) composition. Iron and manganese precipitates are absent in the same gravel layers.

3. Microlayering of the opal coatings has a

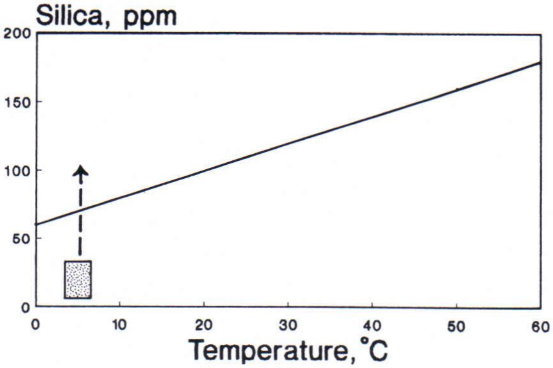

Fig. 6. Chemical equilibrium diagram for the dissolution of amorphous silica (opal) in water according to the data collected by Krauskopf (1959). The box gives the ranges of the silica contents and prevailing temperatures in Finnish ground waters. This data is collected from Kauranne et al. (1972) and Lahermo et al. (1990). The arrow indicates the suggested concentration path of the waters from silica-undersatured to silica-satured conditions. This leads to the precipitation of opal via evaporation model.

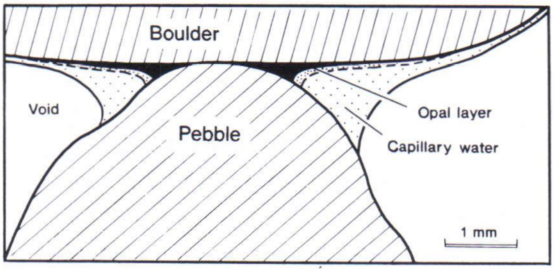

Fig. 7. Sketch depicting the proposed model of opal precipitation by slow evaporation of vadose water in soil water zone in a gravel layer. The sketch shows a section through contacting clasts. The slow evaporation of vadose water transforms the conditions to silica-saturated and leads to opal deposition.

thickness of about 0.5 micrometers. This fact, and the presence of microstalactites, suggests rhythmical and episodical deposition.

These features show that the opal precipitate formed by partial or complete evaporation cycles of vadose water in the soil water zone. The possibility of complete evaporation is excluded because there are no indications of relict evaporite minerals or gypsum as inclusions in the opal coatings.

Similarly, the dissolution diagram of silica (Fig. 6) suggests, that the most logical explanation for deposition is by evaporation. Considerable evaporation of water is required to raise the silica concentration (see the arrow in Fig. 6) above the saturation limit. This is about 65 ppm of silica at the temperatures generally prevailing in Finnish groundwaters (about 6°C). In the oversaturated region silica is expected to be precipitated as opal from capillary waters in the gravel layers. The proposed model of opal precipitation via evaporation is sketched in Fig. 7.

In Finnish eskers and ice-marginal formations the precipitation of opal has similarities with the laboratory synthesis of gem opals (see Nassau and Nassau 1980, O'Donoghue 1983). The opal synthesis is based on the following stages: 1) Manufacturing of silica spheres as suspension in liquid, 2) slow sedimentation of the spheres by evaporation of the water-alcohol mixture, and 3) solidification of the gel either by drying of the excess water or, with an adhesive. These stages require unusually stable conditions with slow changes in the solvent properties likewise for natural opal formation.

Discussion and conclusions

The fluorescent opal occurring as precipitates on pebbles and boulders is a new type of hydromorphic precipitate found in Finland. It is known that in podzol horizons the main hydromorphic components are Fe, Al, Mn, organic compounds, and Si. In the presence of Fe, silica is preferentially co-precipitated with iron in limonitic masses (Carlson 1982, Ojanperä and Ritari 1984) and not as chemically pure silica or opal. However, especially in tropical and subtropical regions, occurrences of opal-forming pedogenic and groundwater silcretes are common. The key studies on these silcretes have been recently summarized and critically reviewed by Drees *et al.* (1989).

The geochemical behaviour of silica at low temperatures in water differs significantly from that of, for example, iron and manganese, whose deposition is mainly governed by abrupt pH—Eh changes in groundwaters. For silica, slow cooling and evaporation leading to supersaturation and coagulation are the main mechanisms. The evaporation model has been proposed by Small (1973) to explain the formation of silcretes. Mineralogically and petrographically they are similar to Finnish hydromorphic opal precipitates. The main difference is that in silcretes, proper, the silica minerals (opal, chalcedony, etc.) commonly fill most of the void spaces (see Thiry and Milnes 1991).

The Finnish hydromorphic opal precipitates can be considered as the first products of the silcretization process. The prerequisite for their deposition in Finnish gravels seems to be a porous texture. Empty voids characterize all gravel layers, in which hydromorphic silica was found (Fig. 7). Similarly, in Australia, Darragh *et al.* (1976) concluded that free spaces formed during dissolution of carbonate veins, or cement, were essential to the deposition of gem opals in conglomerates.

In southern Finland, the areal distribution of the observed localities of fluorescent opal conforms to the highest contents of silica and uranium in groundwaters (Lahermo *et al.* 1990, figs. 23 and 35). Because we have only a very small number of observations from northern Finland, the correlation on the scale of the entire Finland is not justified. However, in southern Finland, it can be concluded that the distribution of opal correlates with the areas characterized by high silica and low Fe contents in groundwaters (Figs.

23 and 29 in Lahermo *et al.* 1990). This correlation can be explained by the co-precipitation of silica and iron in the areas of high iron contents in groundwaters. Opal precipitates have not formed in these areas because silica has been precipitated together with iron in oxidate accumulations.

Besides the geochemical importance, the discovery of the fluorescent opal precipitates has some practical implications. In the compilation of the data on fluorescent minerals in Finland (Kinnunen 1989, 1990, 1991), it was noticed that in a few cases the misidentification of scheelite was sometimes possible. Hydromorphic opal may be easily mistaken for scheelite with high powellite content and additionally for many secondary uranium and thorium minerals or mineraloids (Kinnunen 1990).

In prospecting, the green fluorescence of opal is potentially useful as an exploration guide (Zielinski 1980). This is based on the observation (verified in laboratory tests) that uranium tends to be enriched in the silica precipitates. The enrichment reaches up to 1000 times compared to its original concentration in groundwater (Zielinski 1980). This establishes the fluorescence of the opal precipitates as a sensitive indicator for soil water uranium concentrations. In Finland, the localities of fluorescent opal have no direct correlation to the uranium indications in local scale (Geological Survey of Finland Mineral Indication Data Bank). However, both of these distributions show an enrichment in southern Finland.

The presence of fluorescent opal may have use as an indicator for the former presence of soil water contaminated with uranium. This may be significant in environmental geology, because eskers and ice-marginal formations are major groundwater aquifers in Finland.

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