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Agate as an indicator of impact structures: An example from Sääksjärvi, Finland

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Abstract–Mineralogical, petrographical and chemical determinations were made for 743 agate (banded variety of chalcedonic quartz) nodules (diameters from 5 mm to 5 cm) formed during postimpact, low-temperature hydrothermal activity as vesicle fillings in the melt rocks of the Sääksjärvi meteorite impact structure (diameter 5 km) in southwest Finland. Other hydrothermal vesicle fillings in the impact melt rocks include chlorite, mordenite, smectite and kaolinite. The agates were classified into two types, whose mineralogical properties and chemical compositions fall within the range of volcanic agates (basaltic and rhyolitic host rocks). The relatively high age (~510 Ma) of the Sääksjärvi impact melt rocks, however, is reflected by the presence of recrystallization textures, which are rare in younger volcanic agates. The Sääksjärvi structure was initially located after following the fortuitous discovery of agate "path-finders" in the glacial overburden. It is recommended that wherever volcanic type agates are found as float in Precambrian shield areas devoid of younger volcanic rocks, the possible presence of impact (or volcanic) craters in the vicinity should be considered.

INTRODUCTION

The current global data base of proven impact structures reveals that 27 structures of meteorite origin have been identified in Fennoscandia (Pesonen, 1996; L. J. Pesonen, pers. comm., 1997). Several strategies (*e.g.*, Grieve and Robertson, 1979; Henkel and Pesonen, 1992; Pesonen, 1996) have been developed in the search for impact structures. Although the commonly accepted criteria (see *e.g.*, Grieve and Robertson, 1979) have been successful, additional "path-finders" are necessary in tracing new impact craters in metamorphosed terrains affected by glaciation. Henkel and Pesonen (1992) noted that impact-generated rocks occurring in glacial float are among the criteria used in Fennoscandia for the search and identification of meteorite craters. However, distinctive mineralogical features within detrital mineral grains, such as planar deformation features in quartz and the presence of minerals newly generated during the impact process and impact breccias, have not yet been of practical use because of the effect of dilution within glacial deposits and difficulties in their identification. We have found that in some cases, however, vesicle fillings (including silica minerals and zeolites) of the impact melt rocks may survive erosion and can be observed easily, in spite of strong dilution in the glacial sediments. One such indicator is agate (a concentrically banded type of fibrous chalcedony), which has been found within vesicles of the Sääksjärvi impact structure in the Precambrian shield area of southwest Finland (Fig. 1).

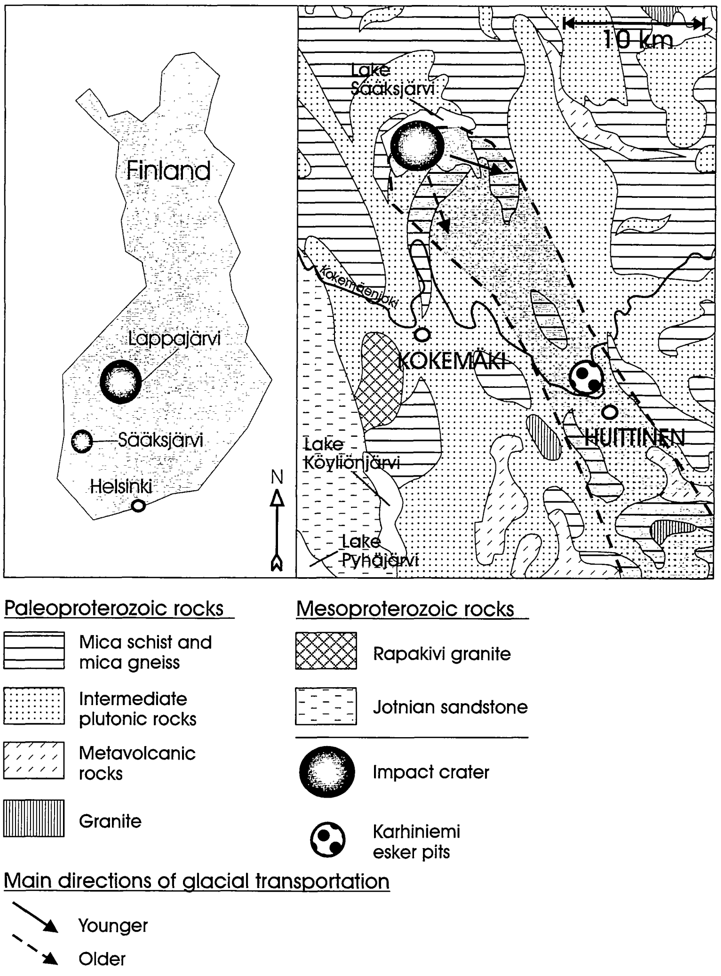

FIG. 1. Location of Finnish impact structures with amygdaloidal impact melt rocks: Lappajärvi and Sääksjärvi. The detailed map shows the Sääksjärvi impact crater, Karhiniemi agate locality and the glacially transported boulder train of impactites and agates (overshaded area). Proterozoic bedrock types are delineated according to Koistinen (1996). The main directions of glacial transportation are indicated according to Salonen and Aumo (1984). The boulder train was constructed according to the maps in Papunen (1973), Halme (1974) and Salonen and Aumo (1984).

Because of their time-dependent recrystallization (Williams and Crerar, 1985) and preferential occurrence in near-surface environments (Heaney, 1993), agates are typically restricted to Cenozoic and Mesozoic rocks (Pabian and Zarins, 1994). The occurrence of unrecrystallized agates in Precambrian shield areas, therefore, indicates the presence of geologically much younger material. To our knowledge, the occurrence of agates in vesicular impact melt rocks has not been previously described in connection with their use as "path-finders" for impact craters, although agates have been reported from other impact structures, including the Ilyinets crater in Ukraine, described by E. P. Gurov (V. L. Masaites, pers. comm., 1996). In this paper, we describe the properties of agates associated with the Sääksjärvi impact structure, using mineralogical, petrographical and chemical methods. This agate "path-finder" method is thought to have potential in discovering impact structures in other glaciated Precambrian terrains.

THE SÄÄKSJÄRVI IMPACT STRUCTURE

The Finnish bedrock represents a fairly typical Precambrian shield area. The northern and eastern part of Finland is largely of late Archaean age, while much of the bedrock of southern Finland formed during the Svecofennian orogeny ~1900 Ma ago (Vaasjoki, 1996). The Sääksjärvi impact structure in southwestern Finland (Fig. 1) lies within the Svecofennian tonalitic migmatite zone, which consists mainly of intermediate plutonic rocks and mica schists and gneisses (Koistinen, 1996). This Pre-Vendian (*i.e.*, ~0.65 Ga) peneplained Paleoproterozoic bedrock is overlain by tills formed during and after the Weichselian glaciations (Nenonen, 1995), recording two main transport directions, an older 325–335° trend and a younger 290–295° trend (Salonen and Aumo, 1984). The length of boulder fans in Finland is normally ~1–5 km but may occasionally reach 50–100 km (Salonen, 1986). As in the case of Sääksjärvi, subsequent glaciofluvial transport has significantly increased transport distances.

The Sääksjärvi impact structure has a diameter of 5 km and was found on the basis of agate pebbles occurring in glaciofluvial material (Papunen, 1969). Agates (Fig. 2), observed in gravel pits in the Huittinen and Kokemäki area some 30 km southeast of the lake Sääksjärvi by local collectors in the late 1960s, were originally identified by Mr. Y. Vuorelainen (Outokumpu Mining Company), who first believed them to be flint, which was a common component of ballast material dumped by ships in old Finnish harbours. It was later discovered, however, that some agates were embedded in vesicles of impactite-like lava boulders in gravel pits within the Karhiniemi esker at Huittinen (Papunen, 1969). These boulders were tentatively interpreted as impactite rocks by Papunen (1969, 1973). Detailed studies at the Max Planck Institute in Germany verified the impact origin, and an age of 514 ± 12 Ma (^{40}Ar-^{39}Ar) was obtained for three whole rock melt samples (Müller *et al.*, 1990). The boulder train of agates and impact melt rocks occurs mainly to the southeast of the lake Sääksjärvi and has been mapped by Papunen (1973), Halme (1974) and Salonen and Aumo (1984). Regional gravity and low-altitude aerogeophysical measurements over the lake Sääksjärvi site revealed a circular Bouguer anomaly of –6.5 mGal ~5 km in diameter (Elo *et al.*, 1992). Microbrecciation found in deep drill holes verified that the Sääksjärvi area was the boulder source (Elo *et al.*, 1992). Later deep drillings revealed impact melt, suevite and impact breccia. The concentrations of siderophilic elements from impact melt rocks suggest that the Sääksjärvi projectile was most probably a chondritic stone meteorite (Palme *et al.*, 1980; Schmidt *et al.*, 1995). Boulders of impact melt breccias and suevites were found in great numbers on the shore line of lake Sääksjärvi and particularly to the southeast of the lake (Salonen and Aumo, 1984).

The petrography and chemical composition of the impact melt breccias (all boulders) have been studied by Papunen (1969, 1973), Maerz (1979), Mutanen (1979) and Müller *et al.* (1990). Papunen (1969, 1973) classified the boulders into four types: (1) impact melt, dark greenish gray, similar to andesite in composition, and small dark green amygdales occasionally filled with silica, (2) vesicular impact melt breccia with crystalline matrix divided to greenish and light brown subtypes, the latter frequently containing agates, (3) impact melt breccia with aphanitic matrix lacking open vesicles, and (4) impact breccia. Müller *et al.* (1990) describe their sample used for isotope determinations (and corresponding to Papunen's type 1) as a cryptocrystalline melt breccia, in which the matrix (composed of plagioclase laths, prismatic pyroxene and a mesostasis with opaques) comprises 68 vol%, vesicles, 7 vol% and partially melted mineral clasts and rock fragments, the remainder of the rock. Detailed petrographic descriptions of other impact types have not been published.

MATERIAL AND METHODS

Agate is a subvariety of chalcedony (microfibrous quartz) showing distinct banding. Agate generally occurs as secondary filling of

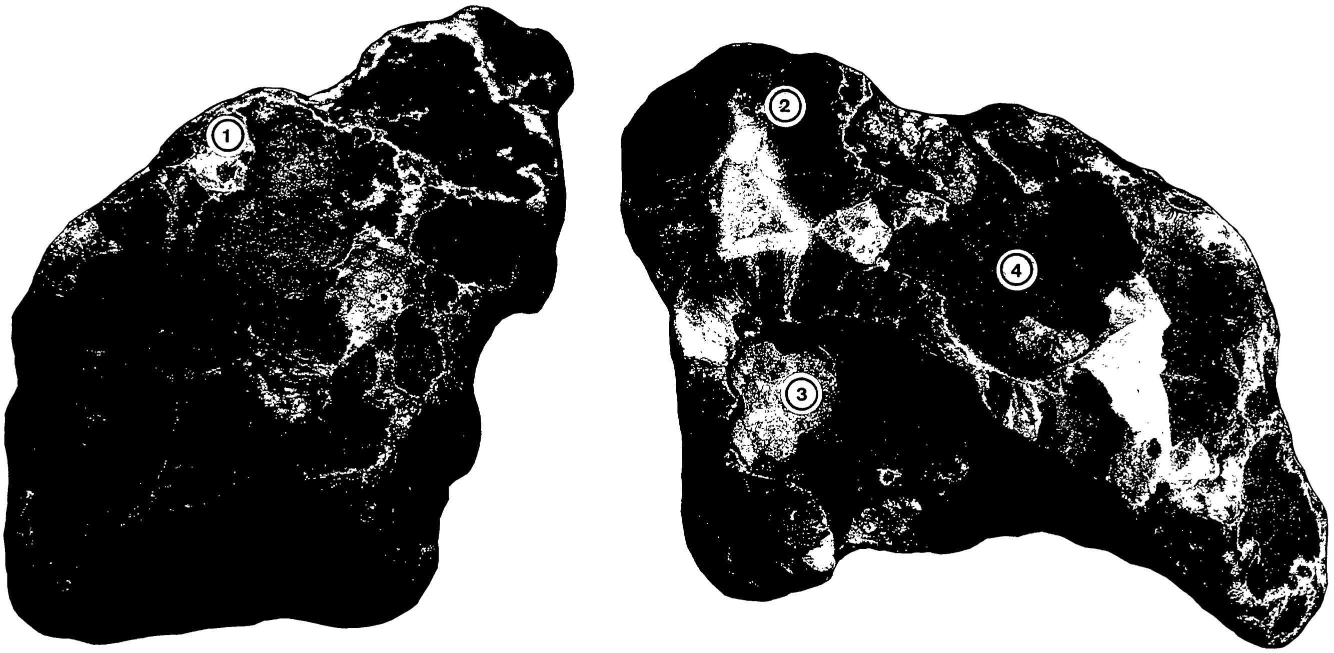

FIG. 2. A typical A-type agate pebble (front and back) from Karhiniemi esker pit. The pebble measures 34 × 24 × 18 mm. It is banded (2) and the corners (1) are glacially abraded. The cavities are covered with chlorite and mordenite (4) and remains of impact melt breccia (3). The irregular shape of the agate pebble is inherited from the shape of the walls of the original amygdaloidal cavity in which the agate was formed.

gas cavities in basic and intermediary lavas. Agate also commonly replaces material in porous pyroclastics and other sedimentary rocks forming irregularly shaped aggregates (so-called thunder eggs and various pseudomorphs). The genesis of agates has been controversial for centuries (see Landmesser, 1984), but recent studies (^{18}O/^{16}O of silica, D/H of bound water and minerals associated with the nodules) have shown that agates represent low-temperature (<100 °C) precipitates in open cavities from fluids that are partly or mostly meteoric (Fallick *et al.*, 1985; Heaney, 1993). Volcanic agates are interpreted to have formed in a cooling lava pile at shallow levels (Harris, 1989).

Impact melt rocks and detached agate nodules of the Sääksjärvi impact structure occur in a glacial dispersal fan that can be traced for at least 50 km from the crater (Fig. 1). The impact rocks range in size from granules to boulders in tills and glaciofluvial material. In the Karhiniemi esker pits, impact melt and breccia rocks comprise 0.3% of the total material based on pebble counts (Kinnunen, 1993), although the agate content itself could not be reliably determined. The material studied are agates collected by local collectors over some twenty years from the Karhiniemi esker pits. A total of 743 agate specimens, mainly whole nodules, were studied, with diameters ranging from 5 mm to 5 cm, the typical size being 1–3 cm. Some agates showed remnants of impact melt breccia on their surface cavities (Fig. 2). Two impact melt breccia pebbles with agate-fillings in vesicles (Fig. 3) were among the material studied.

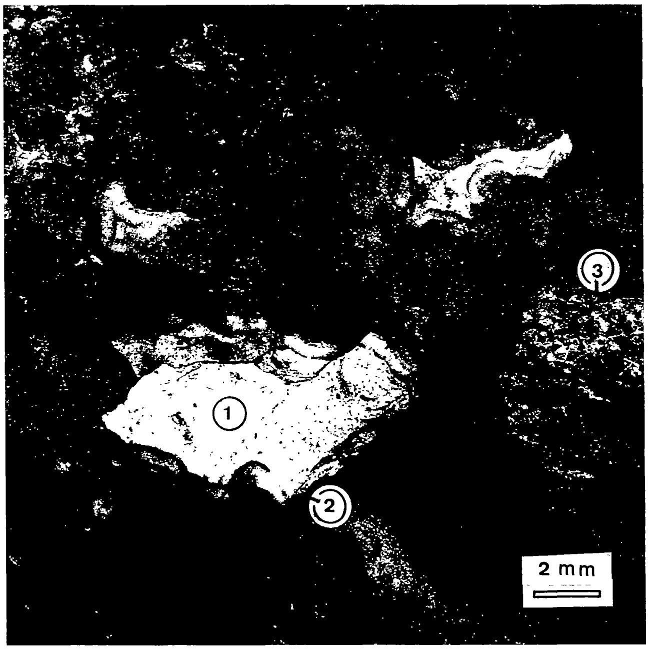

FIG. 3. Agate fillings in amygdales of an impact melt breccia pebble from Karhiniemi esker pit. The centre is composed of B-type agate (1) and the rim of A-type agate (2). The surrounding impact breccia rock contains rock fragments (3).

The material was classified under the stereomicroscope (Nikon SMZ-1) into two main types from which thin sections for petrographic studies and polished thin sections for electron microprobe analyses were prepared. The silica types and microstructures were determined from polished slabs and from thin sections under a polarizing microscope (Leitz Ortholux II POL-BK). About 100–200 points were analyzed from each agate type with the electron microprobe. The electron microprobe instrumentation (Cameca SX50) and related procedures at the Geological Survey of Finland are described in Johanson and Kojonen (1995). The refractive indices were measured with a Rayner Duplex refractometer from polished thin sections using Na light. The density determinations were based on hydrostatic weighing. The two main agate types and other vesicle fillings were studied with x-ray diffraction methods and petrographical techniques. X-ray powder diffraction studies were carried out with a Philips wide-angle goniometer using Ni-filtered Cu-radiation. The 2Θ-range from 2° to 70° was scanned at a speed of 1°/min. The crystallinity index (CI) for quartz was determined according to the procedures described by Murata and Norman (1976). The cathodoluminescence effects were observed with a cold cathodoluminescence instrument CITL 8200 MK4 using 400 μA beam and 20 kV energy.

AGATE TYPES

The properties of the main agate types (A and B) are summarized in Tables 1 and 2 (volcanic agate included for the purpose of comparison). The silica types classified according to the terminology presented by Hesse (1989) are: (1) length-fast chalcedony, which comprises most of the agate nodules; (2) zebraic chalcedony in botryoidal inner rims caused by twisted quartz fibers; (3) microcrystalline quartz filling the spherule inclusions; and (4) megaquartz in the central cavity. The chalcedony textures classified according to the terminology of Flörke *et al.* (1991) are presented in Table 1. The possible presence of moganite, a silica polymorph composed of length-slow chalcedony (cf., Heaney and Post, 1992), was checked from the main agate types with the powder diffraction method; samples were found to be devoid of moganite.

In both agate types, the chalcedony is microbanded (Fig. 4) and shows textures common to volcanic agates worldwide (Table 1). Recrystallization textures in some, or occasionally all, chalcedony layers are diagnostic features of the B-type agates. In some B-type specimens, recrystallization produces a so-called chicken-wire texture (Fig. 5); in others, it reflects coarsening of the chalcedony fibrous texture (Fig. 6). Such textures are *absent* in most volcanic agates of younger geologic age (from Mexico, California, Brazil, Tanzania, Germany, Russia) examined as reference material (Kinnunen, 1993; and this study). However, similar recrystallization textures were observed in agate pebbles of Precambrian age from the agate conglomerate in Dala sandstone located in Horrmund, Middle Sweden (Kinnunen, 1993). Most probably, the age of the agates in general is reflected in their texture: chalcedony recrystallizes slowly to microcrystalline quartz. The same trend as seen in the recrystallization textures is observed in the crystallinity indices: A-type agate without petrographically observable recrystallization texture shows the lowest degree of crystallinity. The refractive indices and density correlate inversely with the crystallinity index.

The crystallization order of the two agate types was determined from nodules composed of both agate types. In all cases, the A-type agate is paragenetically oldest, followed by the B-type. Vesicles filled with only one type of agate are the most common. Accordingly, the centre (youngest) is composed of B-type agate (if both agate types are present in the same nodule) or of a crystal druse (clear quartz or pale amethyst).

TABLE 1. Mineralogical and petrographical properties of the Sääksjärvi postimpact agate types A and B based on 743 samples collected from the Karhiniemi esker pits, Huittinen.

	Type A (this study)	Type B (this study)	Volcanic agate (data from the literature)
Locality	Huittinen, Karhiniemi	Huittinen. Karhiniemi	worldwide
Number of samples (percentage)	76 (10%)	667 (90%)	published data
Diaphaneity	transluscent	weakly transluscent, opaque	transluscent to opaque
Colour (Munsell code)	blue (5PB7/2-5 PB5/2)	white, light grey, light brown, reddish orange (N9-N8, 5YR6/4-5YR5/6, 10R6/6)	varies widely
Density (g/cm^3)	2.59 ± 0.04	2.42 ± 0.04	2.60 ± 0.05
Refractive indices	$\omega = 1.534 \pm 0.001$ $\epsilon = 1.539 \pm 0.001$	$\omega = 1.529 \pm 0.002$ $\epsilon = 1.533 \pm 0.002$	$\omega = 1.535$ (typical) $\epsilon = 1.539$ 1.526–1.543 (total range)
Crystallinity index for quartz	0.7	2.1–3.6	<1.0–4.7
Microbanding (mean N/1mm)	100	100–200	16–600
Cathodoluminescence effect	inert	weak orange	typically blue
Main silica types	length-fast chalcedony zebraic chalcedony megaquartz	length-fast chalcedony microcrystalline quartz	length-fast chalcedony zebraic chalcedony microcrystalline quartz megaquartz (moganite)
Main chalcedony textures	wall-layered (botryoidal)	wall-layered recrystallization features	wall-layered botryoidal (horizontally-layered)
Inclusions in chalcedony	hematite stars silica spherules	hematite stars	varies widely
Rind material composition	chlorite, mordenite	chlorite, mordenite	zeolites, phyllosilicates

Data for volcanic agates from Murata and Norman (1976), Landmesser (1984), Rykart (1989), Heaney and Post (1992), Heaney (1993) Pabian and Zarins (1994) and Taijing and Sunagawa (1994) included for the purpose of comparison. The classification criteria of main silica types used in this table are explained in detail in Hesse (1989) and those of the the chalcedony textures in Flörke *et al.* (1991).

TABLE 2. Chemical composition of the Sääksjärvi postimpact agate types A and B from Karhiniemi esker pits, Huittinen, determined with the electron microprobe as weight percentages (analyst B. Johanson).

Wt%	Type A (this study)	Type B (this study)	Volcanic agate (data from the literature)
SiO_2	99.29	98.66	—
TiO_2	0.01	0.01	0.002–0.083*
Al_2O_3	0.02	0.17	0.005–1.5†
Cr_2O_3	0.01	0.01	—
FeO	0.01	0.11	0.01–3.6†
MnO	0.01	0.01	—
MgO	0.01	0.01	0.00–0.4†
CaO	0.03	0.05	0.00–0.3†
ZnO	0.02	0.02	—
Na_2O	0.06	0.07	0.02–0.25†
K_2O	0.01	0.02	0.0–6.0†
P_2O_5	0.02	0.02	—
F	0.05	0.07	0.010–0.030*
Cl	0.01	0.03	—
Total	99.56	99.26	
Number of analyses	100	198	

Data of volcanic agates from the literature:

*Sixteen basalt agates from Germany, Brazil, Uruguay, Russia and Mongolia; 11 rhyolite agates from Germany; Blankenburg and Schrön (1982) and Burchardt (1986) shown as ranges of reported emission spectral analysis.

†About 75 volcanic agates from Brazil, India, Australia and Germany (Harder, 1993) analyzed by spectrophotometric methods, titration and AAS.

FIG. 4. Photomicrograph showing microbanding (1) and megaquartz (2) in A-type agate from Karhiniemi esker pit. The chalcedony fibers are unrecrystallized. Transmitted, crossed polarized light.

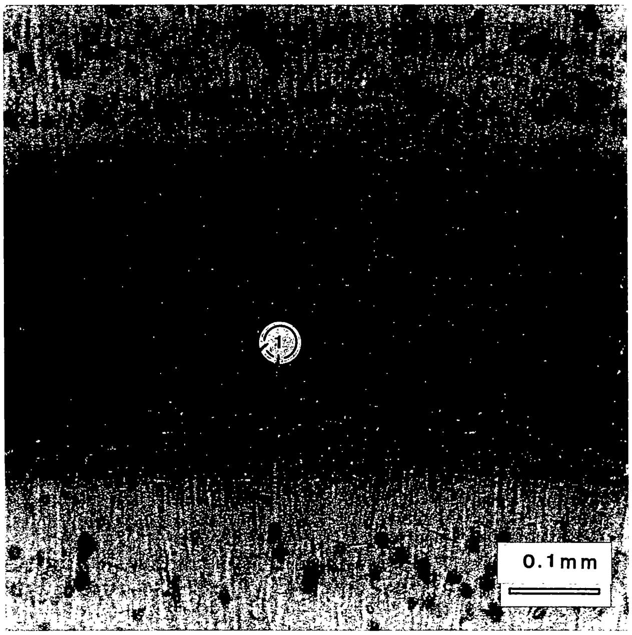

FIG. 5. Chicken-wire like recrystallization (1) in the chalcedony layers of B-type agate from Karhiniemi esker pit. Transmitted, plane-polarized light.

FIG. 6. Recrystallization in the form of coarsening (1) of the chalcedony fiber texture (2) of B-type agate from Karhiniemi esker pit. Transmitted, crossed polarized light.

In chemical composition (Table 2), the A-type agate differs from the B-type with lower Al and Fe contents. Possible explanations for the chemical differences of the agate types include hydrothermal fluid-rock interaction leading to chemical alteration or, more likely in this case, primary precipitation. According to ion-probe data by Merino *et al.* (1995), the chalcedony layers in agates from Brazil flood basalts alternately contain high and low abundances of the elements Al, Fe, K and Na. This distribution is attributed to a primary crystallization phenomenon (Frondel, 1985) leading to typical textures seen on agates and, eventually, to the enrichment of Fe minerals and zeolites typical for agate assemblages. According to Wang and Merino (1990), Al^{3+} acts as a catalyst in agate crystallization, while Flörke *et al.* (1982) argue that Al^{3+} and Fe^{3+} substitute Si in the quartz (chalcedony) structure.

The trace element concentrations of the A and B types of the impact agates in question generally lie within the range reported for volcanic basaltic and rhyolitic agates (see Table 2). The same applies to the mineralogical properties (see Table 1). Burchardt (1986) found that in volcanic agates, the Al content shows positive correlation with Fe, K, Na, Mg, Ti, Ba, Ca and F. His work is based on emission spectral analyses of Blankenburg and Schrön (1982), in which maximum values of trace elements correlating with Al occur in rhyolitic agates, and minimum values occur in basaltic agates. It can be concluded that the type A Sääksjärvi agates are near the low basaltic values and the B type near the high rhyolitic values. This suggests that impact agates may show a wide range of trace element contents, which is indicative of both acid and basic volcanic host rocks. According to Harder (1993), the sum of nonvolatile impurities is 6.75–0.045 wt% in agates from volcanic rocks. In the Sääksjärvi postimpact agates, the sum of nonvolatile impurities is 0.27 wt% (Type A) and 0.60 wt% (Type B).

OTHER VESICLE FILLINGS

In addition to agates (composed of chalcedony and megaquartz), other vesicle fillings in the impact boulders and pebbles from Sääksjärvi contain mordenite, chlorite, smectite (montmorillonite?) and kaolinite, based on x-ray powder diffraction determinations. The deduced crystallization sequence is chlorite and mordenite (oldest), through agate (chalcedony and megaquartz) to the youngest clay minerals (smectite, kaolinite). Smectite, mordenite and chalcedony are indicative of a low-temperature (epithermal) hydrothermal system (cf., Simmons and Browne, 1996). When the mineral assemblage is compared to the mineralogy of modern geothermal systems (Ellis, 1979), it can be estimated that the vesicle fillings precipitated when the temperature was declining from ~150 °C; some vesicle fillings may even have formed during weathering processes.

DISCUSSION AND CONCLUSIONS

Agate is widespread in various geological environments: in gas cavities, in acid and basic volcanic rocks, in fractures and cavities within various rock types, and as replacement material in sedimentary rocks (Frondel, 1962; Hesse, 1989; Pabian and Zarins, 1994). When agate fills cavities, their primary shapes are preserved. Agates crystallized in gas cavities are, thus, distinguished by their vesicle-like ovoidal shape, especially in melt rocks of intermediate or basic composition.

The postimpact agate types of Sääksjärvi (all glacial pebbles) are morphologically, mineralogically and chemically similar to agates from volcanic source rocks (Tables 1 and 2). To our knowledge, the genesis of the host rock (impact melt or volcanic) cannot be deduced from the agate nodules themselves, although the presence of two different agate types may be such an indication. This uncertainty is understandable, because, according to modern genetic models, agates in general are formed by low-temperature polymerized silica-rich fluids showing internal rhythmic fluctuations (Heaney, 1993; Taijing and Sunagawa, 1994). The simple prerequisites for agate formation (and for other vesicle filling types) are voids, the circulation of low-temperature fluids during postimpact alteration, an available source of silica (overlying breccia lens or suevite deposits?) and time. According to models for agate formation, external fluctuations of geothermal or other origin do not significantly contribute to the banding characteristics or to the microtextures (Heaney and Davis, 1995). Therefore, the differences in processes of formation of impact *vs.* volcanic vesicle fillings are not necessarily reflected in the properties of the agates.

In our opinion, the presence of nodular "volcanic-type" agates has a potential value in the search for eroded impact structures within Precambrian shield areas. Although agates are common in younger volcanic and sedimentary rocks, they are rare in most Precambrian shield areas (Pabian and Zarins, 1994). In addition, agates are resistant to comminution compared to the more common but friable minerals formed during postimpact hydrothermal alteration in gas cavities of impact melt rocks. Therefore, the value of agate is enhanced as a "path-finder" for impact structures (or young volcanic craters) in shield areas. Information concerning agate finds in virgin terrain spreads quickly among mineral collectors and the presence of accompanying impactite clasts can easily be checked in the field. This technique is, therefore, considered as a fruitful addition to the criteria in the search for new impact structures.

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