

## BIOGENIC SAPONITE FROM AN ACTIVE SUBMARINE HOT SPRING, ICELAND

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**Abstract**—A study of the mineralogy, chemical composition and structure of poorly-crystalline saponite precipitated from a submarine hot spring in Eyjafjordur, northern Iceland is reported. Special emphasis was placed on the microstructures of the minerals and a possible connection with biological activity during their precipitation. The microstructures of the minerals were found to be very similar to specific clay minerals precipitated from geothermal vents in oceanic rift zones. The composition of the minerals was, however, found to be similar to magnesium silicate scales formed in geothermal installations in Iceland where geothermal waters were mixed with cold fresh waters. High contents of organic substances were found in the clay mineral samples as compared to geothermal precipitates from other localities. Microstructural features of the layer silicates in one of the samples suggest that a gelatinous substance was a precursor of the saponite clay. The organic matter content appears to be greater when the precipitates are more crystalline.

**Key Words**—Active Submarine Hot Spring, Authigenic Formation, Microbial Formation, Organic Matter, Saponite.

### INTRODUCTION

Submarine geothermal activity, in the form of black and white smokers, is known in several localities at sea-floor spreading ridges. Around Iceland several localities with submarine geothermal activity have been reported, especially off the western and northern shores of the country. The existence of submarine hot springs in the Eyjafjordur Fjord, northern Iceland has been known for several decades. The exact location of the site was, however, not recorded until 1996. In 1997 and 1998 its depth, extension and form were mapped. Samples of the precipitates were collected from the submarine hydrothermal vents during diving expeditions in 1997 and 1998. This paper describes the results of an investigation of samples collected around vent outlets during the expeditions. Also reported is the chemistry of water pumped up from a vent by a device specially designed for the task (Marteinsson *et al.*, 2000) to collect uncontaminated samples from the hydrothermal vents on the sea floor.

The clay minerals precipitated have been studied by optical microscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM), and analyzed chemically by energy-dispersive X-ray (EDX) and X-ray fluorescence (XRF) methods, and by wet-chemical analytical methods. Special emphasis was placed on the study of microstructures that might indicate biomorphous activity during the precipitation of the clay minerals. The water was preserved at the sampling site and subsequently analyzed by standard analytical

methods for geothermal water, developed at the Orkustofnun chemical laboratory, and speciation and mineral equilibria were calculated by the Watch program (Bjarnason, 1994).

### GEOHERMAL ACTIVITY IN THE EYJAFJORDUR REGION

Geothermal activity is widespread in the Eyjafjordur region, North Iceland. The bedrocks are basaltic lavas 6–10 My old (Björnsson and Saemundsson, 1975; Björnsson *et al.*, 1978) cut by mostly NE-striking dikes. The lavas generally dip 5–7° to the North, but a flexure to the NE of the fjord increases the dip abruptly to 10–20°. Geothermal occurrences in the area are commonly connected with NE or NNE tectonic features dominating in the area, dikes or faults (Björnsson, 1981). Sometimes the geothermal activity also appears to be connected with NW-striking faults or intersections of the two tectonic directions. Most of the geothermal fields in the region have rather limited capacity. The active hot springs had rather low yield-rates of the order of 0.1–5 l/s prior to exploitation of the fields. When produced, the fields tend to decline rapidly. The geothermal resources within the younger formations connected to the NW fault zone appear to be more permeable and yielding than those within the older rock formation. The reservoir temperatures of the fields in the region are in the range of 50–100°C. The geothermal fluids are of meteoric origin, with low mineral concentration and high pH value (Kristmannsdóttir and Johnsen, 1982). The stable isotopic ratios suggest meteoric water recharge from the high inland mountains to the south.

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## SETTING AND GEOTHERMAL CHARACTERISTIC OF THE VENT

The geothermal hot spring in this study is located 1.8 km offshore in the northeastern part of Eyjafjörður (Figure 1). The site is formed like a broad mound rising from 100 to ~60 m below sea level. The lateral extent of the mound is ~0.5 km<sup>2</sup>. The submarine hot spring appears to be connected with intersections of the active part of the NW fault zone and the predominant NE tectonic trend in the area (Figure 1). From the mound,

two sharp cones rise to 35 and 15 m below sea level, respectively. The cones are on a line oriented approximately E–W. Several active vents are found on each cone as well as numerous extinct ones. Measuring and even estimating the flow rate from the vents is very difficult due to the location and number of the outlets. The flow amounts to a minimum of tens of liters per second or even up to a hundred. The mound is composed of sediments, shells and precipitates from the fluids, but the cones appear to contain a higher proportion of precipitates. The maximum measured temperature of water discharged from the vents is 71.6°C. Samples were collected during both the 1997 and the 1998 diving expeditions. The water samples obtained in 1997 were mostly contaminated by seawater, but in 1998 water samples which were virtually uncontaminated were collected by the use of a submersible pump connected by a hose to an active vent (Marteinsson *et al.*, 2000). The geothermal water (Table 1) was found to be almost completely fresh and very similar in composition to geothermal waters ashore. Apart from a very slight seawater content of ~0.1%, both chemical properties and stable isotope ratios are almost identical to waters of similar temperature from other geothermal fields in the Eyjafjörður region (Kristmannsdóttir and Johnsen, 1982). As is common in Iceland, the pH of the water is high, ~10.0, and according to calculated geothermometers (silica and alkali feldspar temperatures) the water appears to be near equilibrium at reservoir temperatures of ~80°C. The stable isotopic ratios ( $\delta D$  and  $\delta^{18}O$ ) suggest water recharge from the high inland mountains to the south. The <sup>14</sup>C apparent age of the water is comparable with terrestrial geothermal waters of similar temperature and settings elsewhere in Iceland (Sveinbjörnsdóttir *et al.*, 1998), which indicates substantial water-rock interaction. Thermophilic bacteria and archaea were identified in the hydrothermal vent fluid (Marteinsson *et al.*, 2000).

## MINERALOGICAL INVESTIGATION OF PRECIPITATES

### Preparation and methods of investigation

Sample E-2 was collected by a small submarine from the tallest cone of the geothermal submarine spring at 57 m below sea level during the diving expedition in Eyjafjörður in 1997. It consists of several solid pieces (4.5, 2.0, 1.0, 0.5, 0.3, 0.2 cm in length) and loose silt substance (~0.3 cm<sup>3</sup>). Sample E-3 was collected by a scuba diver at ~30 m depth during the second submarine expedition in 1998. It is visibly distinct from sample E-2. All the pieces of this sample are white, have a thread-like structure, and are very brittle. Before analysis the sample was carefully washed with distilled water in order to remove marine salts. Initially all samples were studied by binocular microscope. Distribution of terrigenous components, fossils and characteristic features of

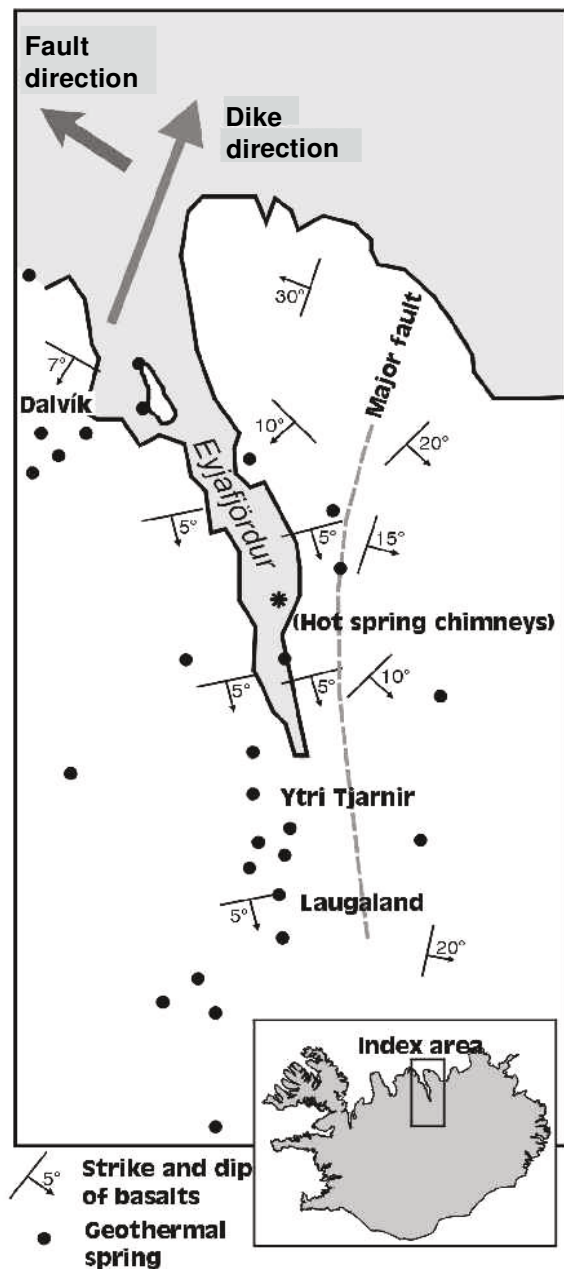


Figure 1. Map of the vent field in Eyjafjörður showing the main fault, dike and dip directions.

Table 1. Chemical composition of geothermal water pumped up from an active chimney at 30 m depth in Eyjafjörður. The composition of a typical geothermal water from an onshore well in the Eyjafjörður valley and standard seawater composition are shown for comparison (Turekian, 1969).

	Vent fluid	Onshore geothermal water	Seawater
Temperature (°C)	71.4	80	
pH	10.03 (at 24°C)	9.95 (at 20°C)	8.0 (at 25°C)
H <sub>2</sub> S (mg/l)	0.32	0.09	0
Total carbonate (CO <sub>2</sub> ) mg/l	25	13	102
Total dissolved solids (TDS) mg/l	291	223	
SiO <sub>2</sub> (mg/l)	93.7	92.3	2.9
Na (mg/l)	79.2	53	10800
K (mg/l)	1.62	1.0	390
Ca (mg/l)	2.45	3.6	410
Mg (mg/l)	2.59	0.006	1290
SO <sub>4</sub> (mg/l)	19.5	43	2700
Cl (mg/l)	44.7	11	19400
F (mg/l)	0.86	0.47	1.3
Br (mg/l)	0.19	-	67.3
B (mg/l)	0.19	0.16	4.45
Al (mg/l)	0.122	0.10	0.001
Fe (mg/l)	0.0081	0.012	0.003
Mn (mg/l)	0.0001	0.002	0.0004
δ <sup>18</sup> O‰	-13.13	-14.12	0
δD‰	-92.9	-102.2	0
δ <sup>13</sup> C‰	-9.44	-	-
Apparent <sup>14</sup> C age in Y	11000 ± 90	-	-
Hg (mg/l)	0.000014	-	0.00015
Cu (mg/l)	0.0012	-	0.0009
As (mg/l)	0.0208	-	0.0026
Cd (mg/l)	0.00011	-	0.0001
Pb (mg/l)	0.0002	-	0.00003
Cr (mg/l)	0.0010	-	0.0002
Zn (mg/l)	0.0008	-	0.005

- not measured

authigenic clay minerals were studied in thin-section using an optical microscope, and X-ray data were obtained from pieces of pure clay minerals selected under a binocular microscope. All these pieces were taken from structures suggestive of biological shapes (winding tubes and worm-like structures, filaments). The same types of pieces were selected for examination by SEM in conjunction with EDX analysis (Link-860 system). Sample E-3 was also analyzed by wet-chemical analysis.

#### Optical investigation

There is strong evidence that the cones and vents were formed jointly by marine and hydrothermal activity. Thin-section study shows that there are some remnants of marine micro-organisms as inclusions in samples, and sample E-2 consists mainly of a marine terrigenous sediment cemented by clay minerals. This sediment consists of coarse, poorly sorted siltstone and in some pieces sandy siltstone. The small portion of terrigenous pelitic material shows that relatively strong currents, which removed fine particles, shaped the characteristics of the sedimentary environment in this part of the fjord. Remains of siliceous sponge spicules

and foraminifera shells were only rarely found in all thin-sections of sample E-2. In the larger pieces of sample E-2, some zoning can be seen in color, density and composition. Sharp boundaries of some zones, differing in the amount of sedimentary particles, suggest that this material was accumulated in open fissures. This was further confirmed by the finding of deformed and flattened foraminifera shells immediately at the sharp boundary between two of the zones.

The terrigenous material consists mainly of plagioclase and pyroxene fragments and a small amount of palagonitized sideromelane and pieces of green-colored clay minerals. The authigenic minerals consist of layer silicates, calcite and Fe hydroxides. The authigenic clay minerals comprise white, translucent and semi-translucent (in thin-sections) globules, worm-like and thread-like structures. The structures of clay minerals found are similar both in shape and size to the clay mineral structures found in a Miocene flood-basalt pile (Geptner *et al.*, 1995; Geptner *et al.*, 1996). Translucent clay minerals, which have a refraction index of ~1.490 and low birefringence index of ~0.01, form cemented siltstone, as well as worm-like and filamentous structures precipitated in open spaces. Some fissures are

partly or completely filled with translucent clay minerals showing colloform texture. The textural features of the cement suggest that the deposition of the clay minerals followed the mineralization of all original pore-spaces and the precipitation of potentially biomorphous structures in voids and open fissures.

Euhedral calcite crystals, precipitated after clay mineralization, were found in open spaces on the surface of globular, worm-like and filamentous clay structures. Very fine needles of aragonite are unevenly distributed in a terrigenous matrix. At least two stages of calcite precipitation can be distinguished. Calcite crystals of the first stage are partly dissolved and replaced by clay mineral pseudomorphs.

Sample E-3 has a very fine filamentous structure. It is composed of a translucent material that has a very low refractive index ( $\ll 1.540$ ) and a very weak birefringence. It appears to be a gelatinous substance forming a filamentous, spiderweb-like structure. Very small crystals of calcite and some rounded brown particles of Fe oxide are unevenly distributed throughout the sample. A small remnant of a marine organism was found trapped in the spiderweb-like structure.

#### Scanning electron microscopy

The pieces selected for SEM investigation were taken from sample E-2 in the zone of clay mineral precipitation into pore-space (various voids and fissures), and from sample E-3, in different zones of threadlike structures. Four types of microstructures were distinguished in sample E-2: (1) filaments; (2) globules and hemispherical bodies; (3) chains of globules; and (4) dense masses.

(1) The diameter of the filaments range from 5 to 8  $\mu\text{m}$ , and they are branched and crossed (Figure 2a). The maximum observed length is up to 60  $\mu\text{m}$ . In cross-section it can be seen that these filaments consist of radiating, tubular-shaped crystals (Figure 2b). A few filaments have a hole in the central part and are tubular (Figure 2c). Inside one of the filaments a sand grain was found (Figure 2d). (2) The globules also consist of radiating tabular-shaped crystal bodies and range from 1 to 30  $\mu\text{m}$  in diameter. Many globules are formed from clusters of several rounded or hemispherical bodies. Their size varies considerably. (3) The extended globular clusters look like chains and consist of rounded structures that are either touching each other or joined by

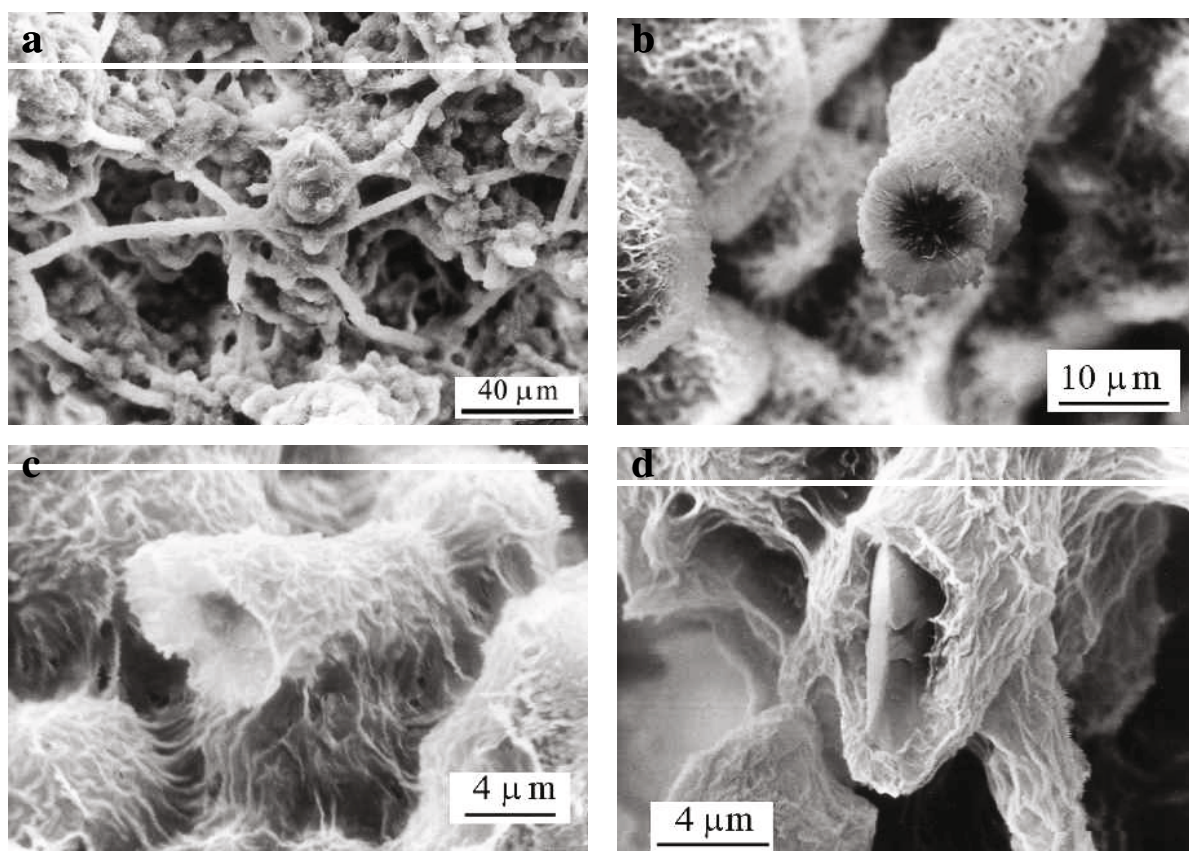


Figure 2. Types of microstructures in saponite clay, sample E-2. (a) Branched and crossed filaments associated with microglobules on its surface and in between. (b) Radiating tabular-shaped crystals on the cross-section of a filament. (c) Filamentous structure consisting of microglobules and displaying a hole in the center. (d) Hole and terrigenous particle situated inside a filament; a characteristic open space surrounds a rock particle.

short filaments (Figure 3a,b). (4) The dense masses have flat or uneven surfaces. On the cross-sections between the dense masses with hilly surfaces, concentric zonation is commonly observed.

On the surface of all the studied microstructures, there are many oval and round holes (diameter 0.5–1  $\mu\text{m}$ ) present (Figure 3c). A shaded surface on the inner wall of a round elongated canal was observed in one of the filamentous structures (Figure 3d). The pattern on the wall looks like furrows and tiny ridges, which may suggest the disappearance of bacteria from a mineralized sheath (Gerasimenko *et al.*, 1996).

Three types of filamentous structures can be distinguished in sample E-3: (1) structures with flat and even surface; (2) structures with sectioned surfaces; and (3) structures formed by a chain of globules clinging close together (Figure 4a–c). The edges of unbroken filaments have a rounded shape. There are many branched and crossed filaments of all structure types (Figure 4a,b,d,f). The diameter of the smallest filaments is <0.5  $\mu\text{m}$ , but most of them are 5–10  $\mu\text{m}$  or more in diameter. In cross-section they display a homogeneous

and dense structure. In one cross-section of a filament, a zoned structure was commonly found and in a few cross-sections, small holes in the central part of the filaments were observed (Figure 4d). A sequence of sections evenly arranged on the surface of such filaments is assumed to indicate biomorphous origin and are commonly observed in sample E-3. Filaments with and without such sectioned structures were found in close association independently of the size and diameter of the thread. Very often the section structure is masked by later globular precipitation.

Many small globular structures are found on the surface of all types of filaments (Figure 4b,d). The small globes have an even surface, whereas the coarse globular surface of thick filaments looks uneven and displays a layer of numerous globules of different size. In dense parts of the spider web structures, globes stick closely together and form a layer with a globular surface. The web of thin threads, with an even surface situated on the thick-sectioned thread, suggests that their formation was successive and that the whole filament construction was growing continuously (Figure 4e). In sample E-2 the

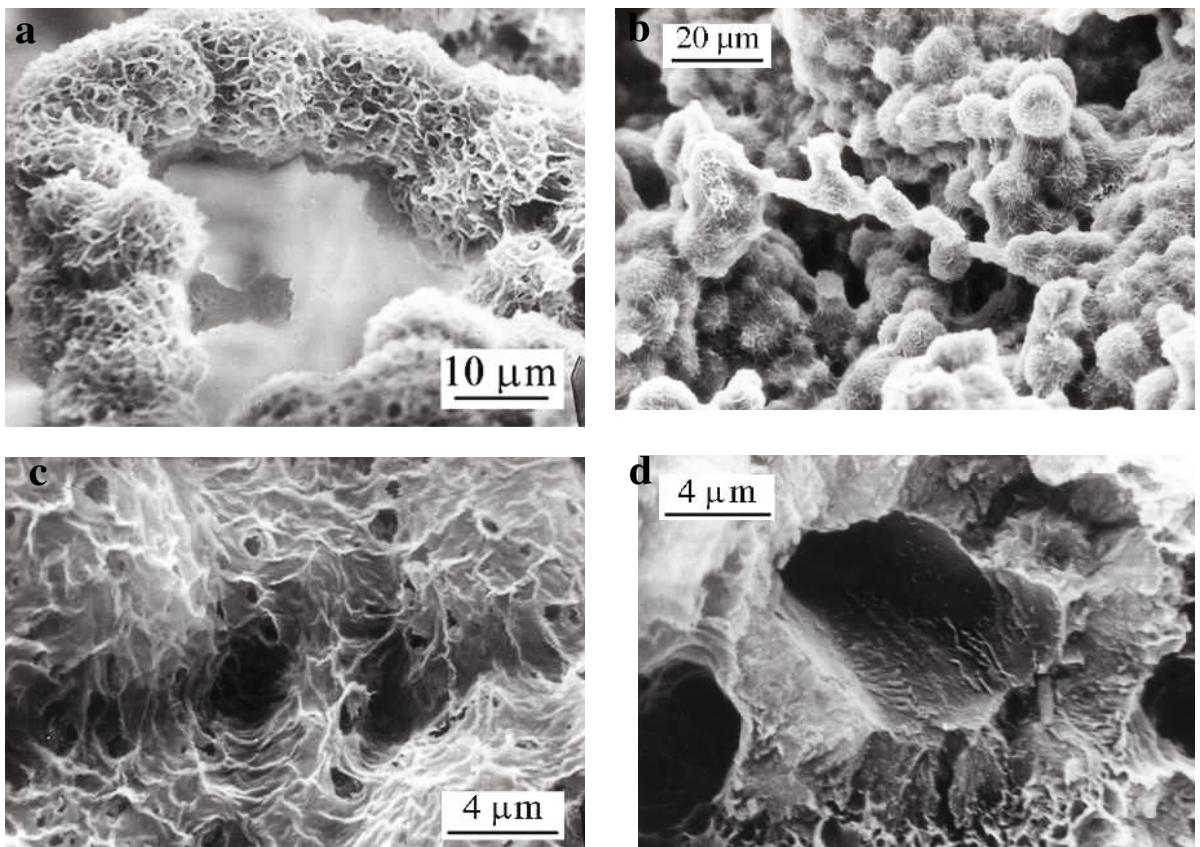


Figure 3. Types of microstructures in saponite clay, sample E-2. (a) Filamentous structure composed of a chain of globules with numerous holes on its surface. (b) Clusters of globular structures joined by filaments. (c) Surface of globular chain displaying numerous holes of oval and round form. (d) Shaded surface on inner wall of elongate canal of filamentous construction suggesting formation by filamentous bacteria leaving fossilized sheath.

section structure is manifested very rarely and is altered by recrystallization and formation of clay mineral leaflets on the surface of the filaments.

In sample E-3 there is a close association of filament structures and calcite crystals. Very often one thin filament is located inside several calcite crystals. Several small calcite crystals strung-grown on one filament are common features in sample E-3 (Figure 4f), which shows later calcite precipitation.

The microstructures described above strongly suggest that the clay structures in sample E-2 were recrystallized from a hydrothermally precipitated gel substance, similar to that of sample E-3. The globules observed in sample E-3 have an homogeneous and dense structure whereas the globules of sample E-2 display a distinct crystal structure. The round elongate canals inside the filaments give strong evidence for the existence of some organic matter around which coagulation and recrystallization took place.

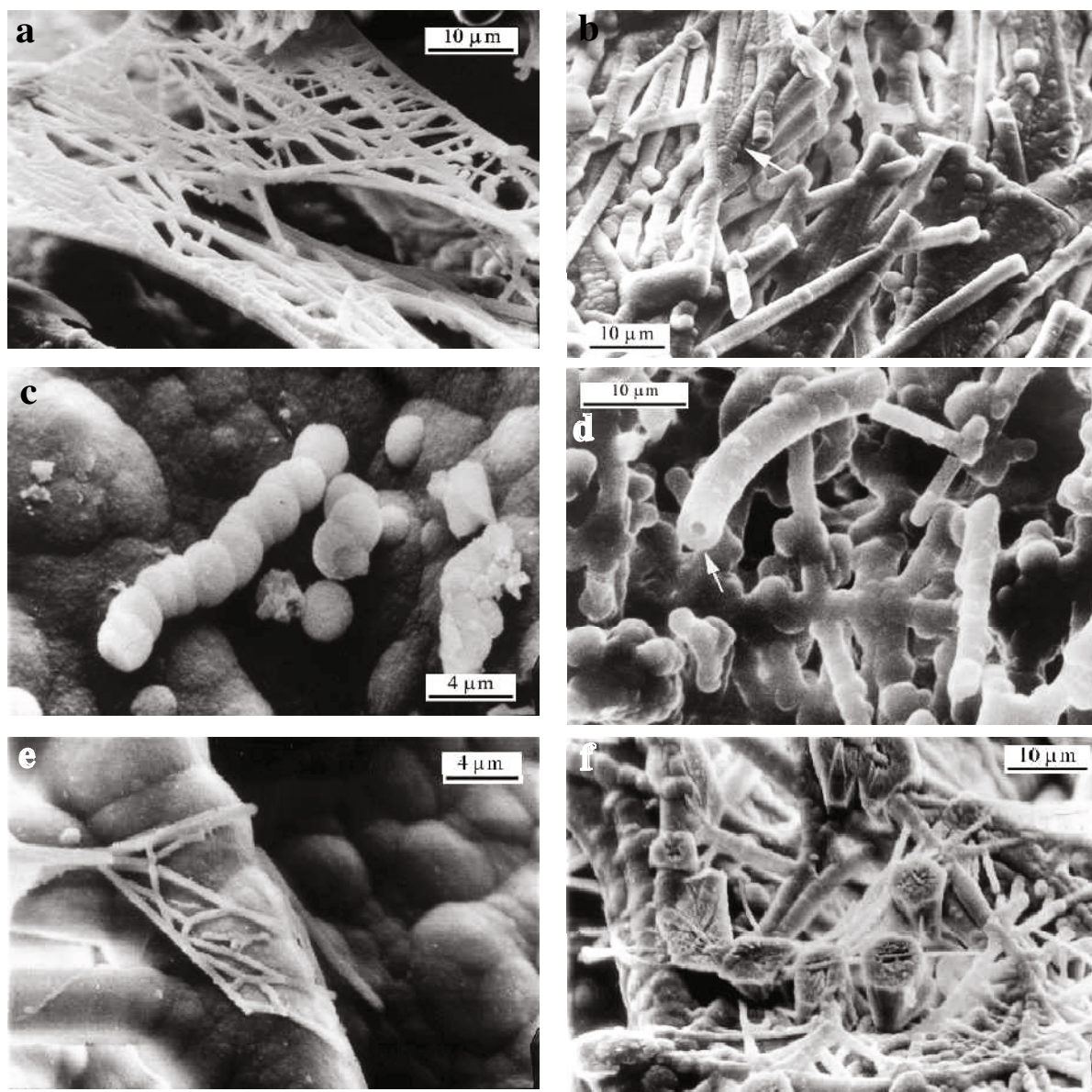


Figure 4. Types of microstructures in a weakly crystallized substance, probably a precursor of layer silicate (saponite), sample E-3. (a) Web-like structure consisting of branched and crossed filaments with a flat and even surface of threads. (b) Dense part of a web-like structure consisting of sectioned thread structures (arrow) and microglobules on its surface. (c) First stages of formation of filaments composed of globules stuck close together. (d) A small elongate hole in the central part of filament (arrow). (e) Web-like structure of thin threads superimposed on the surface of a thick filament with an uneven globular surface. (f) Association of filamentous structures and euhedral calcite crystals.

### X-ray diffraction data

The samples were selected under a binocular microscope in order to select layer silicates with biomorphous-like structures and to avoid X-ray detectable impurities. The clay minerals of sample E-2 were identified by XRD analysis as almost monomineralic, trioctahedral ( $d_{060} = 1.529 \text{ \AA}$ ) swelling smectites, (saponite) (Figure 5a). The XRD patterns for air-dried samples (Figure 5a, I) are characterized by broad peaks centered at 16–18 Å. This is a strong indication that the smectites are saturated with some natural organic substance. This was later proven by the identification of polycyclic aromatic hydrocarbons (1336 ng/g) (diphenyl+fluorene, naphthalenes, phenanthrenes, benzfluorenes) in the clay minerals of this sample (Geptner *et al.*, 1999).

The XRD patterns of powder specimens of sample E-3 show only weak and broad peaks centered at 3.43, 2.45 and 1.547 Å (Figure 5b, I). Diffractograms of oriented specimens are also characterized by broad and very weak peaks (Figure 5b, II–IV). The data show that this sample

is a very poorly crystallized substance and may suggest that it is a precursor of the layer silicate (saponite) found in sample E-2. A much smaller amount of polycyclic aromatic hydrocarbons (27 ng/g) (diphenyl+fluorene, naphthalenes, phenanthrenes, benzfluorenes and pyrene) was detected in this sample than in E-3, supporting this assumption. These data strongly suggest that hydrocarbons migrate with hot water and accumulate in the secondary minerals (Geptner *et al.*, 1999). The results of the XRD analysis suggest that some amorphous silica could be mixed with the clay precipitates in this locality.

### Chemical composition

The chemical compositions of clay minerals (sample E-2) that make up the globular, worm-like, and filamentous structures, as well as of euhedral calcite crystals are listed in Table 2. Total Fe is reported as FeO. It was impossible to select enough material for ignition loss analysis. To evaluate the chemical composition of the clay minerals, an ignition loss of ~16% was

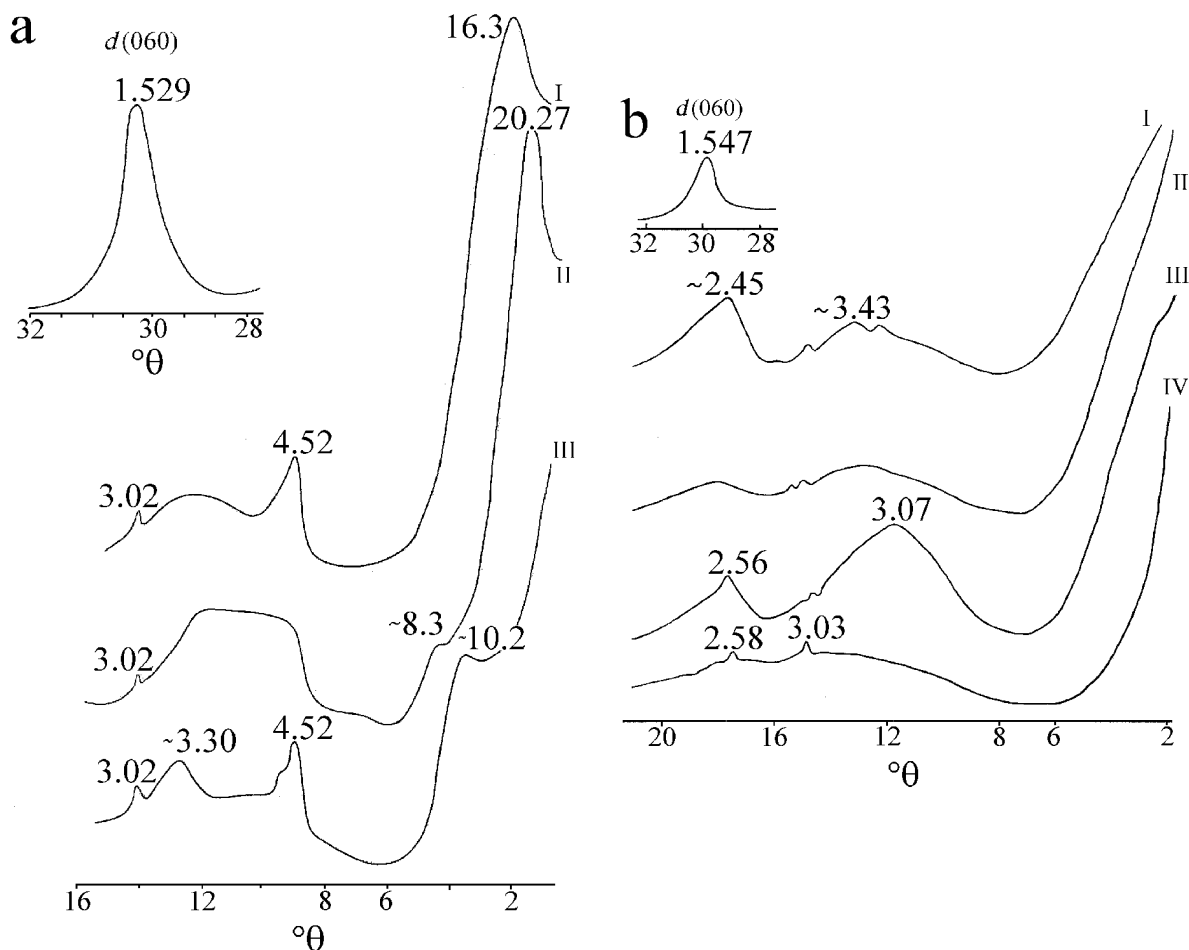


Figure 5. (a) X-ray data for saponite in sample E-2; (b) a weakly crystallized substance from sample E-3. (a) diffraction patterns of oriented specimens; I – air-dry; II – saturated by ethylene glycol; III – heated at 550°C. (b) I – powder specimen; II–IV – diffractograms of oriented specimens: II – air-dry; III – saturated by ethylene glycol; IV – heated at 550°C. Spacings in Å.

assumed, in accordance with that of similar saponites studied in hydrothermally-altered basalts (Drits and Kossowskaya, 1990) (Table 3). Analyses 1–5 are of clay minerals with biomorphous-like structures, 1, 3 and 4 from the surface of ball- and worm-like structures and 2 and 5 from natural cutoff (without selection). Analysis 6 (Table 2) shows data obtained from a small cluster of euhedral crystals situated on the surface of a clay mineral with a worm-like structure. Silicon, Mg and Al are the major elements of the clays and their composition compares well with that observed for many saponites from submarine hydrothermally altered basalt piles (Drits and Kossowskaya, 1990). Smectites enriched in Mg were revealed in the low-temperature zone of the Reykjanes geothermal area (Geptner *et al.*, 1987) where groundwater is of marine origin. Magnesium silicates of very similar composition have been recorded from several geothermal installations in Iceland (Kristmannsdóttir *et al.*, 1999). The precipitates have a

very variable composition indicating a mixture of different mineraloids. This is similar to what has been recorded in studies of geothermal scales (Kristmannsdóttir *et al.*, 1999). Due to the soft structure and poorly crystalline nature of the precipitate it is not viable to separate individual grains or minerals for analysis by microprobe. A calculation of the mineral formula from the analysis is therefore less meaningful, but gives a useful range:  $(\text{Ca}, \text{Na}, \text{K})_{0.2-0.3} \text{Mg}_{3.8-6.2} \text{Si}_{6.4-8.6} \text{Al}_{0.2-1.2} (\text{OH})_4 \cdot n\text{H}_2\text{O}$ . High As and Ba concentration levels are found in the precipitates. The As is known to be precipitated in association with the process of bacterial fossilization in recent hydrothermal environments (Eroshchev-Shak *et al.*, 1996). High As and Ba concentrations have also been recorded from high-temperature hydrothermal solutions of marine origin (Kristmannsdóttir, 1984).

The EDX analysis of sample E-3 revealed a chemical composition that is similar to those obtained for the saponite from sample E-2 (Figure 6). Results of wet-chemical analysis of sample E-3 are shown in Table 4 and compare very well with data obtained by EDX analysis. Data from the XRF analysis of Hg, B, Zn, As, Cu and Mn (Table 5) differ significantly between samples E-3 and E-2. The concentrations of Hg, Zn, Cu and Mn are distinctly higher in sample E-2 than E-3, whereas B and As concentrations are greater in sample E-3 than E-2. The significance of this observation is not clear, but Hg, Zn, Cu and Mn might be expected to be stable with ageing of the hydrothermal precipitate while B and As might be expected to be somewhat volatile.

## DISCUSSION

Clay minerals with micro- and nano-structures connected to biological activity have been identified in some precipitates in submarine hydrothermal environments (black and white smokers) at sea-floor spreading axes (Marteinsson *et al.*, 1997). Iron-rich smectites are often reported as precipitates from submarine hydrothermal fluids. The main features of hydrothermally-formed Fe-smectites from the smokers are: “(1) purity and monomineralic character; (2) extremely low Al content; (3) relatively low content of accessory minor elements, particularly Ba; and (4) their oxygen isotopic composition, which suggested relatively warm formation temperatures” (Köhler *et al.*, 1994). Clay minerals of hydrothermal origin enriched in heavy metals are reported from some localities and As is among the enriched heavy metals present. Filamentous structures are common and may indicate the impact of the microbial communities on clay minerals precipitation in all of these environments.

There is evidence of bacterial impact on precipitation of carbonate, Fe-silica, phosphate, arsenic, magnetite and layer-silicate minerals (Lowenstam, 1981; Ferris *et al.*, 1986; Eroshchev-Shak *et al.*, 1996; Köhler *et al.*,

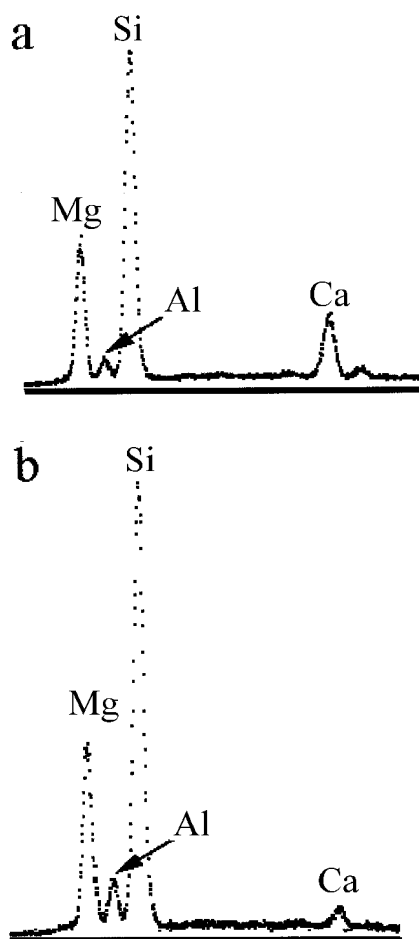


Figure 6. EDX data for samples E-3 (a) and E-2 (b); (a) results were obtained from the surface of the microtubular structure shown in Figure 5d; (b) data from the surface of the filamentous structure.



Table 2. EDX analysis data (LINK-860 analyzer) for clay minerals (1–5) and calcite crystals (6) in sample E-2.

Oxides wt.%	1	2	3	4	5	6
SiO <sub>2</sub>	64.740	62.991	67.364	71.603	69.002	6.886
TiO <sub>2</sub>	0.000	0.141	0.000	0.215	0.250	0.000
Al <sub>2</sub> O <sub>3</sub>	7.954	6.065	6.139	2.957	3.873	0.302
FeO <sup>#</sup>	0.482	0.074	0.846	0.000	0.778	0.000
MnO	0.247	0.000	0.000	0.244	0.000	0.038
CaO	1.292	1.231	1.699	0.576	2.053	82.608
MgO	22.256	29.123	22.766	23.158	23.334	6.296
Na <sub>2</sub> O	0.099	0.000	0.000	0.144	0.111	0.742
K <sub>2</sub> O	0.197	0.147	0.136	0.428	0.007	0.285
Cr <sub>2</sub> O <sub>3</sub>	0.117	0.094	0.270	0.323	0.158	0.540
As <sub>2</sub> O <sub>3</sub>	2.112	0.000	0.344	0.353	0.440	1.007
BaO	0.494	0.087	0.432	0.000	0.000	0.498
S	0.000	0.000	0.000	0.000	0.000	0.314
Total	99.99	99.953	99.996	100.001	100.006	99.516

<sup>#</sup> All Fe as FeO

1994; Petersen *et al.*, 1986; Geptner *et al.*, 1995; Folk, 1993; Folk and Lynch, 1997; Chafetz and Folk, 1984; Tazaki, 1997). Remnants of fossilized bacteria are reported from several regions of the world, freshwater lakes in Japan and Iceland, recent freshwater hot springs in Kamchatka, Russia, hot springs in Yellowstone National Park, USA and in Italy, submarine hydrothermal chimneys of the Galapagos Rift and Mariana Trough, and from the Guayamas Depression in the Gulf of California. These deposits have varying mineral and chemical compositions. However, the nanostructures of the clay precipitates are similar to those described from submarine hydrothermal chimneys of the Galapagos Rift and Mariana Trough (Köhler *et al.*, 1994). Smectites are rather common precipitates in hydrothermal environments. Nontronite is the most commonly reported smectite mineral (Köhler *et al.*,

Table 3. Evaluated chemical composition of the clay minerals after EDX analysis assuming ~16% loss on ignition, in sample E-2.

Oxides wt.%	1	2	3	4	5
SiO <sub>2</sub>	54.38	52.94	56.59	60.15	57.96
TiO <sub>2</sub>	0.00	0.12	0.00	0.18	0.21
Al <sub>2</sub> O <sub>3</sub>	6.68	5.1	5.16	2.48	3.25
FeO <sup>#</sup>	0.40	0.06	0.71	0.00	0.65
MnO	0.21	0.00	0.000	0.20	0.00
CaO	1.09	1.03	1.43	0.48	1.73
MgO	18.70	24.47	19.12	19.45	19.60
Na <sub>2</sub> O	0.08	0.00	0.000	0.10	0.09
K <sub>2</sub> O	0.17	1.12	0.11	0.36	0.01
Cr <sub>2</sub> O <sub>3</sub>	0.10	0.08	0.23	0.27	0.13
As <sub>2</sub> O <sub>3</sub>	1.77	0.00	0.29	0.30	0.37
BaO	0.42	0.07	0.36	0.00	0.00
S	0.00	0.00	0.00	0.00	0.00
Total	84.00	84.99	84.00	83.97	84.00

<sup>#</sup> All Fe as FeO

1994) in hydrothermal environments, but saponite has also been encountered. Saponite, together with hydrated talc in thread-like and dendritic aggregates, was found in hydrothermal structures on the floor of the rift trough in the Gulf of California (Drits *et al.*, 1989). The chemical characteristics (SiO<sub>2</sub> = 56.28, Na<sub>2</sub>O = 0.20, Al<sub>2</sub>O<sub>3</sub> = 2.49, MgO = 25.53, FeO = 0.60) of these minerals are similar to those of the saponite under consideration. Increased temperatures (not <100°C) and a reducing environment in a neutral or weakly acid medium with high concentrations of Fe<sup>2+</sup>, Mg<sup>2+</sup> and SiO<sub>2</sub> were suggested for hydrated talc precipitation. Saponite was precipitated in a medium where the alkalinity was apparently relatively increased.

The composition of the minerals studied in the submarine hot springs in Eyjafjörður is found to be rather similar to magnesium silicate scales from geothermal waters mixed with cold fresh waters in geothermal installations in Iceland (Kristmannsdóttir, 1989; Kristmannsdóttir *et al.*, 1999; Sværriðóttir *et al.*, 1992). Those precipitates also show a variable composition and are often found to be a mixture of poorly crystalline saponite- and serpentine- and talc-like structures. Calculation of mineral equilibria of mixed sea-water and geothermal water from the hydrothermal vent show a distinct supersaturation with respect to several magnesium silicates as is found in the case of the scales in geothermal installations. The microstructures of some of the scales may resemble those of samples E-2 and E-3, but a possible connection with micro-organisms has not been studied in the case of the scales. Microbial impact on the formation of aluminum silicate scales in geothermal installations has, however, been demonstrated recently in Iceland (Kristmannsdóttir *et al.*, 2000). There is proof that thermophilic bacteria and archaea live in the hydrothermal vent fluid and inside the chimney walls (Marteinson *et al.*, 2000). It seems very likely from the observed structural features that those

Table 4. Wet-chemical analysis of sample E-3.

	Wt.%
SiO <sub>2</sub>	38.91
TiO <sub>2</sub>	<0.1
Al <sub>2</sub> O <sub>3</sub>	1.05
Fe <sub>2</sub> O <sub>3</sub>	0.52
FeO	0.14
MnO	<0.01
CaO	0.96
MgO	28.87
Na <sub>2</sub> O	0.36
K <sub>2</sub> O	0.09
P <sub>2</sub> O <sub>5</sub>	0.02
LOI*	28.70
Total	99.62
H <sub>2</sub> O <sup>+</sup>	14.03
H <sub>2</sub> O <sup>-</sup>	12.76
CO <sub>2</sub>	1.93
C	<0.1
Cl	0.13

\* LOI: loss on ignition

micro-organisms participated in the recrystallization of the precipitate samples from the hydrothermal vents in Eyjafjörður. Unfortunately, the precipitate samples were not preserved at the sampling point in order to detect DNA and so any possible trace of DNA will have degraded and is undetectable.

Microstructural features of the layer silicates studied in sample E-2 suggest that a gel substance was a possible precursor of saponite. The SEM investigation and X-ray data indicate that globules and filaments in sample E-3 are a non-crystalline or very weakly crystallized substance. The data suggest that the gelatinous substance coagulated around or within some biological matter (microalgae or cyanobacteria). Very small, round elongated canals inside of the filaments are probably molds of living organisms. Globules, filaments and microtubules revealed in the samples are very similar to those described in biogenic nontronite from marine white smoker chimneys (Köhler *et al.*, 1994) and in precipitates obtained during the experimental phosphatization of cyanobacteriae (Gerasimenko *et al.*, 1996). According to the data reported, the process of mineralization (phosphatization) and the formation of globules and microtubules on the filaments of cyanobacteria was completed within a few hours. Comparison between samples E-2 and E-3 shows that microstructures with similar form and dimensions have different structures. X-ray data for sample E-2 show it to have a clearly-defined crystal structure, whereas in

sample E-3 the silicates are poorly crystalline according to XRD analysis. Sample E-3, as described above, consists of amorphous, globular matter. The microstructures observed strongly suggest that the clay structures in sample E-2 were formed by a gelatinous substance, similar to that of sample E-3 precipitated from hydrothermal solutions. The assumption that the precursor of the clay minerals was a colloidal, gelatinous substance, is supported by the observed difference between samples E-2 and E-3. As described above, sample E-3 was collected from a shallower part of a cone than E-2, strongly supporting an age difference between the precipitates, caused by the fact that during build-up of a cone the lower outlet vents will gradually be clogged and new ones become active and build the cone up to shallower depth levels. Colloform structures studied in the precipitates suggest that during the formation of the filaments, globules and their associations, there is a stage when the precipitate behaves as a fairly coherent gel. The globules of sample E-3 have an homogeneous and dense structure whereas the globules of sample E-2 display a better defined crystal structure. The round elongated canals inside the filaments are strong evidence for the existence of some organic matter around which coagulation and recrystallization took place. Recrystallization and formation of a crystal structure probably took a rather short time in the hydrothermal environment. The difference in hydrocarbon content between crystalline clay minerals and their amorphous predecessors must be examined in more detail, as it appears to be of great importance in this context.

The diameter of most of the filamentous structures radiating crystals of saponite is not more than 5 µm, close to the average diameter of biogenic microtubules with a secondary intergrowth of nontronite found in submarine hydrothermal chimneys of the Galapagos Rift (Köhler *et al.*, 1994), but considerably larger than the structures described by Folk (1993) and Folk and Lynch (1997) assumed to be due to the activity of nanobacteria on diagenesis. In the process of further mineralization, most of the voids might be filled up with gelatinous substance as suggested by the sectioned filaments observed and described above.

Concentrations of As and Ba are very high. A high As concentration may support the hypothesis that the formation of the clays is related to bacterial activity, as As is reported as one of the elements precipitated in association with bacterial fossilization from recent hydrothermal environments (Eroshchev-Shak *et al.*, 1996). High Ba concentrations have been recorded in high-temperature hydrothermal solutions of sea-water origin (Kristmannsdóttir, 1984). The concentrations of Hg, B, Zn, As, Cu and Mn in the samples differ significantly between samples E-3 and E-2, possibly reflecting their state of recrystallization and ageing by variable accumulation of the heavy metals and release of the more volatile elements.

Table 5. XRF analysis data (ppm).

Elements	B	Hg	Zn	Pb	As	Cu	Mn
Sample E-2	36	0.7	35	<1	18	22	310
Sample E-3	400	0.05	<1	<1	55	4	50

## CONCLUSIONS

The hydrothermal vents in Eyjafjörður are mainly composed of precipitates of magnesium silicates of similar composition and structure to scales in geothermal installations. Optical observations show numerous microstructures resembling micro-organisms in all the samples. Very high concentrations of organic substances are encountered in the samples and the higher they are, the more crystalline the clay minerals are. Taking those reasons into consideration it seems plausible that the filamentous and globular saponite structures studied in samples E-2 and E-3 from the submarine hot spring in Eyjafjörður are fossilized sheaths of micro-organisms composed of recrystallized silicate gel. Sample E-3 is probably a bit younger than sample E-2 as the data suggest that the substance in sample E-3 corresponds to the non-crystalline precursor of the saponite encountered in sample E-2. It is also sampled from shallower depths than E-2, supporting the assumption of younger age. Our contention is that observations and measurements strongly support the conclusion that the precipitation of the saponite clays and calcite depends at least partly on the bacterial impact on the process of hydrothermal mineralization.

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