

26. TEXTURAL AND FLUID INCLUSION EVIDENCE FOR HYDROTHERMAL ACTIVITY IN THE VOLCANICLASTIC APRON OF GRAN CANARIA¹

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ABSTRACT

Drilling in the volcanoclastic apron of Gran Canaria during Leg 157 has provided material for extending land-based studies of volcanism back to >15 Ma. Earlier shield stage and earlier eastern island pyroclastic rocks were penetrated, making possible a variety of studies. The one presented here focuses on hydrothermal activity and vein/vug deposition in those sections. The results indicate that the fluid activities at Sites 953, 954, and 956 were different. Site 954 is closest to the island and shows strong visible alteration of the host basaltic rock along veins. It provides the only measurable fluid inclusion data (from aragonite). The results indicate a hot, saline fluid environment, acting in the shield stage with temperatures from 185° to 284°C (without pressure correction) and salinity between 4.6 and 15 wt% NaCl equivalent. Sites 953 and 956 exhibit less alteration. Single-phase inclusions indicate formation at lower temperatures from solutions of lower salinity.

Textures and Raman spectrometry analyses further reveal a complex evolution of vein and vug fillings in the shield stage at Sites 954 and 956 and during the pre-shield (eastern islands) stage at Site 953. Site 953 give a paragenesis of prehnite, apophyllite, and phillipsite over a large section, with natrolite, analcime, and gmelinite occurring at distinct levels. Site 954 gives a paragenesis of carbonate, calcite, aragonite, siderite, phillipsite, and smectite. Site 956 gives a paragenesis of smectite, zeolite, siderite, calcite, aragonite, phillipsite, and analcime. Mineral stability and fluid inclusions together indicate an environment with relatively high, but varying salinity at all three sites and formation temperatures at 100°–150°C (Site 953), 200°–300°C (Site 954), and 100°–150°C (Site 956).

INTRODUCTION

The Canary Islands form an east-west chain of volcanic islands off the coast of Northwest Africa. This coast is also the passive continental margin of the African Plate (Holk et al., 1991; Wilson, 1991). The islands owe their existence to hotspot volcanism that has created new islands on a moving plate, which is revealed by the successively younger ages of the shield stages of the islands to the west (McDougall and Schmincke, 1977; Schmincke and von Rad, 1979; Le Bas et al., 1986; Hoernle and Schmincke, 1993).

Several aspects of the Canary volcanoes are similar to other oceanic island volcanoes, such as the Hawaiian islands (Schmincke, 1976, 1982). Studies of the Canaries may therefore be helpful in constructing models of ocean island development. Leg 157 provided material to extend terrestrial island studies into the surrounding ocean environment. Sampling extended into the nonexposed part of the volcanic shield phase of Gran Canaria, the island that has been studied in greatest detail and which exhibits the greatest variety in volcanic activity.

One aspect of volcanic activity not often studied in ocean islands is the successive infilling of fractures and cavities by hydrothermal solutions. These solutions and their precipitates form a distinct expression of the volcanic activity. During igneous activity magmatic gases and fluids are mixed with seawater. Fluid inclusions may record the resulting fluid environments and the temperatures at which the host minerals were formed. Hydrothermal activity is usually studied in connection with either ore deposits or geothermal systems. In the case of ore deposition and hydrothermal systems, it has long been a mystery why no ore deposits of value occur on oceanic islands, un-

less they are part of subduction systems such as the Fiji Islands. The seafloor has demonstrated deposition of minerals through emanating hydrothermal solutions. It is at mid-ocean ridges that we have the most spectacular demonstration of this phenomenon, which has also been taken as precursor activity for the formation of mineral deposits. At the East Pacific Rise, continued emanation of vent fluids provides an environment on the seafloor that gives rise to abundant growth of biological species. This is a continued hydrothermal process that also provides deposition of sulfides and other minerals. A contrasting environment with similar hydrothermal activity is the Loihi Seamount (Malahoff et al., 1982), but here, no enhanced growth of marine life forms has occurred. The Loihi seamount is the youngest emerging expression of the Hawaiian hotspot chain of islands. Stüben et al. (1992) and McMurtry et al. (1992) found chemical evidence for sulfide deposition within the edifice in hydrothermal vents and deposits on submarine arc volcanoes. Sedgwick et al. (1992) suggested that sulfide deposition was occurring within the Loihi edifice, and this has been confirmed for Loihi by recent diving into the pit crater there (G.M. McMurtry, pers. comm., 1996). The lack of enhanced biota compared to the East Pacific Rise is explained by the noncontinuous activity of volcanism and associated hydrothermal processes. Additional studies of barren hydrothermal systems may contribute to a better understanding of global element redistribution processes in crustal fluids. This study focuses on submarine hydrothermal activity during the shield stages of volcanism of Gran Canaria and the eastern islands.

SAMPLES AND METHODS

Forty-eight samples were recovered from Site 953, 13 samples from Site 954, and 21 samples from Site 956 (Figs. 1, 2). From these samples, the most representative were selected for the study of fluid inclusions. Such a study requires that the crystals be transparent and large enough to be polished on both sides in a thin section. Large crystal size, however, is no guarantee that suitable inclusions are

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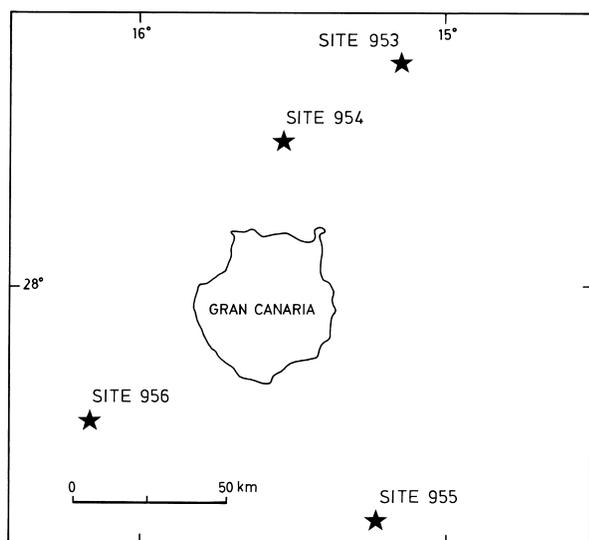


Figure 1. Map showing Gran Canaria and the locations of Sites 953, 954, and 956.

present. Many of the fracture fillings examined consist of a mosaic of very fine crystals, rendering the material completely opaque. On the other hand, vugs may contain small, clear crystals that display a few inclusions very well. Doubly polished thin sections were made from 37 samples, as described in Tables 1–3.

Sample preparation for thin-section manufacture began with the selection of suitable materials. We focused primarily on specimens that would most likely provide fluid inclusion evidence of hydrothermal activity. Each thin section required many hours at the microscope, just for petrographic analyses alone.

The thin sections were made as doubly polished sections, 200 μm thick. This is a compromise between being thick enough to retain large inclusions and too thick to prevent good visibility into the thin section interior. Some sections down to 100 μm were also studied, but did not give additional information.

Ideally, crystals for study should be polished on both sides for the best light conditions. Another advantage of thicker-than-normal thin sections is that they can provide a three-dimensional view. Open vug textures may be retained (Pl. 1, Fig. 1; Pl. 2, Figs. 2, 3, and 6) and give valuable paragenetic and depositional information.

Microthermometry was performed according to procedures described by Lindblom (1982) and Shepherd et al. (1985), using a modified Leitz Laborlux polarizing microscope and a Chaixmeca heating/cooling stage. X-ray diffraction (XRD) analyses were performed with a Siemens X-ray diffractometer with Ni-filtered CuK alpha radiation, at 40 kv and 30m A. The air-dried samples were scanned from 2° to 70° 2 θ at 0.03°/25 with a rotating sample holder (Gérard and Person, 1994). Raman spectrometry was performed with a DILOR XY spectrometer, using an incident laser beam of 514.5 mm and an Innova 70 argon laser (Burke and Lustenhouwer, 1987) as a light source. Minerals were identified by a combination of microscopy, XRD, and Raman spectrometry.

RESULTS

Textures

This work describes secondary infilling minerals that are a result of hydrothermal activity in association with volcanism, but postdating the actual emplacement of the host rock. Host rock is of pyroclastic origin and comprises lapilli tuff, lapilli breccia, lapillistone, sandstone,

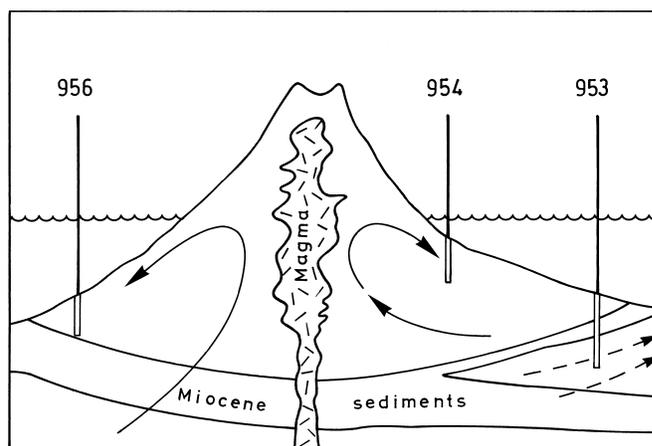


Figure 2. Sketch showing the distance between sites and the center of Gran Canaria. Whole arrows = possible hydrothermal circulation during shield stage and later, and broken arrows = circulation pattern before the formation of Gran Canaria.

and vitric tuff of mainly basaltic composition. There are three main features of secondary infilling minerals:

1. Monomineralic veins that contain one main mineral, but may have other smaller constituents that elude microscopic or XRD analysis.
2. Multistage or complex veins that have a paragenetic sequence of one or more minerals. We have identified up to three minerals in one individual vein. One mineral may be deposited in several stages.
3. Deposition in vugs mean infilling of vesicles produced by gas expansion of the cooling lava. As seen by the sedimented vugs, the vugs must have been interconnected, giving an identical chemical environment in the vugs in the sample. The infilling minerals show original crystal growth, with no later deformation of the minerals.

Cavities varying in size from 1 to 20 mm have been formed by gas expansion during cooling of the basalt. Those cavities are filled with secondary minerals like carbonate or zeolite. At certain intervals, there is a prolific abundance of mineralized vugs or voids. Most cavities are filled completely with precipitated minerals, although open vugs and partially filled vugs are common. Vugs occur in basaltic clasts and also surrounding the clasts. The walls of the vugs are frequently lined with a fine-grained crystal layer and later filled with a radial or pillar growth texture. The following minerals were identified in vugs and veins (Tables 1–3): calcite, apophyllite, prehnite, smectite, aragonite, phillipsite, natrolite, analcite, and siderite. Both vugs and veins may contain one or several minerals.

A monomineralic vein in Sample 157-953C-84R-1, 127 cm, has a crooked “ptygmatic” texture. This indicates that fracturing took place in a not completely lithified sediment, followed by deposition before further lithification. For further information on vein occurrence, refer to Table 1, where veins are classified by their characteristics.

The multistage vein type is further illustrated in Plate 1, Figure 4. A fine-grained lining of the fracture wall is followed by successively larger crystals. The largest pillar crystals occur as a random pile and have triangular open pores. Zeolites may show several crystal habits in a single vein. Vugs may also display zoned growth. Centers may be open. A square pattern of crystal growth was noted in Sample 157-953C-92R-1, 70 cm. This was found to be phillipsite, a variety of zeolite.

Table 1. Description of samples from Sites 953, prepared as doubly polished thin sections.

Core, section, interval (cm)	Volcanic stage	Depth (mbsf)	Vein/vug	Vein/vug (mm)	Vein minerals	Mineral/vein texture	Rock type	Visible rock alteration
157-953C-83R-7, 25	Pre-shield	973.89	Vein	3 to 5	Natrolite Smectite	Hazy-opaque vein	Fine-grained, dark brown sandstone	No
84R-1, 102	Pre-shield	976.62	Vein	1 to 2	Natrolite	Complex vein	Brown, vitric tuff	No
84R-1, 127	Pre-shield	976.87	Vein	0.3 to 2	Natrolite Smectite	Ptygmatic vein	Fine-grained, dark sandstone	No
84R-4, 76	Pre-shield	979.73	Vein	0.5 to 1	Apophyllite	Monomineralic vein	Dark greenish brown vitric tuff	Strongly altered
89R-2, 76	Pre-shield	1019.38	Vein	1 to 6	Apophyllite	Complex, hazy vein	Dark green vitric tuff	No
90R-2, 99	Pre-shield	1026.08	Vein	2 to 3	Prehnite	Monomineralic vein	Dark green lapillistone	No
90R-4, 100	Pre-shield	1028.96	Vein	7	Apophyllite Prehnite	Complex vein	Dark green lapillistone	No
91R-2, 10	Pre-shield	1034.80	Vein	3 to 7	Apophyllite	Complex vein	Dark green sandstone	No
92R-1, 70	Pre-shield	1043.60	Vug	0.5 to 8	Natrolite Prehnite	Large, complex vug Small vugs, empty	Dark green lapillistone	No
93R-2, 28	Pre-shield	1054.34	Vug	2 to 15	Phillipsite Prehnite	Complex vug	Dark green lapillistone	No
93R-3, 42	Pre-shield	1055.89	Vug	0.5 to 2	Analcime Phillipsite Natrolite	Monomineralic vein and vug	Dark green lapillistone	Alteration along vein
93R-5, 104	Pre-shield	1059.20	Vug	1 to 5	Natrolite	Complex vugs	Dark gray green, crystal lapillistone	No
94R46, 38	Pre-shield	1066.78	Vein	2	Natrolite	Single mineral	Dark green breccia	No
98R-6, 48	Pre-shield	1108.21	Vug	1 to 9	Prehnite Phillipsite	Zoned growth	Dark green basalt	Alteration in vugs
100R-5, 114	Pre-shield	1127.03	Vug	1 to 10	Apophyllite Natrolite	Sediment-filled vug with graded bedding	Dark green basalt	Altered lowered part of vug
101R-2, 44	Pre-shield	1131.58	Vug	10	Gmelinite	Monomineralic vugs	Dark green basalt	No
101R-3, 86	Pre-shield	1133.41	Vug	0.5 to 8	Gmelinite	Zoned growth	Dark green basalt	No

Note: Minerals are given in paragenetic sequence for each sample.

Table 2. Description of samples from Site 954.

Core, section, interval (cm)	Volcanic stage	Depth (mbsf)	Vein/vug	Vein/vug (mm)	Minerals	Mineral/vein texture	Rock type	Visible rock alteration
157-954B-35R-3, 42	Shield	411.19	Vein	3	Aragonite	Porous clasts in fine matrix	Breccia	Prominent alteration
36R-1, 34	Shield	417.19	Vein	2 to 7	Calcite Phillipsite	Monomineralic vein/pillar, crystal growth	Dark brown lapillistone with light green matrix	Color alteration near vein
36R-1, 68	Shield	417.98	Vein (vug)	0.1 to 3	Calcite Smectite	Porous clasts in fine matrix	Brown lapillistone green matrix	Color alteration along vein
36R-2, 10	Shield	418.83	(Vug) vein	0.1 to 0.5	Phillipsite Smectite	Intergrain vug fill followed by variable size monomi veinlet	Dark brown lapillistone with green matrix	Color alteration along veinlets
37R-1, 45	Shield	427.25	Vein	1 to 5	Aragonite	Monomineralic vein	Basaltic dark lapillistone, large pyroxene clasts	No
37R-2, 64	Shield	428.94	Vein	0.1 to 2	Aragonite	Monomineralic split	Large pyroxene clasts in a gray lapilli breccia	Color alteration near vein
38R-3, 112	Shield		Vein	0.2 to 3	Aragonite	Monomineralic vein split into smaller	Crystal breccia. Px and olivine in a dark brown fine-grained matrix	Color alteration near vein
38R-4, 0	Shield	440.67	Vein	1 to 5	Aragonite	Complex vein, very irregular shape	Dark green basalt breccia	Color alteration near vein
38R-4, 94	Shield	441.61	Vein vugs	1 to 2	Smectite Siderite	Complex vein empty vugs	Dark grey basalt breccia	Strongly altered clasts
39R-1, 67	Shield	441.87	Vein	1 to 2	Aragonite Phillipsite	Monomineralic vein	Greenish basalt breccia	Strongly altered clasts
39R-1, 105	Shield	442.25	Vein	0.5 to 3		Complex vein		Dark green basalt breccia, strongly altered clasts

Table 3. Descriptions of samples from Site 956.

Core, section, Volcanic interval (cm) stage	Depth (mbsf)	Vein/vug	Vein/vug (mm)	Vein minerals	Mineral/vein texture	Rock type	Visible rock alteration
157-956B-44R-3, 17	Shield	573.87	Vug	0.5	Smectite	Vugs and void between clasts, crystal-lined vugs	Grayish brown lapilli stone
45R-1, 17	Shield	580.57	Vein	1 to 4	Phillipsite Analcime Smectite	Vein with irregular appearance	Fine-grained brown tuff
45R-2, 1	Shield	581.61	Vein	1 to 4	Smectite	Hazy vein with sugary crystals around hazy grains	Grayish green fine-grained tuff
45R-4, 23	Shield	584.43	Vein	1	Smectite	Hazy vein, pillar crystal, open center	Grayish green tuff
47R-1, 7	Shield	599.67	Vug	1 to 5	Smectite Phillipsite	Several empty vugs and voids	Grayish green breccia
49R-3, 40	Shield	622.40	(Vug) vein	0.1 to 1	Smectite Smectite Phillipsite	Opaque vein, very fine-grained, very small vug grained, and very small vug	Dark gray green sandstone
							Palagonite Palagonite Pale green color alteration No

Paragenesis

Judging by successive crystallization in the veins/vugs, certain paragenetic successions may be established at different points. One such paragenesis is the sequence prehnite-apophyllite-phillipsite. This occur wholly or in part in several samples at Site 953. There is no systematic variation of the type of zeolite or the other minerals with depth or at certain depth intervals. There is no apparent variation of vein minerals with rock type.

Site 954 samples only comprise ~30 m. Calcite occurs at the top, and lower down aragonite is the carbonate phase. Smectite appears frequently as a hydrothermal vein mineral. There is a dominance of veins over vugs. Aragonite indicates a hotter deposition environment than calcite. Site 954 show mostly monomineralic veins, but smectite seems to precede other minerals, and carbonates come before zeolites. Site 956 show similar relations.

Sedimented Vugs

Sample 157-956B-47R-1, 7 cm, shows a curious additional feature. Several juxtaposed cavities were first filled with sediment up to a similar level. Following this, deposition of mainly zeolite occurred. (Pl. 1, Fig. 2).

Sedimentation within the voids probably means that they were both interconnected and connected to an outside source. Water with a suspension of fine-grained material entered the voids, leaving the sedimented material. This was followed by a fairly saline solution, which precipitated zeolite at relatively low temperatures. These minerals have one-phase inclusions, indicating a temperature of formation below 100°C.

Fluid Inclusion Petrography

Site 953

Twenty doubly polished thin sections were prepared. Fracture fillings contain zeolites in a variety of habits, the most common being a radial prismatic texture with a triangle-shaped pore between crystals. During sample preparation, air trapped in the pores increased their visibility.

Many one-phase inclusions were observed within the staff-shaped, individual crystals. The radial aggregates of crystals precluded clear observation deep into the thin section. A typical example is shown in Plate 1, Figure 3. The size of inclusions is limited by the size of the crystals. Although inclusions can be trapped between crystals, this type was not observed here. It should be noted that when we discuss “vugs,” we mean open spaces between larger clasts in lapillistone or breccia or open or filled-in large voids created by gas expansion in basaltic fragments.

Site 954

Carbonates in fracture fillings contain fluid inclusions. Only a few crystals per sample had two-phase fluid inclusions that could be used for temperature and composition determinations.

Several hundred crystals were studied, but only a small number had measurable fluid inclusions. There are numerous one-phase inclusions. Many of those were probably filled with a water solution, but no data could be recorded about the melting point of ice in the one-phase inclusions. Zones of small, dark, irregular inclusions were found in many crystals or at certain distances from the walls of the veins. These inclusions could not be analyzed. Plate 1, Figure 3, shows the distribution and zoning of inclusions in some crystals, Plate 1, Figures 5 and 6, shows two-phase fluid inclusions in aragonite.

Site 956

Most inclusions are one phase. Many are dark and give the impression of being trapped air bubbles. Like the pores described under Site 953, they are triangular, but on a smaller scale.

Microthermometry

Site 954

Aragonite in fracture and vug fillings contains two-phase inclusions that were measured with respect to homogenization temperatures and final melting temperatures of ice. Only a few measurable inclusions were found, which precluded statistical treatment. The measured inclusions are of irregular shape and occur at random. They are probably primary inclusions. Two groupings of the melting temperatures were found to be about: (1) -2.7° to -5.2° C, and (2) -10.5° C. (Table 4; Fig. 3) The accuracy was $\pm 0.3^{\circ}$ C. Ten inclusions could be measured. Measurements were repeated several times, giving the same values. In all these inclusions, the ice phase could be seen melting very clearly.

Few homogenization temperatures were obtained because of fracturing of the mineral at higher temperatures. The inclusions measured did not fracture, but the fractures caused a darkening of the field of view precluding further observation. Repeated runs confirmed obtained temperatures values (Table 4).

Sites 953 and 956

No two-phase inclusions were found. No homogenization temperatures could be obtained. Freezing runs were performed on several chips, but no ice or hydrate melting could be observed between -130° C and room temperature.

Raman Spectrometry

Results from Raman analysis are summarized from all sites. The most important result is the demonstration that the only carbonate mineral hosting the measured inclusions is aragonite (Fig. 4). The carbonate line at 1085 cm^{-1} is very strong, and characteristic aragonite lines at 701 and 212 cm^{-1} are diagnostic in these samples.

Raman spectra of smectite are included for comparison where intensity is much lower than for aragonite. Aragonite is typically formed at low temperatures in connection with seawater action (Kim-

Table 4. Fluid inclusion data from Site 954 samples.

Core, section, interval (cm)	Depth (mbsf)	Inclusions	Size (μm)	Salinity			Th C
				Ts C	T mice C	(wt% NaCl eq.)	
157-954B-							
35R-3, 42	411.19	2	20	-45	-2.8	4.7	—
37R-2, 64	428.94	1	25	-45	-2.8	4.7	205.8
37R-2, 64	428.94	2	40	-56	-10.1	14.1	—
37R-2, 64	428.94	4	20	-51	-2.9	4.9	173.2
38R-4, 0	440.67	1	25	-47	-2.7	4.6	238.9
39R-1, 67	441.87	1	15	—	-11.0	15.0	—
39R-1, 67	441.87	5	42	-45	-3.7	6.1	275.7
39R-1, 67	441.87	6	60	-48	-4.5	7.3	350.8
39R-1, 67	441.87	9	15	-46	-5.2	8.3	—
39R-1, 67	441.87	11	30	-45	-3.7	6.1	278.5

Notes: Vapor volume in the two-phase inclusions is 5 to 10 vol%. Th refers to homogenization to the liquid state. Ts C =freezing temperature $^{\circ}\text{C}$, T mice C = last melting of ice $^{\circ}\text{C}$, and Th = homogenization temperature $^{\circ}\text{C}$. — = not obtained.

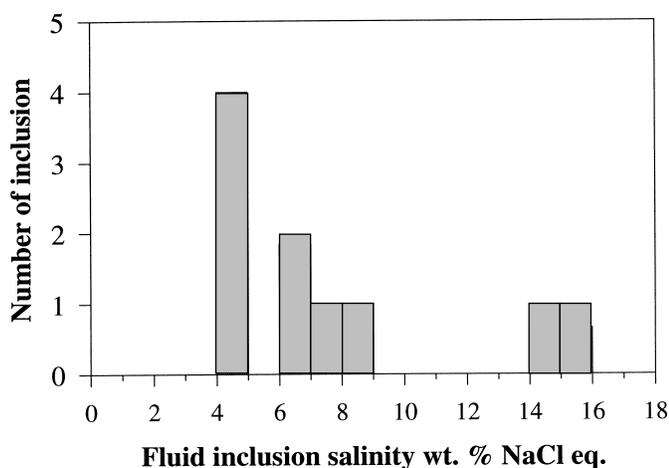


Figure 3. Salinity histogram of data from Site 954.

bell and Humphrey, 1994). Radial minerals in many samples show similar Raman lines. This set of minerals (the strongest lines) shows nearly the same values in all samples. However, the variable intensity of the lines and their slight variation in position probably result from a strong dependence on crystal direction relative to the light path. Recent work by P. Frogner (unpubl. data) has shown a strong orientation dependency of feldspar in Raman measurements. Hansteen and Burke (1994) showed orientation-dependent Raman spectra of fluid inclusion daughter minerals.

Most of those minerals are tentatively identified as zeolites. It is difficult to assign Raman peaks to specific minerals of the zeolite group. Reference spectra (Griffith 1987) indicate that the set of lines (at 532 and 442 cm^{-1}) refers to a mixture of zeolite minerals, with two phases dominant in most samples.

Another identified mineral is apophyllite (Samples 157-953C-90R-4, 100 cm, and 100R-5, 11 cm; Fig. 5). Most of the characteristic lines could be matched to references in these cases.

DISCUSSION

Volume of Hydrothermal Activity

A hydrothermal cell, sustained by a magma chamber and volcanic center, will affect a volume of the crust that is many times the volume of the actual island to which we have access. The volume of clastic material surrounding the island surpasses the volume of the island itself. By drilling into the clastic apron at sea, we can thus extend our sampling of the island system, reach depths not otherwise possible, and obtain information on the extent of hydrothermal activity.

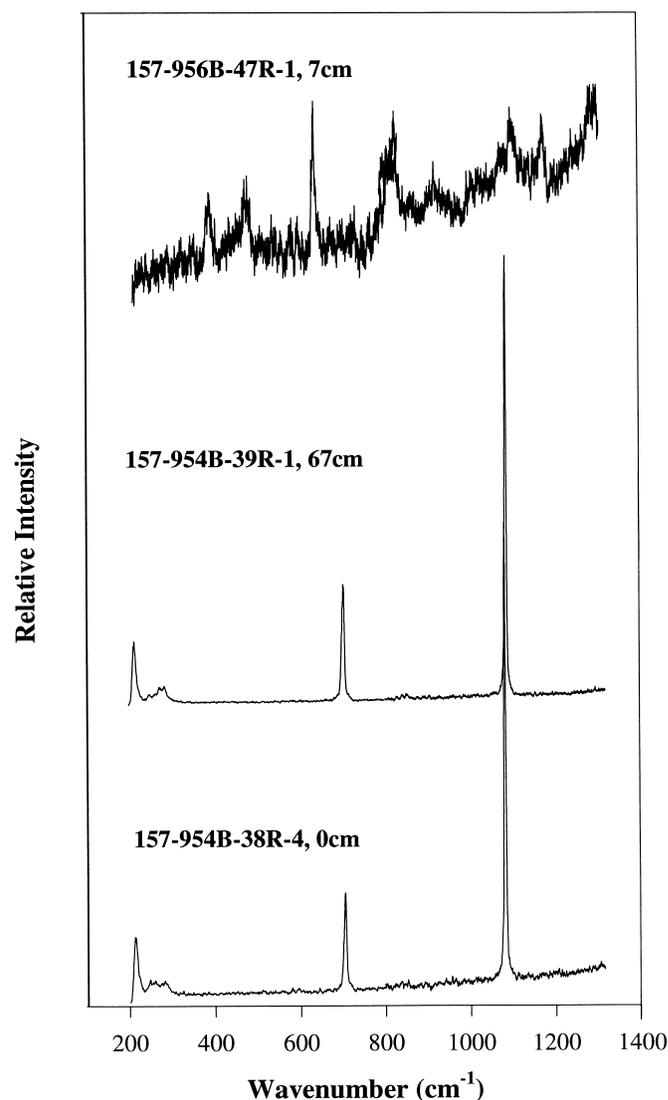


Figure 4. Comparison of Raman spectra from Samples 157-956B-47R, 7 cm (smectite), 157-954B-39R-1, 67 cm (aragonite) and 38R-4, 0 cm (aragonite).

Hydrothermal Circulation

The infilling minerals, which are the subject of this study, are the result of an active hydrothermal cell providing an environment of deposition involving circulating seawater in the pile of pyroclastic rocks. There may be a component of magmatic water involved. The host rock appears to have changed from a porous, vug-filling, poorly lithified sediment, to a compact rock that fractured easily. This in turn produced a change from vug-dominated to vein-dominated infill, which is especially pronounced in the Site 953 samples. This concerns the pre-shield or eastern island stage of volcanism. In Figure 2, this is shown in the lower right-hand corner of a general sketch where hydrothermal fluid circulation is indicated.

Evidence of Hydrothermal Activity

Sites 953, 954, and 956 reveal distinct differences in their hydrothermal activities. In this study, we focused on the petrographic evidence of vug- and vein-filling minerals. These minerals provide direct evidence of the hydrothermal solutions that have permeated the volcanic pile. The indirect evidence of alteration in the form of geochemical imprints on the rock matrix and clasts will be the subject

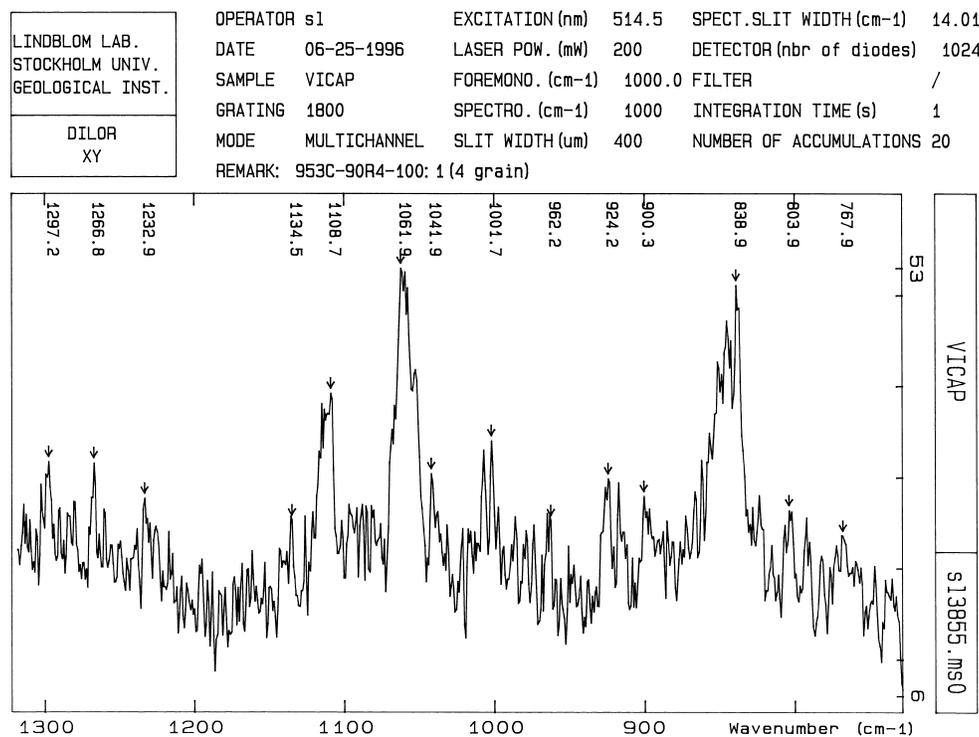
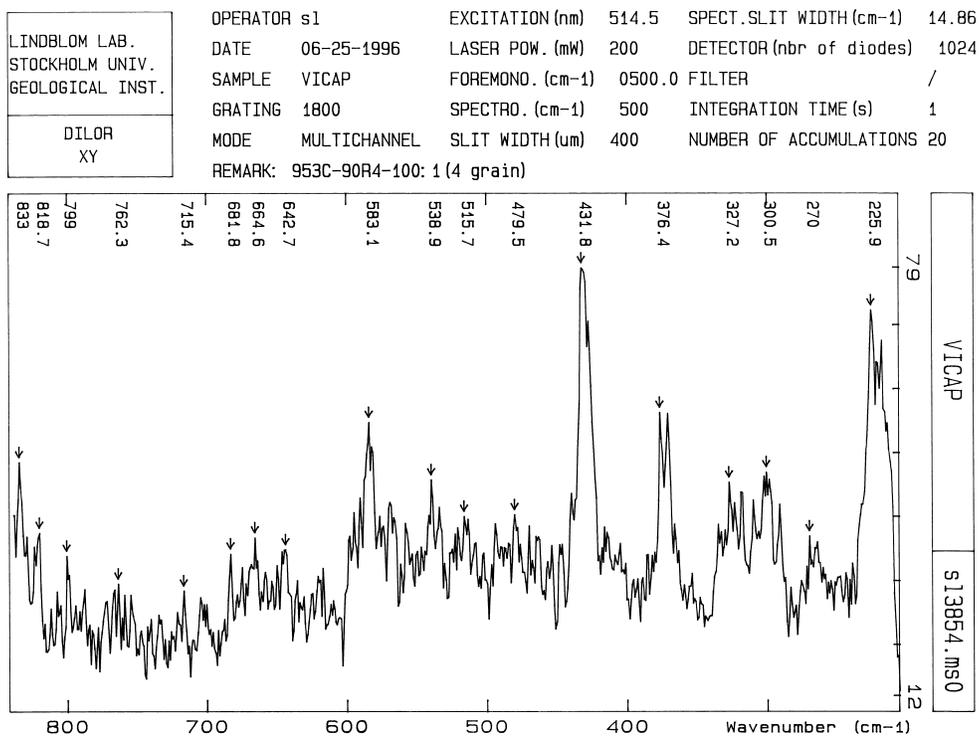


Figure 5. Raman spectra of apophyllite.

of further study. The hydrothermal fluids were a consequence of a magma chamber acting as a heat source on a large volume of rock. The fluids in this rock volume created a hydrothermal convection cell driven by the magma heat source.

At Site 953, hydrothermal minerals were formed at low temperatures. The fluid inclusion evidence (one-phase inclusions) indicates formation below 150°C. The lack of visible alteration, around the veins studied, also points to a low formation temperature and a possibly less corrosive fluid. A curious feature is the sedimented vugs. Apart from providing the upwards direction in the samples, microscopy shows them to consist of fine particles. This could be explained by either (1) flocculated sedimentation by chemical precipitation in the fluid as distinct from crystal growth or (2) transport as a suspension of fine particles in a fluid permeating the porous rock.

The common occurrence of inclusions and solid material as inclusions (seen as dark spotted zones in the growth zones of crystals, e.g., Pl. 3, Fig. 3) indicates that the solutions permeating the volcanic rock pile contained fine particles in suspension at many times. The inclusions were too small to give any measurable Raman spectra, precluding further identification. The solutions were episodic and probably followed intermittent volcanic activity. Vugs dominate in the lower part (below 1040 meters below seafloor [mbsf]) of the section. The absence of veins means that the rock was porous and not lithified enough to develop fractures. The rock was sufficiently porous to let fluids through to fill the former gas voids in the basalt. This also implies that this part of the Hole 953C section was filled before the overlying sections were emplaced. Timewise, the stratigraphic section of the pre-shield stage at Site 953 could be divided at ~1040 mbsf for a possible change in hydrothermal activity.

Site 954 provides direct fluid inclusion data on the composition and temperature of hydrothermal fluids. The data show that the fractures were filled from a relatively high-temperature (210°–310°C), moderately saline solution. However, the presence of numerous one-phase inclusions and open intracrystalline voids also indicates that there was a lower temperature stage of deposition at 100° until 150°C with veins dominating.

At Site 956, there are only one-phase inclusions, indicating a low formation temperature. Visible alteration suggests that the solutions were saline. Vug occurrence increases toward the bottom of the sequence, and veins are more common in the upper part of the lithified clastic rock sequence.

Alteration

In Table 1, we note observations on alteration in hand specimens and under the microscope. This refers only to an ocular survey and implies no chemical analytical work. In reality, we should talk about degrees of alteration or alteration referring to (1) submarine emplacement and reaction with seawater or (2) hydrothermal alteration (Gérard and Person, 1994). In the present study, a relative scale of visible alteration between the three sites can be used in which Site 953 has the least altered samples and Site 954 the most altered samples.

Site 954 is the only site where we have obtained microthermometric data indicating hydrothermal, moderately saline solutions at elevated temperatures (>180°C). The veins are surrounded by a visibly altered zone. Hydrothermal solutions with a salinity of 5 to 15 wt% NaCl equivalent (eq.) are very corrosive at temperatures at ~200°C.

Site 953 is situated farther from volcanic centers than both Sites 954 and 956; therefore, there is much less or no visible alteration at Site 953. The rocks represent a pre-Gran Canaria shield stage, probably reflecting volcanic activity from the eastern islands, Fuerteventura is the nearest one (Ancochea et al., 1996). The veins exhibit sharper contacts with the host rock, and no visible color changes were seen.

Site 956 displays both vugs and fractures. Filling minerals appear to be similar to those at Site 954, and visible alteration was noted

around the veins. This site is slightly farther away from the volcanic centers on the island of Gran Canaria than Site 954. The distance from Gran Canaria seems to directly influence the type of alteration found in the core material.

Timing of Hydrothermal Activity

The timing of the hydrothermal processes, seen as the mineralization of veins and vugs, is difficult to assess. Deposition is necessarily closely related to emplacement of the host rock, but the heat source must be linked to volcanic activity. The amount of heat available at close quarters raises the temperature. This may be related to the proximity of the magma chamber. The center of the heat source may move. For example, volcanism has moved from a central-southern area to a northern location in recent times (Schmincke, 1982).

For Site 953, farthest away from Gran Canaria, the veins appear between 1090 and 980 mbsf. This is below the shield stage and emplaced in the upper sections of the pre-shield stage or earlier stages of the eastern islands volcanism. There is a break between the pre-shield and shield stages, where the veins disappear and only open vugs occur.

This implies that the pre-shield phase rocks had been lithified to an extent that tectonic activity would fracture the rock before emplacement of the veins took place. It further implies that the hydrothermal activity had ceased before Gran Canaria volcanism began.

No thin sections were made from the shield phase mainly because of a lack of suitable material. The material available contains mostly empty vugs, implying very little or no hydrothermal activity in the area during or in relation to the shield stage. At Site 954, veins dominate with very little vug filling. This means that the rock had lithified and fractured before hydrothermal solutions entered the shield stage, which all samples here represent.

Site 956 is on the southwestern side of the island and the drilled section covers ~125 m of shield stage history. Here we found a mixture of veins and vugs. Site 956 is farther away from volcanic activity than Site 954, but alteration evidence indicates higher temperatures than at Site 953. Hydrothermal activity was probably associated fairly closely with the emplacement of the pyroclastic rocks.

Pressure Considerations

Normally, fluid inclusion temperature determinations are subject to pressure corrections. The temperatures measured are from Site 954. The uppermost sample is from 427 mbsf, and the water depth at the Site is 3580 m, giving an overburden of 4010 m.

The solutions show no evidence of boiling. In the case of boiling, we would expect a considerable amount of gas phase to have been trapped. This would appear as a large variation in the vapor-to-liquid ratios in the fluid inclusions.

The total overburden today is 430 + 3580 = 4010 m. This translates into ~400 kp/cm² ~0.4 kbar of hydrostatic pressure. A pressure correction may thus be added of 25°–50°C. (Potter, 1977). The overburden at the time of emplacement of the vein/vugs may have been less. The three sites probably had a similar overburden.

Temperature of Formation

At Site 954, average homogenization temperatures for the three levels are 429 mbsf, 185°C; 440 mbsf, 239°C; and 442 mbsf, 284°C. One temperature determination of 350.2°C was obtained from a very large, irregular inclusion. We interpret this inclusion to have leaked earlier or suffered from “necking down” processes and do not believe that this temperature pertains to formation conditions.

The other temperatures mean that there was a 99°C decrease over a 13-m interval from 429 to 442 mbsf. This agrees with a heat source at deeper levels. The decrease in temperature may have been caused by a successive mixing and/or cooling by seawater. The indicated

temperature gradient supports the conclusion that these temperatures represent primary conditions during crystallization in the veins.

The pressure at the time of crystallization is unknown. A pressure correction may be necessary. Maximum pressure resulting from overburden is 0.4 kbar, which would indicate a correction of 25°–50°C (Potter, 1977), depending on total salinity and on the mineral species in solution. The data from the one-phase inclusions at Sites 953 and 956 imply formation below 150°C. (Roedder, 1984). These temperatures are also subject to a pressure correction of 25°–50°C. The overburden was probably less at the time of vug/vein filling emplacement than it is today.

Composition of the Hydrothermal Solution

The evidence from Site 954 indicates a total salinity of an aqueous solution varying between 4.6 and 15 wt% NaCl eq. This is a very corrosive solution at the temperatures indicated. This is corroborated by the visible alteration around the veins.

There was no sign of dissolved gases, although the presence of CO₂ gas was noted in some core as it was brought on deck. These core sections, however, were from a stratigraphically higher position. The high salt content could be attributed to dissolved evaporites. It is generally too high for directly derived magmatic fluids, but would be common after evolving through salt-rich sediments. The variation in salinity implies mixing with seawater, which also may have cooled the fluids. Another possibility is that seawater salinity was increased by boiling.

At Site 956, there is less visible alteration, indicating that the hydrothermal solution could have been less saline or cooler. No further data could be obtained to support this conclusion.

At Site 953, an even less saline solution or even cooler temperature is implied, judging from the lack of alterations. There are many sources of salinity, but magmatic-related water generally is indicated by a lower salinity and Na-K-Cl affiliation. The first melting temperature was very difficult to observe but occurred in the interval –25° to –35°C, indicating a Na-K composition rather than a Ca-Mg composition. Chemically the solution contained Na-K(-Ca)-Cl fluid, calcium appearing to be a minor component because of lack of calcite in vein/vug minerals. Fluid inclusion first melting temperatures also indicate an absence of Ca in a chloride solution.

Hydrothermal Solutions and Mineral Precipitation

When studying hydrothermal activity in connection with oceanic islands, one is puzzled by the absence of precipitated ore minerals. Hydrothermal systems are associated with many mineral deposits. Even geothermal systems, which are a special variety near surface, are known for their deposition of ore-related minerals. One reason why geothermal/hydrothermal systems are barren could be that when they are found emanating near the surface, pressure has been released and the solution has deposited minerals at depth before escaping.

Two reasons why oceanic islands are barren in their hydrothermal systems could be that the hydrological regime surrounding hotspot activity is limited in its circulation volume or that the percolated rock volumes are devoid of a sufficient amount of metal constituents.

It has been shown that hot-water emanations in hot springs on Iceland have mainly a seawater isotopic signature in their sulfur content (Torssander, 1987). This indicates a natural lack of metal content in the hydrothermal/geothermal water if it is derived from seawater. One explanation for the lack of mineral deposits in oceanic islands is that the rock volume concerned in the thermal circulation pattern is too small to be leached of enough metal constituents to form an ore solution. The salinity and temperatures obtained here are comparable to many ore-forming solutions. The sulfides deposited on seamounts and mid-ocean ridges are not found when these topographical highs reach above the ocean surface and become islands. Maybe the sul-

fides are contained within the island rock volume, but remain undiscovered. A petrogenetic grid for low grade metabasite shows stability fields of zeolite, prehnite-pumpellyite, prehnite-actinolite and blue shist facies (See Frey et al, 1991, and references therein.)

The stability field of prehnite-actinolite ranges from 220° to ~320°C, at pressures <4.5 kbar. Transition to green shist facies occurs at 250°–300°C at 1 to 3 kbar and 250°–350°C at 3 to 8 kbar. Zeolites are found at lower P-T regions and very low partial pressures of CO₂.

If we look at prehnite as an index mineral, this is found at Site 953, where maximum temperatures deduced from the appearance of fluid inclusion are 150°–200°C, depending on pressure. Actinolite is not found as a mineral, and fluid inclusion evidence tends to coincide with prehnite-zeolite occurrence. Zeolite follows prehnite at Site 953, but carbonates are lacking which emphasize the stability of zeolites in later stages. At Site 954, carbonates are frequent and zeolites less common which both agree with a higher CO₂ partial pressure and a higher temperature of deposition as given by fluid inclusion evidence.

CONCLUSIONS

This is a study of epithermal vein deposition at the root of a volcanic island. Fluid inclusion evidence agrees with mineral stability data to indicate an environment of deposition for vein/vug filling minerals: at 100°–150°C (Site 953), 200°–300°C (Site 954), and at 100°–150°C (Site 956).

Mineral deposition occurred at a maximum 334°C from a solution varying in salinity between 4.6 and 15 wt% NaCl eq. This refers to the shield stage at Site 954, which is 50 km from the center of Gran Canaria.

The evidence at 90-km distance from Gran Canaria center (Site 953) is a temperature of deposition <150°C from a less saline solution; however, this reflects hydrothermal conditions in a pre-shield phase that is probably the shield phase of Fuerteventura or associated with a nearby seamount.

There is a break in the sequence at Site 953 ~1040 mbsf: above this depth only veins occur and below vugs dominate. This implies that fracturing occurred above 1040 mbsf when the rock was well lithified. Below 1040 mbsf, cavities were produced by gas expansion in a semi consolidated host rock. This vug/vein transformation is independent of host rock, or vein/vug mineralogy.

At Site 953 the minerals deposited as infilling are natrolite, smectite followed by prehnite, apophyllite, phillipsite, with gmelinite occurring at the bottom of Site 953. At Site 954, we find (1) calcite, phillipsite, smectite, which further down is superseded by (2) aragonite in the interval 425–440 mbsf, followed by (3) smectite, siderite, and phillipsite.

Site 956B has smectite and zeolites as infilling minerals in the studied interval. No sulfides or other ore minerals were found. Hydrothermal fluids acting in the shield stage section at Site 954 were hot (<180°C) and corrosive (5–15 wt% NaCl eq.) Fluids of lower temperature (<150°C) and salinity were active at Site 956 (shield stage) and Site 953 (pre-shield stage). By paying careful attention to the orientation of the mineral, Raman spectroscopy could be successfully used to identify vug/vein minerals. Distinct spectra were obtained for several minerals and aragonite was uniquely identified as the crystal host for the fluid inclusions measured.

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REFERENCES

- Ancochea, E., Brändle, J.L., Cubas, C.R., Hernán, F., and Huertas, M.J., 1996. Volcanic complexes in the eastern ridge of the Canary Islands: the Miocene activity of the island of Fuerteventura. *J. Volcanol. Geotherm. Res.*, 70:183–204.
- Burke, E.A.J., and Lustenhouwer, W.J., 1987. The application of a multi-channel laser Raman microprobe (Microdil-28) to the analysis of fluid inclusions. *Chem. Geol.*, 61:11–17.
- Frey, M., de Capitani, C., and Liou, J.G., 1991. A new petrogenetic grid for low-grade metabasites. *J. Metamorph. Geol.*, 9:497–509.
- Gérard, M., and Person, A., 1994. Low hydrothermal impact in volcanoclastic sediments of the North Aoba Basin: Sites 832 and 833. In Greene, H.G., Collot, J.-Y., Stokking, L.B., et al., *Proc. ODP, Sci. Results*, 134: College Station, TX (Ocean Drilling Program), 131–176.
- Griffith, W.P., 1987. Advances in the Raman and infrared spectroscopy of minerals. In Clark, R.J.H., and Hester, R.E. (Eds.), *Spectroscopy of Inorganic-Based Materials*: London (Wiley), 119–186.
- Hansteen, T., and Burke, E.A.J., 1994. Aphthitalite in high-temperature fluid inclusions in quartz from the Eikeren-Skrin granite complex, the Oslo paleorift. *Nor. Geol. Tidsskr.*, 74:238–240.
- Hoernle, K., and Schmincke, H.-U., 1993. The petrology of the tholeiites through melilite nephelinites on Gran Canaria, Canary Islands: crystal fractionation, accumulation, and depth of melting. *J. Petrol.*, 34:573–578.
- Holk, J.S., Rabinowitz, P.D., and Austin, J.A., Jr., 1991. Effects of Canary hotspot volcanism on structure of oceanic crust off Morocco. *J. Geophys. Res.*, 96:12039–12067.
- Kimbell, T.N., and Humphrey, J.D., 1994. Geochemistry and crystal morphology of aragonite cements of mixing-zone origin, Barbados, West Indies. *J. Sediment. Res.*, A64:604–614.
- Le Bas, M.J., Rex, D.C., and Stillman, C.J., 1986. The early magmatic chronology of Fuerteventura, Canary Islands. *Geol. Mag.*, 123:287–298.
- Lindblom, S., 1982. Fluid inclusion studies of the Laisvall sandstone lead-zinc deposit Sweden [Thesis], Medd. Stockholms Univ. Geol. Inst.
- Malahoff, A., McMurtry, G.M., Witshire, J.C., Hsueh-Wen, Y., 1982. Geology and chemistry of hydrothermal deposits from active submarine volcano Loihi, Hawaii. *Nature*, 298:234–239.
- McDougall, I., and Schmincke, H.-U., 1977. Geochronology of Gran Canaria, Canary Islands: age of shield-building volcanism and other magmatic phases. *Bull. Volcanol.*, 40:1–21.
- McMurtry, G.M., Sedwick, P.N., Fryer, P., Vonderhaar, D.L., Yeh, H.W., 1992. Unusual geochemistry of hydrothermal vents on submarine arc volcanoes: Kasuga Seamounts, northern Mariana Arc. *Earth Planet. Sci. Lett.*, 114:517–528.
- Potter, R.W., 1977. Pressure corrections for fluid-inclusion homogenization temperatures based on the volumetric properties of the system NaCl-H₂O. *J. Res. U.S. Geol. Surv.*, 5:603–607.
- Roedder, E., 1984. Fluid inclusions. *Rev. Mineral., Mineral. Soc. Am.*, 12.
- Schmincke, H.-U., 1976. The geology of the Canary Islands. In Kunkel, G. (Ed.), *Biogeography and Ecology in the Canary Islands*: The Hague (W. Junk), 67–184.
- , 1982. Volcanic and chemical evolution of the Canary Islands. In von Rad, U., Hinz, K., Sarnthein, M., and Seibold, E. (Eds.), *Geology of the Northwest African Continental Margin*: Berlin (Springer), 273–306.
- Schmincke, H.-U., and von Rad, U., 1979. Neogene evolution of Canary Island volcanism inferred from ash layers and volcanoclastic sandstones of DSDP Site 397 (Leg 47A). In von Rad, U., Ryan, W.B.F., et al., *Init. Repts. DSDP*, 47 (Pt. 1): Washington (U.S. Govt. Printing Office), 703–725.
- Sedgwick, P.N., McMurtry, G.M., and Mac Dougall, J.D., 1992. Chemistry of hydrothermal solutions from Pele's Vents, Loihi Seamount, Hawaii. *Geochim. Cosmochim. Acta*, 56:3643–3667.
- Shepherd, T., Rankin, A.H., and Alderton, D.H.M., 1985. *A Practical Guide to Fluid Inclusions Studies*: Glasgow (Blackie).
- Stüben, D., et al., 1992. First results of study of sulphur-rich hydrothermal activity from an island-arc environment: Esmeralda Bank in the Mariana Arc. *Mar. Geol.*, 103:521–528.
- Torssander, P., 1987. Origin of volcanic sulfur on Iceland. *Medd. Stockholm Univ. Geol. Inst.*
- Wilson, M., 1991. *Igneous Petrogenesis*: London (Harper Collins Academic).

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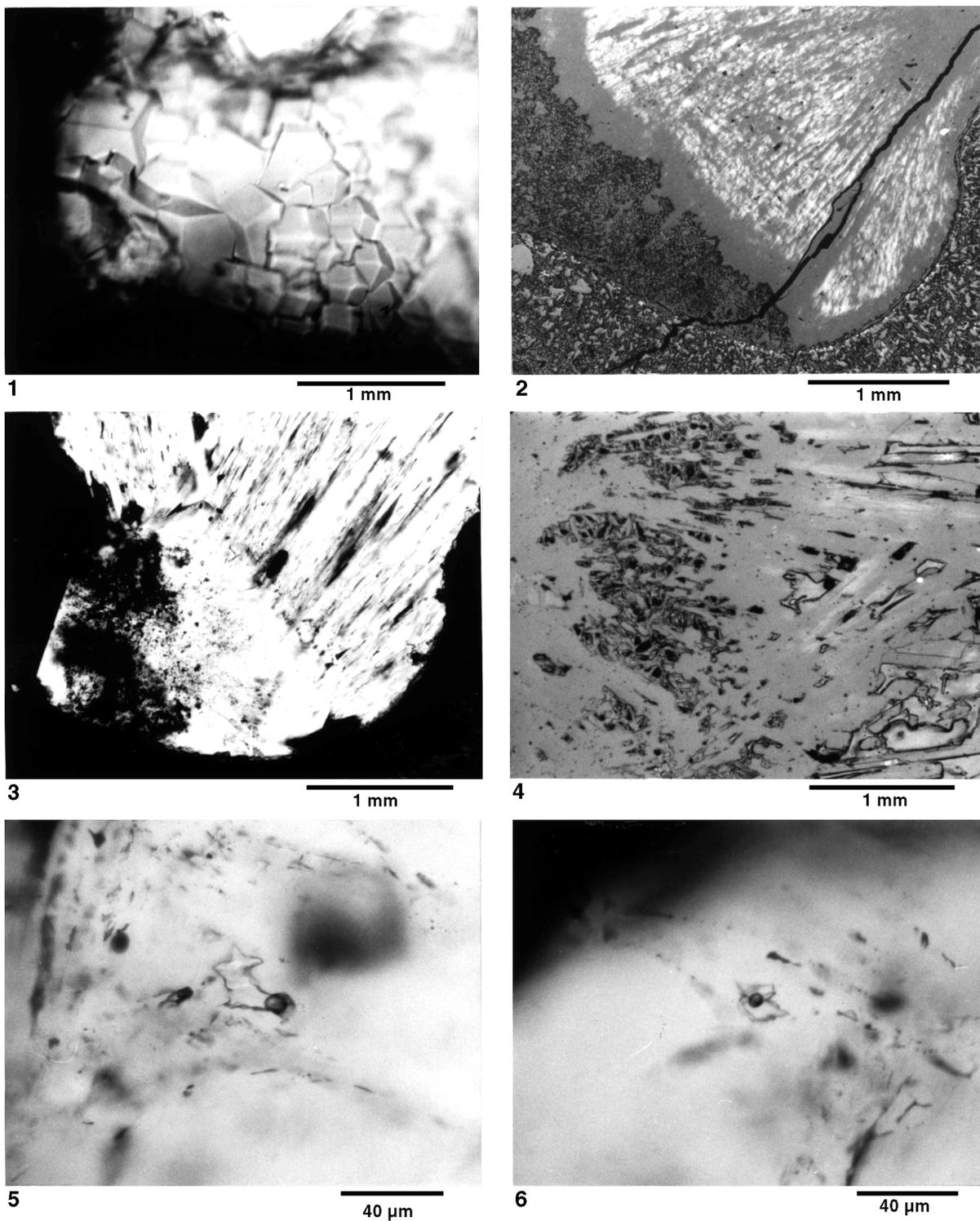


Plate 1. **1.** Crystal faces growing into an open vug (Sample 157-956B-47R- 1, 7 cm; phillipsite). **2.** Radial crystal in a vug filling that begins with a sedimented layer to the right, pointing northeast (Sample 157-953C-100R-5, 114 cm; natrolite). **3.** Equant-shaped crystal with a core of numerous dark inclusions superseded by a growth of radially growing crystals (Sample 157-953C-100R-5, 114 cm; apophyllite). **4.** Crystal growth in multistage vein. Finer crystals in initial growth at right are followed by larger crystals. In between is an area with numerous open pores (Sample 157-953C-90R-4, 100 cm; apophyllite). **5.** Isolated two-phased fluid inclusion in aragonite (Sample 157-954B-39R-1, 64 cm). **6.** Isolated two-phased fluid inclusion in aragonite (Sample 157-954B-38R-4, 0 cm).

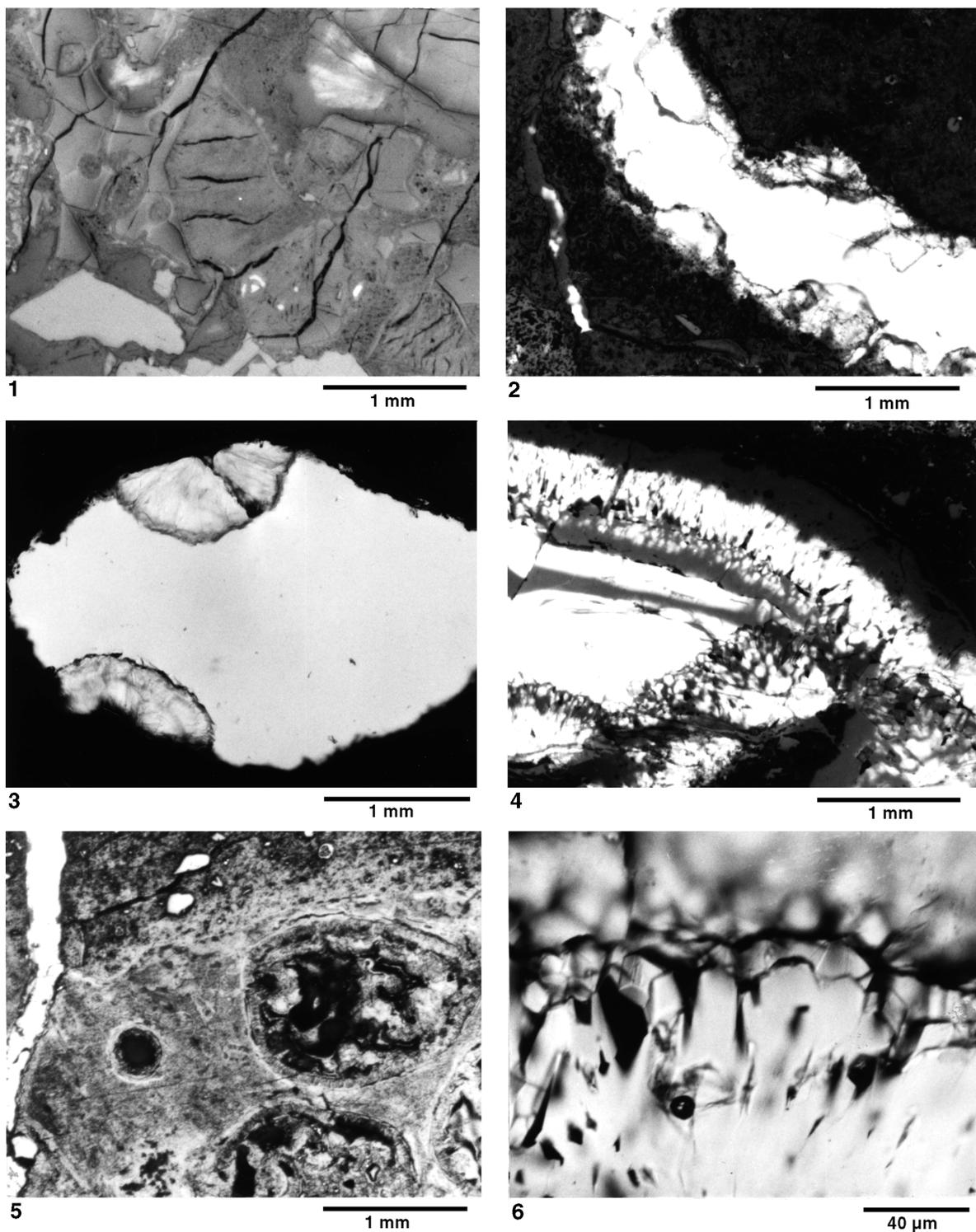


Plate 2. **1.** Cooling fractures in basalt breccia. Note the absence of alteration despite an open channel (Sample 157-953C-94R-4, 38 cm). **2.** Open vein with precipitated minerals on the walls (Sample 157-956B-44R-3, 17 cm; smectite). **3.** Open vug with crystallized siderite radial aggregates on the walls. (Sample 157-954B-38R-4, 94 cm). **4.** Multistage vein calcite and phillipsite (Sample 157-954B-36R-1, 34 cm). **5.** Hydrothermal aragonite vein and adjacent alteration of matrix and clasts. (Sample 157-954B-38R-4, 0 cm). **6.** End of crystal stage showing open intracrystalline inclusions with glue trapping air bubbles (Sample 157-954B-36R-1, 34 cm; phillipsite).