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25. GEOCHEMISTRY OF SIDEROMELANE AND FELSIC GLASS SHARDS IN PLEISTOCENE ASH LAYERS AT SITES 953, 954, AND 956[1]

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ABSTRACT

Sideromelane and felsic glass shards from unconsolidated Pleistocene volcaniclastic sediments drilled at Sites 953, 954, and 956 are thought to have derived from submarine and subaerial volcanic eruptions on Gran Canaria (Sites 953 and 954) and Tenerife (Sites 954 and 956). We analyzed these glasses by electron microprobe for major elements and sulfur, chlorine, and fluorine. Sideromelane glasses represent a spectrum from alkali basalt through basanite, hawaiite, mugearite, and tephrite to nephelinite. Felsic glasses have compositions similar to benmoreite, trachyte, and phonolite. Vesiculated mafic and felsic glass shards, which are characterized by low S and Cl concentrations (0.01–0.06 wt% S and 0.01–0.04 wt% Cl), are interpreted to have formed by pyroclastic activity on land or in shallow water and appeared to have been strongly degassed. Vesicle-free blocky glass shards having 0.05–0.13 wt% S are likely to have resulted from submarine eruptions at moderate water depths and represent undegassed or slightly degassed magmas. Cl concentrations range from 0.01 to 0.33 wt% and increase with increasing MgO, suggesting that Cl behaves as an incompatible element during magma crystallization. Concentrations of fluorine (0.04–0.34 wt% F) are likely to represent undegassed values, and the variations in F/K ratios between 0.02 and 0.24 are believed to reflect those of parental magmas and of the mantle source.

INTRODUCTION

One of the surprises in drilling the clastic apron north and south of Gran Canaria during Leg 157 was the paucity of volcaniclastic material within sediments younger than 2 Ma. (Schmincke, Weaver, Firth, et al., 1995), although alkali basalts, basanites, nephelinites, tephrites, and phonolites were erupted on Gran Canaria and Tenerife during this time (e.g., Schmincke, 1982, 1994; Ancochea et al., 1990; Hoernle and Schmincke, 1993). We studied sideromelane and felsic glasses from Pleistocene mafic volcaniclastic deposits drilled at Sites 953, 954, and 956 to find out (1) which volcanic phase is represented by these materials, (2) if the potential sources, Gran Canaria or Tenerife, can be identified, and (3) if both subaerial and submarine eruptive environments can be distinguished from each other.

STRATIGRAPHY, LITHOLOGY, AND SAMPLE DESCRIPTION

Four sites (Sites 953 through 956) were drilled into the volcanic apron north and south of Gran Canaria (Schmincke, Weaver, Firth, et al., 1995; Fig. 1). Site 953 is located 68 km northeast of Gran Canaria, 90 km west of Fuerteventura, and 98 km east of Tenerife. Drilling at Site 953 recovered an almost complete Quaternary to middle Miocene 1159-m-thick section, in which the stratigraphy of volcaniclastic deposits corresponds closely to the lithostratigraphic subdivision of the volcanic rocks exposed on Gran Canaria. Site 954, the second of four sites drilled, is located 34 km northeast of Gran Canaria, 130 km west of Fuerteventura, and 60 km east of Tenerife. Drilling at Site 954 recovered a 446-m-thick succession of middle Miocene to Holocene sediments, consisting dominantly of fine-grained sediments interbedded with bioclastic and volcaniclastic material. At Site 956, located in the southwestern Canary Channel, fine-grained hemipelagic sediments with Pliocene/Pleistocene volcaniclastic interbeds were drilled in the uppermost part of the 700-m-thick section.

We studied eight samples of calcareous biogenic sands containing volcanic clasts and crystals, two samples of carbonate-free residue from bioclastic sand, and one sample of volcanic ash recovered in the upper part of Holes 953A, 954A, and 956A (Table 1). The main criterion for sample selection was the presence of fresh volcanic glass shards. The glasses are characterized by a broad range in vesicularity, ranging from vesicle-free blocky shards to strongly vesiculated ones. We restricted our studies to those samples, which contain mafic brown or reddish brown glass shards. Composition of felsic pumice

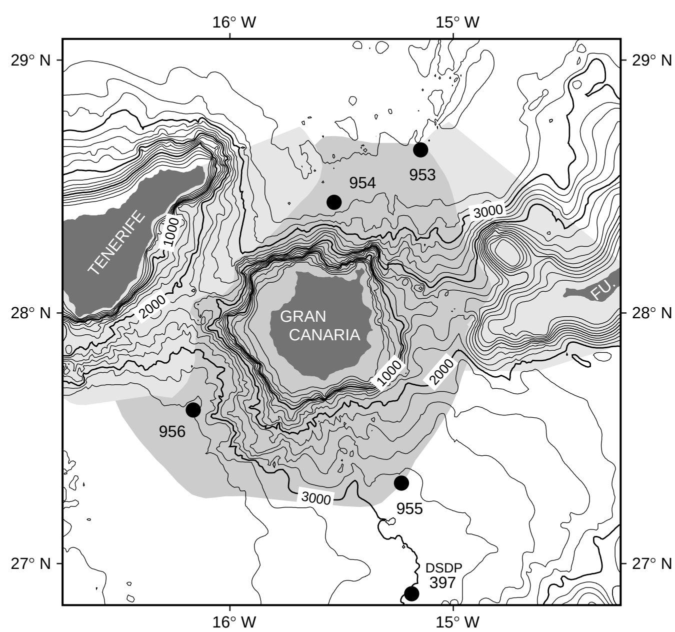

Figure 1. Schematic map showing locations of Sites 953 through 956 in relation to the Canary Islands (after Funck, 1995). Fields are seismically defined volcaniclastic aprons of Fuerteventura, Gran Canaria, and Tenerife.

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Table 1. Sample description.

Core, section, interval (cm)	Depth (mbsf)		Age (Ma)	Sediment Name	Texture Data (%)			Rock Particles (%)					Minerals (%)						Biogenic (%)		
	Top	Bottom			Sand	Silt	Clay	Sider	Pum	Tach	Bas	Fels	Ol	Cpx	Ampf	Pl	Feldsp	Zeol	Biocl	Foram	Nanno
157-953A-																					
16H-2, 45-47	142.55	142.57	1.95*	Lithic-vitric ash with foraminifers	60	30	10	35	0	tr.	20	0	0	tr.	1	2	10	0	0	30	0
157-954A-																					
2H-6, 80-82	9.30	9.32	<0.30**	Carbonate-free residue from bioclastic sand	90	10	0	10	tr.	15	25	5	5	15	5	tr.	15	0	0	0	0
7H-6, 104-106	57.04	57.06	0.77**	Calcareous sand with volcanic clasts and crystals	80	15	5	10	tr.	10	30	5	3	10	tr.	2	5	tr.	25	0	0
8H-3, 87-89	61.87	61.89	0.84**	Calcareous sand with volcanic clasts and crystals	80	10	10	10	5	5	25	5	2	15	3	3	tr.	tr.	15	10	tr.
9H-3, 140-141	71.90	71.91	0.96**	Calcareous sand with foraminifers, volcanic clasts and crystals	75	15	10	tr.	35	15	5	5	5	5	0	10	5	0	0	15	tr.
9H-5, 130-132	74.80	74.82	0.98**	Carbonate-free residue from bioclastic sand	95	5	0	30	25	tr.	20	15	0	5	1	tr.	4	0	0	0	0
157-956A-																					
3H-3, 86-92	19.46	19.52	0.58*	Calcareous sand with volcanic clasts and crystals	60	25	15	5	10	0	2	3	5	10	5	5	10	tr.	25	15	5
5H-4, 92-94	40.02	40.04	1.34*	Calcareous sand with volcanic clasts and crystals	75	15	5	3	15	tr.	2	15	0	15	10	5	7	1	10	15	tr.
6H-1, 4-5	44.14	44.15	1.34*	Calcareous sand with volcanic clasts and crystals	80	10	5	5	15	5	5	15	0	10	tr.	10	10	tr.	5	15	5
7H-6, 58-60	61.68	61.70	1.95*	Calcareous biogenic sand with volcanic clasts and crystals	35	55	10	tr.	5	tr.	tr.	15	tr.	tr.	tr.	tr.	5	tr.	20	45	5

Notes: * = Schmincke, Weaver, Firth, et al. (1995) and ** = Rodehorst et al. (Chap. 18, this volume). Sider = sideromelane, Pum = pumice, Tach = tachylite, Bas = basaltic rock fragments, Fels = felsic rock fragments, Ol = olivine, Cpx = clinopyroxene, Amph = amphibole, Pl = plagioclase, Feldsp = feldspathoids, Zeol = zeolites, Biocl = bioclasts, Foram = foraminifers, and Nanno = nannofossils. tr. = traces.

particles from the same samples and samples of similar age are studied and discussed in more detail by Rodehorst et al. (Chap. 18, this volume).

Site 953

Unit I (0–197 meters below seafloor [mbsf]; Holocene to late Pliocene) consists predominantly of pelagic clayey nannofossil ooze and graded nannofossil clay-silt. The remarkable coarse sands rich in neritic biogenic material recovered in the upper 100 m are interpreted as beach sands and redeposited as turbidites possibly related to glacially controlled changes in sea level (Shipboard Scientific Party, 1995a). The only mafic tephra deposit recovered in the lower part of the Pleistocene interval consists dominantly of angular vesicle-free brown and brown-yellow glass shards (Sample 157-953A-16H-2, 45–47 cm). Pleistocene planktonic foraminifers recovered from Cores 157-953A-1H through 15H (younger than 1.95 Ma), and Pliocene planktonic foraminifers (older than 2.6 Ma) recovered starting only from Sample 157-953A-16H-CC, 0–2 cm (Shipboard Scientific Party, 1995a), allows us to ascribe the age of Sample 953A-16H-2, 45–47 cm, to the Pleistocene (Table 1).

Site 954

In the upper part of Unit I (0–158 mbsf; Pleistocene to late Pliocene), sediments are dominated by clayey nannofossil ooze with foraminifers, clayey nannofossil mixed sediment, and calcareous sand with volcanic lithic clasts. Minor interbeds of crystal lithic sand, pumice sand, and vitric ash layers occur throughout the upper part of Unit I (Shipboard Scientific Party, 1995b). We studied three samples of calcareous sand with volcanic clasts and crystals, and two samples of carbonate-free residue from bioclastic sand, whose age ranges from 0.30 to 0.98 Ma (Shipboard Scientific Party, 1995b; Rodehorst et al., Chap. 18, this volume; Table 1).

Glass shards are classified by their color, morphology, and vesicularity. Sample 157-954A-2H-6, 80–82 cm, contains shards ranging from dark-brown to brown-yellow and from slightly to strongly vesicular with elongate or round vesicles. Shards are generally altered (fresh glasses represent <5%), and contain microphenocrysts of clinopyroxene (*Cpx*), apatite *(Ap)*, opaque minerals, and numerous plagioclase (*Pl*) microlites. Samples 157-954A-2H-6, 80–82 cm, 7H-6, 104–106 cm, 8H-3, 87–89 cm, 9H-3, 140–141 cm, and 9H-5, 130–132 cm, contain fresh brown, yellow-brown, and reddish brown glass shards. About 5%–15% of the shards contain no or trace amounts of microlites and vesicles, and ~80% of the shards are strongly vesiculated, have microphenocrysts of olivine (*Ol*), *Cpx, Ap,* and opaque minerals, and abundant *Pl* microlites.

Site 956

Unit I (0–158 mbsf; Pleistocene to late Pliocene) consists mostly of nannofossil mixed sediments with foraminifers interbedded with coarse debris flow deposits, typically rich in pumice, which were most likely derived from Tenerife (Shipboard Scientific Party, 1995c; Rodehorst et al., Chap. 18, this volume). Because the Pleistocene sequence of Site 956 contains many slumps and debris flows, the biostratigraphy should be regarded with caution (Shipboard Scientific Party, 1995c). We studied four samples of calcareous sands containing volcanic clasts and crystals that are thought to have been deposited within the time interval from ~0.58 to 1.95 Ma.

Samples 157-956A-3H-3, 86–92 cm, 5H-4, 92–94 cm, and 6H-1, 4–5 cm, contain reddish brown, brown, and green glass shards, varying from slightly to strongly vesiculated, and colorless pumice shards as well. Brown shards contain trace to significant amounts of *Cpx* and *Pl* microlites. Reddish brown and green shards are mostly microlite free, or have trace microliths. Sample 157-956A-7H-6, 58–60 cm, contains traces of slightly to strongly vesiculated brown shards with microphenocrysts or microliths of *Ol, Cpx, Pl,* and *Ap.*

ANALYTICAL METHODS

Major elements and S, Cl, and F were analyzed with a Cameca SX-50 electron probe at GEOMAR Research Center (Kiel, Germany). For major elements, analytical conditions were 15 kV of accelerating voltage, 10 nA of beam current, and 10 s of peak counting time. Analyses were performed with an electron beam rastered to 10 µm × 12 µm. Cameca synthetic oxides, basaltic glasses USNM 111240/52 and USNM 113498/1, apatite USNM 104021, microcline USNM 143966 (Jarosewich et al., 1980), and spinel Yb-126 (Lavrentev et al., 1974) were used as standards for calibration.

S, F, and Cl were measured with accelerating voltage of 15 kV and beam current of 10–40 nA. The electron beam was rastered to 10 µm × 12 µm, and peak counting times were 20–40 s. Standards used were chalcopyrite for S, scapolite USNM R6600-1 for Cl, and fluorapatite USNM 104021 for F, respectively (Jarosewich et al., 1980). Four to ten spots were measured within each glass shard. The detection level was estimated to be better than 0.01 wt% with uncertainties of 5%–15% relative for volatile concentrations >0.05 wt%, and up to 20%–40% relative for the concentrations <0.05 wt%.

MAJOR ELEMENTS

Major element compositions of the volcanic glasses are listed in Table 2 and plotted in Figure 2. Some mafic and especially felsic glasses have totals <98%–100%. One possible explanation might be high water concentrations in the glasses, which are impossible to measure with the electron microprobe technique. The low totals are mostly characteristic of felsic glasses, which have elevated K_2O contents and are poorly vesiculated. If H_2O positively correlates with K_2O, as shown for mid-ocean-ridge basalt (MORB) and ocean-island basaltic glasses (e.g., Johnson et al., 1994; Sobolev and Chaussidon, 1995, and references therein), and its solubility increases from mafic to silicic compositions while H_2O is preferentially incorporated into aluminosilicate liquids (e.g., Fisher and Schmincke, 1984; McMillan, 1994, and references therein), we suspect that these low totals are due to the presence of H_2O in the glasses.

All glasses from Sample 157-953A-16H-2, 45–47 cm, are mafic and show a narrow compositional range from alkali basalt to basanite (Fig. 2A). Glasses drilled at Hole 954A have the widest compositional range among all glasses studied. Most glasses from Hole 954A range from alkali basalt to basanite, and one glass shard from Sample 157-954A-7H-6, 104–106 cm, corresponds to nephelinite. More evolved glasses have compositions similar to hawaiite, mugearite, and tephrite (Fig. 2B). Sample 157-954A-2H-6, 80–82 cm, contains glass shards whose compositions range from basanite through phonolitic tephrite and benmoreite to phonolite, interpreted to reflect a crystallization trend (Fig. 2B). Two of four samples drilled at Hole 956A (Samples 157-956A-5H-4, 92–94 cm, and 7H-6, 58–60 cm) contain two populations of glass shards: (1) mafic glasses corresponding to basanite, and (2) felsic glasses, which are close to benmoreite and trachyte (Fig. 2C). This bimodal distribution is also a feature of the third sample (Sample 157-956A-3H-3, 86–92 cm), except that it contains glasses, which are more alkali rich and range from basanite and tephrite to phonolite and trachyte. Glasses from the fourth sample (Sample 157-956A-6H-1, 4–5 cm) show a narrow compositional range and correspond to basanite (Fig. 2C).

VOLATILE ELEMENTS

Sulfur and Chlorine

Concentrations of S and Cl are listed in Table 2 and presented in Figures 3 and 4. Glass compositions are subdivided into two populations based on their S concentrations (Fig. 3A): glasses with elevated S concentrations (0.05–0.13 wt% S and in the MgO range between ≈6.8 and ≈1 wt%), and with low S concentrations (0.01–0.06 wt% S

Table 2. Major element compositions and concentrations of S, Cl, and F in sideromelane and felsic glasses, Holes 953A, 954A, and 956A.

Core, section, interval (cm)	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	NiO	Total	S	Cl	F
157-953A-															
16H-2, 45-47															
1	46.99	3.21	14.15	11.06	0.20	6.75	11.88	2.91	0.83	0.56	0.07	98.61	0.034	0.038	0.135
2	45.41	3.62	14.39	11.14	0.19	6.09	11.05	2.92	1.02	0.63	0.02	96.48	0.064	0.046	0.208
3	44.97	3.46	13.96	11.57	0.18	6.10	12.66	2.91	1.07	0.54	0.02	97.45	0.056	0.055	0.163
4	44.50	3.64	13.77	11.91	0.15	6.89	11.33	2.99	1.22	0.73	0.02	97.13	0.066	0.057	0.179
5	45.23	3.53	14.37	11.51	0.21	5.87	11.68	3.08	1.06	0.65	0.06	97.24	0.049	0.054	0.182
6	45.21	3.56	13.92	11.56	0.18	5.99	10.83	3.19	1.36	0.64	0.02	96.45	0.055	0.056	0.168
7	45.82	3.36	14.90	11.14	0.18	5.91	9.98	3.26	1.20	0.68	0.01	96.44	0.077	0.059	0.146
8	45.12	3.52	13.84	11.57	0.20	6.53	11.99	2.85	1.03	0.61	0.05	97.30	0.045	0.078	0.165
9	44.35	3.76	14.32	13.36	0.20	4.98	11.45	3.24	1.48	0.64	0.02	97.79	0.020	0.037	0.214
10	44.23	3.41	13.86	11.58	0.18	6.75	11.27	3.05	1.29	0.65	0.02	96.30	0.079	0.067	0.206
157-954A-															
2H-6, 80-82															
1	55.31	1.76	20.32	4.31	0.11	1.26	5.03	6.39	4.10	0.45	0.04	99.08	0.034	0.200	0.176
2	50.33	3.06	18.06	7.27	0.18	3.30	6.48	6.24	4.01	1.15	0.05	100.12	0.030	0.165	0.019
4	58.49	1.19	19.87	3.52	0.26	1.08	1.43	7.45	5.01	0.35	0.03	98.68	ND	ND	0.341
7	48.11	3.23	16.92	8.04	0.18	3.29	8.36	5.37	3.36	1.62	tr.	98.48	0.016	0.184	0.336
8	54.74	1.79	19.68	4.92	0.17	1.58	5.27	6.71	4.45	0.51	0.04	99.84	0.061	0.213	0.156
10	52.73	2.24	19.46	6.11	0.19	2.17	5.82	6.53	4.21	0.76	0.02	100.23	0.041	0.207	0.197
11	53.55	2.09	19.36	5.73	0.15	1.85	5.01	6.78	4.50	0.64	0.01	99.67	0.042	0.243	0.199
12	60.39	0.88	19.73	3.00	0.20	0.52	1.04	7.93	5.66	0.14	0.05	99.52	0.042	0.196	0.159
14	53.52	2.31	19.10	6.11	0.21	2.11	5.69	6.28	4.26	0.71	0.02	100.33	0.034	0.229	0.177
15	52.50	2.47	18.78	6.56	0.20	2.23	6.64	6.65	3.90	0.79	0.02	100.72	0.048	0.187	0.196
16	49.41	3.05	17.64	7.53	0.20	3.52	7.23	7.32	3.97	1.16	0.03	101.05	0.032	0.012	0.134
157-954A-															
7H-6, 104-106															
1	43.51	4.36	14.83	13.32	0.22	4.39	11.27	4.07	1.92	1.07	0.02	98.97	0.045	0.087	0.255
2	48.39	3.61	15.93	11.01	0.22	3.17	7.85	5.23	3.22	1.31	0.02	99.96	0.045	0.058	0.255
3	44.34	3.77	15.06	12.36	0.18	5.04	11.56	3.84	1.62	0.83	0.03	98.61	0.012	0.039	0.212
4	44.43	4.06	14.99	13.14	0.23	4.20	10.81	4.30	2.04	0.93	tr.	99.13	0.036	0.093	0.248
5	44.78	3.47	14.86	13.23	0.18	4.79	11.47	3.96	1.58	0.80	tr.	99.12	0.021	0.048	0.181
6	40.29	4.97	13.41	11.04	0.21	5.20	13.09	5.09	2.37	2.15	0.05	97.86	0.088	0.208	0.284
7	46.25	4.31	15.38	11.65	0.14	3.86	9.50	4.46	2.63	1.11	0.03	99.32	0.028	0.057	0.246
8	45.60	4.61	14.97	12.36	0.26	3.75	9.46	4.69	2.40	1.26	0.03	99.39	ND	ND	0.259
9	46.58	3.94	15.93	11.11	0.22	3.47	8.74	5.05	2.88	1.19	tr.	99.10	0.046	0.067	0.255
10	46.21	3.92	15.01	11.98	0.27	4.02	9.71	4.47	2.21	0.91	0.04	98.74	ND	ND	0.182
11	46.57	4.09	15.43	10.95	0.18	3.99	9.75	4.26	2.17	0.96	0.05	98.40	ND	ND	0.274
12	49.65	3.36	14.98	10.13	0.24	2.90	6.30	4.25	3.65	1.08	0.05	96.58	0.021	ND	ND
13	45.39	3.92	14.99	11.43	0.26	4.41	10.00	3.98	1.81	1.45	0.04	97.67	ND	ND	0.264
157-954A-															
8H-3, 87-89															
1	46.90	3.59	14.05	12.72	0.20	5.13	10.72	3.74	1.20	0.70	0.04	98.99	0.027	0.036	0.160
2	46.07	3.79	14.39	12.77	0.24	4.77	10.29	3.91	1.71	0.70	0.02	98.66	0.017	0.035	0.182
3	44.63	4.64	14.58	13.04	0.20	4.29	10.23	4.07	2.00	0.76	0.03	98.47	0.040	0.028	0.211
4	50.91	2.84	17.17	8.47	0.21	2.55	5.78	6.42	4.00	1.12	0.01	99.49	0.047	0.079	0.265
5	45.63	3.84	14.00	12.91	0.16	5.28	11.30	3.66	1.33	0.74	0.02	98.88	0.020	0.047	0.183
6	56.05	1.66	18.57	5.95	0.19	1.80	4.98	4.55	2.55	0.74	0.02	97.05	0.072	0.082	0.126
7	50.11	3.06	17.02	9.47	0.19	2.71	6.35	6.21	3.52	1.15	0.01	99.79	0.056	0.075	0.250
8	45.41	3.83	14.17	12.73	0.16	5.21	11.52	3.52	1.32	0.70	0.04	98.60	0.018	0.032	0.172
9	47.00	3.67	15.40	10.68	0.22	4.24	8.49	4.74	2.04	1.73	tr.	98.21	0.028	0.068	0.317
10	46.55	3.75	14.58	12.46	0.21	4.68	10.04	4.04	1.85	0.80	0.06	99.03	ND	ND	0.219
157-954A-															
9H-3, 140-141															
1	47.70	3.62	15.92	10.45	0.23	4.03	8.71	4.62	2.27	1.21	0.04	98.81	0.027	0.069	0.239
2	48.06	3.51	15.81	10.15	0.19	3.84	8.25	4.76	2.56	1.24	0.01	98.37	0.029	0.063	0.229
3	46.18	4.07	14.10	12.28	0.20	5.18	10.86	3.57	1.59	0.69	0.04	98.76	0.009	0.026	0.182
4	47.64	3.92	13.90	12.30	0.17	5.23	10.54	3.37	1.37	0.54	0.06	99.03	0.022	0.022	0.175
5	47.86	4.04	14.20	12.42	0.17	5.22	10.52	3.33	1.47	0.58	0.02	99.85	0.010	0.026	0.161
6	47.14	4.11	13.41	12.50	0.22	4.87	10.17	3.52	1.45	0.52	0.03	97.95	0.020	0.022	0.188
7	46.33	4.00	13.80	12.28	0.15	5.03	10.67	3.63	1.49	0.60	0.02	98.00	0.020	0.017	0.194
8	48.39	3.58	16.09	10.44	0.19	3.82	8.15	4.64	2.46	1.31	0.03	99.10	0.039	0.055	0.221
9	47.74	3.93	13.83	12.02	0.14	5.17	10.37	3.33	1.36	0.51	0.02	98.41	0.008	0.014	0.176
10	48.94	3.37	16.12	10.14	0.23	3.50	7.68	4.56	3.01	1.41	0.02	98.98	0.029	0.072	0.265
12	47.63	4.00	13.86	12.50	0.20	5.16	10.43	3.33	1.42	0.54	0.03	99.11	0.013	0.030	0.195
14	47.52	3.94	14.12	12.04	0.18	5.24	10.64	3.36	1.43	0.56	0.04	99.07	0.011	0.024	0.182
15	48.09	3.65	15.93	10.40	0.18	4.05	8.66	4.54	2.31	1.18	0.02	99.01	0.021	0.063	0.223
16	43.67	4.65	14.81	13.02	0.15	4.91	10.89	3.73	1.91	0.85	0.02	98.61	0.035	0.019	0.110
18	47.70	3.91	14.15	12.35	0.17	5.25	10.59	3.36	1.45	0.61	0.03	99.57	0.013	0.026	0.147
19	47.22	3.96	13.93	12.35	0.19	5.11	10.50	3.41	1.48	0.58	tr.	98.72	0.014	0.024	0.190
20	47.54	4.07	13.93	12.53	0.18	5.00	10.29	3.42	1.50	0.59	0.03	99.08	0.012	0.019	0.189
157-954A-															
9H-5, 130-132															
1	46.83	3.64	15.48	11.01	0.24	4.08	8.98	4.37	2.28	1.26	tr.	98.17	0.038	0.074	0.253
2	47.17	3.05	16.14	10.75	0.23	4.37	8.37	4.39	2.19	1.24	0.05	97.96	0.035	0.061	0.207
3	46.87	3.56	15.85	10.79	0.22	4.01	9.12	4.39	2.18	1.23	0.03	98.24	0.027	0.077	0.248
4	49.35	2.47	16.96	9.61	0.23	3.39	7.10	4.78	2.66	1.44	0.02	98.01	0.016	0.082	0.267
5	47.94	3.15	15.86	10.82	0.26	4.16	8.26	4.42	2.42	1.32	0.02	98.63	0.033	0.080	0.198
6	44.47	4.29	14.93	12.59	0.21	4.96	11.16	3.51	1.48	1.06	0.03	98.69	0.082	0.045	0.243
7	42.70	4.93	14.79	12.85	0.21	4.72	11.48	3.78	2.15	0.81	0.01	98.45	0.037	0.044	0.219
8	46.44	3.60	15.37	11.02	0.21	4.18	8.96	4.39	2.28	1.29	0.03	97.77	0.035	0.087	0.261
9	42.24	5.02	13.23	13.13	0.25	4.64	11.14	3.89	1.70	2.76	0.01	98.00	0.024	0.072	0.359
10	43.83	4.85	13.63	12.76	0.25	4.49	9.81	4.06	1.85	2.18	0.07	97.77	0.04	0.070	0.288
11	48.09	2.41	19.34	8.09	0.17	3.05	9.42	4.37	1.70	0.98	0.08	97.69	0.038	0.066	0.209
12	47.04	3.70	15.48	10.97	0.26	3.96	9.10	4.28	2.37	1.26	tr.	98.42	0.031	0.088	0.251
13	45.60	3.72	15.45	11.05	0.25	4.77	8.98	4.35	2.01	1.81	0.01	98.00	0.047	0.063	0.304

Table 2 (continued).

Core, section, interval (cm)	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	NiO	Total	S	Cl	F
157-956A-															
3H-3, 86-92															
1	60.75	0.59	19.97	3.07	0.22	0.31	0.60	8.68	5.45	0.07	0.04	99.75	ND	ND	0.261
5	60.48	0.62	20.22	3.04	0.23	0.30	0.60	8.35	5.46	0.06	0.03	99.39	0.029	0.325	0.255
6	60.63	0.57	20.05	2.79	0.19	0.27	0.66	8.68	5.61	0.08	tr.	99.54	ND	ND	0.205
8	60.21	0.65	18.46	4.05	0.33	0.54	0.65	8.40	3.81	0.14	0.05	97.29	0.080	0.257	0.120
9	42.70	3.20	16.26	10.86	0.19	4.55	10.89	5.26	2.30	1.90	0.04	98.14	0.039	0.111	0.220
10	60.59	0.65	20.00	2.85	0.15	0.34	0.54	10.07	5.12	0.06	0.04	100.41	ND	ND	0.254
11	59.14	0.67	19.51	3.06	0.23	0.29	0.62	7.69	5.27	0.05	0.04	96.56	ND	ND	0.297
13	61.50	0.84	19.77	2.92	0.18	0.52	1.05	7.66	4.90	0.12	0.04	99.50	ND	ND	0.230
14	43.62	3.20	16.29	10.50	0.22	4.44	10.67	5.32	2.37	1.79	0.02	98.44	ND	ND	0.256
17	61.37	0.75	19.02	3.00	0.24	0.37	0.62	8.62	5.47	0.10	0.03	99.59	0.033	0.265	0.179
22	62.78	0.59	19.05	2.52	0.19	0.27	0.96	8.14	5.25	0.05	0.01	99.82	ND	ND	0.198
25	48.54	3.03	18.41	8.67	0.20	3.04	7.14	5.86	3.80	1.14	0.09	99.94	0.074	0.150	0.278
26	61.38	0.74	19.05	2.72	0.21	0.40	0.88	8.00	6.06	0.09	0.01	99.54	0.046	0.143	0.171
28	46.21	4.00	16.99	10.39	0.19	3.49	8.44	5.02	3.19	1.36	0.01	99.29	0.026	0.113	0.340
29	58.72	0.66	19.81	3.16	0.20	0.32	0.65	7.37	5.00	0.07	0.03	95.99	0.050	0.326	0.206
157-956A-															
5H-4, 92-94															
30	61.10	0.63	17.09	2.76	0.21	0.34	0.53	5.30	5.14	0.09	tr.	93.19	0.062	0.188	0.161
32	61.30	0.72	17.78	2.66	0.18	0.48	0.91	4.56	5.07	0.11	0.01	93.77	0.060	0.139	0.115
35	61.33	0.73	18.64	3.16	0.23	0.47	1.06	7.83	5.30	0.14	0.05	98.94	0.040	0.274	0.184
36	61.61	0.68	18.93	3.05	0.24	0.40	0.89	7.91	5.26	0.11	0.02	99.11	0.032	0.261	0.172
37	61.55	0.72	18.81	3.08	0.25	0.43	0.89	7.86	5.35	0.10	0.07	99.10	ND	ND	0.212
38	57.61	0.92	17.51	3.10	0.15	0.69	3.01	6.19	4.64	1.55	0.04	95.41	0.059	0.117	0.205
40	61.52	0.59	17.28	2.87	0.24	0.34	0.54	5.65	5.06	0.06	0.01	94.16	ND	ND	0.162
41	43.28	4.38	14.70	12.57	0.21	4.88	12.03	3.29	1.52	0.71	0.07	97.64	0.099	0.051	0.203
42a	42.69	4.42	14.86	12.79	0.17	4.94	12.09	3.26	1.51	0.73	0.06	97.52	0.096	0.059	0.229
42b	43.51	4.39	15.25	12.66	0.20	5.04	12.11	3.21	1.55	0.80	0.07	98.78	0.102	0.060	0.185
44	43.11	4.31	14.52	12.54	0.19	4.91	12.11	3.28	1.49	0.75	0.06	97.28	0.100	0.058	0.215
46	60.41	0.78	17.96	2.53	0.18	0.54	1.12	5.44	5.48	0.17	0.02	94.62	ND	ND	0.117
52	58.36	0.80	17.33	3.10	0.18	0.52	2.50	5.65	5.26	1.46	0.02	95.20	ND	ND	0.174
157-956A-															
6H-1, 4-5															
1	43.73	4.38	15.09	12.14	0.19	5.22	12.19	3.22	1.36	0.77	0.03	98.30	0.095	0.055	0.199
2	43.29	4.24	14.82	12.07	0.23	5.12	12.07	3.28	1.35	0.72	0.01	97.20	0.079	0.060	0.219
3	43.56	4.04	15.11	12.17	0.17	4.91	11.87	3.44	1.40	0.76	tr.	97.43	0.102	0.076	0.247
4	44.10	5.35	13.61	11.73	0.17	5.13	11.96	3.29	1.89	0.67	0.04	97.93	0.087	0.067	0.240
5	43.17	5.39	13.22	12.58	0.18	5.11	12.28	3.26	1.89	0.70	0.01	97.79	0.101	0.066	0.222
157-956A-															
7H-6, 58-60															
1	43.33	4.28	15.03	12.76	0.22	4.76	11.49	3.50	1.62	0.85	0.01	97.86	0.127	0.057	0.214
4	61.83	0.52	18.68	2.69	0.22	0.26	0.61	8.35	5.04	0.07	0.04	98.30	0.039	0.278	0.180
5-1	60.72	0.84	18.65	3.02	0.20	0.54	0.94	6.52	4.21	0.18	0.02	95.84	0.050	0.188	0.166
5-2	61.80	0.78	18.17	2.75	0.15	0.37	0.38	7.90	6.17	0.10	0.04	98.60	0.017	0.142	0.133
8	62.03	0.50	18.78	2.60	0.22	0.31	1.06	8.16	4.79	0.09	0.01	98.55	0.043	0.236	0.178
10	43.99	4.21	14.36	13.19	0.25	4.64	11.16	4.09	1.66	1.03	0.03	98.61	0.083	0.084	0.177
11	60.64	0.65	18.32	2.22	0.17	0.43	1.31	6.69	4.89	0.13	0.02	95.46	0.063	0.150	0.136
12	43.59	4.35	14.95	12.41	0.20	4.86	11.86	3.64	1.54	0.75	0.03	98.17	0.094	0.070	0.213

Notes: Numbers below the core, section, and interval = the numbers of the glass shards analyzed. ND = no data. All values are reported in weight percent.

in the MgO range between ≈5.3 and ≈1 wt%). Cl ranges from 0.01 to 0.33 wt% increasing with the increase of MgO in the melt (Fig. 3B). Although some glasses may have also been degassed with respect to Cl, this increase of Cl concentrations suggests that Cl mostly behaves as an incompatible element during magma crystallization (Fig. 3B). Sulfur and chlorine concentrations do not correlate between each other and show a large range of S/Cl ratios from 0.04 to 2.68 (Fig. 4A). The upper boundary of S concentrations measured in glass shards from Sites 953, 954, and 956 is similar to those found in Hawaiian and MORB submarine basaltic glasses (with a mean value of 0.11 ± 0.03 wt%; Johnson et al., 1994; Jambon, 1994, and references therein).

Our observations showed that strongly vesiculated glass shards are commonly characterized by lower S concentrations, whereas vesicle-free or poorly vesiculated shards are S-rich. We therefore suspect that vesiculated glass shards with low S concentrations represent products of explosive eruptions, either on land or in shallow water. Vesicle-free glass shards enriched in sulfur are likely to have resulted from submarine eruptions at moderate water depths (>500 m; e.g., Moore and Schilling, 1973; Sakai et al., 1982).

Chlorine is a volatile element, which is preferentially retained in the melt (e.g., Fisher and Schmincke, 1984, and references therein). On the other hand, for samples that are characterized by high S and low Cl concentrations, significant magma degassing during eruption is not expected. We thus suggest the following interpretation for the S and Cl data. First, glasses with relatively high S (>0.05 wt%) and Cl (>0.04 wt%) concentrations are believed to represent undegassed or slightly degassed magmas. Second, strongly vesiculated glasses that are characterized by low S and Cl concentrations, we interpret to be degassed. Third, glasses with low S concentrations and varying concentrations of Cl represent magmas that were probably subjected to continuous degassing, where the first degassing event was accompanied by the loss of sulfur followed by varying chlorine exsolution.

Fluorine

Concentrations of F are listed in Table 2 and presented in Figures 3C, 4B, and 4C. Sideromelane and felsic glasses are characterized by a wide spectrum of F concentrations ranging from 0.12 to 0.34 wt% F. Fluorine shows a weak correlation with MgO and Cl (Figs. 3C, 4B). On the basis of relationships between MgO and F concentrations, and F/K ratios ranging from 0.02 to 0.24, the mafic glasses are subdivided into two populations of high (F/K ≈0.15) and low (F/K between 0.03 and 0.05) F concentrations. Similarly to sulfur, fluorine does not correlate with chlorine (F/Cl ratio ranges from 0.47 to 12.6),

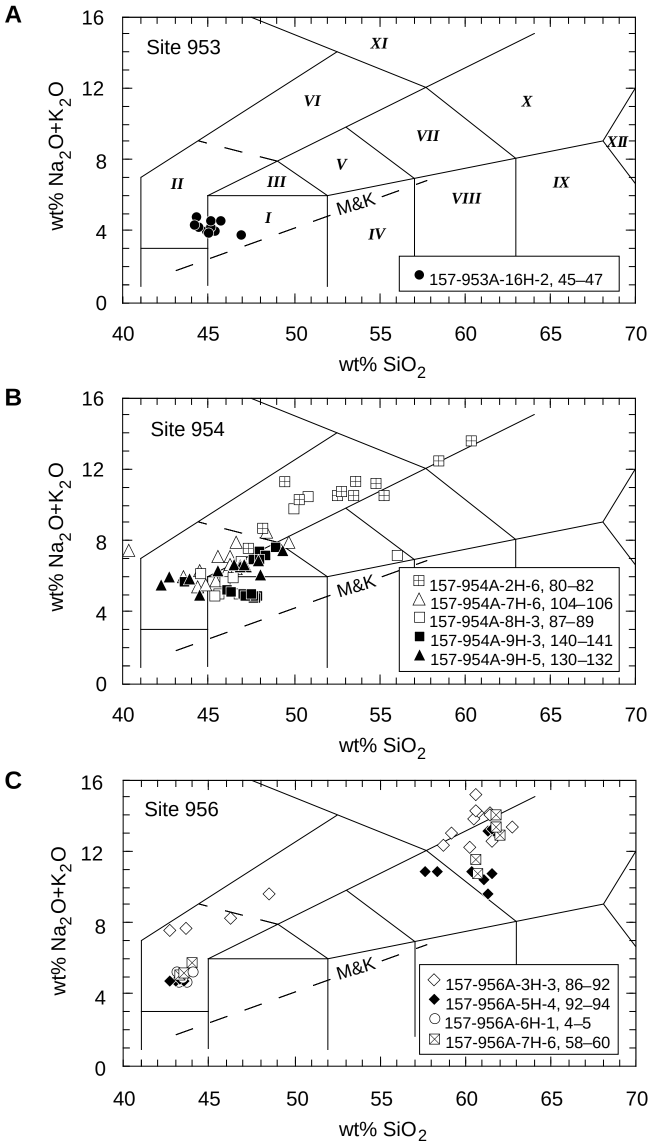

Figure 2. Classification of glass shards drilled at Holes 953A, 954A, and 956A in alkali-silica variation diagram after Le Maitre (1984) and Le Bas et al (1986). **A.** Hole 953A. **B.** Hole 954A. **C.** Hole 956A. Major groups of volcanic rocks are *I*= basalts, *II* = basanites and tephrites, *III* = hawaiites, *IV* = basaltic andesites, *V* = mugearites, *VI* = phonolitic tephrites, *VII* = benmoreites, *VIII* = andesites, *IX* = dacites, *X* = trachytes, *XI* = phonolites, and *XII* = rhyolites. Dividing line is after Macdonald and Katsura (1964).

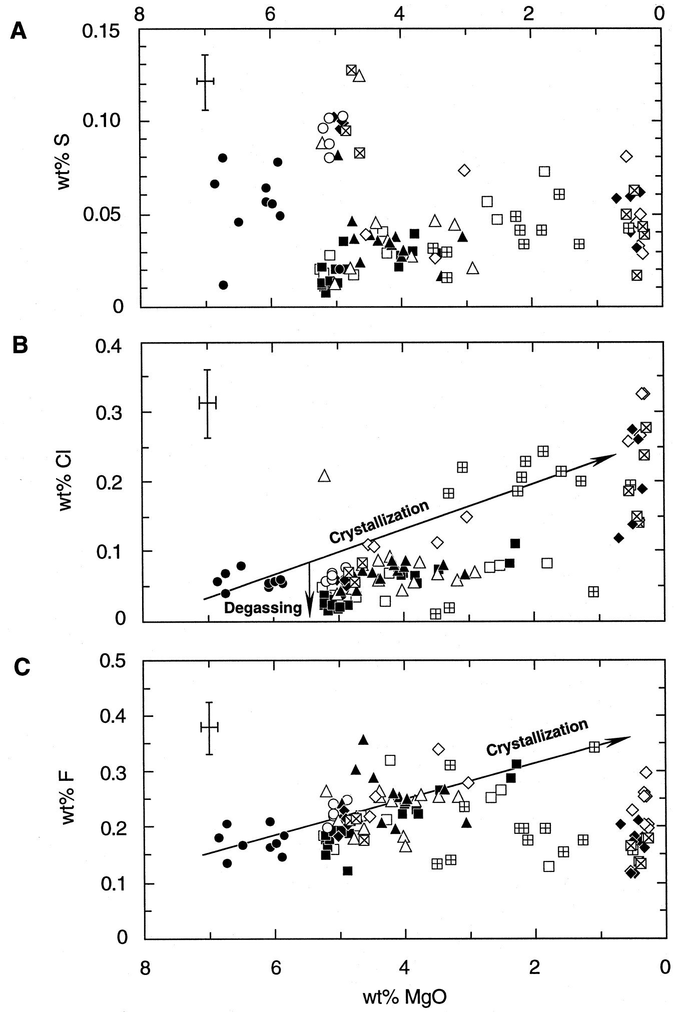

Figure 3. Concentrations of S, Cl, and F in sideromelane and felsic glass shards. **A.** S vs. MgO. **B.** Cl vs. MgO. **C.** F vs. MgO. Error bars represent standard deviation (2σ) analytical precision. For legend see Figure 2.

and the highest F concentrations were found in the glasses that have lost S and Cl, as for instance, Samples 157-954A-7H-6, 104–106 cm, 8H-3, 87–89 cm, and 9H-3, 140–141 cm (Fig. 4A, B).

The highest F concentrations occurred in the samples, which we postulate to have already degassed with respect to sulfur and chlorine (see above), allow us to suggest that the concentrations of F in the mafic glasses are likely to represent undegassed concentrations. Observed F/K ratios therefore reflect those of parental magmas and might be explained by heterogeneous mantle source.

SOURCE OF UNCONSOLIDATED GLASS-BEARING VOLCANICLASTIC SEDIMENTS FROM THE PLEISTOCENE SECTIONS

Although the evidence is strong that the felsic tephra layers younger than ~3 Ma at all three sites represent explosive eruptions of Teide Volcano on Tenerife (Rodehorst et al., Chap. 18, this volume), the correlation of mafic volcanic clasts with distinct volcanic phases on Gran Canaria or neighboring islands is less straightforward. Magmas presented by glass shards with high S concentrations (Samples 157-953A-16H-2, 45–47 cm; 157-954A-7H-6, 104–106 cm; 157-954A-9H-5, 130–132 cm; 157-956A-5H-4, 92–94 cm; 157-956A-6H-1, 4–5 cm; and 157-956A-7H-6, 58–60 cm) are likely to have erupted at moderate to deep water depths. Other lines of evidence indicate that the area northeast of Gran Canaria probably experienced submarine eruptions during the last 2–3 m.y. For one, all late Pliocene to Holocene volcanism took place in the northeastern half of Gran Canaria. The submarine morphology northeast of the island indicates the presence of at least three cones (T. Funck and H.-U. Schmincke, unpubl. data). We, thus, tentatively conclude that volca-

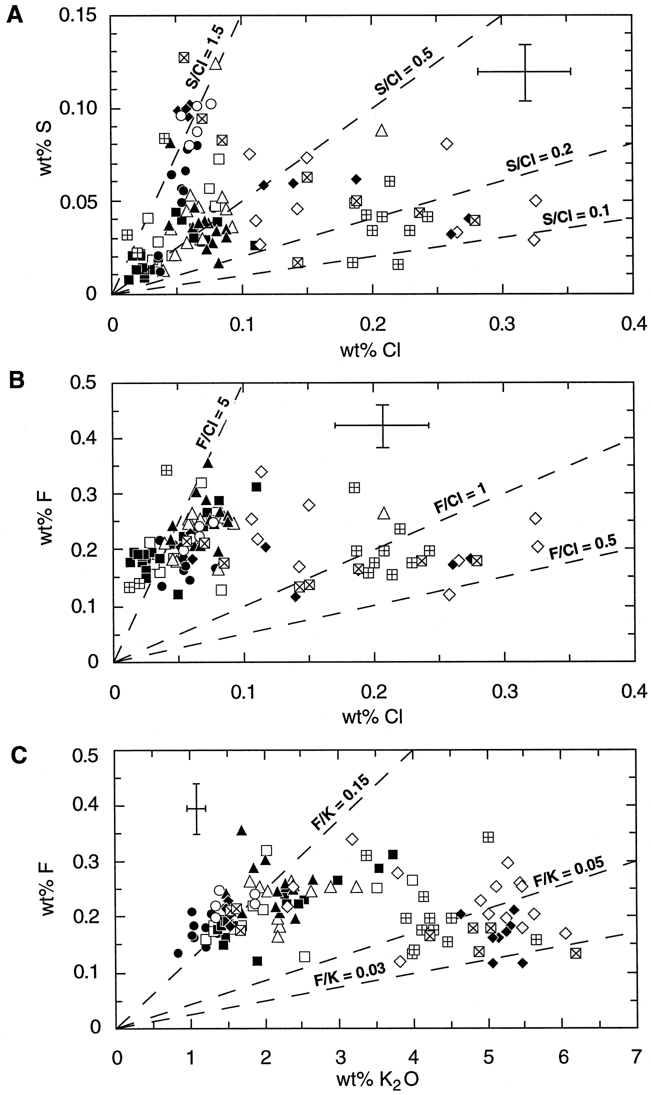

Figure 4. Variations of S and F vs. Cl and K_2O in sideromelane and felsic glass shards. **A.** S vs. Cl. **B.** F vs. Cl. **C.** F vs. K_2O. Error bars represent standard deviation (2σ) analytical precision. For legend, see Figure 2.

nism during late Pliocene/Pleistocene time in this part of the Canarian Archipelago was not restricted to the subaerial part of Gran Canaria but also took place below sea level. The submarine cone of Gran Canaria may have grown appreciably in a northeast direction during this time interval.

The mafic and felsic glass shards in the other samples with varying S and Cl concentrations are probably of diverse origin. Because many Pleistocene lava flows entered the sea both along the northeastern coast of Gran Canaria, as well as the eastern coast of Tenerife, spalled-off glassy flow margins should be ubiquitous. Shallow-water submarine explosive eruptions are equally likely as well, because young cones are observed on the submarine flanks of Tenerife (Schmincke and Rihm, 1994). We suggest, therefore, that glass shards in unconsolidated ashes from the Pleistocene sediments at Site 953 are mainly derived from Gran Canaria, probably from Gran Canaria and Tenerife at Site 954, whereas those at Site 956 were derived only from Tenerife, because no Pleistocene volcanism is known to have occurred in southwestern Gran Canaria.

CONCLUSIONS

1. Mafic volcanic glasses represent a spectrum from alkali basalt through basanite, hawaiite, mugearite, and tephrite, to nephelinite, whereas felsic glass shards have compositions similar to benmoreite, trachyte and phonolite.
2. Magmas represented by mafic and felsic glass shards were subjected to different degrees of degassing. Vesicle-free glasses that are characterized by high concentrations of S, are likely to represent undegassed or slightly degassed magma compositions. Strongly vesiculated glasses with low concentrations of S and Cl resulted from prolonged magma degassing. Glasses with low S concentrations and varying concentrations of Cl represent magmas, which probably were subjected to continuous degassing, while the loss of sulfur was followed by varying degrees of chlorine exsolution.
3. Glass shards at Sites 953 and 954 are believed to have resulted from volcanic activity on Gran Canaria and Tenerife, and those at Site 956 were derived from Tenerife.

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REFERENCES

Ancochea, E., Fúster, J.M., Ibarrola, E., Cendrero, A., Coello, J., Hernán, F., Cantagrel, J.M., and Jamond, C., 1990. Volcanic evolution of the island of Tenerife (Canary Islands) in the light of new K-Ar data. *J. Volcanol. Geotherm. Res.,* 44:231–249.

Carroll, M.R., and Webster, J.D., 1994. Solubilities of sulfur, noble gases, nitrogen, chlorine, and fluorine in magmas. *In* Carroll, M.R., and Holloway, J.R. (Eds.), *Volatiles in Magmas.* Rev. Mineral., Mineral. Soc. Am., 30:231–279.

Fisher, R.V., and Schmincke, H.-U., 1984. *Pyroclastic Rocks:* New York (Springer-Verlag).

Funck, T., 1996. Structure of the volcanic apron north of Gran Canaria deduced from reflection seismic, bathymetric and borehole data [Ph.D. dissert.]. Univ. Kiel.

Hoernle, K., and Schmincke, H.-U., 1993. The role of partial melting in the 15-Ma geochemical evolution of Gran Canaria: a blob model for the Canary Hotspot. *J. Petrol.,* 34:599–627.

Jambon, A., 1994. Earth degassing and large-scale geochemical cycling of volatile elements. *In* Carroll, M.R., and Holloway, J.R. (Eds.), *Volatiles in Magmas.* Rev. Mineral., Mineral. Soc. Am., 30:479–517.

Jarosewich, E., Nelen, J.A., and Norberg, J.A., 1980. Reference samples for electron microprobe analysis. *Geostand. Newsl.,* 4:43–47.

Johnson M.C., Anderson, A.T., Jr., and Rutherford, M.J., 1994. Pre-eruptive volatile contents of magmas. *In* Carroll, M.R., and Holloway, J.R. (Eds.), *Volatiles in Magmas.* Rev. Mineral., Mineral. Soc. Am., 30:281–330.

Lavrentev, Y.G., Pospelova, L.N., and Sobolev, A.V., 1974. Rock-forming mineral compositions determination by X-ray microanalysis. *Zavodsk. Lab.,* 40:657–666. (in Russian)

Le Bas, M.J., Le Maitre, R.W., Streckeisen, A., and Zanettin, B., 1986. A chemical classification of volcanic rocks based on the total alkali-silica diagram. *J. Petrol.,* 27:745–750.

Le Maitre, R., 1984. A proposal by the IUGS Subcommission on the Systematics of Igneous Rocks for a chemical classification of volcanic rocks based on the total alkali silica (TAS) diagram. *Austr. J. Earth Sci.,* 31:243–255.

Macdonald, G.A., and Katsura, T., 1964. Chemical composition of Hawaiian lavas. *J. Petrol.,* 5:82–133.

McMillan, P.F., 1994. Water solubility and speciation models. *In* Carroll, M.R., and Holloway, J.R. (Eds.), *Volatiles in Magmas.* Rev. Mineral., Mineral. Soc. Am., 30:131–156.

Moore, J.G., and Schilling, J.-G., 1973. Vesicles, water, and sulfur in Reykjanes Ridge basalts. *Contrib. Mineral. Petrol.,* 41:105–118.

Sakai, H., Casadevall, T.J., and Moore, J.G., 1982. Chemistry and isotope ratios of sulfur in basalts and volcanic gases at Kilauea volcano, Hawaii. *Geochim. Cosmochim. Acta,* 46:729–738.

Schmincke, H.-U., 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.

————, 1994. *Geological Field Guide: Gran Canaria* (7th ed.): Kiel, Germany (Pluto Press).

Schmincke, H.-U., and Rihm, R., 1994. Shipboard scientific party. *Report METEOR cruise,* M24.

Schmincke, H.-U., Weaver, P.P.E., Firth, J.V., et al., 1995. *Proc. ODP, Init. Repts.,* 157: College Station, TX (Ocean Drilling Program).

Shipboard Scientific Party, 1995a. Site 953. *In* Schmincke, H.-U., Weaver, P.P.E., Firth, J.V., et al., *Proc. ODP, Init. Repts.,* 157: College Station, TX (Ocean Drilling Program), 317–394.

————, 1995b. Site 954. *In* Schmincke, H.-U., Weaver, P.P.E., Firth, J.V., et al., *Proc. ODP, Init. Repts.,* 157: College Station, TX (Ocean Drilling Program), 395–431.

————, 1995c. Site 956. *In* Schmincke, H.-U., Weaver, P.P.E., Firth, J.V., et al., *Proc. ODP, Init. Repts.,* 157: College Station, TX (Ocean Drilling Program), 497–557.

Sobolev, A.V., and Chaussidon, M., 1996. H_2O concentrations in primary melts from supra-subduction zones and mid-ocean ridges: Implications for H_2O storage and recycling in the mantle. *Earth Planet. Sci. Lett.,* 137:45–55.

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