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The Petrochemistry of a Unique Cordierite-Bearing Lava from St. Helena Island, South Atlantic[1]

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Abstract

The dominant petrochemical evolution of St. Helena volcanics is from undersaturated alkali olivine basalt through nepheline normative trachybasalt and trachyandesite to trachyte and phonolite. A unique lava is described that shows extreme iron enrichment and internal fractionation towards a granitic mesostasis, and hence is quite unlike previously described volcanic rocks from this or any other Atlantic island. The unique chemistry is also reflected in the remarkable mineral assemblage andesine-titanomagnetite-ilmenite-ferrohypersthene-iron cordierite. Contamination is surmised to have played some role in the history of the lava, but the details of its evolution remain enigmatic.

Introduction

St. Helena is a volcanic island situated in the South Atlantic (5°40′W; 16°00′S), some 800 km east of the Mid-Atlantic Rise. Its geology and geochemistry have been described in detail by Baker (1968, 1969). Alkali olivine basalts (AOB) predominate, and are associated with trachybasalts, trachyandesites, trachytes and phonolites. Similar alkaline, undersaturated rock series have been described from Tenerife (Ridley, 1970), Gough Island (Le Maitre, 1962), Tristan da Cunha (Baker *et al*, 1964), Ascension Island (Daly, 1925), and, with the exception of Iceland, appear to be the characteristic type of subaerial assemblage of nearly all Atlantic islands. Fractional crystallization of undersaturated alkali olivine basalt has been considered the dominant process whereby the undersaturated, intermediate, and salic rocks are produced. Fractionation under constant or increasing P_{O_2} conditions is reflected in the steady decrease in CaO, MgO, total iron, TiO_2, and increase in alkalis and silica, from basic through intermediate to salic members.

An exceptional lava crops out on St. Helena, the chemistry and mineralogy of which are unrelated to the normal fractional descent of alkali olivine basalt magma. Major and trace element data indicate that the rock is substantially fractionated, not in the same direction as the undersaturated intermediate and salic rocks, but with iron content abnormally great. Further fractionation has occurred within the lava as it cooled, producing interstitial patches of 'granitic' composition.

Microprobe analyses of the main rock-forming minerals also reflect initial iron enrichment. Abundant titanomagnetite and ilmenite have crystallized along with andesine feldspar and ferrohypersthene, an iron-rich orthopyroxene. In addition, the rare igneous mineral iron-cordierite has also crystallized, and both tridymite and cristobalite have been identified by X-ray methods as mesostasis components.

We do not propose a name for the rock type; for convenience, and to avoid confusion in the text, we will refer to it as the FHIC lava (ferrohypersthene, iron-cordierite).

Field relations of the FHIC lava

The field relationships of this lava flow are slightly ambiguous because of its exposure in an area of more or less highly altered rocks and patchy vegetation. It is exposed in the headwaters of Thompson's Valley, in the extreme west of the island, and lies approxi-

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mately 500 m west of the cottages at Thompson's Wood, and the same distance east of Wild Cattle Pound, at an elevation of 525 m. The fresh part of the flow covers an area measuring a hundred or so meters by a few tens of meters, capping a flattish spur locally known as Rush Knoll. It has been extensively eroded and a maximum thickness of 2 m is preserved; remnants of the flow are largely vegetation covered. The flow, which is weakly jointed with broadly spaced vertical joints and horizontal partings, is fine-grained and non-vesicular; erosion has removed any surface features. Where exposed, the base rests on a fine (now altered) scoria horizon; no obvious scoriaceous base to the flow is seen, but the lack of a chilled margin, characteristic of intrusive rocks elsewhere on the island, supports its origin as a lava.

The related lavas at this locality are from the later stages of the Main Shield stage (Baker, 1969), and several hundred meters of AOB and trachybasaltic lavas would have been extruded on top of the flow. The thin ash horizon beneath the flow immediately overlies a small salic 'dome' subsequently intruded into the lava pile. The 'dome,' now largely altered (one fresh analysis shows it to be a phonolitic-trachyte), measures only approximately 250 m by 175 m. Like several other bodies of its shape and origin on St. Helena, the top few meters (topographic top) of the 'dome' are highly altered and vesicular, a feature which from field evidence appears to result from the upward migration of volatiles during cooling after emplacement. The weathering of the lava pile in which the FHIC flow occurs is widespread, and there is no evidence to indicate that the alteration of the lava sequence was brought about, or influenced, by the much later alkaline intrusion (the lava pile is approximately 10 m.y. old here, the intrusion approximately 7.5 m.y.—Baker, Gale, and Simons, 1967).

The specimens studied were collected from two sub-vertical traverses some 25 m apart; one set was partially weathered, displaying iron oxide veinlets, the other was perfectly fresh. All analyses were made on the fresh materials of the second traverse.

Major and trace element characteristics

Major element data of the FHIC lava sample SH239 are presented in Table 1, plus data for an AOB, a trachybasalt, and a trachyandesite (from Baker, 1969) for comparison. The FHIC lava is enriched in Al_2O_3, TiO_2, and total iron, but depleted in Na_2O and K_2O relative to the trachyandesite and the trachybasalt. These differences are such that 20 percent quartz, 9 percent corundum and 13 percent iron-titanium oxides appear in the norm. No other rock on St. Helena even remotely approaches this composition. Since the trachyandesite and trachybasalt are typical members of the AOB-phonolite suite, it is evident that a rather specialized process has been operative to produce the FHIC lava. The low MgO and CaO contents suggest that the FHIC lava is at least as differentiated as the regular trachybasalts and probably as differentiated as the trachyandesites (compare with Baker, 1969, Table 2). However, the high TiO_2, P_2O_5, and low total alkalis are not consistent with a highly fractionated lava.

The FHIC lava sample SH239 is enriched in rare-earth elements (R.E.E.-320 ppm) compared to a typical St. Helena alkali olivine basalt SH786 (200 ppm). Figure 1 indicates a marked fractionation of light relative to heavy R.E.E. in SH239, but no europium anomaly. This would be compatible with a

TABLE 1. Major Element Data and Normative Compositions of St. Helena Volcanic Rocks*

	SH786	SH780	SH239	SH613
SiO_2	45.03	50.09	50.9	54.09
Al_2O_3	14.60	16.09	20.45	17.38
TiO_2	3.36	2.34	3.48	0.80
Fe_2O_3	2.53	4.55	4.50	2.77
FeO	10.50	7.33	9.34	6.58
MnO	0.25	0.25	0.28	0.30
MgO	6.93	3.23	2.12	1.66
CaO	8.82	6.80	4.34	4.20
Na_2O	4.15	5.42	2.36	5.99
K_2O	1.60	1.82	0.53	2.90
P_2O_5	0.67	0.87	0.55	0.43
H_2O	1.73	1.19	0.90	2.87
Total	100.17	99.98	99.75	99.97
QZ	--	--	20.34	--
OR	9.46	10.71	3.13	17.14
AB	18.33	39.61	19.97	45.71
AN	16.49	14.20	18.30	11.97
NE	9.09	3.39	--	2.69
CO	--	--	9.29	--
OL	14.75	6.41	--	7.90
DI	18.73	11.36	--	5.14
HY	--	--	13.49	--
MT	3.67	6.60	6.52	4.02
IL	6.38	4.44	6.61	1.52

*Analyses of specimens SH786 (alkali olivine basalt), SH780 (trachybasalt), and SH613 (trachyandesite) are from Baker (1969). Specimen SH239 (FHIC lava) was analyzed in duplicate by K. V. Rodgers and also checked with unpublished data from Baker.

TABLE 2. Microprobe Analyses of Cordierite and Orthopyroxene*

	Cordierite	Ortho-pyroxene			
	Weight Percent Oxides		Structural Formulae$^+$		
SiO_2	45.46	46.14	Si	4.690	1.877
Al_2O_3	35.42	4.05	Al	4.306	0.194
TiO_2	--	0.42	Ti	--	0.013
FeO	11.84	38.95	Fe	1.022	1.325**
MnO	0.29	1.20	Mn	0.025	0.041
MgO	7.24	9.02	Mg	1.113	0.547**
CaO	--	0.38	Ca	--	0.017**
Total	100.25	100.16	Total Cations	11.156	4.014

*Analyses in Tables 2, 3, and Fig. 1 were carried out using an ARL-EMX microprobe. Corrections were made for background, drift, deadtime, and matrix effects using a combined EMX-MK5 computer program.
+Cordierite recalculated on basis of 18 oxygens, orthopyroxenes on basis of 6 oxygens
**Relative proportions of Ca, Fe, Mg, recalculated as Ca, 0.89; Fe, 70.16; Mg, 28.95.

moderate degree of pre-eruption fractionation not involving a large amount of plagioclase. The normalized R.E.E. pattern (Fig. 1) suggests that the FHIC lava is related to a parental magma itself enriched in rare earths and moderately fractionated in light rare earths. The normal (fine grained) AOB from St. Helena (SH786) shows an enrichment in rare earths and a fractionated pattern that would be compatible with such a parent magma. A Sr 87/86 ratio of 0.7029 for the FHIC lava is not significantly different from that obtained for SH786 (0.7028). Moreover, the Pb isotopic data (S. Church, personal communication) for the FHIC lava is compatible with the Pb systematics for other St. Helena volcanics (Oversby and Gast, 1970).

Mineralogy

The texture of the FHIC lava is best displayed in the freshest sample 239/5. Feldspar, the most abundant mineral, dominantly occurs as small laths and irregular interstitial patches. In some areas the laths impart a poorly developed fluidal texture to the rock, but overall the feldspar is randomly oriented. Titanomagnetite, although less abundant than feldspar, has crystallized extensively as small anhedral grains. It is commonly enclosed within early crystallized feldspar and also occurs as tiny interstitial grains, thus indicating a long and continuous period of crystallization. Ilmenite, although rare relative to titanomagnetite, is associated with titanomagnetite in composite grains. Ferrohypersthene occurs as small anhedral grains, discrete and in clusters, recognized by a pronounced pink to green pleochroism. Rarely, ferrohypersthene occurs as elongate, sub-poikilitic grains almost 1 mm in length. In slightly altered sections, the orthopyroxene may be partially altered to an unidentified brown mineral. Cordierite occurs as subhedral plates or anhedrally with interstitial feldspar. It has a distinct violet to colorless pleochroism, but often shows an extensive turbid alteration. Some patches, although having the same mineralogy, are distinctly coarser grained.

Pyroxene

No clinopyroxene has been observed in the FHIC lava. The composition and structural formula of the pale brown ferrohypersthene are shown in Table 2. The orthopyroxene structure of the mineral has been confirmed by single-crystal studies (H. Takeda, per-

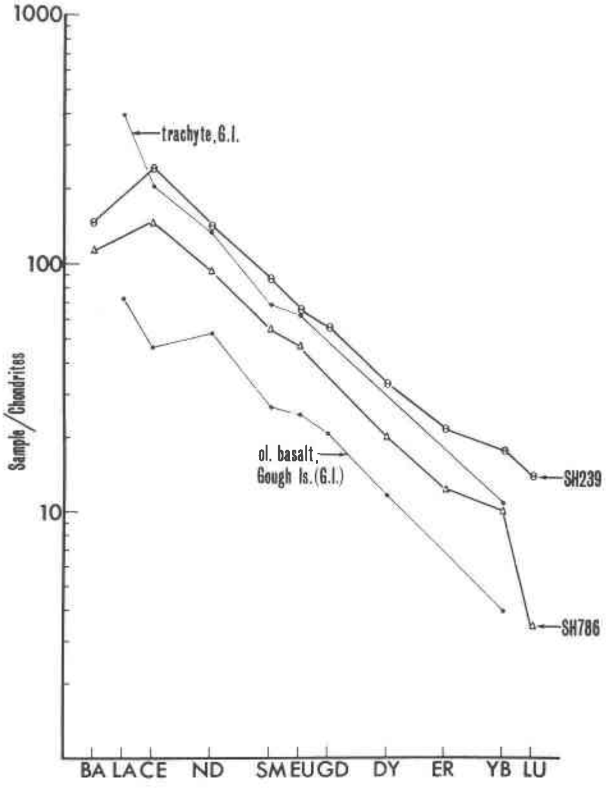

FIG. 1. Rare-earth element patterns, normalized to an average chondritic abundance, for the FHIC lava (SH239) and an alkali olivine basalt (SH786) from St. Helena. The rare earth elements were determined by isotope dilution mass spectrometry; W. I. Ridley, analyst. For comparison are plotted R.E.E. data for an olivine basalt and trachyte from Gough Island (Zielinski and Frey, 1970).

sonal communication). The aluminous nature of the pyroxene reflects the aluminous environment of crystallization. Iron-rich, low calcium orthopyroxenes of this type are rare in igneous rocks, although iron-rich clinopyroxenes crystallize from many types of fractionated magma. In undersaturated liquids, the clinopyroxene is a hedenbergite-acmite solid solution (Scott, 1970) reflecting the strongly alkaline environment. Iron-rich orthopyroxenes are unknown in alkaline, undersaturated rock series.

Ferrohypersthene has been described in dacites (Kuno, 1969), and ferropigeonites from acid pitchstones (Emeleus *et al,* 1971), but these pyroxenes invariably co-exist with an iron-rich olivine ± calcium-rich clinopyroxene. The presence of iron-rich, low-calcium pyroxenes in volcanics that are strongly quartz-normative is consistent with the crystallization of ferrohypersthene from the FHIC lava, when it is remembered that silica phases have been identified in this rock. Thus, a high silica activity, approaching unity in the final stages of consolidation, would promote the crystallization of iron-rich orthopyroxene rather than olivine.

Iron-titanium oxides

Titanomagnetite is more abundant than ilmenite. Composite ilmenite-titanomagnetite grains are common; oxidation exsolution is rarely observed. Eight analyses of composite grains are given in Table 3, the analyses being taken near to the ilmenite-titanomagnetite boundaries. These analyses give an estimate of the oxygen partial pressure (P_{O_2}) and temperature (T) for the final equilibration of ilmenite-titanomagnetite pairs. Different oxide pairs give different $P_{O_2} - T$ values, ranging from 800°C at log $P_{O_2} = -15.5$ bars, and 705°C at log $P_{O_2} = -19.1$ bars. Since individual oxide pairs cannot be unequivocally placed in a paragenetic sequence, the significance, if any, of the range of $P_{O_2} - T$ values is uncertain. However, the highest temperature value (800°C) is substantially lower than the liquidus temperature (850–860°C, assuming $P_{H_2O} = 1000$ kg/cm^2) estimated by Baker (1969) from the curves of Hamilton and MacKenzie (1965) for the phonolitic trachyte underlying the FHIC lava. It therefore seems unlikely that the estimated $P_{O_2} - T$ conditions for the FHIC lava approach the liquidus value, but they may reflect equilibration of oxide pairs at a variety of sub-liquidus temperatures.

TABLE 3. Microprobe Analyses of Co-Existing Ilmenite-Titanomagnetite Pairs*

	Ilmenites				Titanomagnetites			
	1	2	3	4	1	2	3	4
FeO	45.85	45.73	45.99	45.71	71.08	70.01	69.67	69.09
TiO_2	51.12	50.72	52.30	52.26	18.21	18.22	18.96	20.65
MgO	1.00	0.67	0.96	1.01	0.55	0.36	1.41	0.63
Al_2O_3	0.40	0.39	0.44	0.41	5.35	5.75	5.78	5.69
MnO	0.89	0.83	0.82	0.81	0.68	0.66	0.66	0.68
	FeO recalculated as ilmenite				FeO recalculated as ulvospinel			
FeO	43.29	43.58	44.49	44.37	45.90	46.22	44.52	48.12
Fe_2O_3	2.85	2.39	1.67	1.48	27.98	26.44	27.95	23.31
Total	99.55	98.58	100.68	100.35	98.67	97.65	99.28	99.07
	Mole % ilmenite				Mole % ulvospinel			
	96.51	96.99	97.67	97.89	53.88	55.89	52.44	61.51
					FeO recalculated as ilmenite			
FeO					33.63	33.51	32.60	34.32
Fe_2O_3					41.62	40.56	41.20	38.64
Total					100.04	99.06	100.61	100.61
T°C					800	780	725	705
log PO_2					-15.5	-16.1	-18.1	-19.1

*Analyzed pairs are homogeneous grains in contact.

The $P_{O_2} - T$ curve is slightly below but parallel to the quartz-fayalite-magnetite buffer curve. This is consistent with the mineralogy [tridymite, Fe orthopyroxene, titanomagnetite] observed in the rock, assuming some displacement of the curve due to the aluminum substitution in the oxide and pyroxene phases.

Cordierite

This mineral occurs as pleochroic crystals showing no reaction with the surrounding minerals. The analysis (Table 2) indicates it is an iron-rich variety, consistent with the iron-rich nature of the rock, and implies a primary rather than xenocrystal origin.

Miyashiro (1957) in a study of cordierite-indialite relations examined only a few iron-rich cordierites, all apparently from pegmatites and characterized by very low distortional indices (Δ). The cordierite examined here has Δ = 0.29 (M. Bass, personal communication) and hence is a high perdistortional type according to the nomenclature of Miyashiro (1957). This value is similar to those for cordierite in xenoliths in a Japanese andesite (Δ = 0.30) but exceeds those for the porphyritic cordierites in andesite at Kasyo-to (Δ = 0.25; Miyashiro, 1957). The chemical composition of these latter cordierites is unknown, but it is evident that the high Δ value for the FHIC cordierite is in keeping with its relatively high temperature, volcanic environment.

Feldspar and mesostasis

Small laths of plagioclase, the principal mineral in the FHIC lava, produce a sub-trachytic texture. Microprobe analyses (Fig. 2) show that most laths have calcic andesine cores ($An_{48}Ab_{49}Or_3$) and are regularly zoned to sodic andesine rims ($An_{32}Ab_{60}Or_8$). In many cases the laths grade outwards into irregular interstitial patches of feldspar, which also have sodic andesine compositions. Figure 2 illustrates the range in feldspar compositions observed in laths and interstitial plagioclase patches.

The plagioclase cores are more sodic than the liquidus feldspar, crystallized from St. Helena alkali olivine basalts, that was optically determined to be An_{74} composition (Baker, 1969). The liquidus plagioclase in trachybasaltic compositions is also more calcic (An_{66}, *op. cit.*) than the FHIC lava, although within the trachybasalts zoning of plagioclase to An_{30} has been observed. Hence the plagioclase data suggest that although the FHIC lava is chemically distinct from any member of the AOB-phonolite series, it is about as fractionated as the trachybasalt-trachyandesite stage of that series.

Electron microprobe X-ray scanning images indicate that although feldspar is the major interstitial mineral, there are rare interstitial regions rich in Si, K and low in Ca, Fe, Mg, Ti. In addition, X-ray diffraction powder patterns indicate the rock to contain both tridymite and cristobalite, and since neither of these minerals has been identified optically, it has been assumed that they form part of a granitic mesostasis. Electron microprobe analyses of mesostasis areas for Ca, Na, K show them to be extremely variable in composition, as shown in Figure 2, defining an unusual trend through the ternary feldspar system towards the composition of K-feldspar.

Phase relations in the system Ab-An-Or-Qz (Carmichael, 1963) deny that the trend in Figure 2 represents a liquid line of descent, since the intervention of the two-feldspar phase boundary effectively prohibits continuous potash-enrichment in the liquid. It is therefore assumed that the high potassium analyses (probably all those analyses with >55 mole percent Or) represent mesostasis areas rich in potassium feldspar. However, it is also possible that those mesostasis areas with <55 mole percent Or represent 'frozen' stages in the fractionation of the residual liquid. Such a trend could reach fairly potassic regions because of the relatively high Ca content of the magma, with tridymite and cristobalite finally precipitating at the quartz-feldspar boundary.

Within the FHIC lava, extreme internal fractionation towards a potassic granite composition results ultimately in the precipitation of a silica phase and orthoclase. This fractionation is in marked contrast to the trend of crystallization in the AOB series, in which the salic rocks are invariably strongly undersaturated.

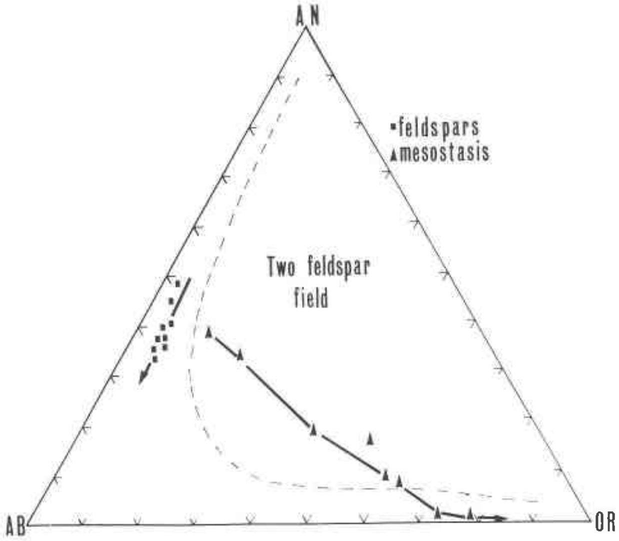

FIG. 2. Microprobe analyses of plagioclases (filled squares) and interstitial "granitic" material (filled triangles), after recalculation of the analyses into normative albite (AB), anorthite (AN), and orthoclase (OR). The limit of ternary solid solution in feldspars is taken from Carmichael (1963).

Discussion

Two distinct fractionation trends are required to produce the FHIC lava. The pre-eruptive history, surmised largely from the whole rock chemical data, must have involved a decrease in CaO, MgO, Na_2O, K_2O and an increase in Al_2O_3, total Fe, and possibly TiO_2. These variations are considered in relation to the 'normal' St. Helena AOB phonolite series, and they clearly indicate very different pre-eruptive conditions.

Extensive post-eruptive fractionation within the lava is also evident. Eruption apparently terminated the iron-enrichment trend, for the final residuum has a 'granitic' composition, as a result of the eventual precipitation of a silica phase, although the Fe-Ti oxide data suggest continuously decreasing P_{O_2} during cooling. This in turn could be brought about by the silicate system being strongly internally buffered by the precipitating phases.

Two sets of conditions, pre- and post-eruptive, thus set this lava apart from the remainder of the St. Helena volcanic sequence. The post-eruptive conditions are unusual but explicable, but the pre-eruptive conditions are inexplicable. Assuming that the magma was in the general position of the most alkaline trachybasalts in the St. Helena fractionation series (based on silica, R.E.E., P_2O_5 values and feldspar compositions), one must account for the very low alkalis, low CaO and MgO, high iron and titania and very high Al_2O_3. However, the oceanic setting of St. Helena rules out sialic crustal contamination, and the Pb isotopic data effectively eliminates oceanic sediment involvement.

Much of the surface of the St. Helena volcanic pile is at present highly altered. The intensity of this alteration is variable and field evidence suggests that it results from a combination of sub-aerial weathering and (probably less important) hydrothermal activity. Alteration extends a few tens of meters below the surface. Alteration takes the form of *in situ* breakdown of lavas and pyroclastics alike into clay-rich assemblages; segregation veins, pods and stringers of halloysite ($Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$) occur in intensely altered areas (R. M. Davis, personal communication). The altered volcanics, which are laterite-type residues, are therefore rich in alumina, H_2O, and probably iron, and may be enriched in TiO_2 relative to their parental rocks. The overall silica value is unknown, but is probably lower than that of the parent (see Rankama and Sahama, 1960, p. 209). As a contaminant these materials could be used to explain a number of features of the FHIC whole rock chemistry. As part of the young volcanic sequence, they would have little or no effect on the low Sr 87/86 ratio of the lava. They could easily account for the high Al_2O_3, total iron, and probably the TiO_2 values; the SiO_2 content may be unaffected or slightly reduced. One is also faced with the problem of how the altered materials could have come into contact with the melt and what mechanism allowed such thorough mixing to produce a perfectly 'normal' looking lava flow with such unusual chemistry.

The origin of the FHIC lava remains an enigma. Its unique chemistry and mineralogy, compared to the 'normal' St. Helena volcanics, and its small volume indicate local, highly specialized conditions that may involve some degree of contamination. However, the isotopic evidence restricts the contaminant to materials within the volcanic pile and effectively rules out local oceanic sediment as a possible source of contamination.

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