

Post-eruptive alteration of silicic ignimbrites and lavas, Gran Canaria, Canary Islands: Strontium, neodymium, lead, and oxygen isotopic evidence

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Abstract—Isotopic analyses of Miocene comenditic, pantelleritic, and trachyphonolitic ignimbrites and lavas from Gran Canaria, Canary Islands, provide evidence for post-eruptive mobility of Rb, Sr, and O. Calculated initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in whole-rock samples from basaltic lavas and feldspar mineral separates from ignimbrites define a magmatic trend in the stratigraphic section, from ratios of 0.70340 at the base of the Mogan Formation to 0.70305 in the lower Fataga Formation. However, calculated apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in hydrated vitrophyre and devitrified matrix separates range from 0.7035 to 0.7090. $\delta^{18}\text{O}$ ratios in basalts and feldspars vary little, from +5.7 to +6.1, yet range from +6.5 to +15.0 in the ignimbrite matrices. In contrast to the Sr and O isotope ratios, Pb and Nd isotope ratios are identical within analytical error in feldspars and their silicic ignimbrite matrices. Sequential leaching experiments and the oxygen data suggest that low-temperature, post-eruptive interaction with meteoric water, perhaps containing a small seawater component, has modified Rb and Sr concentrations in the matrices, such that calculated apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are not those of the magmas when they were erupted. Mobilization of Rb and Sr must occur significantly after eruption. Nd and Pb isotope systems appear to be unaffected by this process. Therefore, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios determined by whole rock analysis of silicic rocks from hotspot-type oceanic islands are suspect and should not be incorporated into mantle tracer studies, although analysis of phenocrysts may produce useful data.

INTRODUCTION

THE ISOTOPIC COMPOSITION of lavas from oceanic islands provides important information about the composition and evolution of the Earth's mantle (e.g., ZINDLER and HART, 1986). It is critical to establish that the isotope ratios measured in the lavas are representative of their source. This requirement is especially relevant in studies of silicic lavas on oceanic islands. Most petrologic studies have concluded that the silicic rocks evolved by multi-stage fractional crystallization from parental basaltic magmas (ZIELINSKI and FREY, 1970; HARRIS, 1983; LE ROEX, 1985; HOERNLE, 1987, 1990; COUSENS et al., 1990), a process which does not affect isotope ratios in the residual liquid except in rare cases where Rb/Sr ratios evolve to extraordinarily high values (MC CARTHY and CAWTHORN, 1980; SOUTHER and HICKSON, 1984; HALLIDAY et al., 1989). Yet, silicic lavas often have significantly higher calculated initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{in}}$) than enclosed feldspar phenocrysts or closely associated basaltic lavas (Fig. 1), whereas initial Nd and Pb isotopic ratios in the silicic and basaltic lavas are similar (see Fig. 1 for references). Suggested causes of ^{87}Sr isotopic enrichment in silicic magmas on oceanic islands include post-crystallization seawater contamination (DUPRÉ et al., 1982), seawater contamination of magmas in magma chambers (WEST and LEEMAN, 1987) or within feeder dikes (PALACZ and WOLFF, 1988), post-emplacement hydrothermal alteration by meteoric water mixed

with seawater (GRANT et al., 1976), or incorporation of altered oceanic crust or submarine shield by differentiated magma (WEIS et al., 1987).

Silicic ignimbrites on Gran Canaria exhibit Sr and oxygen isotopic disequilibrium between feldspar (anorthoclase) phenocrysts and their matrices. In contrast to Sr and O, initial $^{143}\text{Nd}/^{144}\text{Nd}$ and Pb isotope ratios are similar in feldspar phenocrysts, matrices, and intercalated basaltic lavas. The isotopic data, combined with acid leaching experiments on ignimbrite matrix separates, indicate that the glassy matrices of the ignimbrites have been altered at low temperature by meteoric waters after emplacement. Rubidium and strontium mobility and exchange during alteration has modified the original magmatic Rb/Sr ratios in the matrices such that it is not possible to correctly calculate $^{87}\text{Sr}/^{86}\text{Sr}_{\text{in}}$ in the matrices.

GEOLOGIC SETTING

Gran Canaria, amongst the best studied of hotspot-type oceanic islands, is remarkable for its relatively large volume of silicic ignimbrites and their excellent exposure (summarized in SCHMINCKE 1976, 1987). The bulk of the island edifice is composed of basaltic rocks of the Guigui and Hogarzales formations, 14.1 Ma in age and older. The overlying evolved rocks studied here are the extracaldera facies of the Mogan and Fataga formations, which erupted from a shallow magma reservoir (6–12 km) that was periodically replenished by basaltic magmas (CRISP and SPERA, 1987). The Mogan Formation consists largely of trachytic to pantelleritic lava flows and ignimbrites, erupted between 14.2 and 13.4 Ma (MCDUGALL and SCHMINCKE, 1976; VAN DEN BOGAARD et al., 1988; CLARK and SPERA, 1990), and includes four basalt lava flows in its lower part. The ignimbrites become increasingly peralkaline with height in stratigraphic section. The overlying Fataga Formation consists of trachyphonolitic ignimbrites and lava flows, including one basalt flow near its base. The

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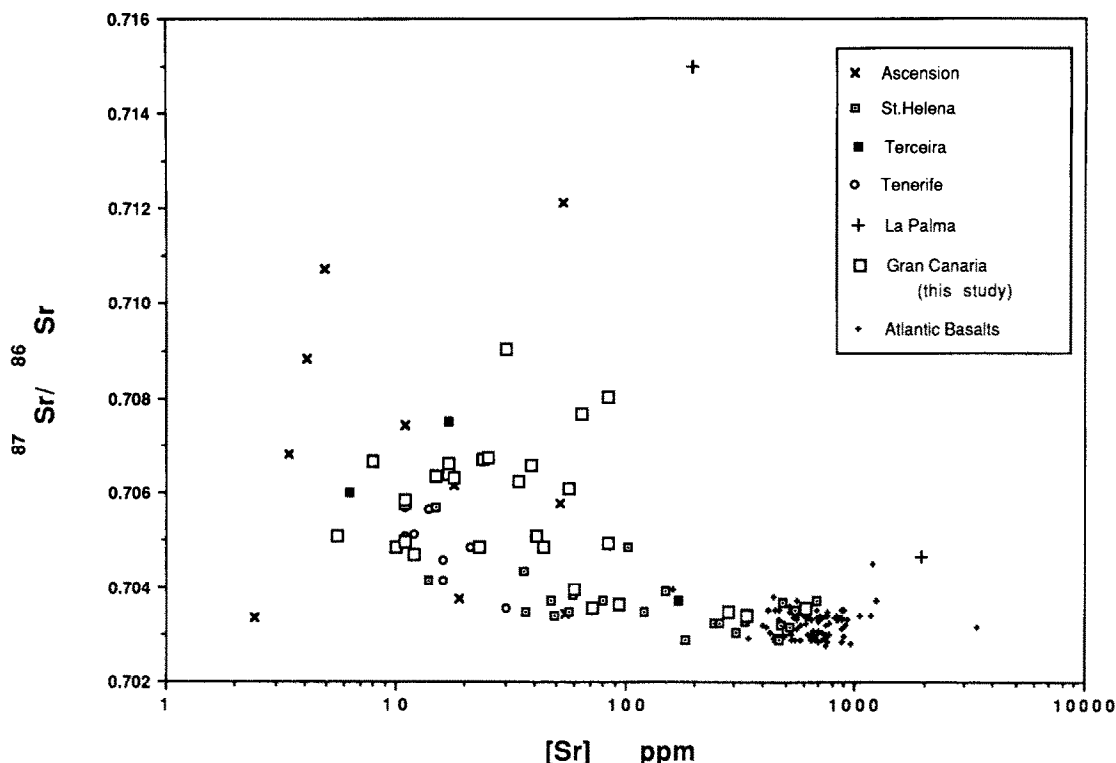


FIG. 1. Age-corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vs. Sr concentration in silicic rocks from several Atlantic oceanic islands. Basalts from these islands are grouped and shown as small plus symbols. Samples with less than 100 ppm Sr have variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, up to 0.7140. Sources: DUPRÉ et al., 1982; GAST et al., 1964; GRANT et al., 1976; MENDES and VIALETTE, 1974; O'NIONS et al., 1977; PALACZ and WOLFF, 1988; WEIS et al., 1987.

Fataga Formation volcanic rocks are intruded by late stage syncline bodies and a cone sheet swarm, referred to as the Tejada Formation (SCHMINCKE, 1976). The oldest extracaldera Fataga ignimbrite has been dated at 12.9 ± 0.3 Ma, whereas the youngest Tejada intrusion is 8.6 ± 0.1 Ma in age (McDOUGALL and SCHMINCKE, 1976). This Miocene phase of volcanic activity was followed by separate Pliocene and Quaternary Recent phases of dominantly basaltic volcanism (McDOUGALL and SCHMINCKE, 1976; HOERNLE, 1990).

SAMPLE DESCRIPTIONS

Most of the ignimbrite samples analysed during this study were collected by J. Crisp and FJS (CRISP, 1984), supplemented by sampling (BLC) in 1989. Due to the highly welded nature of these ignimbrites, analyses were performed on whole-rock samples rather than separated fiamme. To minimize the effects of vapour-phase alteration, samples were chosen from basal vitrophyres or from the lowermost three metres of each flow. One ignimbrite, Unit E, was sampled vertically at one locality to ascertain the isotopic homogeneity of the matrix of a single flow. Petrographically, there is no clear evidence for extensive vapour-phase alteration or post-depositional alteration in any of the samples analysed in this study. Hand specimens of Mogan and Fataga Formation basal vitrophyres were selected based on fresh appearance. In thin-section, the samples often have perlitic cracks due to hydration ($\text{H}_2\text{O}^+ = 1-5\%$). Basal samples with eutaxitic textures have variably devitrified fiamme and matrices. The whole-rock major- and trace-element composition of the samples analysed for isotopic compositions are discussed by CRISP (1984), COUSENS (1990), and COUSENS et al. (1990); mineral chemistry data are presented in CRISP and SPERA (1987); and isotopic data from basalts and feldspar separates are presented in COUSENS et al. (1990).

ANALYTICAL PROCEDURES

Between 50 and 100 grams of each ignimbrite were crushed by hand in a steel mortar and pestle. Anorthoclase feldspar phenocrysts

and matrix were separated using a Frantz isodynamic separator, and only the matrix material in the 0.18 to 0.71 mm size fraction was retained. The matrix separates were hand-picked to remove lithic fragments, small phenocrysts, and altered matrix, leaving only hydrated glass or variably devitrified, eutaxitic matrix. The processed matrix material contained less than 1% of phenocryst phases such as anorthoclase, clinopyroxene, amphibole, and trace amounts of apatite and Fe-Ti oxides (CRISP and SPERA, 1987). Matrix separates were then washed in distilled water in an ultrasonic bath. For radiogenic isotopes, approximately 100 mg of matrix separate (or whole-rock powder for the trachyphonolitic lavas) were dissolved in HF-HClO_4 , then split in half to determine isotope ratios and elemental concentrations separately. Concentrations were determined by isotope dilution mass spectrometry (precision 0.5–1%), using ^{208}Pb – ^{235}U – ^{230}Th , ^{87}Rb – ^{84}Sr , and ^{150}Nd – ^{149}Sm spikes. Blanks for Sr, Nd, and Pb are 0.3, <1.0, and 0.3 nanograms, respectively, which are negligible. Samples were analysed on the UCSB Finnigan MAT 261 multicollector mass spectrometer running in the static mode. Rb, Sr, and Pb were run using single Re filaments, whereas Nd, Sm, U, and Th were determined using a double Re filament technique. A $\sim 0.1\%$ /mass unit Pb fractionation factor was applied to all samples, using NBS 981 as a standard (TODT et al., 1984). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are normalized within-run to $^{86}\text{Sr}/^{88}\text{Sr} = 0.11940$, and the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio obtained for NBS 987 was 0.71021 ± 1 (2-sigma, eight analyses). All $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reported in Table 1 have been adjusted by +0.00004, to be directly comparable to $^{87}\text{Sr}/^{86}\text{Sr}$ data for feldspars reported by COUSENS et al. (1990) where the average obtained for NBS 987 was 0.71025. $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are normalized within-run to $^{146}\text{Nd}/^{144}\text{Nd} = 0.72190$. The average value measured for the La Jolla standard was 0.51185 ± 2 (2-sigma, 7 analyses). Initial (age-corrected) isotopic ratios were calculated using $^{39}\text{Ar}/^{40}\text{Ar}$ ages from VAN DEN BOGAARD et al. (1988) and CLARK and SPERA (1990). For oxygen isotope measurements, oxygen was liberated from the samples by reaction with BrF_3 at 600°C (using a procedure modified from CLAYTON and MAYEDA, 1963), and converted to CO_2 for isotopic analysis on a Finnigan MAT 251 mass spectrometer at Unocal Science

Table 1. Trace Element and Isotopic Compositions of Ignimbrite Matrices and Lavas.

Unit	Sample	Type	Age	[Rb]	[Sr]	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}_m$	2 SD _m	$^{87}\text{Sr}/^{86}\text{Sr}_{ai}$	2 SD _{ai}	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$
FATAGA														
O*	91 GL	DT	12.9	123.0	10.8	32.76	0.71203	2	0.70603	32	0.51291	39.65	15.60	19.85
N	81 GL	DT	12.9	129.4	33.9	11.02	0.70832	2	0.70631	14	0.51289	39.67	15.60	19.88
L2	H14 WR	TL	12.9	135.8	41.1	9.55	0.70693	3	0.70518	11	0.51293	39.37	15.59	19.69
K	13H GL	DT	12.9	113.0	64.4	5.08	0.70861	2	0.70768	7	0.51290	39.64	15.60	19.87
J	12H GL	DT	12.9	90.8	16.9	15.50	0.70934	2	0.70651	12	0.51289	39.54	15.59	19.80
I	15J GL	HV	12.9	91.0	24.9	10.58	0.70873	2	0.70679	14	0.51290	39.65	15.59	19.92
I	8H GL	DT	12.9	156.3	16.8	26.98	0.71178	2	0.70685	27	0.51291	39.65	15.60	19.88
H	18J GL	DT	12.9	95.6	39.4	7.03	0.70789	1	0.70660	7	0.51291	39.58	15.60	19.82
G	3H WR	DT	12.9	82.4	84.0	2.84	0.70527	1	0.70475	4	0.51289	-	-	-
T6	685 WR	BL	11.8	*31	*3387	0.03	0.70308	2	0.70308	2	0.51291	39.59	15.59	19.87
L1	5H WR	TL	12.9	115.0	85.1	3.91	0.70878	3	0.70806	6	0.51289	39.32	15.58	19.61
MOGAN														
F up	17J GL	HV	13.4	111.1	71.9	4.47	0.70438	1	0.70353	4	0.51291	39.52	15.61	19.67
F mid	16J GL	HV	13.4	56.0	44.3	3.66	0.70548	2	0.70479	3	0.51291	39.39	15.60	19.69
F low	79 GL	DT	13.4	91.9	17.7	15.05	0.70915	2	0.70629	11	0.51289	39.43	15.61	19.67
ET	V18 GL	DT	13.4	97.6	7.85	36.00	0.71301	1	0.70616	16	0.51290	39.39	15.60	19.69
E	O6 GL	HV	13.4	167.2	23.6	20.55	0.71075	2	0.70684	10	0.51289	39.43	15.61	19.68
D	153 GL	DT	13.6	53.1	9.7	15.69	0.70806	2	0.70499	10	0.51290	39.41	15.60	19.71
C	13G GL	HV	13.8	110.1	30.3	10.53	0.71110	2	0.70903	9	0.51289	39.33	15.59	19.61
B	V14 GL	HV	13.9	33.5	5.4	17.98	0.70930	1	0.70575	9	0.51289	39.14	15.58	19.44
A	10D GL	HV	14.0	77.2	59.9	3.73	0.70466	2	0.70395	4	0.51289	39.18	15.59	19.45
T4	I1 WR	BL	14.0	42.1	*25	876.5	0.70337	2	0.70333	2	0.51289	38.84	15.57	19.09
T4	619 WR	BL	14.0	*25	*925	0.08	0.70334	2	0.70333	2	-	39.43	15.60	19.70
O	4G GL	HV	14.0	114.5	5.5	60.16	0.71709	2	0.70485	24	0.51291	39.33	15.59	19.64
O	T1 GL	DT	14.0	62.9	23.5	7.75	0.70646	1	0.70491	5	0.51290	39.29	15.59	19.61
X	5D GL	DT	14.0	170.1	14.8	33.18	0.71297	2	0.70612	4	0.51291	39.33	15.59	19.62
TL	C2 GL	HV	14.0	89.6	10.9	23.70	0.70978	1	0.70507	10	0.51290	39.38	15.61	19.58
P2	W6 GL	DT	14.0	69.0	335.5	0.60	0.70356	1	0.70346	2	0.51291	39.21	15.59	19.49
V1	V1 GL	HV	14.1	130.0	11.8	31.89	0.71098	2	0.70459	18	0.51295	39.22	15.59	19.47
U	10B GL	HV	14.1	147.3	280.7	1.52	0.70374	1	0.70344	3	0.51292	38.98	15.45	19.35
R	695 WR	BL	14.1	*85	*828	0.30	0.70347	2	0.70341	2	0.51292	39.24	15.58	19.54
R	20 GL	HV	14.1	65.7	609.7	0.31	0.70356	2	0.70351	2	0.51295	39.26	15.58	19.53
T1	J9 WR	BL	14.1	15.3	872.3	0.05	0.70333	2	0.70332	2	0.51289	39.23	15.59	19.50
P1	K8 GL	HV	14.1	126.7	94.2	3.89	0.70440	1	0.70363	3	0.51293	39.17	15.58	19.52
UNIT ESECCION														
E	646 GL	DT	13.4	127.7	8.4	44.01	0.71424	3	0.70587	23	-	39.45	15.61	19.74
E	644 GL	DT	13.4	113.8	4.68	70.37	0.71526	2	0.70187	11	-	-	-	-
E	642 GL	DT	13.4	125.8	11.3	32.36	0.71230	4	0.70619	19	-	-	-	-
E	641 GL	DT	13.4	118.8	11.0	31.35	0.71258	2	0.70662	18	-	39.46	15.60	19.75
E	639 GL	DT	13.4	128.5	7.05	52.75	0.71324	3	0.70320	24	-	39.37	15.60	19.72
E	637 GL	DT	13.4	67.5	2.58	75.30	0.71353	3	0.69913	31	-	-	-	-
E	635 GL	DT	13.4	121.3	10.9	32.06	0.71193	3	0.70579	16	-	39.44	15.60	19.75
E	633 GL	DT	13.4	67.7	9.3	21.13	0.70907	3	0.70505	11	-	39.43	15.60	19.66
E	631 GL	DT	13.4	80.4	7.7	30.24	0.71064	2	0.70488	19	-	39.50	15.63	19.70
E	629 GL	HV	13.4	83.6	10.5	23.08	0.70874	2	0.70435	40	-	39.43	15.60	19.71

NOTES: Sample types: GL = matrix separate, WR = whole-rock, HV = hydrated vitrophyre, DT = devitrified tuff, BL = basaltic lava, TL = trachyphonolitic lava. * indicates no data collected. Rb and Sr analysed by isotope dilution or XRF (%), concentrations in ppm. Ages are interpolated from McDougall and Schmincke (1976), van den Bogaard et al. (1988), and Clark and Spera (1990). For $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, m = measured, ai = apparent initial. 2-sigma uncertainties for Sr isotope ratios (2 SD) are in parts per 10⁵. 2-sigma uncertainties for $^{143}\text{Nd}/^{144}\text{Nd}$ = ± 0.00002 , $^{208}\text{Pb}/^{204}\text{Pb}$ = ± 0.03 , $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ = ± 0.02 .

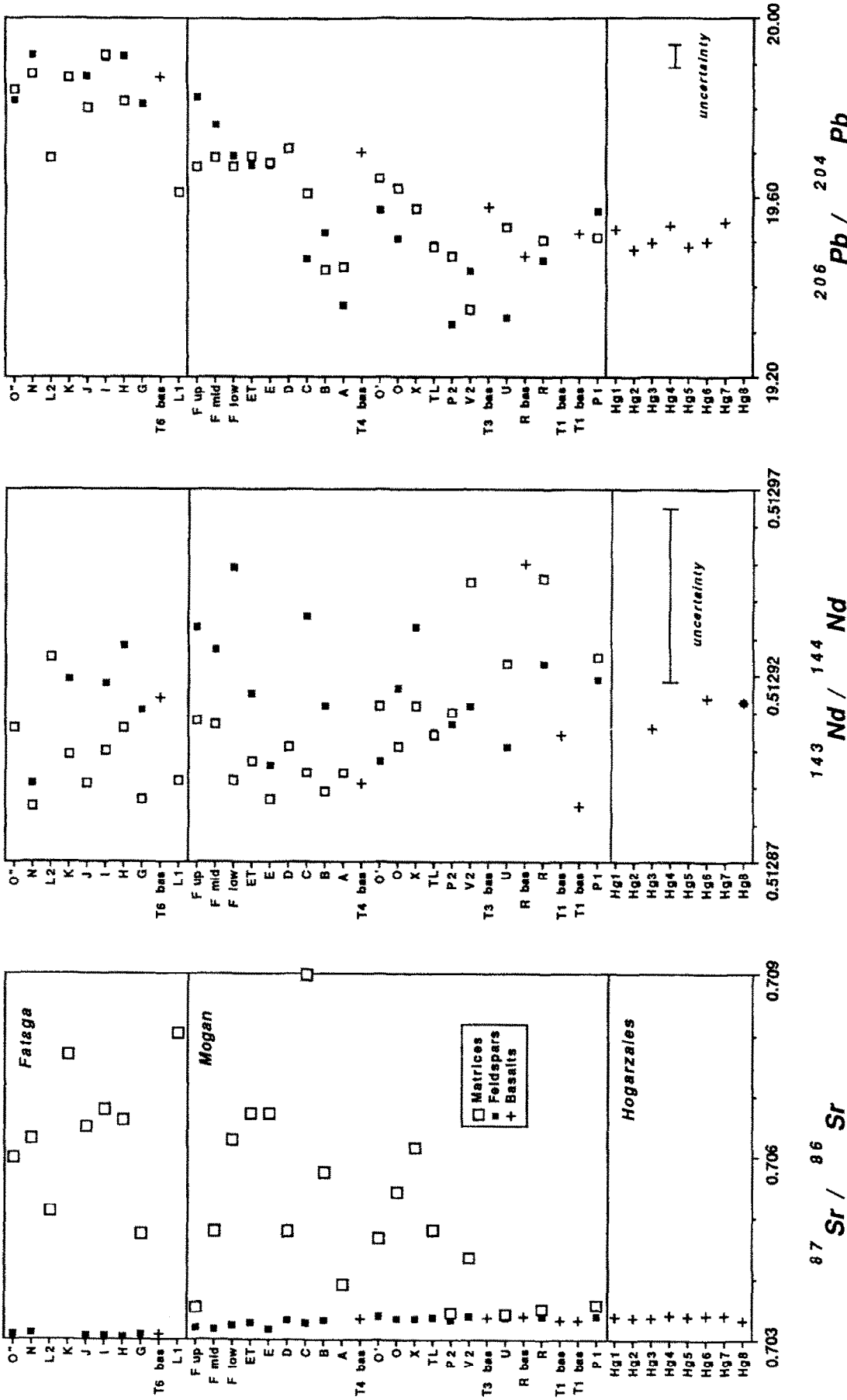


FIG. 2. Age-corrected $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios in basaltic lavas, feldspar (largely anorthoclase) phenocrysts and matrix separates, plotted against stratigraphic height. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in feldspars decrease upsection, the apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the matrices increase erratically. The analytical error in $^{87}\text{Sr}/^{86}\text{Sr}$ is smaller than the size of the data points. Although some minor differences exist, feldspars and matrices are in equilibrium with respect to Nd and Pb (Note that although feldspars appear to consistently have higher $^{143}\text{Nd}/^{144}\text{Nd}$ ratios than matrices above Unit T4, anorthoclase and matrix analyses fall well within analytical error). Phenocryst data from COUSENS et al. (1990).

and Technology Division. Replicate analyses of samples and standards, reported relative to V-SMOW, indicate that analytical reproducibility is $\pm 0.2\%$.

ISOTOPIC RESULTS

Calculated initial isotope ratios of the ignimbrite matrix separates and feldspar phenocrysts, as well as those of trachyphonolitic and basaltic lava whole-rock powders, are plotted versus stratigraphic height in Fig. 2. Within analytical error, $^{143}\text{Nd}/^{144}\text{Nd}_{\text{in}}$ ratios remain constant from the Hogarzales shield basalts through the Mogan Formation into the lower Fataga Formation. $^{143}\text{Nd}/^{144}\text{Nd}_{\text{in}}$ ratios in the matrix and feldspar phenocrysts of each flow are indistinguishable, within analytical error. $^{206}\text{Pb}/^{204}\text{Pb}_{\text{in}}$ ratios are constant at ~ 19.5 in the Hogarzales basalts, increase in a step-wise manner going up through the Mogan Formation, and level off at 19.8–19.9 in the lower Fataga Formation. $^{206}\text{Pb}/^{204}\text{Pb}_{\text{in}}$ ratios for feldspar and matrix are different in some units, sometimes by as much as 0.2, and the differences are not consistent, i.e., the matrix $^{206}\text{Pb}/^{204}\text{Pb}_{\text{in}}$ is not always higher than the feldspar. The apparent initial (i.e., corrected for radiogenic ingrowth assuming that the measured Rb/Sr ratio was the ratio during the period of ingrowth) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the ignimbrite matrices increase erratically going up the section, ranging from 0.7034 at the base of the Mogan Formation to an average of 0.7065 in the lower Fataga Formation. Apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are as high as 0.7091 in Unit C and 0.7077 in Unit K. The increase in apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ of the matrix samples coincides with a general decrease in [Sr] going up the stratigraphic section, but the correlation between apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ and [Sr] is poor (Fig. 1). The apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ of the matrix separates is always higher than enclosed feldspar phenocrysts, and, as the apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the matrix separates increase going upsection, the $^{87}\text{Sr}/^{86}\text{Sr}_{\text{in}}$ ratios in the feldspars decrease. Thus, the silicic matrices are neither in Sr isotopic equilibrium with phenocryst phases, nor similar in Sr isotopic composition to intercalated basaltic volcanic rocks, a phenomenon also noted at St. Helena, Gough, Ascension, and Tenerife (WEIS et al., 1987; GRANT et al., 1976; GAST et al., 1964; PALACZ and WOLFF, 1988).

The oxygen isotopic composition of matrix separates from the basal portions of nine ignimbrites, a trachyphonolitic lava, and a basaltic lava, expressed in the δ notation relative to SMOW, are listed in Table 2. $\delta^{18}\text{O}$ values range from +6.5 to +15.0 in the ignimbrite matrices and the silicic lava, whereas basalt T1 has a lower value of +6.1. The silicic rocks all have $\delta^{18}\text{O}$ values higher than those of anorthoclase phenocryst separates from Mogan and Fataga Formation ignimbrites, which have normal magmatic values of +5.7 to +6.1 (CRISP and SPERA, 1987). There is no trend in O isotopic composition with stratigraphic position. $\delta^{18}\text{O}$ correlates with H_2O^+ (Table 2), indicating that the O isotopic composition of the matrices is controlled by hydration. The samples with the highest H_2O^+ contents are the basal, hydrated vitrophyres, whereas devitrified samples from just above the base have lower H_2O^+ contents.

DISCUSSION

Analytical Uncertainties

It is critical in this kind of study to demonstrate that the apparent Sr isotopic disequilibrium between feldspar phenocrysts and matrix cannot be explained simply by uncertainties in the eruption age, Rb/Sr ratio, and measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of each unit. Units P1, X, B, and E of the Mogan Formation have been dated by $^{40}\text{Ar}/^{39}\text{Ar}$ methods utilizing plagioclase (T1) and anorthoclase phenocrysts (single crystal laser fusion, VAN DEN BOGAARD et al., 1988; incremental heating of mineral separates, CLARK and SPERA, 1990), whereas these and other units of the Mogan and Fataga formations have been dated by the K-Ar technique on both anorthoclase separates and whole-rock samples (MCDONOUGH and SCHMINCKE, 1976). Combining the analytical uncertainties in age, Rb/Sr ratio, and measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, the range in uncertainty of the calculated apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is ± 0.00003 to ± 0.00032 for samples with $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of 3 to 33, respectively. Sample 644 GL from the detailed section of Unit E has an extraordinarily high uncertainty due to a poor Rb determination, but still has an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio slightly different from the value of 0.70317 ± 2 measured in Unit E feldspars. Thus analytical errors can

Table 2. Oxygen Isotope and Water Content Data.

Sample	Unit	$\delta^{18}\text{O}$ (matrix)	H_2O^+ (%) (whole rock)	Matrix Type
K16	T1	+6.1	0.47	Basaltic Lava
K8	P1	+13.7	2.39	Hydrated Vitrophyre
V1	V	+14.5	3.62	Hydrated Vitrophyre
13G	C	+15.0	2.34	Hydrated Vitrophyre
Q5	E	+7.3	0.54	Devitrified
V18	ET	+6.5	0.54	Devitrified
79	F low	+7.1		Devitrified
16J	F mid	+6.6	0.70	Devitrified
17J	F up	+6.9	0.45	Devitrified
5H	L1	+8.9	2.00	Trachyphonolitic Lava
19J	I	+14.2	3.51	Hydrated Vitrophyre

NOTES: Uncertainty in matrix $\delta^{18}\text{O} \pm 0.2\%$. Whole-rock H_2O^+ data from Crisp (1984), uncertainty $\sim 5\%$. Samples are designated as either devitrified or hydrated vitrophyre matrix, except for lavas T1 and L1.

only account for a maximum of 10–15% of the observed Sr isotopic disequilibrium in these samples. While eruption ages of Mogan Formation ignimbrites are well constrained, those of the Fataga Formation are not. MCDUGALL and SCHMINCKE (1976) determined an age of 12.9 ± 0.4 Ma for two basal Fataga units at Barranco de Taurito, Units G and L1, and apparent initial ratios for all overlying Fataga ignimbrites have been calculated using this age. 12.9 Ma is almost certainly a maximum age for the oldest Fataga flows, since two intracaldera flows that closely precede the first extracaldera Fataga flows have been dated at 12.9 and 13.0 ± 0.2 Ma (CLARK and SPERA, 1990). Some of the samples analysed here may be slightly younger than 12.9 Ma; a basal Fataga ignimbrite from Barranco de la Data has been dated at 12.1 ± 0.2 Ma (CLARK and SPERA, 1990). Using a younger age magnifies the degree of apparent disequilibrium.

Causes of Isotopic Disequilibrium

It is difficult to envision a magmatic process (e.g., fractional crystallization, magma mixing) in a large magma chamber that could result in a series of ignimbrites with such highly variable Rb/Sr and apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios where there is absolutely no isochronous relationship (see HALLIDAY et al. (1989) for discussion of isochrons and magmatic processes). As well, whatever process has produced this Sr isotopic disequilibrium appears to have had no effect on Sm-Nd and, at most, only minor effect on U-Th-Pb systematics. However, some non-magmatic, post-emplacement processes could explain this. One possibility is that the ignimbrite matrices have been enriched in radiogenic strontium. Analysis of meteoric waters on Iceland show that sea spray can be carried inland several tens of kilometres by winds (GISLASON and EUGSTER, 1987), so that small amounts of seawater Sr in meteoric waters on Gran Canaria could exchange with the matrices. A second possibility is that infiltration of seawater or stoping of altered roof rock into the Tejeda magma chamber may have added radiogenic Sr to silicic magmas near the roof of the chamber (e.g., TAYLOR, 1987; MICHAEL and SCHILLING, 1989). However, if a seawater component was introduced into the magma chamber and mixed with evolved magma, some of the anorthoclase phenocrysts should have incorporated seawater Sr as well, unless infiltration and mixing occurred just prior to eruption. We see no evidence of this in any of the analysed phenocrysts. Further, Mogan and Fataga matrix samples do not lie on a mixing line in a $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/[\text{Sr}]$ plot (not shown). Lastly, partially disaggregated and metasomatized basaltic xenoliths are not common in the Mogan and Fataga ignimbrites.

A third possibility is that magmas at the roof of the chamber have assimilated pelagic sediments, which have distinctive $^{87}\text{Sr}/^{86}\text{Sr}$ and Pb isotope ratios (GOLDSTEIN and O'NIONS, 1981; CHOW and PATTERSON, 1962). Gran Canaria sits on >10 km-thick pile of pre-Miocene sediments (SHIPBOARD SCIENTIFIC PARTY, 1979), so the potential for contamination is high. In a $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/[\text{Sr}]$ diagram (not shown), the Gran Canaria data do not lie on a mixing line between uncontaminated magma and average Atlantic pelagic sediments. Pb isotope ratios are similar in both feldspars and matrix, and in Pb-Pb plots the Mogan and Fataga Formation rocks

do not trend towards the field of Atlantic sediments (COUSENS et al., 1990). This is especially true for Fataga ignimbrites, which show the greatest degree of Sr-isotopic disequilibrium. Thus, there is no evidence of contamination of these magmas by pelagic sediments.

O-Sr Isotopic Relationships and Meteoric Water Alteration

The elevated $\delta^{18}\text{O}$ values of many of the Mogan and Fataga ignimbrites are typical of volcanic rocks that have been altered at low temperatures by meteoric waters (TAYLOR, 1968; CERLING et al., 1985; MUEHLENBACHS, 1987). $\delta^{18}\text{O}$ correlates positively with H_2O^+ contents of analysed samples, indicative of progressive exchange of groundwater and matrix O. However, there is no correlation between either the degree of devitrification or the volatile content and apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Fig. 3a). In Fig. 3b, Mogan and Fataga ignimbrites plot in two groups, the vitrophyres with $\delta^{18}\text{O}$ values

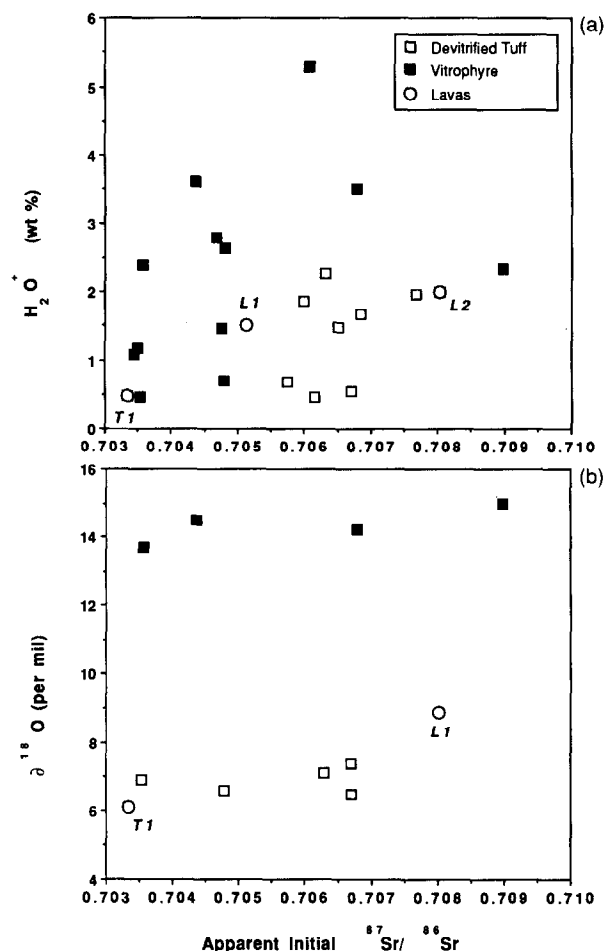


FIG. 3. (a) Apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (matrix separate) vs. H_2O^+ (whole rock; CRISP, 1984) for Mogan and Fataga ignimbrites. No correlation is apparent. Unit T1 is the lowermost basalt in the Mogan Formation, while L1 is a trachyphonolite flow from the Fataga Formation. (b) $\delta^{18}\text{O}$ vs. apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ for Mogan and Fataga Formation matrix separates. The samples plot in two groups: the hydrated vitrophyres at high $\delta^{18}\text{O}$, and the devitrified matrices at low $\delta^{18}\text{O}$. Both groups cover the same range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

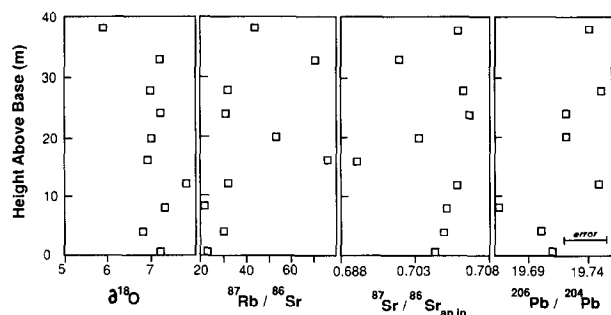


FIG. 4. Variations in $\delta^{18}\text{O}$, $^{87}\text{Rb}/^{86}\text{Sr}$, apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios as a function of height within Unit E at Baranco de la Data. Note that, except for the uppermost sample, the matrix separates have higher $\delta^{18}\text{O}$ values than do feldspar phenocrysts from this ignimbrite (+6.0; CRISP and SPERA, 1987). $^{87}\text{Rb}/^{86}\text{Sr}$ ratios fluctuate between 20 and 80, while apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ranges from 0.6991 to 0.7066. Pb isotope ratios remain approximately constant throughout the flow.

> 13.7 and the devitrified tuffs with $\delta^{18}\text{O}$ values < 7.5. The trachyphonolite lava plots between the two. Thus the hydrated vitrophyres have exchanged oxygen more readily than samples from above the vitrophyres. The vitrophyres may also have interacted with a larger volume of groundwater than did the interior portions of the flow, if groundwater flow was heavier along the contacts between ignimbrite units due to its relatively high permeability. But the range of Sr isotopic disequilibrium is identical in both types of samples. This decoupling of O from Sr isotopes is common in rocks that have interacted with water due to the stronger partitioning of O into the fluid compared to Sr (e.g., BICKLE, 1992).

The susceptibility of all parts of the ignimbrite to post-eruptive modification is best exemplified by a series of samples from one 40 m thick exposure of Unit E (Fig. 4). Except for the sample taken at 8 m height, $^{206}\text{Pb}/^{204}\text{Pb}_{\text{in}}$ ratios are within analytical error. However, apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary from 0.69913 to 0.70662 while $^{87}\text{Rb}/^{86}\text{Sr}$ ratios range from 21.1 to 75.7. The apparent initial ratio of 0.69913 ± 31 in sample 637 GL is certainly not a magmatic ratio, but its extraordinarily high Rb/Sr ratio of 75.7 clearly indicates that Rb and/or Sr have been mobile in this rock.

Rb-Sr Mobility from Acid Leaching Experiments

To further test Rb and Sr mobility in the ignimbrites, matrix separates from Units K (sample 13H), TL (G2), and C (13G), and a whole-rock powder of trachyphonolite lava L1 (5H) were subjected to a sequential leaching experiment, using the following procedure. Matrix separates and the powdered sample, initially weighing 400 mg, were leached using a four-step process. Steps 1 and 2 were in cold 2N HCl in an ultrasonic bath for 10 minutes, Step 3 was in warm 6 N HCl in an ultrasonic bath for 10 minutes, and Step 4 was in hot 6 N HCl (hotplate for 7 minutes, cool ultrasonic bath for 5 minutes). After each leach step, leachates were decanted, residues carefully washed with distilled H_2O , and ~100 mg. of residue saved for isotopic analysis, along with the leachate. For Units K and L1, the residue from the last step was spiked with a mixed $^{87}\text{Rb}/^{84}\text{Sr}$ spike and analysed for [Rb] and [Sr]. Residues from all the leach steps for Units C and TL were similarly spiked for [Rb] and [Sr] determinations. Apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were then calculated for these spiked residues.

Table 3. Sr Isotopic Data from Leaching Experiments.

Unit	Sample	Leach Step	$^{87}\text{Sr}/^{86}\text{Sr}_m$	Rb	Sr	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{ai}}$	2 SD	$^{87}\text{Sr}/^{86}\text{Sr}_l$
K	13H WR	0	0.70861	113.0	64.4	5.08	0.70768	0.00011	
K	13H L1	1	0.70143						0.70808
K	13H L2	2	0.71174						0.70811
K	13H L3	3	0.71216	31.9	2.2	42.93	0.70429	0.00005	0.70863
L1	5H WR	0	0.70875	115.0	85.1	3.91	0.70806	0.00006	
L1	5H L1	1	0.70877						0.70876
L1	5H L2	2	0.70873						0.70897
L1	5H L3	3	0.70901	63.3	9.7	18.73	0.70557	0.00003	0.70851
C	13G WR	0	0.71104	110.0	30.3	10.52	0.70902	0.00009	
C	13G L1	1	0.71142	115.8	26.1	12.83	0.70898	0.00003	0.70789
C	13G L2	2	0.71269	120.8	21.9	16.00	0.70964	0.00005	0.70706
C	13G L3	3	0.71108	114.5	27.2	12.19	0.70876	0.00005	0.70770
C	13G L4	4	0.71406	132.5	19.6	19.57	0.71034	0.00004	0.70909
TL	G2 WR	0	0.70953	89.6	10.9	23.68	0.70507	0.00010	
TL	G2 L1	1	0.71154	95.0	10.5	26.20	0.70641	0.00007	0.70840
TL	G2 L2	2	0.70967	98.7	10.7	26.65	0.70444	0.00006	0.70833
TL	G2 L3	3	0.70928	98.4	10.5	27.23	0.70394	0.00005	0.70851
TL	G2 L4	4	0.70988	109.7	9.7	32.65	0.70349	0.00004	0.70812

NOTES: m=measured ratio, ai= apparent initial ratio, l = measured ratio of leachate. Leach step 0 = unleached powder. Rb and Sr concentrations in ppm. "2 SD" = 2-sigma precision.

Although the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the residues of successive leach steps vary for each sample, the end result of the leaching procedure is that the residue of the final step always has a higher measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than the unleached separate (Table 3, Fig. 5). An easily leachable Sr component with a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is present, probably concentrated along cracks in the matrices. The $^{87}\text{Sr}/^{86}\text{Sr}$ of the leachates range from .7070 to .7090, which are slightly lower than seawater values. This is what would be expected if alteration has added radiogenic seawater Sr to the matrices.

The most important effect of leaching is the difference in Rb/Sr ratios of the residues. For the hydrated vitrophyres of Units C and TL, the residues of Step 4 have lower [Sr] and higher [Rb] compared to the unleached splits. The relative

increase in [Rb] is probably not an artifact of the leaching procedure itself (MACHADO *et al.*, 1986). For the devitrified or crystalline Units K and L1, both [Rb] and [Sr] drop from Steps 0 to 3, but [Sr] decreases to a much greater extent. Thus, although the measured $^{87}\text{Sr}/^{86}\text{Sr}$ increases in the residues from Step 0 to 4, the Rb/Sr ratio increases even more dramatically. With the exception of Unit C, the result is that the apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ for Step 4 residues are much closer to the feldspar value of the flow (Fig. 5). The Step 4 residue for unit TL is almost exactly the same as enclosed feldspars.

The residues from Unit C do not follow the progression of decreasing apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ with leach steps defined by the other three samples. This may be because the net effect of the leach steps depends on the pervasiveness of the alteration; it is more easily removed if it is narrowly concentrated along cracks or along grain boundaries in devitrified rocks, but difficult to completely remove if the alteration is broadly distributed. Thus the hydrated vitrophyre from Unit C, possessing the highest $\delta^{18}\text{O}$ value and highest unleached apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of all the ignimbrites, may be pervasively altered.

The conclusion drawn from these leaching experiments and the oxygen isotope data is that low-temperature interaction between the ignimbrite matrices and groundwater has mobilized Rb and Sr, and may have added radiogenic Sr (~ 0.7090 , but perhaps different in time and space) to the matrices, the effect of which is probably concentrated along cracks and grain boundaries. As the isotopic results from the detailed section of Unit E indicate, the process of Rb and Sr mobilization is extremely variable, even within a single flow. Only a few ppm of Sr need be added to the rock to completely mask its original isotopic composition. The alteration is cryptic, because there is no evidence of alteration in thin-section besides hydration of the basal vitrophyres. The net effect of this alteration is that it is impossible to properly calculate initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The loss or gain of Rb and Sr must significantly postdate eruption of the ignimbrites, otherwise the age corrections would be close to the feldspar values. Therefore, the mobilization of Rb and Sr did not occur during post-emplacement degassing or vapour-phase alteration. Previous work has shown that the hydrated basal vitrophyres of Gran Canaria ignimbrites have lost alkalis (see SCHMINCKE, 1987). Most of the samples studied here are basal vitrophyres, but alkali mobility is also very pronounced in ignimbrite samples taken from above the basal vitrophyre, as well as in the dense trachyphonolitic lava flows. Thus the Sr isotopic disequilibrium between phenocrysts and matrices is not due simply to hydration.

CONCLUSIONS

Radiogenic and stable isotopic analyses of ignimbrites from the Mogan and Fataga formations show that Rb and Sr are mobile elements during low-temperature, post-emplacement interaction with circulating groundwater. Except in very young volcanic rocks where no significant age correction is necessary, this mobility can mask the initial Sr isotopic compositions of silicic whole-rock samples by modifying the Rb/Sr ratio, so that it is not possible to properly calculate an

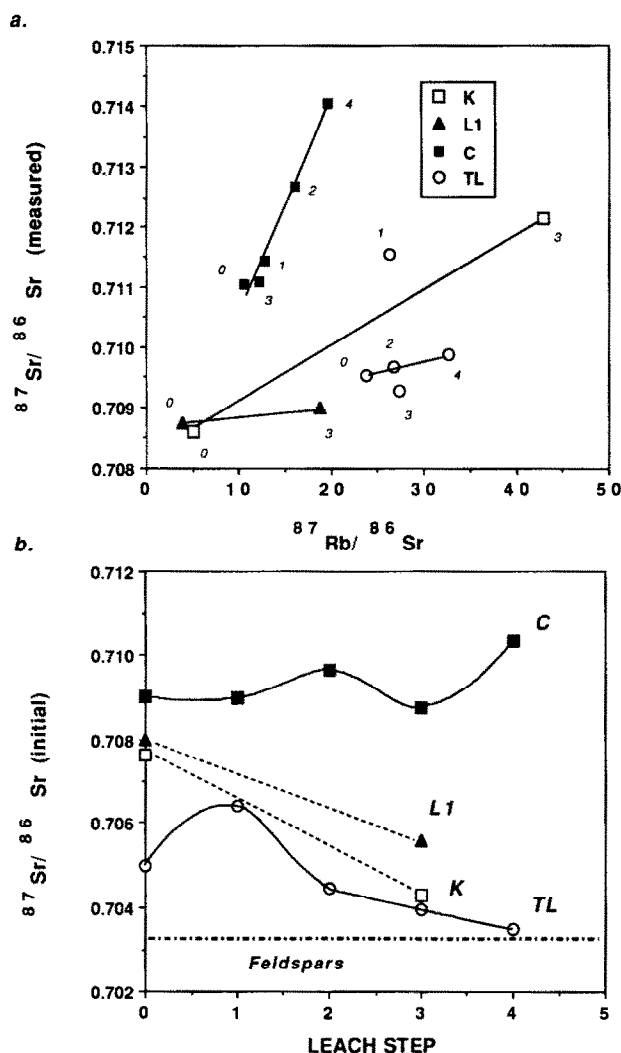


FIG. 5. (a) $^{87}\text{Sr}/^{86}\text{Sr}_{\text{meas}}$ ratios in the four leached samples, plotted vs. $^{87}\text{Rb}/^{86}\text{Sr}$, for all the leach steps. (b) Apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ plotted against leach step. In three out of four samples, the apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the residues of the final step are smaller than those of the unleached samples and approach the feldspar phenocryst values. The matrices have lost Rb and gained Sr along cracks during weathering on the surface, and this altered material is removed during the leaching process. The vitrophyre of Unit C is apparently pervasively altered, such that leaching fails to leave more pristine rock in the residue. Rb and Sr mobility after emplacement means that proper matrix $^{87}\text{Sr}/^{86}\text{Sr}_{\text{in}}$ ratios cannot be calculated.

initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. In this case, significant Rb and Sr mobility is not limited to the hydrated basal vitrophyres of the ignimbrites, but extends patchily throughout the entire pyroclastic flow due to progressive groundwater alteration which begins significantly after deposition. This process may be an ongoing one. Low [Sr] make these rocks especially susceptible to Sr exchange, although samples with as much as 85 ppm Sr exhibit major isotopic disequilibrium. Anorthoclase phenocrysts are resistant to this low-temperature alteration, which is perhaps a reflection of their tectosilicate structure and relatively high Si-O, Al-O, and alkali metal-O bond energies, relative to the amorphous state. Nd and Pb isotope systematics in both phenocrysts and matrices are relatively unaffected by the alteration process.

The results of this study address the problems that are encountered during Sr isotopic analysis of silicic ignimbrites and lavas as part of a mantle tracer study. Whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios should be regarded with suspicion, although they may convey some information about late- or non-magmatic processes, as in this case. Analysis of more resistant phenocryst phases is preferable to whole rocks, but some uncertainty as to the freshness of these phases will always remain.

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