Elemental and isotopic geochemistry of nonhydrated quartz latite glasses from the Eureka Valley Tuff, east-central California

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ABSTRACT

The Eureka Valley Tuff, erupted from the late Miocene Little Walker volcanic center, east-central California, includes two major ash-flow sheets: the more voluminous, widespread, and more silicic Tollhouse Flat Member and the overlying By-Day Member. Nonhydrated quartz latitic glasses from the Tollhouse Flat and By-Day Members have, respectively, 65.5 and 63.3 wt percent SiO_2 and are extremely rich in large-ion lithophile elements. The K_2O contents and K/Rb ratios are 5.3 wt percent and 195 for the Tollhouse Flat glass and 5.5 wt percent and 190 for glasses from the By-Day Member. FeO^*/MgO (FeO^* = total Fe as FeO) ratios are transitional between values characteristic of basaltic and calc-alkalic suites. Initial $^{87}Sr/^{86}Sr$ ratios of 0.7054 to 0.7055 are consistent with the pattern of northwestward decrease in $^{87}Sr/^{86}Sr$ observed for Mesozoic plutonic and Cenozoic volcanic rocks in the western Great Basin and Sierra Nevada provinces. The glasses are higher in Rb than are Mesozoic granitic rocks of the Sierra Nevada batholith that have comparable Sr contents and initial $^{87}Sr/^{86}Sr$ ratios. Pb isotopic compositions fall at the upper end of arrays found for upper Cenozoic calc-alkalic rocks from the Cascade Mountains and nearly on trends found for rocks of the Sierra Nevada batholith. The moderately high FeO^*/MgO ratios, very low Co, Cr, and Ni contents, high Ba/Sr and K/Sr ratios, and approximately 25 percent negative Eu anomalies demonstrate that the glasses are the products of appreciable crystal fractionation. This in turn strongly suggests that the Eureka Valley Tuff was derived from a hypersthene-normative or only slightly quartz-normative parent magma. A model is outlined in which a potassic mafic parent magma was produced by a moderate degree of partial melting of diapirically upwelling, undepleted ultramafic mantle material followed by zone refining of upwelling mantle and other material within the asthenosphere and lithosphere. Extensive fractional crystallization and crystal separation subsequently enriched the melt further in large-ion lithophile elements. The evidence for appreciable plagioclase separation demonstrates that much fractionation took place well within the Earth's crust. The Tollhouse Flat and By-Day Members were erupted from discrete — although closely related — bodies of magma. Lower water and halogen contents of the By-Day magma may have prevented the intratelluric crystallization of biotite and thereby allowed the magmatic liquid to become richer in K and Rb than that of the more highly fractionated Tollhouse Flat Member. *Key words: elemental and isotopic geochemistry, igneous petrology, ash-flow tuffs, nonhydrated glass.*

INTRODUCTION

The Eureka Valley Tuff, the underlying Table Mountain Latite, and the overlying Dardanelles Formation together compose the

Stanislaus Group, a sequence of genetically related lava flows, tuffs, and related rocks of late Miocene age (approximately 10 to 8 m.y. old) in the central Sierra Nevada of California and in adjacent Nevada (Ransome, 1898; Slemmons, 1966; Noble and others, 1974). Since chemical analyses of several rocks of the Stanislaus Group were published by Ransome (1898), the unit has been known for its highly potassic character. Additional major-element analyses presented by Halsey (1953) confirmed the potassic nature of the Stanislaus Group, and optical emission spectrographic analyses by Nockolds and Allen (1954) showed that rocks of the unit contained unusually high concentrations of Rb, Ba, Sr, Y, and Zr. In addition to the petrogenetic and tectonic importance of this suite of rocks, the Stanislaus Group is important in that two of the included units — the Table Mountain Latite and the Tollhouse Flat Member of the Eureka Valley Tuff — may be considered the type examples of the common rock types latite and quartz latite.

The Little Walker volcanic center (Fig. 1), the vent area from which the Eureka Valley Tuff was erupted (Noble and others, 1969, 1974; Priest, 1974; Priest and others, 1975), is located near the northwestern end of a west-northwest–trending belt of late Tertiary (6 to about 14 m.y. old) volcanic centers of moderately to very highly potassic character (Noble, 1972). Rocks of these centers range from moderately calc-alkalic to moderately basaltic in character. Silicic tuffs and lavas from most of the centers are subalkaline, although appreciable volumes of peralkaline silicic tuff and lava were erupted at the Black Mountain, Silent Canyon, and Kane Springs Wash centers (Noble and Parker, 1975). The belt may reflect a zone of asthenospheric disturbance resulting perhaps from a discontinuity in flow patterns that triggered the rise of a linear array of successive diapiric upwellings or surges of mantle material.

The Eureka Valley Tuff contains two major ash-flow sheets: the Tollhouse Flat Member and the overlying, somewhat less extensive By-Day Member (Noble and others, 1974). The Tollhouse Flat Member is identical with the "biotite-augite-latite" of Ransome (1898). Each ash-flow sheet consists of many individual ash flows that cooled and crystallized in continuum. Imperfectly known volumetric relationships indicate that, with allowance made for fine-

Figure 1. Location of Little Walker volcanic center (LW) and other late Tertiary potassic volcanic centers, southern Great Basin. M, Markleville; BA, Bodie Hills–Aurora; SP, Silver Peak; SM, Stonewall Mountain; BM, Black Mountain; SC, Silent Canyon; PT, Paintbrush–Timber Mountain; KS, Kane Springs Wash; OV, Ox Valley (approximate).
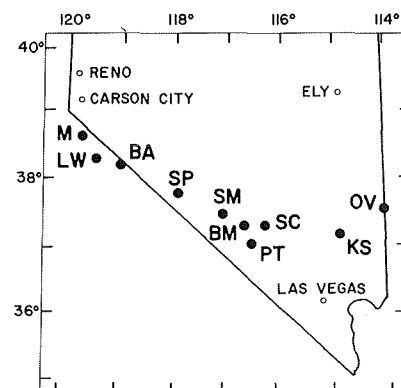
obtained by knowing the size, shape, and orientation of the triangles formed by the marker lines. The magnitude of the principal strain axis normal to the thin section can be obtained from the radial displacement of the triangles during the deformation due to the fact that this strain is equal to the circumferential strain of a circle that is oriented normal to the specimen axis and that passes through the triangle.

Specimen Preparation

It would be desirable for the sample to have no preferred orientation prior to the experiment. However, simple compaction of powdered mica in a cylindrical pellet press results in a strong preferred orientation of the mica with its (001) planes normal to the axis of the cylindrical pellet. Although pellets could not be prepared with random preferred orientation, a technique was developed so that the preferred orientation was either weak or opposite in character to that expected from the deformation in the experiment itself. Pellets with the opposite preferred orientation were prepared by coring compacted pellets parallel to their diameter. Pellets with a weak preferred orientation were prepared using a two-stage orthogonal compaction process (T. Tullis, 1971, p. 92).

X-ray Preferred-Orientation Measurement

A modified Norelco pole-figure goniometer was used in transmission to measure the preferred orientation of the experimental samples. Only the preferred orientation of the basal plane has been measured. Although this plane is termed (001) in this discussion, the d-spacing measured was the 10 Å basal spacing whose Miller indices are (002) for a 2M mica. Spiral transmission scans were made for all samples in order to get as complete coverage of the pole figures as possible. The x-ray beam was collimated to produce an irradiated area that was 1 mm in diameter. This allowed study of small regions that have nearly homogeneous strain.

Details of the procedures used in this study are described in T. Tullis (1971, p. 65–74). More complete descriptions are given by von Gehlen (1960, 1971), Barrett and Massalski (1966, p. 193–208), and Baker and others (1969).

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TABLE 1.   MAJOR-ELEMENT ANALYSES OF NONHYDRATED GLASSES
FROM THE TOLLHOUSE FLAT MEMBER OF THE EUREKA VALLEY TUFF

	SQL-2 A*	TF-L-18P B*	TF-L-18P C*	BW-L-6 B*	BW-L-15A B*	BW-L-15B B*	BW-L-30 B*
SiO_2	65.71	65.5	..	65.5	65.4	65.6	65.4
Al_2O_3	16.56	16.57	15.9†	16.55	16.54	16.55	16.66
Fe_2O_3	1.23	3.10§	3.19§	3.21§	3.15§	3.15§	3.19§
FeO	1.73	..	..	..	..	..	..
MgO	0.84	0.81	..	0.83	0.82	0.81	0.82
CaO	2.03	2.01	..	2.03	2.04	2.05	2.01
Na_2O	4.52	4.72	4.91	4.81	4.81	4.77	4.81
K_2O	5.62	5.20	5.4#	5.11	5.13	5.41	5.38
H_2O^+	0.26	..	..	..	..	..	..
H_2O^-	0.01	..	..	..	..	..	..
TiO_2	0.66	0.66	0.62	0.67	0.68	0.66	0.67
P_2O_5	0.19	0.18	..	0.18	0.18	0.17	0.19
MnO	0.09	..	0.080	..	..	..	..
Cl	0.07	0.08	..	0.07	0.07	0.06	0.07
F	0.06	..	..	..	..	..	..
Subtotal	99.69**	..	..	..	..	..	..
Less O	−0.05	..	..	..	..	..	..
Total	99.64	98.8	..	99.0	98.8	99.2	99.2

* A, by standard wet-chemical methods, G. O. Riddle, analyst; B, by electron microprobe methods, M. K. Korringa and D. C. Noble, analysts; C, by neutron activation methods, H. R. Bowman, analyst. All values are in percent.
† ±0.4 wt %.
§ Total Fe as Fe_2O_3.
# ±0.5 wt %.
** Subtotal based on Al_2O_3 value of 16.67 wt % uncorrected for ZrO_2, oxides of rare-earth elements, and so forth.

grained material lost during eruption and transport, the Tollhouse Flat Member and By-Day Member reflect eruptions of at least 200 and 100 km³ of magma, respectively.

During study of the Eureka Valley Tuff and the Little Walker volcanic center, nonhydrated obsidian cores were discovered in collapsed pumice fragments at several exposures of the Tollhouse Flat and By-Day Members. The pumice fragments from which the glasses were obtained also contain about 15 percent phenocrysts, consisting mainly of plagioclase, clinopyroxene, and magnetite-ulvospinel in the By-Day Member and plagioclase, biotite, clinopyroxene, magnetite-ulvospinel, apatite, and (in some samples) hornblende in the Tollhouse Flat Member. The preservation of

nonhydrated glass (Ross and Smith, 1955) was particularly fortunate, because such material has undergone no change in chemical composition since solidification and thus provides completely unaltered samples of the magmatic liquid at the time of eruption. Alkali metals, alkaline earths, and other mobile elements such as H, O, the halogens, and U have not diffused or otherwise moved into or out of the glass (Rosholt and others, 1971, and references cited therein). The purpose of this paper is to present and discuss major- and minor-element analyses and Sr and Pb isotopic data obtained on these glasses.

The specimens studied (Tables 1 through 6) are from three localities, all several miles north of the northern margin of the Little

TABLE 2.   MAJOR-ELEMENT ANALYSES OF NONHYDRATED GLASSES
FROM THE BY-DAY MEMBER OF THE EUREKA VALLEY TUFF

	BW2-M-N1 A	BW2-M-N1 B	BW2-M-K1 A	BW2-M-K1 B	BW-M-42 C	BW-M-13.5 C	BW2-M-N2 D	BW2-M-N2 E	BW-2-M-N3 D	BW-2-M-N3 E
SiO_2	63.6	..	63.2	..	63.1	63.1	..	..	..	..
Al_2O_3	16.7	16.7*	16.7	16.2*	16.64	16.76	..	..	..	..
Fe_2O_3	4.6†	4.26†	4.0	4.37†	4.23†	4.21†	..	..	..	..
FeO	..	..	0.52	..	..	..	..	..	..	..
MgO	1.3	..	1.3	..	1.15	1.15	..	..	..	..
CaO	2.4	..	2.4	..	2.48	2.54	..	..	..	..
Na_2O	4.2	4.41	4.2	4.14	4.45	4.61	4.31	..	4.18	..
K_2O	5.3	5.4§	5.4	5.2§	5.87	5.45	5.67	5.25	5.94	5.48
TiO_2	1.0	0.83	1.0	0.92	0.96	0.98	..	..	..	..
P_2O_5	0.32	..	0.32	..	0.29	0.31	..	..	..	..
MnO	0.10	0.089	0.10	0.084	..	..	..	..	..	..
Cl	..	..	..	..	0.08	0.08	..	..	..	..
Loss on ignition	0.30	0.20	..	..	..	..	..	..	..	..
Total	100	..	99	..	99.2	99.2	..	..	..	..

Note: A, by rapid methods supplemented by atomic absorption, P. Elmore, H. Smith, J. Kelsey, J. Glenn, and R. Moore, analysts; B, by neutron activation methods, H. R. Bowman, analyst; C, by electron microprobe methods, M. K. Korringa and D. C. Noble, analysts; D, by flame photometry, L. B. Schlocker, analyst; E, by x-ray fluorescence, L. F. Espos, analyst. All values are in percent.
* ±0.4 wt %.
† Total Fe as Fe_2O_3.
§ ±0.5 wt %.

TABLE 3. PREFERRED MAJOR-ELEMENT VALUES FOR GLASSES FROM THE EUREKA VALLEY TUFF

	Tollhouse Flat Member (wt %)	By-Day Member (wt %)
SiO_2	65.5	63.3
Al_2O_3	16.5	16.7
Fe_2O_3	1.23	3.8
FeO	1.73	0.5
MgO	0.83	1.25
CaO	2.03	2.45
Na_2O	4.75	4.30
K_2O	5.3	5.5
H_2O^+	0.26	0.25*
H_2O^-	0.01	..†
TiO_2	0.64	0.93
ArO_2	0.07	0.07
P_2O_5	0.19	0.31
MnO	0.08	0.09
Cl	0.07	0.08
F	0.06	..

* Loss on ignition.
† Leaders (..) = not determined.

TABLE 5. Rb AND Sr CONTENTS AND $^{87}Sr/^{86}Sr$ RATIOS OF NONHYDRATED GLASSES FROM THE EUREKA VALLEY TUFF

Specimen no.	Field no.	Rb* (ppm)	Sr* (ppm)	$^{87}Sr/^{86}Sr_o$[†,§]	$^{87}Sr/^{86}Sr_i$[§]
		Tollhouse Flat Member			
1.1	SQL-2	224	380	0.70562	0.70539
2	TF-L-18P	225	384	0.70569	0.70546
		By-Day Member			
3	BW2-M-K1	241	430	0.70569	0.70547
4	BW2-M-N1	240	430	..	..
5	Bw2-M-N2	215	385	..	..
6	BW2-M-N3	230	405	..	..

* By x-ray fluorescence, W. Doering (specimens 1 to 4) and L. F. Espos (specimens 5 and 6), analysts.
† Mass spectrometry by D. C. Noble (specimens 1 and 2) and R. A. Hildreth. Chemical separations by W. T. Henderson. All determinations ±0.9992 (2σ).
§ Subscript $_o$ indicates measured ratio; subscript $_i$ indicates calculated initial ratio; subscript digits are of dubious statistical significance.

TABLE 4. MINOR-ELEMENT ANALYSES OF NONHYDRATED GLASSES FROM THE EUREKA VALLEY TUFF

	Tollhouse Flat Member		By-Day Member			
	SQL-2 Q*	TF-L-18P NA*	BW2-M-N1 SQ*	BW2-M-N1 NA*	BW2-M-K1 SQ*	BW2-M-K1 NA*
Cs	..†	17(1)§	..	14(1)	..	14(1)
Rb	..	245(30)	..	200(25)	..	240(30)
Ba	1,600	1,700(80)	2,000	2,020(95)	2,000	1,980(95)
Pb	30, 50#	48#	50	44#	50	43#
Sr	380	570(200)	700	500(220)	700	570(210)
La	80	69(1)	150	72(1)	150	73(1)
Ce	..	143(4)	200	150(4)	200	150(4)
Nd	..	60(5)	100	61(5)	100	66(5)
Sm	..	8.9(3)	..	10.2(2)	..	10.3(2)
Eu	..	1.65(5)	..	1.92(5)	..	1.94(5)
Tb	..	0.99(7)	..	1.07(7)	..	0.98(7)
Dy	..	4.8(3)	..	6.3(3)	..	5.9(3)
Yb	3	2.7(1)	5	3.1(1)	5	3.1(1)
Lu	..	0.35(2)	..	0.42(2)	..	0.42(2)
Y	40	..	50	..	50	..
Th	..	42(1)	..	36(1)	..	35(1)
U	..	14(1)	..	12(1)	..	12(1)
Zr	510	..	450	..	410	..
Hf	..	13(1)	..	13(1)	..	13(1)
Sn	<20	..	N.D.†	..	N.D.	..
Nb	<20	..	20	..	20	..
Ta	..	1.41(4)	..	1.52(4)	..	1.44(4)
Mo	<10	..	10	..	10	..
Cu	7	..	9	..	10	..
Co	<7	2.7(1)	5	5.0(1)	5	5.7(2)
Ni	<5	<15	<2	<15	<2	<15
Sc	11	7.5(2)	15	10.4(2)	15	10.5(2)
V	35	51(35)	73	88(38)	72	92(34)
Cr	<2	(4)	<2	4(4)	<2	2(4)
Zn	..	86(12)	..	85(12)	..	85(13)
Ga	27	..	20	..	20	..
Be	<5	..	3	..	3	..
B	160	..	70	..	70	..
As	..	22(2)	..	17(2)	..	17(2)
Sb	..	2.7(2)	..	2.0(2)	..	1.6(2)

* Q, quantitative optical emission spectrographic analysis, J. C. Hamilton, analyst; NA, neutron activation analysis, H. R. Bowman, analyst; SQ, semiquantitative optical emission spectrographic analysis (except Zr, Cu, Co, Ni, V, and Cr by quantitative methods) H. R. Bastron and C. Heropoulos, analysts. All data in parts per million.
† Leaders (..) = not determined; N.D. = not detected.
§ The number in parentheses indicates the error at the 68% confidence level (including uncertainties in calibration of the working standard) of the last digit(s) of the tabulated value.
# By x-ray fluorescence, W. P. Doering, analyst.

Walker caldera. Specimens SQL-2 and TF-L-18P from the Toll-house Flat Member are, respectively, from lat 38°24'00"N, long 119°25'20"W, and lat 38°25'35"N, long 119°26'45"W. Specimens prefixed by BW are from lat 38°25'05"N, long 119°25'55"W.

METHODS OF ANALYSIS

The standard major-element analysis was made by the methods of Peck (1964); the rapid analyses were made by the methods of Shapiro and Brannock (1962) supplemented by atomic absorption procedures. Electron microprobe determinations were made on an ARL-EMX instrument using an acceleration potential of 15 or 20 kV depending on the elements being determined. Ten or more spot analyses were made per specimen using a somewhat defocused beam. Nonhydrated glass SQL-2 (Table 1), which had been inter-compared with other chemically analyzed nonhydrated glasses by microprobe methods, was used as the working standard. Corrections using the coefficients of Albee and Ray (1970) were applied as necessary. Neutron activation analyses were made using the techniques of Bowman and others (1973). In addition, K and Na also were determined on several samples by flame photometry using Li as an internal standard (Ingamells, 1970) and by x-ray fluorescence.

Quantitative and semiquantitative analyses by optical emission spectrography were made using techniques similar to those described by Bastron and others (1960) and Myers and others (1961). X-ray fluorescence analyses for Rb and Sr were made using a method similar to that of Doering (1968), but with the addition of a Compton-scattering procedure to correct for matrix effects. The method of Fabbi (1971) was used for several of the x-ray fluorescence analyses.

Sr isotopic composition was determined on a 6-in., 60°-sector, Neir-type mass spectrometer utilizing triple-Re-filament ionization. Data were collected digitally and reduced by computer (Stacey and others, 1968). The mass spectrometer gives a $^{87}Sr/^{86}Sr$ ratio of 0.7080 for the Eimer and Amend standard $SrCO_3$. Pb isotopic analyses were made using procedures identical to those of S. E. Church and M. Tatsumoto (unpub. manuscript).

RESULTS AND DISCUSSION

Elemental Geochemistry

Major- and minor-element analyses of nonhydrated glasses from the Eureka Valley Tuff are given in Tables 1 through 4. With the

Figure 2. Comparison of FeO^*/MgO ratios and K_2O contents of nonhydrated glass from By-Day Member (BDM) with values of selected potassic volcanic suites at the same (63 wt percent) SiO_2 content. BM, Black Mountain, Nevada (Noble and Christiansen, 1974); SP, Silver Peak, Nevada (Robinson, 1972); C, Cimino, Italy (Joplin, 1968); P, Pantelleria, Mediterranean (Korringa and Noble, 1972). NWM represents data from Mount Barcroft and Pellisier Flats plutons, northern White Mountains, California (Crowder and Ross, 1973), the most potassic rocks of Sierra Nevada–White Mountains batholithic complex.

possible exception of K, there is no evidence of compositional variation within the glasses of a given member, and most data scatter is interpreted to be the result of analytical error.

Very few ash-flow tuffs — not to mention their residual glasses — have the low SiO_2 content and the high concentration of Mg and Ca that are found in the glasses from the Eureka Valley Tuff. Equally striking are their extremely high concentrations of K and of a wide range of other large-ion lithophile elements. In spite of their high content of K and total alkali metals, the glasses are not of trachytic or quartz trachytic composition, but rather are best termed quartz latite.[1]

The glasses are transitional in degree of relative Fe enrichment between suites of definitely calc-alkalic character and rocks of basaltic parentage,[2] in which protracted separation of Fe-Mg silicate minerals from hypersthene-normative parent melts has produced residual liquids of intermediate composition with high FeO^*/MgO (FeO^* = total Fe as FeO) ratios. Standard AFM plots are inadequate to distinguish suites of calc-alkalic, transitional, and basaltic character in cases in which the suites differ appreciably in K content. More useful projections are obtained by plotting FeO^*/MgO (or a comparable index) against SiO_2 (Carmichael, 1964) or by plotting FeO^*/MgO against K_2O for rocks of a given SiO_2 content. Figure 2 utilizes this type of projection to compare the glass from the By-Day Member with other potassic suites from the Great Basin and elsewhere.

The glasses of the Eureka Valley Tuff are high in large-ion lithophile elements in comparison not only with calc-alkalic and island-arc tholeiitic series rocks from oceanic regions (Jakeš and White, 1972; Ewart and others, 1973) but also in comparison to the relatively potassic volcanic and plutonic rocks typically erupted through thick sections of continental crust. With a K_2O content of 5.5 wt percent, the glass from the By-Day Member is more potassic than rocks of comparable SiO_2 content from any other Cenozoic

TABLE 6. Pb ISOTOPIC COMPOSITIONS OF GLASSES FROM THE EUREKA VALLEY TUFF AND OTHER UNITS

	Field number	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Tollhouse Flat Member	BW-2F-L1	19.118	15.641	38.78
		19.05*	15.64*	38.74*
By-Day Member	BW2-M-K1†	19.093	15.642	38.80
		19.02*	15.64*	38.76*
Obsidian from Mono Craters, California		19.102	15.643	38.81
		19.08§	15.61§	38.75§
Obsidian from Clear Lake, California		19.172§	15.653§	38.918§

* Value corrected for the growth of radiogenic Pb since the time of eruption.
† The following elemental concentrations have been determined by isotope-dilution methods: U = 11.67 ppm, Th = 34.93 ppm, and Pb = 34.44 ppm.
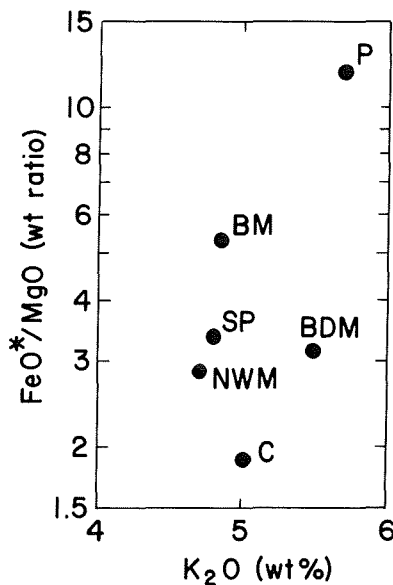§ Data from Doe and Delevaux (1973). All other analyses by S. E. Church.

[1] Simple classification schemes in which boundaries between rock groups of comparable degrees of K_2O enrichment are drawn at arbitrarily chosen SiO_2 contents (MacKenzie and Chappell, 1972) are convenient and petrogenetically meaningful. We thus suggest the following simple breakdown of potassic calc-alkalic and transitional rocks: specimens containing less than 57 wt percent SiO_2 (recalculated free of H_2O and CO_2) are termed "low-silica latite," rocks with 57 to 63 wt percent SiO_2 are termed "latite," and rocks with more than 63 wt percent SiO_2 are termed "quartz latite."

[2] Our distinction between intermediate rocks of "calc-alkalic" and "basaltic" character is very similar to that, for example, of Lowder and Carmichael (1970) and Miyashiro (1974), being based mainly on the degree of relative Fe enrichment. We use "basaltic" instead of "tholeiitic" for the end of the spectrum exhibiting marked Fe enrichment so as to include moderately to highly potassic subalkaline suites with high FeO^*/MgO ratios.

suite in the Great Basin and adjacent areas (Fig. 2) and is appreciably more potassic than virtually all Mesozoic granitic rocks from the Sierra Nevada and White Mountains (Bateman and Dodge, 1970). Rb, Cs, and Ba contents also are unusually high. U and Th contents are twice as high as the average of a number of rhyolitic natural glasses from the western United States (Rosholt and others, 1971), and the calculated heat production (a function of combined K, U, and Th contents) is about twice that found by Tilling and others (1970) for rocks of comparable SiO_2 content in their most radiogenic SiO_2-oversaturated igneous suites. The light rare-earth elements, Y, Pb, Ta, Hf, and Zr are present in unusually high concentrations. Contents of these elements are higher than values found, for example, for early Oligocene latites and quartz latites from the northern Great Basin and potassic calc-alkalic volcanic rocks of Miocene age from the Andes of central Peru (H. R. Bowman, D. C. Noble, and others, unpub. data). The ratios La/K and Ce/K are significantly higher than those of upper Cenozoic volcanic rocks of similar SiO_2 content from the Cascade Range (Condie and Swenson, 1973).

The inference from Fe/Mg ratios that the compositions of the glasses reflect very significant amounts of fractional crystallization is supported by the very low Co, Cr, and Ni contents (Table 4; compare, for example, Siegers and others, 1969; Dodge, 1972), which indicate the separation of large amounts of olivine, pyroxene, and perhaps other ferromagnesian minerals (Hälki and Wright, 1967; Taylor and others, 1969; Hedge, 1971; Ewart and others, 1973). The extremely low Cr contents suggest that clinopyroxene was separating during most of the period of intratelluric crystallization (Ewart and others, 1973; Burns, 1973). The occurrence within the Little Walker volcanic center of appreciable volumes of less highly fractionated lavas with 54 to 60 wt percent SiO_2 having Ni contents of 25 to 85 ppm and comparably high Co and Cr contents (H. R. Bowman, G. R. Priest, and D. C. Noble, unpub. data; Priest, 1974) argues strongly that the low transition-element content of the Eureka Valley Tuff are not the result of a two-stage process involving partial melting of pre-existing mafic rock (eclogite). The somewhat low V contents probably reflect the separation of small amounts of Fe-Ti oxides (Taylor and others, 1969; Ewart and others, 1973). Approximately 25 percent Eu depletion (Fig. 3) and the Ba/Sr and K/Sr ratios of the glasses, which are much higher than

values found for continental latite of more strongly calc-alkalic character, testify to the separation of appreciable amounts of plagioclase (Korringa and Noble, 1971; Dudas and others, 1971).

As discussed above, the glasses show strong evidence of separation of large amounts of plagioclase and mafic minerals. Approximate mass-balance calculations suggest that the present contents of large-ion lithophile elements in the By-Day Member glass are about three times their values in the original mafic or low-SiO_2 intermediate magma. The extreme enrichment in K, Rb, Cs, U, Th, Pb, and other related elements thus is in part the result of residual concentration produced by the separation of large amounts of crystalline material.

The K/Rb ratios of the Tollhouse Flat and By-Day Members are approximately 195 and 190, respectively (Tables 3 and 5). Considerable crystal fractionation is required to markedly lower K/Rb ratios if phases containing appreciable amounts of K do not separate (for example, Noble and Korringa, 1974). The K/Rb ratio of the primary magma(s) thus in all probability did not exceed 300. Although there will be some difference between the K/Rb of a small-volume partial melt compared to that of the source material, the similarity of the partition coefficients for K and Rb between clinopyroxene and other mantle phases and magmatic liquid (Shimizu, 1974) suggests that the amount of fractionation of K and Rb will not be great. The very low K/Rb ratios of the glasses from the Eureka Valley Tuff thus suggest that the source was appreciably less depleted in large cations than the material from which ocean-floor and island-arc tholeiite magmas are generated.

Genetic Relationship of Tollhouse Flat and By-Day Magmas

The nonhydrated glasses of the Tollhouse Flat and By-Day Members are very similar in their major- and minor-element composition. The isotopic compositions of Sr and Pb are identical within the limits of analytical error (Tables 5 and 6). Nearly all the small differences in elemental chemistry can reasonably be explained by separation of small amounts of the phenocryst minerals present in the rocks. For example, glass from the Tollhouse Flat Member contains about 5 percent less La and Ce than does glass from the By-Day Member. The heavier rare-earth elements are even more strongly depleted. The Tollhouse Flat Member contains appreciable apatite, both as individual phenocrysts and as inclusions within other minerals. The P_2O_5 content of the glass from the Tollhouse Flat Member also is lower than that of the glass from the By-Day Member (Table 3). The rare-earth differences can thus be explained by the crystallization of apatite, which has a very strong affinity for the entire range of rare-earth elements (Nagasawa, 1970), and possibly zircon, which preferentially accepts the heavy rare-earth elements. Certain data discussed below, however, suggest that the two members were derived from distinct, although very similar and closely genetically related, bodies of magma rather than from a single body of magma which had become vertically
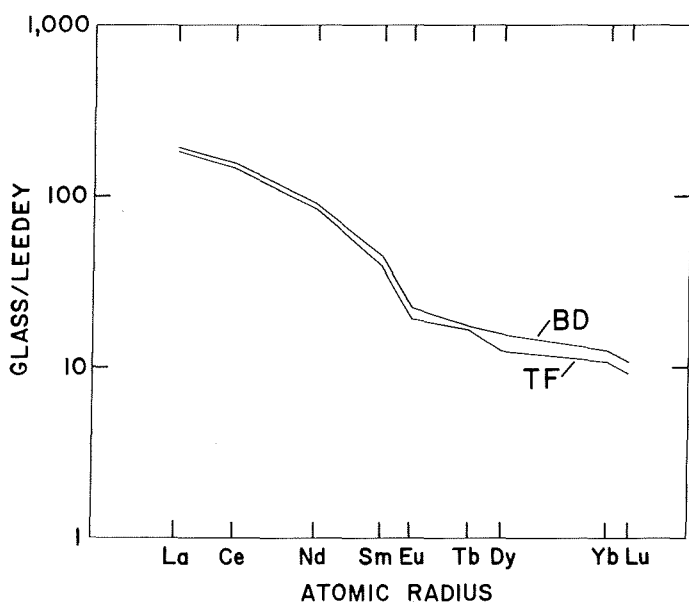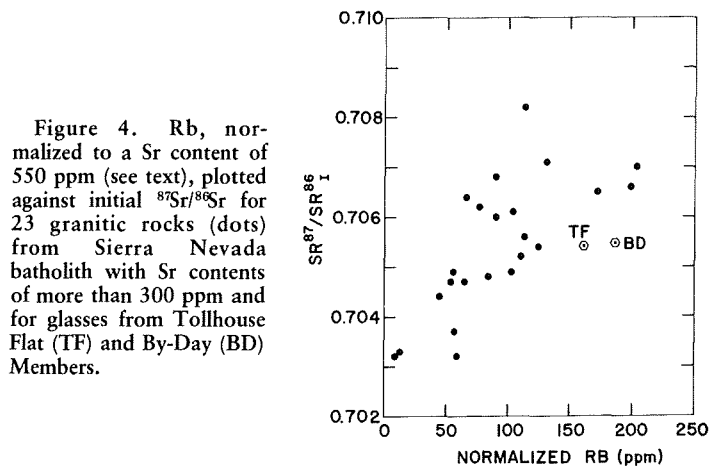

Figure 3. Patterns of rare-earth elements for nonhydrated glasses from Tollhouse Flat (TF) and By-Day (BD) Members of Eureka Valley Tuff. Data normalized to the L-6 chondrite Leedey (Masuda and others, 1973). Atomic radii are those of Templeton and Dauben (1954) adjusted to an O radius, in six-fold coordination, of 1.32 Å.

Figure 4. Rb, normalized to a Sr content of 550 ppm (see text), plotted against initial $^{87}Sr/^{86}Sr$ for 23 granitic rocks (dots) from Sierra Nevada batholith with Sr contents of more than 300 ppm and for glasses from Tollhouse Flat (TF) and By-Day (BD) Members.

compositionally zoned as the result of crystal fractionation and settling within a high-level magma chamber.

The Tollhouse Flat Member contains appreciable intratelluric biotite, both as large euhedra and as inclusions in large plagioclase phenocrysts, whereas the less silicic By-Day Member contains none. Biotite thus appears to have started to form relatively early in the crystallization history of the Tollhouse Flat magma. Calculations based on modal data, glass composition, and assumed phenocryst compositions indicate that the Tollhouse Flat (glass plus contained phenocrysts) had a SiO_2 content of about 63.5 wt percent compared to the SiO_2 content of 63.3 wt percent for the glass from the By-Day Member. Thus, it is difficult to explain the complete absence of biotite in the By-Day Member and particularly in its lowermost ash flows, if the Tollhouse Flat and By-Day Members represent successively deeper portions of a single, compositionally zoned magma body.

Moreover, although the nonhydrated glass of the Tollhouse Flat Member is richer in U, Th, Cs, and so forth[3] than is the glass of the By-Day Member, the latter contains slightly, but significantly, more Rb (Table 5) and probably also more K than does the former. Separation of any reasonable assemblage of phenocrysts from the glass of the By-Day Member would cause an increase rather than a decrease in the K_2O content of the residual liquid; the crystal assemblage would have to contain more than 50 percent biotite to produce even a slight decrease in K_2O, whereas biotite composes less than 20 percent of the phenocryst assemblage of the Tollhouse Flat Member.

The Tollhouse Flat and By-Day Members thus appear to represent two distinct (although closely related genetically) bodies of magma. The Tollhouse Flat magma perhaps was able to retain its volatile constituents throughout the interval of subsequent crystal fractionation, allowing relatively early onset of biotite (and hornblende) crystallization, with a concomitant decrease in the rate of rise of the K_2O and Rb contents of the melt as crystal fractionation proceeded. The second batch of magma, however, may have had lower initial halogen and water contents and (or) may have lost these components during the period of high-level intratelluric crystallization. Biotite did not crystallize from the By-Day melt, and the K_2O content was able to rise unhindered by the separation of a K-rich phase. It is significant that the glass from the Tollhouse Flat Member contains significantly more Cs (17 compared to 14 ppm) than does the glass from the By-Day Member. Cs, with an ionic radius almost 15 percent greater than that of Rb, is strongly partitioned into the melt phase during the crystallization of biotite (Dupuy, 1968).

Sr and Pb Isotopes

The initial $^{87}Sr/^{86}Sr$ ratio of the Eureka Valley Tuff, 0.7054 to 0.7055 (Table 5), conforms well with the general decrease in initial $^{87}Sr/^{86}Sr$ progressively northward along the eastern margin of the Sierra Nevada and the northwestern Great Basin that has been observed for Cenozoic volcanic rocks (Hedge and Noble, 1971; Noble and others, 1972, 1973) and Mesozoic granitic rocks (Kistler and Peterman, 1973). The $^{87}Sr/^{86}Sr$ ratios, although within the range of values found for oceanic basalt (Hedge and others, 1972), are higher than those of almost all oceanic rocks studied. Values greater than 0.7050 are found only for alkalic basalt at a small number of volumetrically insignificant islands; indeed, the percentage of oceanic basalts with $^{87}Sr/^{86}Sr$ ratios above 0.7040 is small. However, in the Great Basin and eastern Sierra Nevada, basalts commonly are found that have $^{87}Sr/^{86}Sr$ ratios of 0.706 to 0.707+ and such high Sr contents and low Rb/Sr ratios that addition of significant amounts of radiogenic Sr through crustal contamination

can be ruled out (Hedge and Noble, 1971; Mark and others, 1974). The Sr isotopic ratio of the Eureka Valley Tuff thus would appear to be compatible with derivation from an ultramafic source within the asthenosphere or possibly the continental lithosphere. Although the Sr isotopic data cannot rule out generation largely or in part from relatively unradiogenic lower crustal material, the high (≥1,000 ppm) Sr contents of less differentiated rocks of the Little Walker center (Hedge and Noble, 1971; H. R. Bowman, G. R. Priest, and D. C. Noble, unpub. data; Priest, 1974) do not favor the interpretation that an appreciable increase in $^{87}Sr/^{86}Sr$ was produced by incorporation of radiogenic crustal material by a magma with a Sr isotopic composition typical of ocean-floor basalt.

The $^{87}Sr/^{86}Sr$ ratio of a magma will tend to reflect the content of large cations in the source materials, although considerable scatter will be present because $^{87}Sr/^{86}Sr$ is a time-integrated function of Rb/Sr and not of Rb/Sr at the time of magma generation. Additional scatter in original content of large-ion lithophile elements will be introduced by variations in the degree of partial melting of the source materials. Nevertheless, for a suite of rocks derived from a source region that is laterally and (or) vertically inhomogeneous relative to $^{87}Sr/^{86}Sr$ and Rb and Sr contents, a general correlation should exist between $^{87}Sr/^{86}Sr$ and both Rb content and Rb/Sr ratio.

As noted by Kistler and Peterman (1973), such correlations are present in the data for the Sierra Nevada batholith. The Rb content and Rb/Sr ratio of a magma is a function of the history of differentiation in addition to the Rb and Sr contents of the source and the degree and conditions of partial melting. We thus have attempted to reduce the amount of data scatter by normalizing the data from the Sierra Nevada and Eureka Valley Tuff to a constant Sr content by assuming a differentiation scheme similar to that observed for andesite and dacite from Crater Lake, Oregon (Noble and Korringa, 1974). In these rocks, Rb behaved as a nearly ideal rest element, and the distribution coefficient for Sr between total crystals and liquid increased markedly (Korringa and Noble, 1971) with differentiation. These effects combined to generate an approximately arithmetically linear decrease in Sr with increasing Rb. Assuming that a comparable percentage increase in Rb corresponds to the same absolute decrease in Sr found for the Crater Lake suite, we have normalized the Rb contents of both the Sierra Nevada and Eureka Valley Tuff specimens to a Sr content of 550 ppm (Fig. 4). This simple model breaks down during the later stages of differentiation of K-rich magma, and we thus have omitted specimens containing less than 300 ppm Sr.

The normalized Rb contents of the Sierra Nevada specimens correlate well with initial $^{87}Sr/^{86}Sr$ ratios (Fig. 4). The data for the Eureka Valley Tuff plot to the right of the Sierra Nevada trend. This suggests that (1) the primary magma or magmas that produced the Eureka Valley Tuff were generated by a smaller effective degree of partial melting than those that produced most of the granitic rocks of the Sierra Nevada batholith or (2) the source was appreciably richer in large-ion lithophile elements than those from which Sierra Nevada magmas of comparable $^{87}Sr/^{86}Sr$ were derived.

The Pb isotopic ratios of the Eureka Valley Tuff (Table 6) plot at the upper end of the array defined by data from upper Cenozoic volcanic rocks from the Cascade Mountains and very slightly below the trend defined by Mesozoic granitic rocks from the Sierra Nevada batholith (Fig. 5). The ratios are virtually identical to those of highly differentiated rhyolite specimens from bimodal suites in the Mono Craters and Clear Lake, California (Table 6).

The $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios of the glasses from the Eureka Valley Tuff are too high for them to be uncontaminated derivatives of oceanic mantle as represented by ocean-floor tholeiite from the Juan de Fuca Ridge–Gorda Rise area (Fig. 5). The isotopic similarity of the Eureka Valley Tuff to spatially related rocks of the Sierra Nevada batholith and temporally associated rocks of the Cascades suggests the possibility that the Eureka Valley magmas may have had a similar history to the magmas of one or both of these provinces.

Pb isotopic arrays with relatively steep slopes obtained on igne-

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[3] The precision of the neutron activation analyses is appreciably better than their absolute accuracy, and the differences in the concentration of these elements and others such as the rare-earth elements between the glasses of the two members are highly significant.
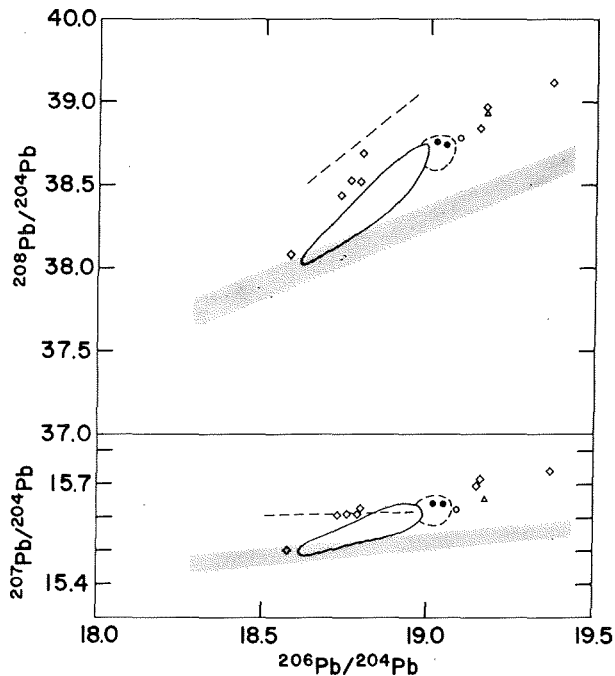
Figure 5. Summary of pertinent Pb isotopic data. New analyses on nonhydrated glasses from the Eureka Valley Tuff, corrected for in situ growth of radiogenic Pb since eruption, are indicated by dots. Analyses are shown as follows: Sierra Nevada batholith by diamonds (Doe and Delevaux, 1973), Mono Craters obsidian by an open circle, and Clear Lake, California, obsidian by a triangle. The stippled fields represent the array of mantle Pb as reported by S. E. Church and M. Tatsumoto (unpub. data). Dashed straight lines represent data for Pb from manganese nodules (Church, 1973). The fields enclosed by solid lines represent the array of Pb isotopic values of basaltic to dacitic rocks from the Cascade Mountains (Church and Tilton, 1973; S. E. Church, unpub. data). The fields enclosed by dashed lines represent isotopic values measured on several silicic volcanic rocks that occur along the Cascade Mountains trend (S. E. Church, unpub. data).

ous rocks and ores from cratonic regions (for example, Stacey and others, 1968; Peterman and others, 1970b) have been interpreted as resulting from the presence of large proportions of Pb from very old systems having variable $^{238}U/^{204}Pb$ ratios. Thus, as pointed out by Doe and Delevaux (1973), a possible source for rocks of the Sierra Nevada batholith would be old upper-mantle material within the lithosphere that had not suffered marked loss or enrichment of U and Th relative to Pb. Such an explanation would be applicable to the Eureka Valley Tuff but probably not to the volcanic rocks of the Cascades.

Armstrong and Cooper (1971) suggested that such steep data arrays are controlled by the Pb in oceanic sediment admixed with down-going ocean crust during subduction. However, Church and Tilton (1973) and Church (1973) argued strongly that this mechanism is not adequate to explain the data from the Cascade Mountains. Although some graywacke sediment from the trough off the coast of Oregon (S. E. Church, unpub. data) and Eocene sediment from the Oregon Coast Ranges (Tatsumoto and Snavely, 1969) may have the correct Pb isotopic compositions to serve as possible source materials for the more radiogenic end of such a mixing array, as pointed out by Peterman and others (1970a) and Church and Tilton (1973), the Sr isotopic composition of the volcanic rocks appears to rule out such a model. Moreover, as pointed out by Doe and Delevaux (1973), it would appear quite fortuitous that mixing of leads characteristic of oceanic basalt and continentally derived sediment, both of which are isotopically quite heterogeneous, should produce steep, well-defined trends. Although the radiogenic character of the Pb in silicic volcanic rocks of the Cascades (Fig. 5) is suggestive of crustal contamination, a similar argument can be made against contamination of magma with Pb from ocean-floor tholeiite by upper crustal rocks, which typi-

cally show wide ranges in Pb isotopic composition. Indeed, it may well be unreasonable to assume that the Pb isotopic composition of the lower continental lithosphere is grossly homogeneous.

The above discussion shows that the Pb and Sr of the Eureka Valley Tuff could have been derived from the lower part of the continental lithosphere or could be a mixture of Pb and Sr of typical oceanic basalt with added radiogenic continental material. However, the steep and very coherent data arrays obtained from the Sierra Nevada batholith and the volcanic rocks of the Cascades argue against the latter interpretation.

Another possible source for the Eureka Valley Tuff and other rocks of the Stanislaus Group is suggested by geochemical studies of volcanic rocks of certain oceanic islands. Schilling (1973) concluded that oceanic volcanic rocks produced by the partial melting of mantle plumes are less depleted in large-ion lithophile elements than are ocean-floor tholeiites, which he suggested are derived from relatively shallow depths within the asthenosphere. Volcanic rocks from oceanic islands also in general have more radiogenic Pb and Sr isotopic compositions. Thus, the relatively radiogenic character of the Eureka Valley Tuff could be explained by derivation from a source region located beneath the convecting portion of the mantle from which ocean-floor basalts are derived. The source would not have suffered an early depletion of U relative to Pb or Rb relative to Sr.

ORIGIN AND EVOLUTION OF THE EUREKA VALLEY MAGMA

It has recently been popular to propose that intermediate magmas of circum-Pacific regions are produced by partial melting of the basaltic (eclogitic) portion of subducted oceanic lithosphere. Such a mechanism does not appear applicable to rocks of the Stanislaus Group. The Eureka Valley Tuff is closely associated with latite and low-Si latite with moderately high concentrations of both large-ion lithophile elements and minor transition elements. Such magmas cannot be produced by direct partial melting of subducted ocean-floor tholeiite. Small degrees of partial melting would produce melts with contents of minor transition elements that are too low, whereas large amounts of melting would generate melts with contents of large-ion lithophile elements that are much too low. Such a melt would have to react with large amounts of superjacent rock to acquire the observed isotopic composition and content of large-ion lithophile elements.

Instead, we believe that it is more likely that the Eureka Valley Tuff was derived from ultramafic material from deep within the mantle. Recent work has emphasized the importance of partial melting of convectively rising bodies of mantle material as the result of adiabatic decompression in the generation of a variety of magma types. The geometric configuration and magmatic history of the Little Walker volcanic center and other centers in the western United States is strongly suggestive of such a model (Noble, 1972, and in Armstrong and others, 1969, p. 486). Anderson and Perkins (1974) presented calculations that provide a theoretical understanding of the generation of diapiric upwellings or surges of mantle material in areas where flow patterns within the mantle have been disturbed. Successive tappings from a partly molten diapir would provide the succession of genetically related, but distinctive, magmas recognized at the Little Walker and other volcanic centers (for example, Noble and Christiansen, 1974). If derived from great depth, the diapir responsible for the Eureka Valley Tuff probably would have had to shoulder aside thin remnants of the subducted East Pacific plate.

Available experimental data (for example, Mysen and others, 1974; Boettcher, 1973) do not appear to rule out the generation of both hypersthene-normative and slightly quartz-normative melts by the partial melting of ultramafic materials under appropriate conditions at various depths in the upper mantle. The strong relative enrichment of the Eureka Valley Tuff in light rare-earth elements (the La/Yb ratio of the glass from the By-Day Member is 23)

suggests generation within a pressure-temperature regime within which garnet, which has a strong affinity for the heavy rare-earth elements, is a stable phase (Green and Ringwood, 1972). The extensive crystal fractionation that the magmas underwent strongly suggests that the parental magma was not appreciably silica oversaturated, for relatively small amounts of crystal fractionation would have been required to produce a residual liquid with 63 wt percent SiO_2 from a mantle-equilibrated melt containing significant normative quartz. Instead, the primary melt probably was hypersthene normative or possibly very slightly quartz normative.

The very high concentration of large-ion lithophile elements in the Eureka Valley Tuff requires that the parent magma also must have been rich in these components. The Sr and Pb isotopic ratios, low K/Rb ratios, and the general abundance of large-ion lithophile elements strongly suggests that the ultimate source for the parent magma also must have been well endowed with large-ion lithophile elements. Mantle material from great depths may have a greater concentration of large-ion lithophile elements than does overlying material from the low-velocity zone (Schilling and Noe-Nygaard, 1974). Nevertheless, even if the source was appreciably richer in K, Rb, and so forth than that from which ocean-floor tholeiite was derived, the final mantle-equilibrated magma from which the Eureka Valley Tuff was produced by differentiation must represent about a fifty-fold increase in the concentration of the more enriched large-ion lithophile components over the concentration of these components in the source. Even if aggregation of small pockets of magma was facilitated by internal shearing (Weertman, 1972) within a still-mobile diapir, it is difficult to envisage how innumerable small pockets of several percent partial melt could coalesce to form a major ($\sim$2,000 km^3) body of magma.

A mechanically more plausible two-stage process would have begun with more extensive (perhaps 5 to 15 percent) partial melting and coalescence of this liquid to form a large body of magma. This relatively light mass would then have ascended, reacting with and extracting large-ion lithophile components from superjacent material of the diapir, the upper asthenosphere, and perhaps the lower lithosphere. Such a zone-refining process (Harris, 1957) would have been greatly facilitated by a small degree of partial melting of the overlying material and by convection within the ascending body of magma. Zone refining could involve material of the lower crust. As the magma moved through the lithosphere and into high-level chambers, crystallization and crystal settling progressively overshadowed assimilation. The concentration of MgO, minor transition elements, CaO, and Sr decreased, and the concentration of SiO_2 and large-ion lithophile elements increased until the process of differentiation was halted by eruption.

In this model, the very high concentration of large-ion lithophile elements in the Eureka Valley Tuff reflects the cumulative effects of (1) a moderate degree of partial melting of upwelling mantle material that was richer in large-ion lithophile elements than is the material from which ocean-floor tholeiite is derived, (2) zone refining of other parts of the diapir, superjacent mantle, and perhaps lower crust, and (3) a high degree of crystal fractionation of the final hypersthene-normative or slightly quartz-normative parental magma. Preliminary data on other rocks of the Little Walker volcanic center (Priest, 1974; Priest and others, 1975) are consistent with this interpretation. Successively younger rocks of the center contain progressively lower concentrations of large-ion lithophile elements. We tentatively interpret this relationship as largely reflecting progressive depletion of large-ion lithophile elements in the source region by the generation and extraction of successive batches of primary magma.

Finally, it should be mentioned that the Eureka Valley Tuff and other rocks of the Stanislaus Group differ markedly in FeO^*/MgO ratio, large-ion lithophile content, and petrography from calc-alkalic andesites, dacites, and so forth of Miocene age that underlie and overlie the Stanislaus Group (Slemmons, 1966). These pronounced differences suggest that the calc-alkalic magmas that formed the Miocene andesites and dacites were derived from fundamentally different source regions than were the magmas from which the Stanislaus Group originated.

ACKNOWLEDGMENTS

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