



Origin of distinct silicic magma types from the Guachipelín Caldera, NW Costa Rica: Evidence for magma mixing and protracted subvolcanic residence

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Abstract

Lower Pleistocene pyroclastic deposits in NW Costa Rica represent sequential eruptions of distinct dacitic–rhyolitic (69–79% SiO₂) magmas from the Guachipelín Caldera that were emplaced in a period of 0.75 myr. This southern segment of the Central American arc, the Chorotega block, evolved on the modified Caribbean Large igneous province, an overthickened oceanic plateau; silicic magmatism is uncommon in settings such as this, void of continental crust. Previously, models have proposed the generation of silicic magmas in this type of setting by the partial melting or extreme crystal fractionation of intermediate source rocks (e.g. [Tamura, Y., Tatsumi, Y., 2002. Remelting of an andesitic crust as a possible origin for rhyolite magma in oceanic arcs: an example from the Izu–Bonin arc. *Journal of Petrology* 43, 1029–1047]). In fact, recent melting experiments performed by Sisson et al. [Sisson, T.W., Ratajeski, K., Hankins, W.B., Glazner, A.F., 2005. Voluminous granitic magmas from common basaltic sources. *Contributions to Mineralogy and Petrology* 148 (5), 542–565] suggest that melting of andesite or high-K basalts, common along the Central American volcanic arc, could produce silicic melts with the characteristic alkali content of these types of eruptives.

Geochemical evaluation of the pumice-clasts through the complete sequence of Guachipelín eruptive products allows for subdivision into two major silica groups. First, the dacites are (66–72 wt.% SiO₂ pumice clast; 75.2–76.5 wt.% SiO₂ glass) orthopyroxene-bearing with plagioclase (An_{36–65})±magnesianhornblende, which are found intermittently from the base of the sequence through the uppermost ash-flow deposit. Second, the rhyolites are (72–79 wt.% SiO₂ pumice clast; 74.5–78.6 wt.% SiO₂ glass) biotite and quartz-bearing, with plagioclase (An_{24–51}) and magnesianhornblende. Chemical heterogeneities were discovered within each of these groups through evaluation of incompatible trace element ratios. Consequently, seven units were defined using the Nb/Ta ratio, which has a significantly wide range, from 3.8 to 29.4, and is interpreted to reflect contributions from more than one intermediate source. Most of these units also display extensive geochemical and petrological evidence of mixing (oxygen isotopes, phenocryst composition, banded pumice clasts, and different glass compositions in single pumice fragments).

The distinct geochemical characteristics of these deposits and the stratigraphic occurrence of each flow unit require both limited fractional crystallization within units coupled with melt extractions and extensive mixing. Hence, individual melts would reside in relatively close proximity in subvolcanic zones for extended periods prior to the inception of a particular eruptive event.

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Considering the temporal (<0.75 Ma) and spatial (single caldera) constraints of this sequence of eruptions, significant chemical variations of the magmas have occurred.

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1. Introduction

Silicic pyroclastic flows and related deposits along the Central American volcanic arc are the result of subduction of the Cocos Plate underneath the Caribbean Plate. This arc can be divided into two large geologic regions based on the composition of the underlying crust: 1) The southeastern Chorotega block underlain by the Caribbean Large Igneous Province (CLIP; non-continental) and 2) The Northwestern Chortis block underlain by Paleozoic crystalline basement (continental). Vogel et al. (2006) have shown that the along-arc variation of selected trace element ratios and oxygen isotopes in silicic pumice fragments mimic the variation observed in the arc-related lavas. These along-arc variations in the lavas have been interpreted to reflect varying contributions from the slab and mantle (Carr et al., 1990; Patino et al., 2000; Eiler et al., 2005) and are not influenced by assimilation of the crustal material (Carr et al., 2003). Although regional scale geochemical variations along arc appear to be the result of subduction zone dynamics, local heterogeneity in the composition of the ignimbrites requires an alternative model. This study focuses on the petrogenesis of silicic magmas in tectonic regions absent of continental crust and the processes governing the geochemical variability in multiple ash-flow sheets associated with a single caldera, the Guachipelín, located in the southeastern segment of the Central American Arc (Fig. 1).

1.1. Silicic volcanism in arc settings

The petrogenesis of silicic magmas in arc settings without old, evolved continental crust, although extensively studied (for a review see: Bergantz, 1989; Hildreth and Fierstein, 2000; Tamura and Tatsumi, 2002; Vogel et al., 2004), is still not well understood. If old, evolved continental crust were present, simply assimilating and/or melting that crust could produce silicic magmas (Perry et al., 1993; Vervoort and Green, 1997; Parker et al., 2005). However, the southern part of the Central American arc is not built on old, evolved continental crust and silicic volcanic deposits are common. Vogel et al. (2004) have suggested that the gen-

eration of these magmas represents the development of new continental crust.

Several models have been presented to account for the presence of high silica volcanic products in arc settings. Tamura and Tatsumi (2002) have argued that slab-derived fluids induce the formation of basaltic mantle melts that would eventually pond at the base of the crust. Subsequent melting of these crystallized basaltic magmas could produce intermediate hydrous magmas that stall within the crust after reaching neutral buoyancy. These plutons are compositionally calc-alkaline andesites, and partial melting of these emplaced crystalline magmas could produce rhyolitic melts (Tamura and Tatsumi, 2002). Alternatively, Bachmann and Bergantz (2004) emphasize the expulsion of interstitial liquid from a crystal mush within a shallow magma chamber as a mechanism to produce voluminous rhyolitic melt.

The silicic pyroclastic fall and flow deposits associated with the Guachipelín Caldera, Costa Rica, contain chemical heterogeneities among and within the individual units (see discussion below). Different processes have been proposed to account for the chemical heterogeneities in other silicic deposits: 1) differentiation of a chemically homogeneous magma body (Mittlefehldt and Miller, 1983; Baker and McBirney, 1985; McBirney et al., 1986; de Silva and Wolff, 1995); 2) discrete magma batches produced by partial melting or melt extraction from chemically distinct sources (Marsh, 1984; Bergantz, 1989; Sawyer, 1994; Mills et al., 1997; Eichelberger and Izbekov, 2000; Eichelberger et al., 2000); 3) magma chamber recharge (Eichelberger et al., 2000); and 4) modification by magma mixing/mingling, and/or assimilation (Eichelberger et al., 2000).

This paper documents the stratigraphic sequence of deposits associated with the Guachipelín Caldera, NW Costa Rica (Fig. 1) and the petrologic characteristics of the pumice-clasts. We present geochemical, mineralogical, and textural evidence that supports the generation of distinct silicic magma batches and demonstrates the importance of both open-system processes and fractional crystallization in the Guachipelín eruptive history. Our model accounts for the chemical variability and

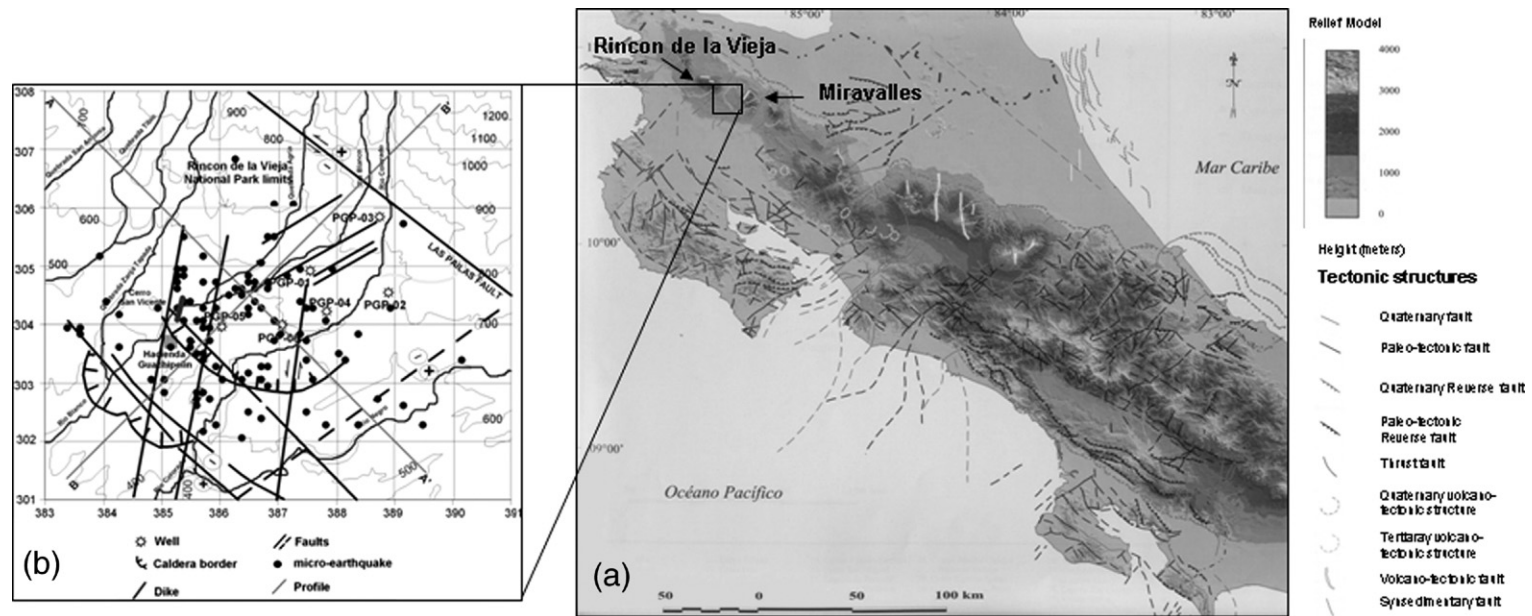


Fig. 1. a, Map of Northwestern Costa Rica showing the field study area which lies between active arc volcanoes: Rincon de la Vieja to the Northwest and Miravalles to the East. Map taken from Denyer et al. (2003). b, Schematic diagram showing part of the collapse structure which defines the Southwestern Guachipelin Caldera. The pumice samples were collected from road cuts and quarries along the South and Southeast Caldera margin.

describes the origin and evolution of the magmatic system.

2. Guachipelín ignimbrite stratigraphy

Ignimbrites associated with the Guachipelín Caldera (Fig. 1) are related to the processes governing the modern subduction zone magmatism and are between 2.06 and 1.31 Ma (Vogel et al., 2004). These units include fall, flow and surge deposits that are crystal-poor, poorly welded tuffs covering an area of 3500–4000 km² with a total eruptive volume of 25 km³ DRE (Chiesa, 1991; Zamora et al., 2004). Although the topographic expression of the caldera is obscured by infill and collapse by younger eruptions, seismic profile data (provided by Waldo Taylor, Observatorio Sismológico y Vulcanológico de Arenal y Miravalles (OSIVAM), Instituto Costarricense de Electricidad (ICE); personal communication) define two arcuate structures between the Rincon de la Vieja and Miravalles volcanoes (Fig. 1), which are interpreted as the southwestern boundary of the caldera.

Kempton et al. (1996) first recognized the association of the Liberia Tuff and the Guachipelín Caldera from the following observations: the structural margins of the caldera truncates all units older than the Liberia Tuff, the radial distribution of the deposits and an increase in the thickness towards the caldera margin, and the largest lithic size (>0.5 m) occur close to the caldera margin. The Liberia Tuff identified by Kempton et al. (1996) is representative of all of the chemically distinct pyroclastic flow units described in the present study, but a more detailed survey of the distribution and clast size for individual units is needed to confirm a relationship to source. Although maximum lithic measurements were obtained for these individual units and are consistent with Kempton et al. (1996) conclusions, heavy vegetation and erosion in this tropical environment prevented a thorough investigation of clast size for each individual flow unit to allow isopleths to be constructed.

This sequence of poorly welded tuffs is further defined in this study using a combination of techniques including field relationships, previously acquired Ar–Ar dates, petrography, and bulk geochemical analyses. Stratigraphic sampling at the various localities constrained the eruptive sequence. It should be noted that the intensity of the tropical weathering and erosion prevented the identification of clear boundaries in the upper section of the sequence. Here we rely on age relationships (e.g. Ar–Ar dates) and distinct contact surfaces between adjacent units that may have intervening flows not recognized at a particular locality

(details below). Following the field work, chemical analyses, particularly trace element ratios (e.g. Nb/Ta), revealed the presence of seven distinct pyroclastic units (see below for details). Geochemically distinct units within the otherwise indistinguishable pyroclastic deposits provide the basis for a more comprehensive determination of stratigraphic succession and the systematic magmatic changes that occur within this succession. Stratigraphic columns at different outcrops illustrate the lateral variations within different units.

The base of the Guachipelín volcanic suite is marked by a paleosol followed by a distinct pale Green Layer (Fig. 2) (all units are informally named). A basal tephra layer, this deposit varies in thickness from 0.1 to 5.0 m and typically consists of lapilli-sized pumice-clasts with sparse lithics averaging 2.2 cm in diameter and grading into a 3–4 cm thick fine ash layer. This tephra grades into the overlying dacitic Santa Fe unit.

Ranging in thickness from 6.0 to 15.0 m, the Santa Fe dacite (Fig. 2) is identified by tan-gray pumice-clasts, with bi-modal pumice-size distribution that occurs normally graded or poorly sorted, with abundant pumice clasts and sparse lithics. Up to 3 sequences of ash-flow sheets with several centimeters of basal ash occur in several outcrops. Glomerocrysts of plagioclase, orthopyroxene, amphibole, and Fe–Ti oxides and light pumice banding are also indicative of this unit. Some Green Layer unit type pumice-clasts (based on similar Nb/Ta ratios) are also found above the graded sequence, occurring as a 0.5–1.0 m thick ash-

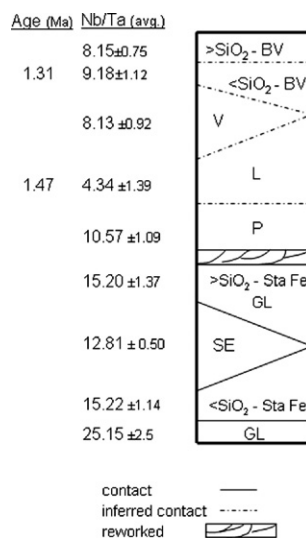


Fig. 2. Composite stratigraphic column constructed based on interpretation of individual outcrop stratigraphic sequences. Nb/Ta ratios are averages for all of the pumice samples within a unit. Ar–Ar dates from Vogel et al. (2004). Abbreviations: BV, Buena Vista; V, Virginia; L, Liberia; P, Pijije; Sta Fe, Santa Fe; SE, Salitral East; GL, Green Layer.

flow deposit, which is distinguished from the deposit below by a decrease in pumice-clast density. These pumice fragments differ from the lapilli-sized Green Layer pumice-clasts found at the base of the Guachipelin sequence in size and color, instead resembling the Santa Fe dacite pumice in size (6–7 cm diameter) and color (tan–gray). This entire sequence is followed by a reworked contact that may represent a time-break.

The Salitral East Unit is located above the Santa Fe dacite (Fig. 2); however, this contact was only observed at one outcrop. This unit is similar to the Santa Fe dacite in thickness (~6.0 m), pumice-clast size distribution (normal grading), color (tan–gray), and lithic abundance. Consequently, we interpret this deposit to represent a continuation of the Santa Fe eruptive episode, which would indicate the aforementioned reworked contact is simply the result of the Salitral East pyroclastic flow scouring the emplaced Santa Fe dacite. Pumice mineralogy is dominated by plagioclase and amphibole with small quantities of biotite and quartz; this is in contrast with the dacitic Santa Fe unit, which contains neither biotite nor quartz.

The next unit in the sequence, the rhyolitic Santa Fe, is found in contact with the Salitral East or the Santa Fe dacite (Fig. 2). This ash-flow sheet ranges in thickness from 0.5 to 1.0 m with randomly distributed tan–gray pumice-clasts and sparse lithics. The contact between Santa Fe dacite and Santa Fe rhyolite is distinguished by a transition from abundant pumice-clasts (up to 30 cm diameter), with a slight normal grading, to a poorly sorted distribution of smaller pumice-clasts (up to 12 cm diameter). Although mineralogically similar to the Salitral East deposits and with no distinct field contacts found, the Santa Fe rhyolite pumice fragments are geochemically distinguishable. In addition, the Santa Fe rhyolite pumice-clasts are also found scattered within or just above reworked ash. Pumice-clast mineralogy is marked by plagioclase, biotite, and quartz with small quantities of amphibole.

Contact between the Santa Fe rhyolite and the next youngest unit, Pijije, is defined by a reworked zone, a feature that consistently occurs where the Santa Fe rhyolite is in contact with the Pijije (Fig. 2). Both the Pijije and Santa Fe rhyolite pumice-clasts are found across this reworked contact, suggesting that the Santa Fe rhyolite was emplaced immediately before the Pijije ash-flow unit. The Pijije deposits are white or pink, ranging in thickness from 3 to 40 m. Lithics are more abundant and larger (average 3 cm diameter, some as large as 18 cm in diameter near the caldera rim) than those found interspersed among the other deposits. Mineralogy consists primarily of plagioclase, biotite, and quartz with trace amounts of amphibole.

Pijije is followed by the Liberia unit (Fig. 2), which is located in the sequence using inferred contacts with the Buena Vista (a younger unit) and Ar–Ar dating. Data for thickness and pumice-clast size are not available. Primary mineralogy consists of plagioclase, biotite, quartz, and small quantities of amphibole. Pumice fragments from this unit were dated at 1.47 Ma (Gans et al., 2003; Vogel et al., 2004).

Similar to the Liberia unit, the Virginia unit lacks firm stratigraphic control and pumice/lithic data are sparse. Only one outcrop is used to indicate the possible placement of this unit above the Liberia unit (Fig. 2), which places it below the Buena Vista. In general, similarities in mineralogy and chemical composition to the adjacent eruptives provide further support for cogenesis. Pumice-clasts contain plagioclase and amphibole.

A distinct unconformity exists between the Liberia and Buena Vista (Fig. 2), the youngest unit in the sequence (1.31 Ma) (Gans et al., 2003; Vogel et al., 2004). Pumice/lithic data are sparse due to extremely limited exposure. Like the Santa Fe deposits, the Buena Vista unit can be divided into two groups: dacite and rhyolite. These pumice-clasts were collected without stratigraphic control within the unit and are therefore assumed to be randomly distributed within the ash-flow sheet. Primary mineralogy consists of plagioclase and amphibole with small amounts of biotite and quartz, which occur only in the rhyolite group.

The composite stratigraphic column in Fig. 2 incorporates the interpretation of all individual outcrops, illustrating a possible eruptive sequence. Dating of the Monteverde Formation, below the Guachipelin sequence, at 2.06 Ma by previous workers (Alvarado et al., 1993; Gillot et al., 1994) constrains the complete eruptive sequence to less than 0.75 myr. Grading from the basal tephra, Green Layer, to the Santa Fe-dacite, reworked contacts, and the lack of paleosol contacts between the fall and flow units through the Pijije suggest this sequence of eruptions occurred over a time period short enough that features like soil horizons had no time to develop. Further work is required to constrain the timing of the upper sequence of eruptions due to poor exposure, but the presence of an unconformity and a 160 ka gap between the Liberia and Buena Vista ash-flow sheets suggests longer periods of quiescence between eruptions.

3. Methods

3.1. Sample collection

Samples of over 380 pumice fragments from the region S-SE of the Guachipelin Caldera were collected. The

Table 1
Pumice-clast bulk geochemical data

Major element oxides (wt.%), trace elements (ppm)																				
Unit	Green Layer		Santa Fe		Salitral East		Santa Fe		Pijije		Liberia		Virginia		Virginia		Buena Vista		Buena Vista	
Type	dacite	S.D.	dacite	S.D.	rhyolite	S.D.	rhyolite	S.D.	rhyolite	S.D.	rhyolite	S.D.	rhyolite	S.D.	dacite	S.D.	rhyolite	S.D.	dacite	S.D.
XRF analyses	n=9		n=74		n=54		n=22		n=31		n=22		n=4		n=4		n=17		n=6	
Majors																				
SiO ₂	68.93	1.19	69.63	1.10	72.86	0.87	73.43	0.63	73.70	1.65	73.59	1.36	72.68	0.35	70.90	0.16	72.63	0.38	69.17	0.89
TiO ₂	0.49	0.05	0.43	0.04	0.33	0.04	0.25	0.03	0.24	0.04	0.25	0.08	0.42	0.03	0.44	0.03	0.32	0.01	0.51	0.02
Al ₂ O ₃	16.84	0.87	15.81	0.94	14.93	0.71	15.47	0.82	15.11	1.18	15.23	0.94	14.92	0.04	15.81	0.28	14.64	0.26	16.17	0.64
Fe ₂ O ₃	3.82	0.43	3.21	0.37	2.53	0.23	1.92	0.24	1.82	0.37	1.85	0.62	3.02	0.39	3.33	0.21	2.53	0.10	3.84	0.28
MnO	0.11	0.04	0.09	0.02	0.08	0.02	0.07	0.01	0.07	0.02	0.06	0.01	0.11	0.04	0.10	0.04	0.08	0.01	0.11	0.03
MgO	0.63	0.16	0.66	0.18	0.46	0.08	0.31	0.06	0.31	0.14	0.37	0.14	0.58	0.05	0.38	0.01	0.65	0.06	0.66	0.23
CaO	2.83	0.34	2.61	0.26	2.21	0.17	1.72	0.19	1.72	0.24	1.70	0.30	2.27	0.03	2.41	0.13	2.27	0.10	3.02	0.23
Na ₂ O	2.68	0.31	2.76	0.25	2.45	0.28	2.52	0.38	2.77	0.31	2.49	0.23	2.39	0.06	2.27	0.12	2.72	0.14	2.75	0.21
K ₂ O	3.64	0.30	3.75	0.34	4.13	0.29	4.28	0.30	3.97	0.42	4.42	0.34	3.54	0.04	4.31	0.11	4.14	0.16	3.73	0.34
P ₂ O ₅	0.03	0.01	0.04	0.03	0.02	0.01	0.03	0.01	0.02	0.02	0.03	0.01	0.06	0.01	0.05	0.00	0.02	0.00	0.04	0.01
Traces																				
Rb	71	10	73	12	79	7	91	8	91	12	103	12	76	0	90	4	81	4	67	9
Sr	391	43	346	51	335	29	249	33	258	28	257	44	312	7	357	17	368	19	398	21
Zr	195	24	192	32	161	24	134	12	134	13	145	27	221	2	207	5	160	5	211	5
Laser ablation ICP-MS analyses																				
Ba	1690	177	1657	180	1799	110	1845	237	1910	339	1776	182	1722	72	1912	73	1729	47	1554	151
Y	24.52	5.45	22.94	4.74	17.23	2.83	17.87	3.30	14.06	2.76	12.99	3.27	21.03	4.00	20.95	0.21	14.28	2.17	19.82	2.05
Nb	11.21	1.37	11.25	1.85	11.98	1.14	11.05	1.88	9.96	0.90	7.58	1.40	8.50	0.42	11.15	1.28	10.49	0.61	8.83	0.16
La	32.66	7.98	30.52	5.69	29.55	2.94	29.04	3.83	26.59	2.51	25.86	4.27	30.01	0.21	36.37	0.13	33.81	2.59	25.79	1.54
Ce	64.99	14.73	57.98	10.50	53.26	5.42	51.94	8.53	47.50	4.62	46.37	7.61	53.53	0.95	66.00	6.36	55.02	5.32	54.75	4.40
Pr	8.09	2.94	6.94	1.52	6.05	0.71	5.92	1.00	5.00	0.61	5.00	1.07	6.72	0.47	8.22	0.25	6.58	0.80	6.13	0.48
Nd	29.38	11.89	24.79	5.85	20.58	2.76	19.40	3.31	16.11	2.49	16.98	4.44	25.14	3.40	29.71	0.26	22.97	3.39	23.14	2.46
Sm	4.44	2.06	4.68	1.14	3.80	0.54	3.15	0.89	2.95	0.50	2.96	0.97	4.50	0.56	5.55	0.04	3.86	0.57	4.64	0.64
Eu	1.09	0.29	1.25	0.24	1.09	0.12	0.82	0.19	0.88	0.11	0.97	0.21	1.29	0.12	1.35	0.01	1.13	0.11	1.38	0.22
Tb	0.54	0.18	0.65	0.14	0.53	0.08	0.43	0.12	0.43	0.07	0.41	0.10	0.69	0.15	0.76	0.03	0.47	0.06	0.63	0.06
Dy	3.20	0.99	3.46	0.78	2.63	0.37	2.29	0.60	2.10	0.41	2.13	0.56	3.46	0.71	3.62	0.08	2.45	0.35	3.19	0.35
Ho	0.56	0.16	0.75	0.17	0.58	0.09	0.47	0.17	0.49	0.11	0.41	0.12	0.69	0.11	0.70	0.01	0.45	0.12	0.59	0.12
Er	1.25	0.41	2.24	0.51	1.84	0.25	1.35	0.61	1.53	0.32	1.30	0.35	2.06	0.39	2.19	0.05	1.52	0.20	2.04	0.13
Yb	1.69	0.25	2.70	0.57	2.26	0.37	2.08	0.64	2.15	0.49	1.96	0.28	2.63	0.34	2.68	0.07	2.05	0.24	2.51	0.23
Lu	0.22	0.04	0.40	0.09	0.36	0.05	0.29	0.09	0.30	0.06	0.27	0.06	0.41	0.06	0.41	0.00	0.32	0.04	0.38	0.04
Hf	3.47	0.42	4.10	0.56	3.69	0.48	2.72	0.46	3.24	0.41	3.80	0.59	5.14	0.16	5.01	0.08	3.63	0.25	4.36	0.82
Ta	0.45	0.09	0.74	0.13	0.94	0.09	0.74	0.16	0.96	0.12	1.66	0.30	1.07	0.06	1.20	0.11	1.29	0.10	0.97	0.12
Th	6.75	1.00	7.18	1.37	7.74	0.60	8.99	1.22	8.33	1.05	8.92	1.54	8.26	0.21	9.22	0.06	7.31	0.75	4.88	0.85
U	3.54	0.80	3.94	0.84	3.73	0.48	5.32	0.98	5.28	1.07	4.57	1.44	5.04	0.04	6.02	0.86	2.68	0.17	2.48	0.23

Analyses are expressed as a mean (wt.%) of samples; S.D. = standard deviation.

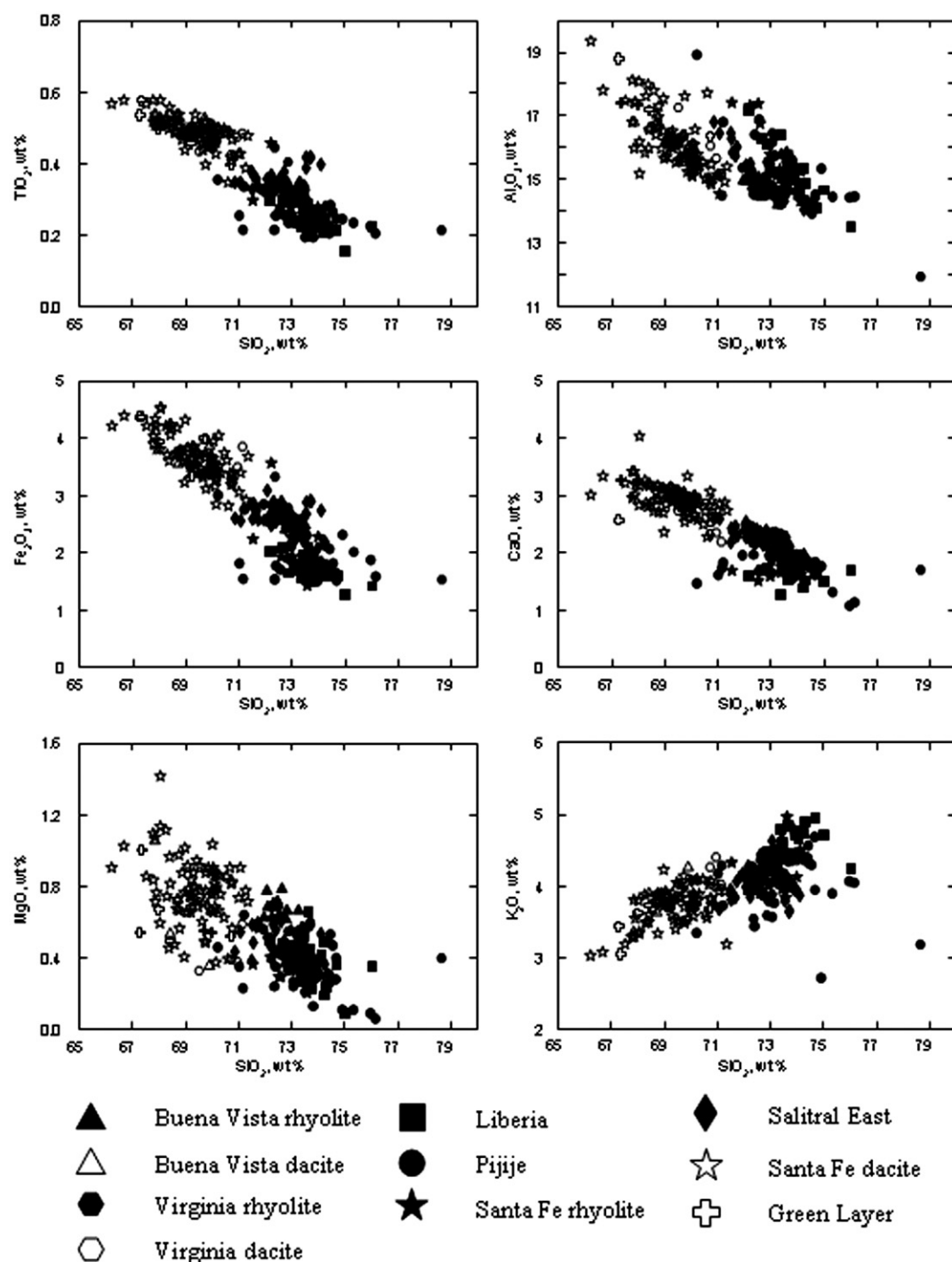


Fig. 3. Variation plots of major element oxides against silica for all of the representative pumice.

locations for pumice sampling were chosen to encompass the region that is thought to represent the pyroclastic deposits of the Guachipelin Caldera (Kempter et al., 1996; Acuna et al., 2000; Zamora et al., 2004). Samples were

taken mainly from road cuts and quarries. To constrain the geochemical boundaries that were apparent within some of the field-identified eruptive deposits, sampling was done in stratigraphic order within individual units.

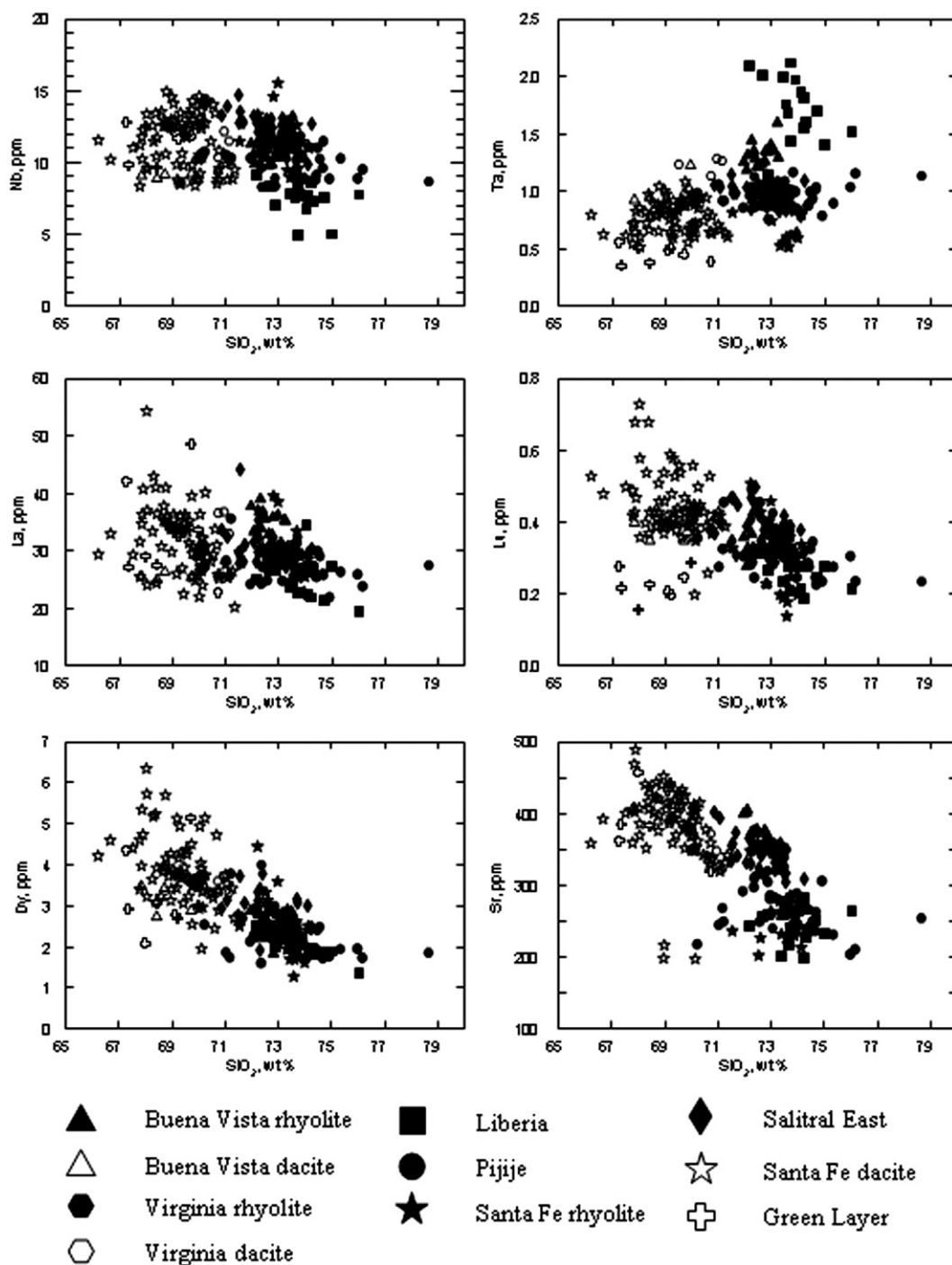


Fig. 4. Variation plots of trace elements against silica for all of the representative pumice.

3.2. Analytical techniques

3.2.1. Bulk geochemical analyses

Over 320 pumice samples were analyzed for major and trace elements. Hand samples selected for analyses

were chosen to represent any macroscopic variations in color, banding, and mineral content and to eliminate weathered samples. X-ray fluorescence (XRF) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) analyses at Michigan State University

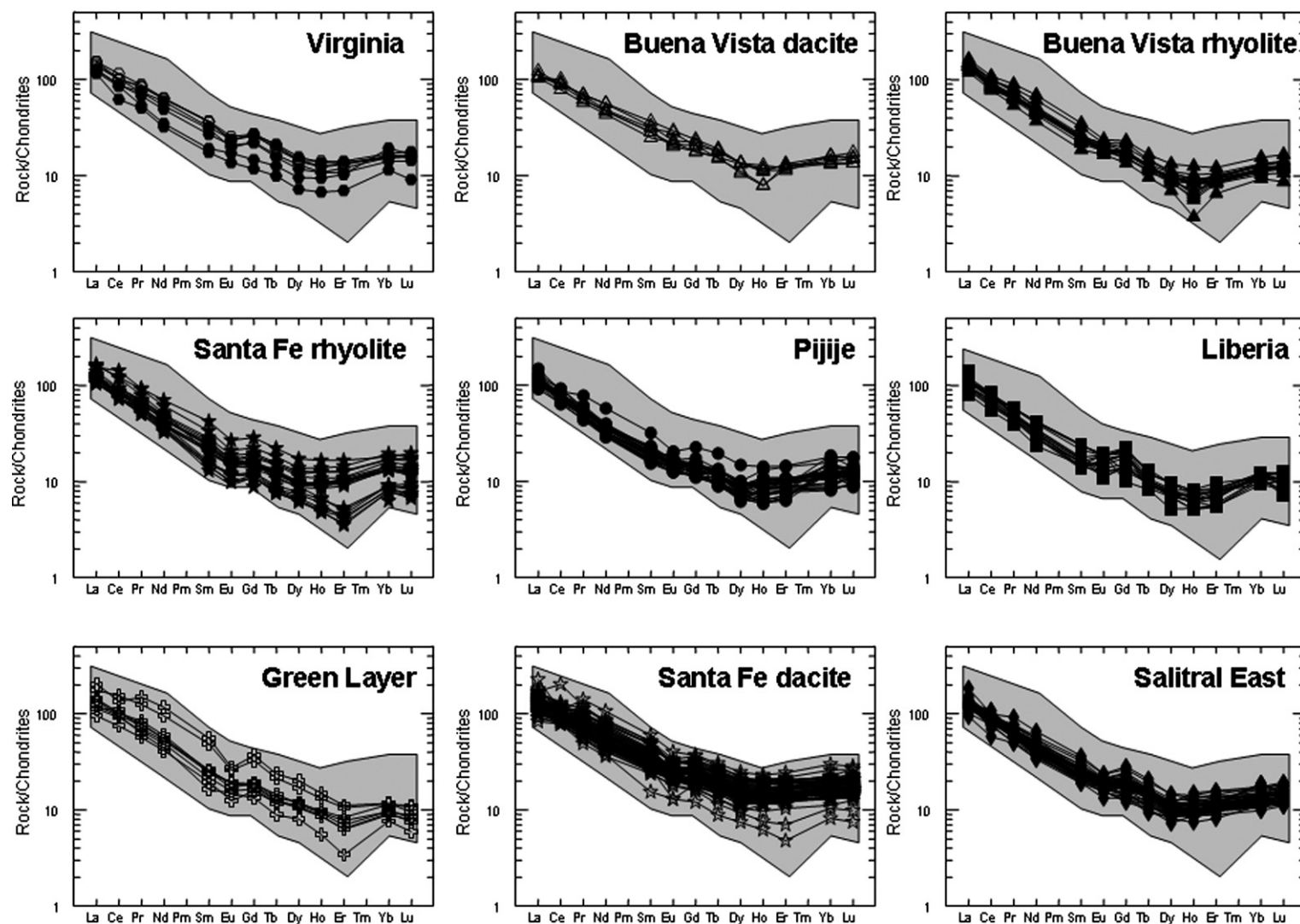


Fig. 5. Rare-earth variation diagrams of representative pumice fragments from each of the seven depositional units including two sub-groups (Santa Fe and Buena Vista) of the Guachipelin–Virginia subgroups are combined on a single diagram. Samples normalized to chondrite value of Sun and McDonough (1989).

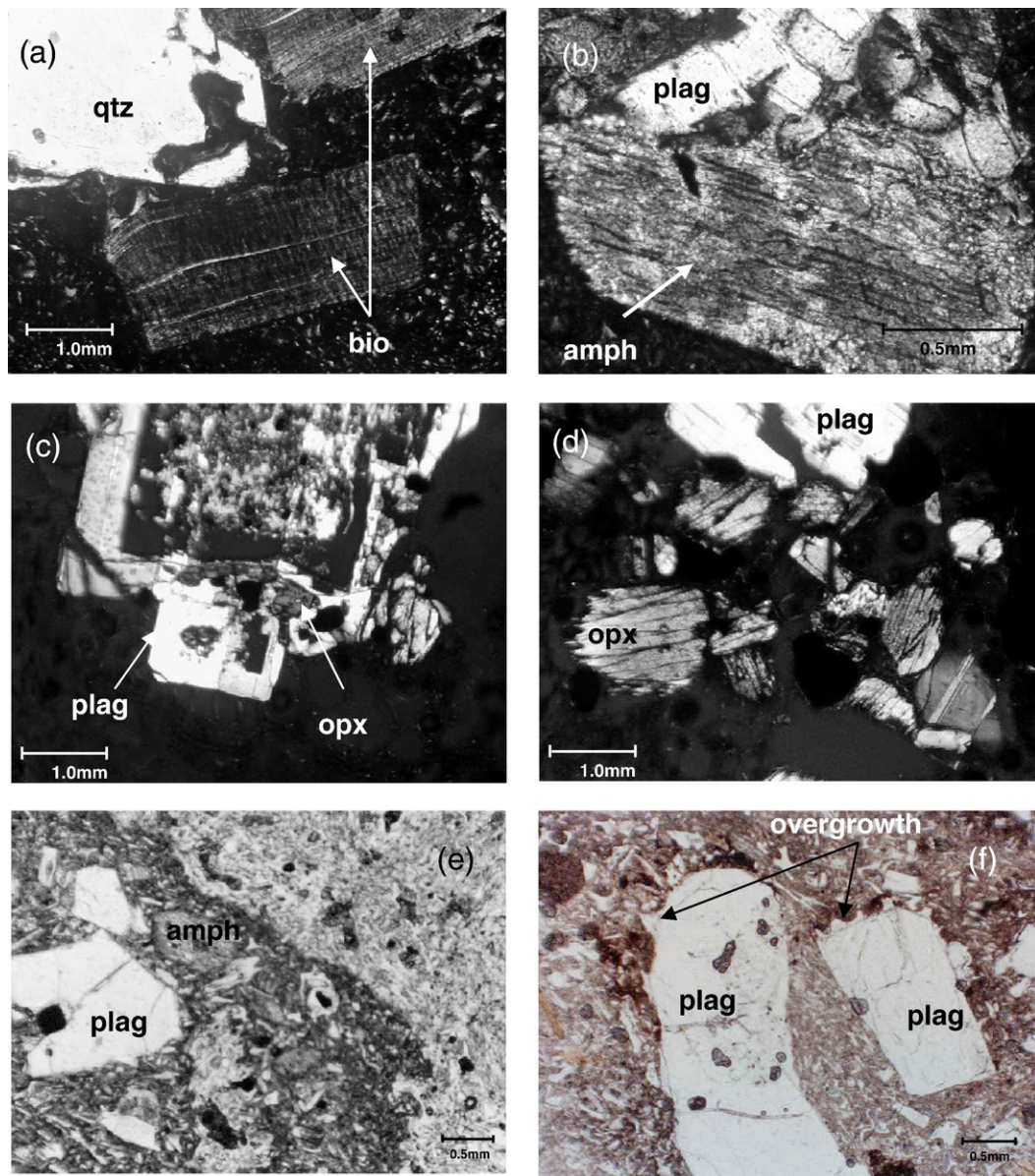


Fig. 6. Photomicrographs (XPL) of representative pumice fragments. Plagioclase, amphibole, biotite and quartz are the most common minerals. Note the resorbed quartz in (a), more than 90% of the quartz found in these pumice samples exhibit this disequilibrium texture. (b) Typical amphibole and plagioclase grains at the edge of a glomeroporphyritic clot (c) Corroded plagioclase found in nearly all of the representative units from the Guachipelin pyroclastic deposits. (d) Glomeroporphyritic clot with resorbed plagioclase and orthopyroxene with 'brush-like' disequilibrium texture from the dacite of the Santa Fe unit. (e–f) Photomicrographs (PPL) illustrating the presence of two distinct glasses in a single pumice fragment from the Pijije unit and plagioclase overgrowths. Note the difference in crystallinity between the two apparently different magmas. This textural variation is consistent with the presence of banded pumice fragments identified in the field.

use fused glass disks. Analytical methods, accuracy and precision are the same as those reported by Vogel et al. (2006). All analyses with totals <96% are excluded from the discussion; major elements are normalized to 100% in the figures.

3.2.2. Individual phase chemistry

Minerals and glass matrix from eighteen samples were selected for electron microprobe (EPMA) analyses at the University of Michigan. These samples represent both the bulk geochemical and physical heterogeneities

observed in the deposits. Microprobe analyses were performed using a Cameca SX 100 EPMA equipped with five wavelength spectrometers using an accelerating potential of 15 kV, a 5 μm beam spot size, counting time of 3 min/mineral, and a 5 nA beam current for mineral phases and a 10 μm defocused beam and 5 nA beam current for glass. The following phases were analyzed for major elements: plagioclase, orthopyroxene, amphibole, biotite, Fe–Ti oxides, and glass.

Trace elements of individual mineral phases and glass analyzed by EPMA were determined using LA-ICP-MS. The location of each point analyzed was recorded for consistency between EPMA and LA-ICP-MS analyses. Laser ablation parameters used included a spot size of 25 μm for plagioclase and 50 μm for amphiboles and glass with a frequency of 20 Hz. The ablation mode was depth profile, where the sample stage was raised at a rate of 1 $\mu\text{m/s}$. The detector was activated before ablation to capture the transient signal. After ~ 0.3 min of data acquisition, ablation was initiated and continued for 5 s. The first 0.3 min of data acquisition was used to measure the background. Once the ablated material reached the detector, the signal for the different elements was clearly observed in well-developed peaks. Results were quantified using the height of the peak above background for each element. The concentrations were calculated following Norman et al. (1996), with

NIST 612 glass as the external standard and calcium determined by microprobe analyses as the internal standard.

4. Guachipelin pumice-clast compositions

Guachipelin pumice clasts can be divided into two primary types, dacite and rhyolite, based on SiO_2 concentrations and mineral content, each representing a wide range of colors (white, pink, green, gray, tan or light-gray/tan banding). The first type, dacite, has pumice clasts with SiO_2 concentrations of less than 72 wt.% and contains plagioclase+hornblende $\pm$ orthopyroxene+Fe–Ti oxides $\pm$ accessory zircon and apatite. The second type, rhyolite, has pumice clasts with SiO_2 concentrations greater than 72 wt.% and contains plagioclase+hornblende+quartz+biotite+Fe–Ti oxides $\pm$ accessory zircon and apatite. The dacite group includes samples from the Green Layer, Santa Fe, Buena Vista, and Virginia units. The rhyolite group includes Santa Fe, Salitral East, Pijije, Liberia, Virginia, and Buena Vista.

4.1. Whole-rock geochemistry

Representative samples from the stratigraphic sequence are in Table 1 and a full dataset is available as an

Table 2
Estimated crystallinities and phenocryst assemblages of selected pumice-clasts from the Guachipelin dacite-rhyolites

Unit/sample	Crystallinity	Plagioclase	Hornblende	Orthopyroxene	Biotite	Quartz	Opaques	Zircon	Apatite
Buena Vista dacite									
990718-2c	20	15	2				3		
Buena Vista rhyolite									
990718-3a	20	15	1		$\ll 1$	2	1	$\ll 1$	$\ll 1$
990718-3-1	14	10	1		< 1	1	1	$\ll 1$	$\ll 1$
Virginia									
010629-1a	22	15	< 1		2	3	< 1		
020709-3a	5	4	< 1				1		
Liberia									
990718-1-1	16	8	< 1		7	< 1	< 1	$\ll 1$	
Pijije									
010629-1c	35	15	< 1		7	10	3		
040708-2a	52	40	10		1		1		
Salitral East									
040706-7f	11	5	4		$\ll 1$	1	1	$\ll 1$	$\ll 1$
Santa Fe dacite									
990718-12g	8	6		2			< 1		
040706-1a	17	15		2			< 1		
Santa Fe rhyolite									
040706-3a	9	5	$\ll 1$		1	2	< 1		
Green Layer									
040706-1j	10	7	1	1			1		

Crystallinity is based on estimated modal percentages determined petrographically.

Table 3

Representative electron microprobe analyses of mineral phases from Guachipelin ignimbrite pumice-clasts

Unit	Green Layer	Santa Fe	Salitral East	Santa Fe	Pijije	Liberia	Virginia	Virginia	Buena Vista	Buena Vista	Green Layer	Salitral East
Type	Dacite	Dacite	Rhyolite	Rhyolite	Rhyolite	Rhyolite	Rhyolite	Rhyolite	Dacite	Rhyolite	Dacite	Rhyolite
Sample	040706-1J	990718-12g	040706-7F	040707-8F	010629-1C	990718-1-1	020709-3a	010629-1A	990718-2C	990718-3-6r	040707-3C	040706-7F
Analysis #	plag 5a	plag 2a	plag 1a	plag 3a	plag 8a	plag 6a	plag 3	plag 2a	plag a	plag 1	opx 2c	amph 1
Mineral	plag	plag	plag	plag	plag	plag	plag	plag	plag	plag	opx	amph
(wt.%)												
SiO ₂	51.13	52.44	58.16	59.85	59.71	62.36	56.37	58.96	57.59	58.47	48.67	49.71
TiO ₂	—	0.02	—	0.02	—	0.01	0.01	0.03	—	0.01	1.77	1.37
Al ₂ O ₃	29.99	29.23	26.25	25.31	24.68	23.90	26.29	24.27	27.34	25.18	7.16	6.88
FeO	0.44	0.32	0.19	0.27	0.25	0.22	0.39	0.24	—	0.22	13.07	11.86
MnO	—	—	—	—	—	—	—	—	—	—	0.49	—
MgO	0.28	0.45	0.01	0.33	0.87	0.04	—	—	—	0.16	15.01	16.13
CaO	13.43	12.09	8.66	7.05	6.34	5.80	8.88	6.29	8.99	7.10	11.15	11.23
Na ₂ O	3.89	4.69	5.92	6.73	7.63	7.12	6.61	7.63	6.47	6.65	1.66	1.38
K ₂ O	0.17	0.23	0.44	0.54	0.60	0.72	0.35	0.65	0.35	0.57	0.38	0.41
SrO	0.20	—	—	—	—	0.14	0.29	—	—	—	—	—
BaO	—	0.05	0.04	0.07	0.15	0.11	0.14	0.09	—	0.06	—	—
Total	99.51	99.53	99.66	100.16	100.28	100.43	99.32	98.16	100.73	98.42	96.31	98.73
An%	64.98	57.96	43.56	35.49	48.90	31.00	41.77	30.11	43.00	35.83		

electronic supplement. All pumice analyzed were secondarily hydrated, but were glassy with no traces of clay alteration.

Variation diagrams show the chemical array for major elements as silica increases (Fig. 3). There is a slight overlap between the two groups and with a few samples from the Virginia, Pijije, and Salitral East units that plot outside their respective silica group. With respect to other major elements, the pumice fragments display similar trends: MgO, Fe₂O₃, CaO, Al₂O₃ and TiO₂ decrease and K₂O increases with increasing SiO₂ (Fig. 3). In addition, there are three sub-parallel to parallel Al₂O₃ trends. One trend includes the dacites from the Green Layer, Santa Fe dacite, Virginia, and Buena Vista dacite. An intermediate trend includes the Salitral East and Buena Vista rhyolite while another trend includes the rhyolites from Santa Fe, Pijije, and Liberia units.

Trace element variations with respect to SiO₂ are illustrated in Fig. 4. The units show little systematic variation with respect to high field-strength elements (HFSE): Nb–Ta with increasing SiO₂ content. The Nb remains constant while there is a slight increase in Ta among units. The Liberia unit is an outlier in regards to both HFSE, containing lower Nb and higher Ta concentrations than the other units. Strontium and the rare earth elements (REE) decrease with increasing SiO₂. However, the Green Layer unit is a notable outlier in heavy rare-earth elements (HREE), displaying lower

values than the other samples within the same SiO₂ range. Light rare-earth elements (LREE) content remains relatively constant between the two SiO₂ groups. Rare-earth element variation diagrams normalized to chondrite for all the seven geochemical units are depicted in Fig. 5. This figure shows all of the units are enriched in LREE and some units are depleted in (MREE) relative to the HREE. The Eu anomaly (Eu/Eu*) in these units ranges from 1.57–0.55. The Green Layer and some selected dacites and rhyolites from the Santa Fe unit do not display the MREE depletion. The range of REE's in the Santa Fe unit encompasses the total range of REE's for the other units.

4.2. Petrography and phase chemistry

4.2.1. Petrography

All pumice samples are hypohyaline with crystallinity typically ranging between 7% and 20% although one Pijije pumice fragment has a crystal content of ca. 50%. All samples contain a glassy groundmass and some contain plagioclase microlites, displaying an intermediate to strong parallel alignment (i.e. Pijije, Santa Fe dacite/rhyolite). The samples contain a phenocryst assemblage of plagioclase + hornblende + magnetite ± orthopyroxene ± biotite ± quartz ± ilmenite, ± accessory zircon and apatite (Figs. 6a and b). Table 2 provides estimated modal percentages from samples representing

Santa Fe	Pijije	Liberia	Virginia	Buena Vista	Buena Vista	Santa Fe	Virginia	Santa Fe	Pijije	Liberia	Virginia	Buena Vista
Rhyolite	Rhyolite	Rhyolite	Rhyolite	Dacite	Rhyolite	Dacite	Dacite	Rhyolite	Rhyolite	Rhyolite	Rhyolite	Rhyolite
040707-8F	010629-1C	990718-1-1	020709-3a	990718-2C	990718-3a	990718-12g	020709-4C	040707-8F	010629-1C	990718-1-1	010629-1A	990718-2D-1
amph 4	amph 3	amph 1	amph 1b	amph 1	amph 3	opx 3a	opx 3d	bio 1a	bio 2	bio 2a	bio 3	bio 4
amph	amph	amph	amph	amph	amph	opx	opx	biotite	biotite	biotite	biotite	biotite
49.68	50.22	50.47	48.62	48.53	49.57	53.18	51.83	39.99	40.38	38.16	39.07	40.15
1.22	1.12	1.14	1.53	1.68	1.25	0.22	0.15	4.84	4.76	4.93	5.00	5.18
6.15	6.07	6.18	6.94	6.88	6.05	0.96	0.84	14.91	14.56	14.46	14.53	14.54
13.04	12.86	12.40	11.89	12.86	11.86	19.80	20.35	17.57	16.29	16.17	15.92	14.29
0.88	0.92	0.79	0.56	0.51	0.60	1.17	1.26	0.20	0.39	0.44	0.29	0.20
15.63	15.34	15.73	16.58	15.46	16.47	23.88	23.53	13.47	14.57	14.88	14.47	15.37
11.37	11.31	11.26	11.50	11.48	11.19	1.05	0.96	0.11	0.12	0.01	0.03	0.10
1.32	1.28	1.27	1.49	1.59	1.22	0.02	0.03	0.31	0.31	0.55	0.57	0.44
0.45	0.47	0.37	0.37	0.37	0.34	0.00	0.00	8.01	8.32	9.55	9.24	8.71
–	–	–	–	–	0.38	–	–	–	–	–	–	–
–	–	–	–	–	0.11	–	–	–	–	–	–	–
97.99	98.70	96.38	96.39	97.58	99.02	100.27	98.94	94.59	94.86	96.37	96.81	96.20

each unit. Twinning is common among both plagioclase and amphibole, and many of the plagioclase grains exhibit oscillatory zoning. Melt inclusions are abundant in plagioclase and amphibole — many are completely devitrified. Several disequilibrium textures (i.e. resorption, embayments, corroded plagioclase cores) are found throughout the sample collection (Figs. 6c and d). Plagioclase and quartz are typically the minerals displaying these textures; however, some amphibole grains display a “brush-like” texture that may be related to disequilibrium or a result of phenocryst dehydration during the ascent (Fig. 6d).

Although, in general, the petrography of the seven units is similar, meaningful variations among units do exist. The size, distribution (i.e. glomeroporphytic clots, bi-modal), and modal abundance of minerals and groundmass are features that differ among units. Most notably, biotite and quartz are only present in rhyolitic pumice fragments. Conversely, orthopyroxene is only present in dacitic pumice fragments. Mineral distribution also varies considerably. Bi-modal size distributions of plagioclase and amphibole are observed in samples from the Green Layer and Virginia units. Some samples have glomerocrysts of several or all of the primary minerals present (Fig. 6d). Another distinct difference is the presence of banded pumice fragments, which contain both dark- and light-colored glass in the Green layer, Santa Fe rhyolite, Buena Vista dacite, and Pijije units (Fig. 6e).

4.2.2. Phase compositions

Representative microprobe analyses of individual mineral samples that reflect each of the seven units and sub-groups are provided in Table 3 and a full dataset including glass analyses is available as an electronic supplement.

Plagioclase compositions range from An₆₅ to An₂₅ and Or₂ to Or₉, with FeO decreasing from 0.44 to 0.17 wt.% (Figs. 7a and b). These parameters do not correlate well with whole-rock composition (Fig. 8a). Although zoning was not systematically investigated, plagioclase from most units display normal zoning; however, some phenocrysts from the Virginia and dacitic Buena Vista units are both normally and reversely zoned An₄₀ to An₄₆ and An₃₇ to An₄₄, respectively. Some phenocrysts from the Buena Vista rhyolite have clear oscillatory zoning (An₄₄ to An₃₀). Other units (Pijije, Liberia, Santa Fe rhyolite) show small compositional variations from core to rim in the plagioclase grains, which also represent the units with the lowest anorthite content (An₃₂ to An₂₅).

The most common amphibole phenocrysts are euhedral with dark green pleochroism. These phenocrysts are calcic (Ca_B > 1.5 atoms) with alkali contents (Na+K)_A from 0.2 to 0.5 atoms (Fig. 7c) and classify as magnesiohornblendes (Mg/Mg+Fe²⁺ > 0.5) according to Leake et al. (1997), with a strong correlation between the alkalis (Na+K)_A, Ti and Al^T (Figs. 7c and d).

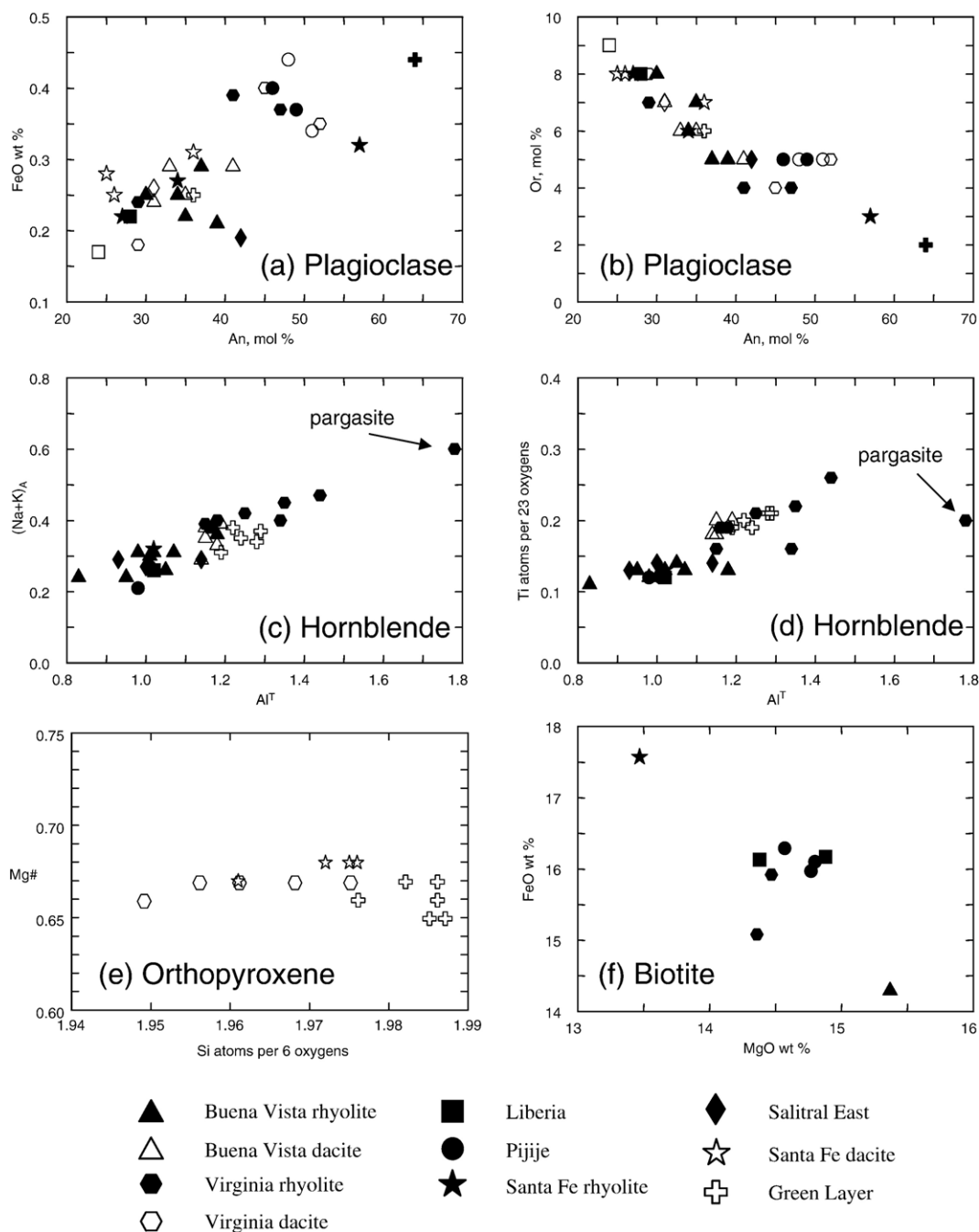


Fig. 7. Plots of mineral compositions in Guachipelin dacite–rhyolite pumices. (a) and (b) Open and filled symbols denote rims and cores, respectively. (c)–(f) See text for discussion.

Variations in the alkali and Ti content of the magnesiohornblendes are continuous, with the rhyolitic pumice clustered near an intermediate composition (Fig. 7c and d). Excluding the Virginia magnesiohornblende and pargasite, magnesiohornblende $(\text{Na}+\text{K})_{\text{A}}$, Ti, and Al^{T} content decrease with increasing whole-rock silica

(Fig. 8b). A rare pargasite ($\text{Ca}_{\text{B}} > 1.5$; $(\text{Na}+\text{K})_{\text{A}} > 0.5$; $\text{Ti} < 0.5$) is found in a Virginia pumice-clast (Fig. 7c and d), which notably includes the reversely zoned plagioclase. Pale yellow orthopyroxenes with weak pleochroism and a ‘brush-like’ disequilibrium texture are restricted to the units from the dacitic group. These phenocrysts are

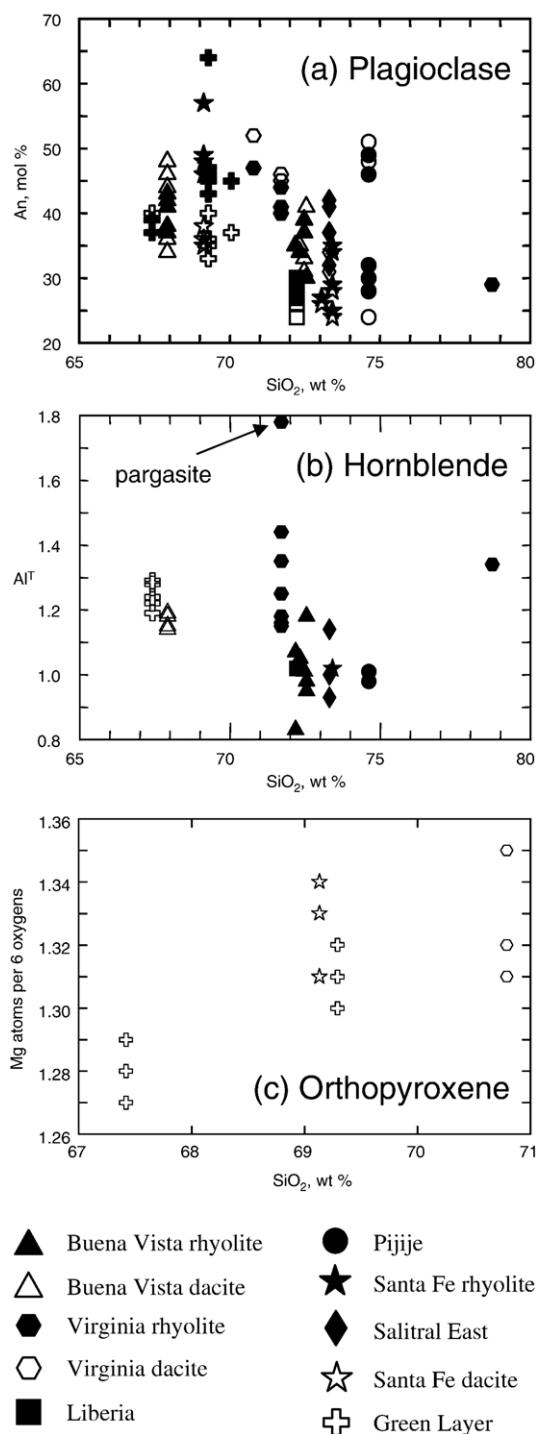


Fig. 8. Plots of mineral compositions in Guachipelín dacite–rhyolites against their host pumice. See text for discussion.

compositionally invariant (Fig. 7e) with respect to Mg#; however, Mg increases with increasing whole-rock silica (Fig. 8c).

Biotite occurs as euhedral flakes and ‘books’, and is restricted to the rhyolites (Liberia, Pijije, Santa Fe, Virginia, Buena Vista). Biotite grains are compositionally distinct with respect to FeO and MgO (Fig. 7f).

EPMA glass analyses of select pumice clasts are given in Table 4. Analyses with raw totals less than 96% are excluded from the discussion. Totals were recalculated to 100% for comparative purposes in all diagrams.

Major element variations with increasing silica contents of pumice-clast matrix glass (Fig. 9a) can be divided into two groups: lower-silica (<76.5 wt.%) and higher-silica (>76.5 wt.%). The lower-silica group is represented by samples from the Green layer, Santa Fe dacite, and Virginia dacite/rhyolites. The higher-silica group is represented by samples from Santa Fe rhyolite, Salitral East, Pijije, Liberia, and Buena Vista rhyolite. The units within these two groups also correspond to the dacitic and rhyolitic groups identified by bulk geochemistry with the exception of the rhyolitic Virginia unit, which is represented in both the high- and low-silica glass groups. Glass analyzed from Virginia sample 020709-3a is comparatively lower in SiO₂ than other rhyolitic Guachipelín pumice-clasts. Large compositional variations also exist within single pumice-clasts representing both the Pijije (Sample: 010629-1c) and Virginia (Sample: 010629-1a) units and are enlarged in the Fig. 9b plot of K₂O against CaO.

5. Petrogenesis

5.1. Origin of silicic magmas

Based on geochemical similarities among silicic deposits and lavas from the active arc in Central America, Vogel et al. (2006) concluded that these silicic magmas are related to partial melting of, or melt extraction from, subduction related calc-alkaline plutons that have ponded in the lower crust. The Guachipelín dacite–rhyolites have a similar origin. Within the southeastern region of the Central American arc, where the Guachipelín Caldera is located, interpretation of seismic data by Sallares and Danobeitia (2001) indicate that mid-crustal heterogeneities exist and could characterize the basaltic–andesitic crystalline bodies thought by many workers to represent intermediate crustal sources (for a review see: Bergantz, 1989; Hildreth and Fierstein, 2000; Tamura and Tatsumi, 2002; Vogel et al., 2004). A combination of this geophysical evidence and the occurrence of large-volume, calc-alkaline plutons in the Cordillera de Talamanca, Costa Rica, also supports a model that invokes the partial melting of those mid-crustal sources to generate silicic magmas (Drummond

Table 4

Representative electron microprobe analyses of glass from Guachipelin ignimbrite pumice-clasts

Unit	Buena Vista	Buena Vista	Virginia	Virginia	Pijije	Salitral East	Santa Fe	Santa Fe	Santa Fe	Green Layer	Green Layer
	Rhyolite	Rhyolite	Rhyolite	Dacite			Rhyolite	Rhyolite	Dacite		
Sample	990718-3a	990718-4-5	010629-1A	020709-4c	010629-1C	040706-7F	040707-8F	010629-21F	990718-12G	040706-1J	040707-3C
Analysis #	glass 3a	glass 2a	glass 5a	glass 3b	glass 6a	glass 1	glass 1	glass 4a	glass 4a	glass 4	glass 1
(wt.%)											
SiO ₂	74.88	75.81	75.84	73.79	75.37	75.57	76.63	75.11	73.50	74.84	74.22
TiO ₂	0.17	0.20	0.12	0.28	0.05	0.16	0.14	0.10	0.24	0.31	0.19
Al ₂ O ₃	12.37	12.02	12.26	12.90	12.54	12.91	12.60	12.09	12.88	12.99	12.28
FeO	0.88	1.16	0.70	1.38	0.47	0.76	0.75	0.67	1.17	1.31	1.56
MnO	0.04	0.06	0.07	0.05	0.00	0.00	0.11	0.12	0.07	0.02	0.04
MgO	0.25	0.23	0.11	0.21	0.01	0.11	0.07	0.08	0.10	0.24	0.12
CaO	0.78	0.74	0.56	1.02	0.39	0.82	0.79	0.66	1.08	1.14	1.10
Na ₂ O	3.29	3.37	3.02	2.98	3.19	3.03	3.53	3.04	3.54	3.46	3.63
K ₂ O	4.40	4.63	5.43	4.85	4.90	4.30	4.90	4.99	4.55	4.33	3.86
Cl	0.29	0.26	0.25	0.26	0.17	0.20	0.24	0.21	0.25	0.27	0.25
Total	97.41	98.53	98.43	97.97	97.10	97.87	99.77	97.14	97.38	98.92	97.31

et al., 1995; DeBoer et al., 1995; Abratis, 1998; Abratis and Worner, 2001).

On the other hand, one inherent difficulty in the generation of silicic magmas using the remelting model is the relatively high K₂O/Na₂O ratios observed (0.4–1.1) — higher than have been produced by experimental studies of melting low-K basaltic or andesitic samples (Beard and Lofgren, 1991; Müntener et al., 2001a; Grove et al., 2003; Villiger et al., 2004). However, Sisson et al. (2005) have shown through high pressure–temperature experiments that silicic magma could be produced by partial melting or extreme fractional crystallization of intermediate to high-K basalts — some basalts in Central America have similar K concentrations as those used in these experiments. The K₂O/Na₂O ratios of the Guachipelin dacite–rhyolites are similar to those produced in these experiments (Fig. 9) and demonstrate that evolved liquids, produced by partial melting or extreme crystal fractionation, could be derived from moderately enriched, medium to high-K basalt. Our interpretation of the Guachipelin data is therefore consistent with a model proposed by Vogel et al. (2006), which invokes the partial melting of mantle-derived, calc-alkaline mid-crustal plutons or melt extraction from a nearly crystalline equivalent to produce high K₂O/Na₂O silicic magmas (Fig. 10).

5.2. Variation in the Guachipelin magmas

Guachipelin dacitic–rhyolitic pumice-clast bulk compositions follow only broadly coherent trends while major elements such as Al₂O₃ and K₂O and trace

elements like La and Lu have separate subparallel trends (Figs. 3 and 4). Chemical heterogeneities within the ignimbrites are best illustrated by evaluating incompatible trace element distributions. Niobium (Nb) and tantalum (Ta) are equally incompatible with the mineral phases present in these magmas and are used to differentiate among chemically distinct magma batches with probability plots (which are cumulative frequency plots with a log scale for the cumulative frequency). These plots contain discrete distributions (heterogeneities) that occur within the Guachipelin ash-flow deposits. On probability plots, samples that occur on a straight line are normally distributed with the slope of the line being a function of the dispersion (the shallower the slope the greater the dispersion of the data). Distinct breaks and/or differences in the slope of the sample distribution indicate that the data are not normally distributed and can be interpreted to indicate more than one process or different source rocks for the units. This is markedly evident in the case of the Nb/Ta ratio, where the distinct distributions among samples are observed (Fig. 11). In this way, chemically distinct magmas are defined and represent the seven ash-flow sheets characterized earlier in this paper within the composite stratigraphic sequence.

In addition, petrologic and phase compositional disparities have been identified among the separate ash-flow sheets characterized in this study and cannot be explained based on a single process such as fractional crystallization, assimilation, or mixing alone. Therefore, the data can be interpreted to elicit two processes that explain the compositional variation.

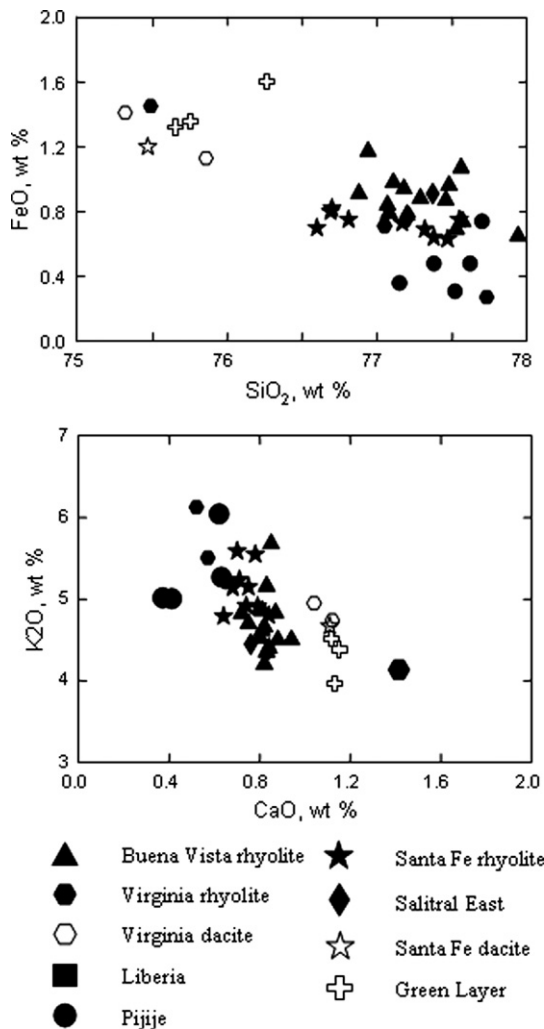


Fig. 9. Analyses of groundmass glass representing each of the Guachipelin eruptive units. a–b) Enlarged symbols of Virginia and Pijije glass analyses represent samples 010629-1a and 010629-1c, respectively. There are no analyses for Buena Vista dacite. Note the low-silica glass content of Virginia rhyolite sample 020709-3a in (a).

5.2.1. Mixing

The following evidence suggests to us that extensive mixing was important in generating the compositional heterogeneities described and precludes fractional crystallization as a single process of differentiation.

- (1) An oxygen isotope study of ignimbrites from Costa Rica by Vogel et al. (2006) concluded that major element correlations with $\delta^{18}\text{O}$ were not consistent with crystal fractionation. Instead, they postulated that variations in the $\delta^{18}\text{O}$ might be explained by assimilation of crustal rocks that have been affected by surface waters low in $\delta^{18}\text{O}$.

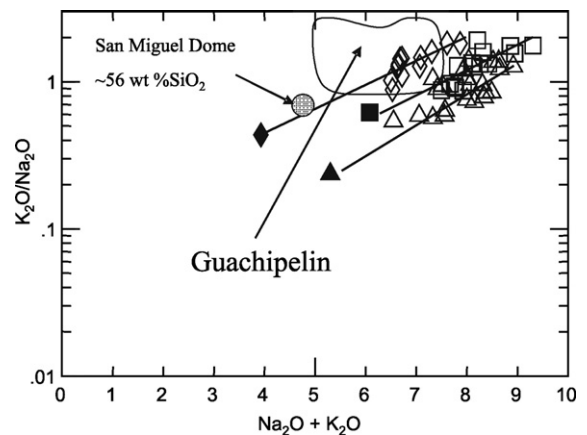


Fig. 10. Modified from Vogel et al. (2006). Melting experiments from Sisson et al. (2005). Solid symbols are the high-K basaltic starting material. Open symbols represent partial melts under varying conditions; melt fractions from 12–34%. Tie-lines are connecting initial materials with the melt fraction produced under the various conditions applied. The San Miguel dome represents andesitic post-caldera activity.

Eaton (2004) demonstrated that the Guanacaste region, which includes Guachipelin, displayed lower $\delta^{18}\text{O}$ values ($<2.0\text{‰}$ $\delta^{18}\text{O}$) than the rest of Costa Rica. A model proposed by Bindeman and Valley (2001) supports this hypothesis, invoking the complete melting and assimilation of hydrothermally altered, down-dropping roots of caldera block to produce low $\delta^{18}\text{O}$ magmas. It is important to note that only three of the seven units described in this study were represented by

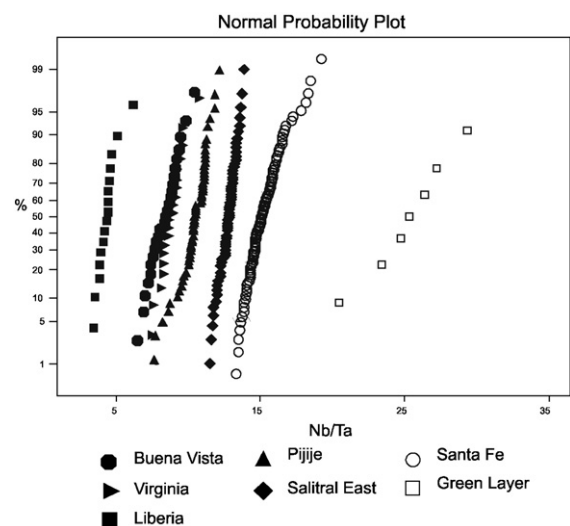


Fig. 11. a) Cumulative frequency plot of the incompatible trace element ratio Nb/Ta. The Nb/Ta ratio demonstrates that clear compositional breaks exist within the Guachipelin pyroclastic deposits.

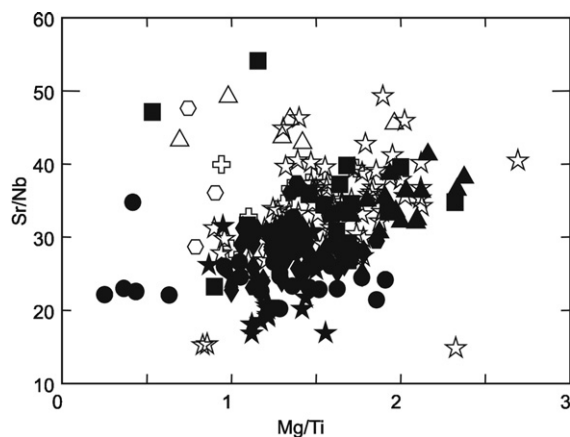


Fig. 12. An example of an element ratio–ratio plot used as a test for magma mixing/mingling among the Guachipelin magmas.

Eaton's work: Liberia, Virginia, and Buena Vista from the upper sequence of the Guachipelin deposits. All of these eruptive events occurred following the deposition of the Pijije unit, which we suggest could indicate the inception of the caldera collapse based on an increase in the size and abundance of lithics found in these deposits. This might explain the low $\delta^{18}\text{O}$ values as a result of caldera collapse, but analyses of pumice from the remaining units and additional lithic distribution data are required to further test this hypothesis. Nevertheless, there is no evidence to support fractional crystallization (FC) or assimilation as the primary process of differentiation relating these magmas.

- (2) Phenocryst compositions are not systematically correlated with the whole-rock compositions (Fig. 8). Hornblende from the less-evolved dacitic pumice-clasts are compositionally indistinguishable from hornblende of the rhyolite group (Figs. 7c and d). Some plagioclase have reverse zoning (An_{30-41} , An_{37-44}), and populations of more calcic plagioclase (An_{46-51}) occur in the more-evolved Pijije pumice-clasts (Fig. 8a). Conversely, sodic plagioclase (An_{28}) and high-Ti, alkali magnesiohornblende (normally associated with the less-evolved units) are found coexisting in a single Virginia rhyolitic pumice-clast. These overlapping trends suggest mineral exchange has occurred during mixing within several of these eruptive units. In contrast, however, orthopyroxene is only found in the less-evolved units.
- (3) Evidence in hand samples of tan–gray compositional banding is widespread. Petrographic analysis of these pumice-clasts reveals disequilibrium textures

from nearly all of the representative units as follows: corroded cores, embayments, or overgrowths in plagioclase; embayments in orthopyroxene and magnesiohornblende; and/or resorbed quartz.

- (4) Some compositional variations occurring in the glasses within single pumice-clasts and glass which is less-evolved than the bulk rock equivalent are present in the Virginia unit. However, additional glass analyses are required to further investigate the heterogeneities throughout the sampled suite and clarify the nature of variations within pumice with respect to magma chamber or open-system processes.

Traditional methods of evaluating mixing among magmas elicit a comparison of element ratios using an x – y plot, correlated by least squares multiple linear regressions, defined by a hyperbolic curve. A ratio–ratio plot of four elements (Sr, Nb, Mg, and Ti) for the Guachipelin pumice-clasts (Fig. 12) clearly provides little support for mixing relationships among these individual magma batches despite the abundant geologic evidence of mixing. These traditional methods fail to produce any usable relationships among the units. However, a multivariate statistical method of analysis termed polytopic vector analysis or PVA was used to evaluate mixing models by Deering (2005), which support extensive mixing among these magmas. Details regarding the use of this technique for evaluating multiple processes

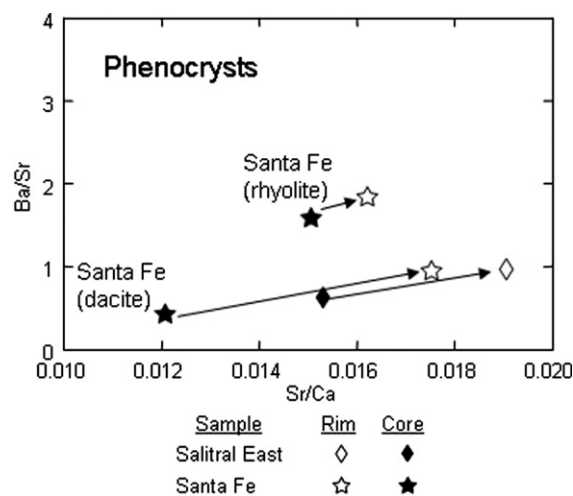


Fig. 13. Ba/Sr vs. Sr/Ca plot for representative plagioclase phenocrysts from the dacitic and rhyolitic pumice clasts from the Santa Fe and Salitral East units. Two separate trends are evident from core to rim of the phenocrysts. The upper group represents the Santa Fe rhyolite (stars); the lower trend includes the Santa Fe dacite (stars) and Salitral East (diamonds).

(fractional crystallization and mixing) in the Guachipelin samples will be presented in a future paper.

5.2.2. Fractional crystallization

Evidence for fractional crystallization exists as coherent geochemical crystal fractionation trends *within* units. For instance, the two sub-groups Santa Fe-dacite and -rhyolite were originally defined as one unit from a distinct source based on the similar Nb/Ta ratios (mean 15.22 and 15.20, respectively); however, a major element compositional gap separates these two groups. Importantly, the Salitral East unit occupies both the compositional gap between these two groups as well as lies stratigraphically between the Santa Fe dacite and rhyolite deposits and was therefore included in the evaluation of limited fractional crystallization.

A first order evaluation of crystal fractionation is implemented using bulk geochemistry and phenocryst compositions. In particular, plagioclase grains are sensitive indicators of melt composition, and any changes that occur throughout the melt evolution are recorded in the mineral growth. Anorthite content and trace elements Barium (Ba) and Strontium (Sr), which have a high partition coefficient with respect to plagioclase, provide additional evidence for a co-genetic relationship among evolving melts at various stages. Consequently, if the Salitral East and Santa Fe rhyolite were melts extracted from the Santa Fe dacite and therefore related by crystal fractionation, the following would be expected: 1) the whole rock concentrations of major elements should vary systematically with SiO₂, 2) the whole rock concentration of Sr should be lower in the more-evolved

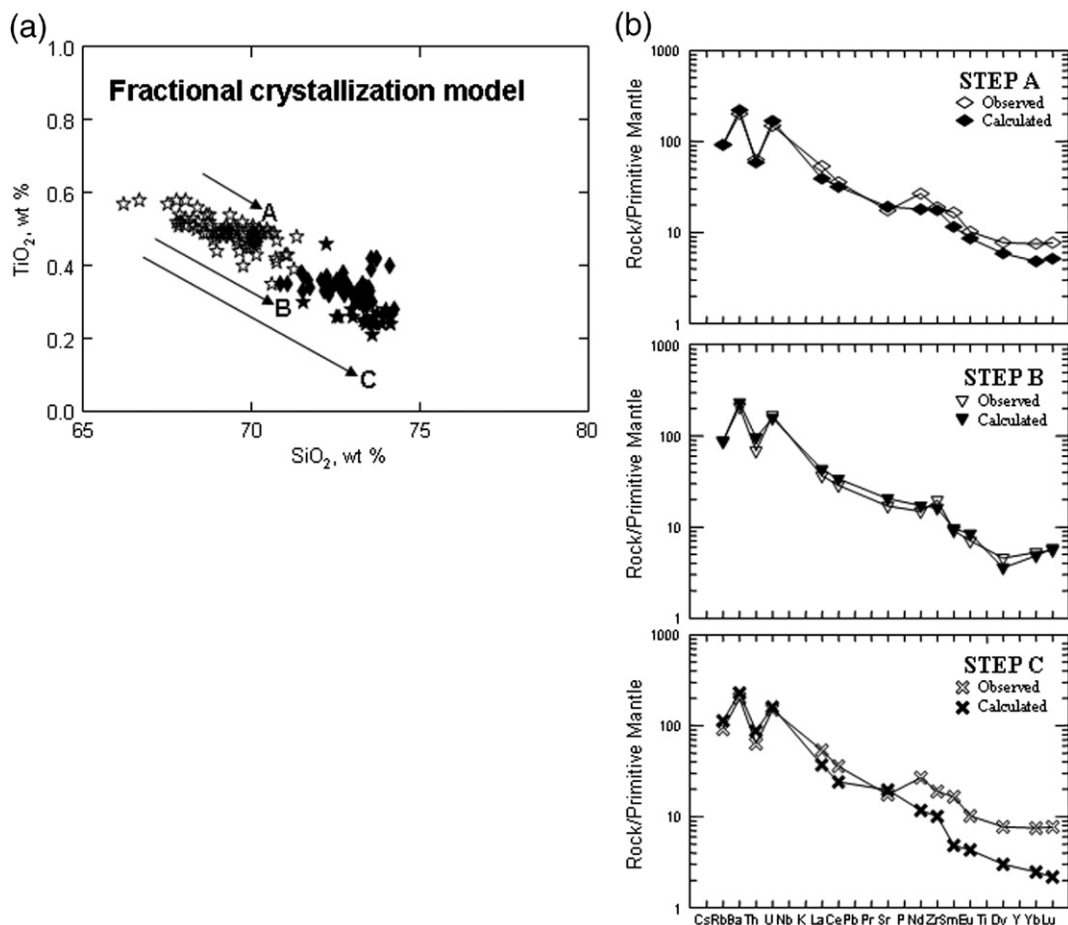


Fig. 14. a) Fractional crystallization (FC) modeling using multiple linear regressions for the Santa Fe dacite and Santa Fe rhyolite. Arrows used to indicate the pathways for Steps A–C. Step A represents the modeling within the Santa Fe dacite (Parent: 010630-4h, Daughter: 010630-4a). Step B shows the model from one of the least evolved Santa Fe dacite samples to an intermediate Santa Fe sample (Parent: 010630-4e, Daughter: 040707-2a). Step C represents modeling extending across the compositional gap *within* the Santa Fe unit from dacite to rhyolite (Parent: 010630-4h, Daughter: 040708-6a). b) Spider diagrams comparing the observed and calculated trace element trends for each step. Symbols are consistent with previous diagrams. Partition coefficients from Rollison (1993) and the GERM on-line database (<http://www.earthref.org/GERM/index.html?main.htm>).

Table 5
Multiple linear regressions

Step A					Step B					Step C				
Parent	010630-4h				Parent	010630-4e				Parent	010630-4h			
Daughter	010630-4a				Daughter	040707-2a				Daughter	040708-6A			
%	Min/rock				%	Min/rock				%	Min/rock			
1.7	Hornblende				2.2	Hornblende				4.2	Hornblende			
5.0	Plagioclase				6.4	Plagioclase				11.2	Plagioclase			
0.2	ilmenite				0.3	ilmenite				0.3	ilmenite			
0.8	Magnetite				0.9	Magnetite				2.2	Magnetite			
0.923	Liquid				90.2	Liquid				82.1	Liquid			
	remaining					remaining					remaining			
Sum of the squares of the residual=0.05					Sum of the squares of the residual=0.09					Sum of the squares of the residual=0.02				
Analyte	Daughter	Obs: 010630-4h	Calc: 010630-4h	Residual	Analyte	Daughter	Obs: 010630-4e	Calc: 010630-4e	Residual	Analyte	Daughter	Obs: 010630-4h	Calc: 010630-4h	Residual
SiO ₂	70.32	68.43	68.41	0.01	SiO ₂	70.89	68.13	68.36	0.09	SiO ₂	73.96	68.44	68.57	0.05
TiO ₂	0.45	0.57	0.57	–	TiO ₂	0.34	0.51	0.53	0.02	TiO ₂	0.26	0.57	0.58	0.01
Al ₂ O ₃	15.88	16.17	16.15	0.01	Al ₂ O ₃	17.69	18.11	18.03	0.04	Al ₂ O ₃	15.06	16.17	16.04	0.07
FeO	3.07	4.04	4.04	–	FeO	2.50	3.48	3.50	0.02	FeO	1.64	4.04	4.05	0.01
MnO	0.07	0.11	0.09	0.02	MnO	0.09	0.07	0.10	0.03	MnO	0.07	0.11	0.10	0.01
MgO	0.74	1.13	1.13	–	MgO	0.38	0.82	0.75	0.07	MgO	0.39	1.13	1.08	0.04
CaO	2.80	3.13	3.21	0.08	CaO	2.24	2.92	3.05	0.13	CaO	1.65	3.13	3.21	0.07
Na ₂ O	2.90	3.06	2.91	0.15	Na ₂ O	2.32	2.66	2.43	0.23	Na ₂ O	3.01	3.05	3.07	0.02
K ₂ O	3.73	3.31	3.45	0.14	K ₂ O	3.53	3.26	3.21	0.05	K ₂ O	3.94	3.32	3.28	0.04
P ₂ O ₅	0.03	0.03	0.03	–	P ₂ O ₅	0.02	0.03	0.02	0.01	P ₂ O ₅	0.02	0.03	0.02	0.01
Prediction based on distribution coefficients					Prediction based on distribution coefficients					Prediction based on distribution coefficients				
RB	61.90	58.00	58.40	0.47	RB	0.29	56.50	60.60	4.05	RB	0.28	58.00	76.70	18.72
SR	347.00	367.50	402.50	34.98	SR	2.87	356.90	409.30	52.40	SR	2.76	367.60	339.90	27.70
ZR	207.70	210.80	195.70	15.10	ZR	0.27	219.90	166.00	54.00	ZR	0.27	210.90	115.40	95.50
BA	1621.80	1399.20	1543.50	144.31	BA	0.39	1457.50	1607.80	150.30	BA	0.38	1399.30	1566.50	167.22
LA	27.80	36.70	26.80	9.91	LA	0.55	25.10	31.90	6.80	LA	0.47	36.70	22.30	14.40
CE	58.20	63.20	56.30	6.85	CE	0.65	50.80	58.60	7.87	CE	0.51	63.20	42.00	21.20
ND	24.70	36.20	24.30	11.90	ND	1.08	20.10	24.40	4.31	ND	0.73	36.20	14.80	21.40
SM	5.14	7.33	5.10	2.23	SM	1.31	4.04	3.83	0.20	SM	0.87	7.33	2.18	5.15
EU	1.31	1.71	1.44	0.26	EU	2.32	1.18	1.18	–	EU	2.15	1.71	0.73	0.98
TB	0.66	1.02	0.63	0.39	TB	0.40	0.60	0.41	0.20	TB	0.36	1.02	0.27	0.75
DY	3.66	5.69	4.32	1.36	DY	1.62	3.35	2.54	0.81	DY	3.17	5.69	2.63	3.06
ER	2.33	3.45	2.66	0.78	ER	1.41	2.17	1.21	0.96	ER	2.82	3.45	1.08	2.37
YB	2.44	3.69	2.37	1.32	YB	1.33	2.59	1.84	0.75	YB	0.60	3.69	1.45	2.24
LU	0.39	0.57	0.38	0.19	LU	1.21	0.41	0.26	0.16	LU	0.58	0.57	0.22	0.35
HF	4.15	4.62	3.91	0.71	HF	0.25	4.71	3.26	1.45	HF	0.22	4.62	2.41	2.22
TA	0.63	0.58	0.76	0.18	TA	0.32	0.69	0.74	0.05	TA	2.04	0.58	0.73	0.14
TH	5.29	5.37	4.98	0.39	TH	0.30	5.82	8.51	2.68	TH	0.17	5.37	7.81	2.43
U	3.79	3.12	3.54	0.42	U	0.16	3.53	3.54	0.01	U	0.11	3.12	3.75	0.63

Salitral East and Santa Fe-rhyolite fragments, 3) a systematic change in the anorthite content from least to most evolved, and 4) Ba and Sr abundance in crystals should reflect the change in melt composition.

First, major elements from the Santa Fe dacite–Salitral East–Santa Fe rhyolite vary systematically, decreasing in MgO, Fe₂O₃, and CaO with an increase in SiO₂ and are consistent with fractional crystallization (FC) trends. Second, Fig. 4 clearly displays a decrease in whole rock Sr content from the least-evolved Santa Fe dacitic pumice-clasts to the more-evolved Santa Fe rhyolitic pumice-clasts. Notably, the Sr content of some Salitral East samples are equivalent to an intermediate pumice-clast concentration from the Santa Fe dacite, consistent with melt extraction from the evolving Santa Fe. Third, Salitral East plagioclase cores, as high as An₄₄, fall within the intermediate ranges (An₅₇ to An₃₆) of the Santa Fe dacite (Fig. 8b). Representing a more evolved unit, the Santa Fe rhyolite is characterized by a lower degree of crystallinity (<10%) than the Santa Fe dacite, and the core An compositions correspond to the rim compositions of the Santa Fe dacite. Sodic rims (An₃₈) of the Santa Fe dacite are within analytical error ($\pm 10\%$ of the actual value) of the Santa Fe rhyolite core (An₃₆) (Fig. 8b). Finally, Ba and Sr concentrations in plagioclase crystals are consistent with the aforementioned sequence of An relationships among these units (Fig. 13).

Multiple linear regression modeling provides additional support for limited FC during the evolution of the Santa Fe dacite–Salitral East–Santa Fe rhyolite. Several different parent/daughter combinations were used in the model to test FC, first within the Santa Fe dacite, then from the dacite to an intermediate (Salitral East), and finally to the Santa Fe rhyolite (Fig. 14a). Table 5 shows the results of this three-part model. The sum of the squares ($\sum r^2$) of the residual determined in this model, 0.023 and 0.05, are well below acceptable limits that other workers have established. In addition, the liquid/melt predictions correspond well with the actual pumice crystallinity and mineral abundances. Fig. 14b displays a comparison of the trace element concentrations of the predicted daughter and the actual pumice sample for steps A, B and C. Steps A and B display a good correlation between the observed and calculated trace element quantities as the melt fractionates out key minerals: amphibole, plagioclase, ilmenite, and magnetite. The lack of a strong correlation between some of the M-HREE in Step C could be the result fractionation of biotite, zircon, or apatite related to the Santa Fe rhyolitic magma, which have high partition coefficients for those elements. Trace element partition coefficients in these minerals were not considered in this model due to the lack of mineral composition data.

Therefore, both the Salitral East and Santa Fe rhyolite are considered to be evolved equivalents of the Santa Fe dacite and the following sequence is envisaged: Step A involves the crystallization within the Santa Fe dacitic magma; in Step B, the Salitral East, a hybrid magma, is proposed to be the product of melt extraction from the evolving Santa Fe dacitic initial melt at some intermediate point of crystallization. This process is represented by Step B in the multiple linear regressions in Fig. 14. Note that the Salitral East is defined as a distinct magma based on the Nb/Ta ratio. The disparity between the Nb/Ta ratio of the Salitral East and Santa Fe unit is considered the result of mixing, which followed the extraction of the Salitral East melt and is discussed in detail by Deering (2005); in Step C, our model represents extraction of a melt from the Santa Fe dacitic magma reservoir after the extraction of the melt involved in producing the Salitral East magma, which could produce the Santa Fe rhyolite.

In general, this type of geochemical relationship does not exist among other units, precluding any further evaluation of FC. Consequently, although the Guachipelin dacite–rhyolites have some coherent bulk rock geochemical trends, which support limited fractional crystallization, the full range of chemical variation is best explicated by a combination of both limited FC and mixing.

6. Conclusion

Compositional data from pumice-clasts associated with the Guachipelin Caldera are interpreted to reflect melting of previously emplaced subduction related sources that had distinct trace element concentrations. Recent experiments by Sisson et al. (2005) demonstrated the effective production of silicic melts with high K₂O/Na₂O by melting medium- to high-K basaltic rock, which are similar in composition to those erupted from the Guachipelin. The aforementioned chemical heterogeneities in the eruptive sequence not only reflect variations in source input to a shallower magma plumbing system, but processes of crystal fractionation and/or melt segregation and mixing.

Although a geochemical relationship among all of the pyroclastic units cannot be explained by fractional crystallization, this process was important in the evolution of several of the most voluminous flows associated with the Guachipelin. However, the inverted depositional sequence of these magmas with respect to magma evolution, where the less evolved dacitic magma is erupted first, precludes the evacuation of a stratified evolving magma chamber. Instead, the evolved magmas must be extracted and stored in subjacent

chambers, which are tapped following the evacuation of the less-evolved magma at the beginning of the eruptive sequence.

The data discussed above (incompatible trace element variations, oxygen isotopes, disequilibrium textures, plagioclase compositions, and banding in pumice-clast glass matrixes) all support the existence of independent magma batches evolving in an open-system with no evidence of mafic input.

As a result, our simplified model necessitates the use of two stages of intracrustal partitioning, which are illustrated in Fig. 15. First, ongoing subduction zone magmatism produced mantle-derived calc-alkaline magmas that ponded at the base of the crust and migrated into the overlying crust, stalling and crystallizing at some mid-crustal level as chemically discrete K-rich basaltic bodies. Pulses of new calc-alkaline magma percolated through the lower crust to heat the existing plutons, triggering melting. Second, the subsequent melting of those sources produces chemically distinct magmas that accumulate at shallow crustal levels, one of which would undergo a limited degree of crystal fractionation with melt extractions — the final emplacement of the nine deposits probably the result of mixing at various stages and different degrees.

In conclusion, the numerous explosive eruptions associated with the formation of the Guachipelin Caldera would require a complex network of magma pathways to allow storage of several independent magma bodies and the crystal fractionation, melt extractions, and magma mixing displayed in this volcanic suite. Ultimately, seven distinct magmas were produced through contributions from several intermediate end-member sources, which must have occurred as discontinuous pulses that required protracted subvolcanic residence.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jvolgeores.2007.05.004](https://doi.org/10.1016/j.jvolgeores.2007.05.004).

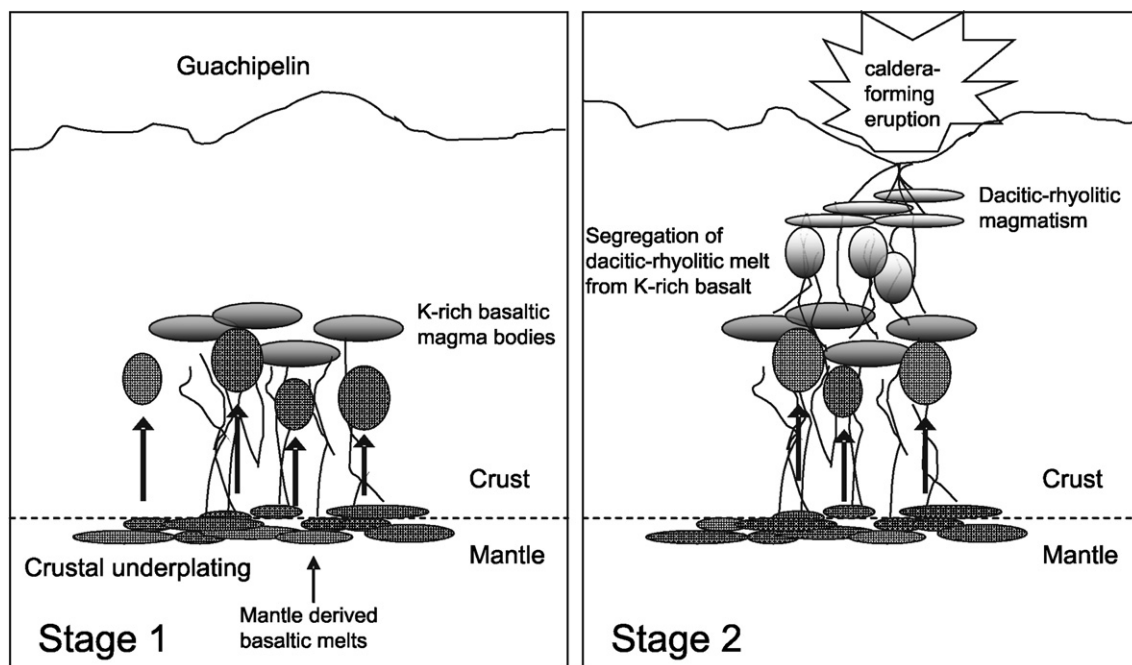


Fig. 15. Schematic summary of the processes involved in the generation and evolution of the Guachipelin eruptives. Stage 1, ponding of subduction related calc-alkaline, K-rich basaltic magma at the base of the crust. Some of this magma migrates to mid-crustal levels and crystallizes into separate plutons. Stage 2, the continuing melt migration from the crust-mantle interface provides heat to partially melt the emplaced plutons, which results in production of compositionally distinct magmas that reside in subvolcanic reservoirs. At this interval, independent magma bodies reside and undergo fractional crystallization and magma mixing prior to eruption.

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