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Original paper

Trace elements geochemistry and origin of volcanic units from the San Luis Potosí and Río Santa María volcanic fields, Mexico: the bearing of ICP-QMS data

Alfredo Aguillón-Robles*, Margarito Tristán-González, Rubén Alfonso López-Doncel, María Elena García-Arreola, Joselin de Lourdes Almaguer-Rodríguez and René C. Maury

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Resumen

Dos campos volcánicos importantes separados por una estructura volcano-tectónica se desarrollaron en la porción meridional de la Mesa Central durante el Cenozoico en la etapa de máxima extensión continental, correspondiente a la porción SE de la Provincia de Cuencas y Sierras en la porción suroriental de la Sierra Madre Occidental. Las rocas volcánicas asociadas a estas estructuras tectónicas varían en composición desde basaltos subalcalinos a basanitas o andesitas basálticas hasta riolitas emplazadas desde el Eoceno y extendiéndose hasta el Cuaternario durante cinco eventos volcánicos. A partir de análisis químicos de unidades volcánicas representativas de los complejos volcánicos en el estado de San Luis Potosí, se interpreta que el vulcanismo derivó de la fusión de la cima del manto y por metasomatismo de la base de la corteza, ligado con grados pequeños de cristalización fraccionada, dando como resultado una diversidad magmática y multiepisódica durante el tiempo y espacio, que se asociaron a estructuras volcanánicas de la región de San Luis Potosí. La interpretación conjunta a los análisis químicos obtenidos por diferentes técnicas para elementos mayores y para elementos traza por el método ICP-QMS, ha ayudado a proponer nuevos modelos sobre el origen y emplazamiento de unidades volcánicas existentes en la región.

Palabras clave: campos volcánicos, unidades volcánicas, elementos traza, ICP-QMS, San Luis Potosí, México.

Abstract

Two main volcanic fields separated by a volcano-tectonic structure were emplaced in the southern part of San Luis Potosí state during the Cenozoic peak of continental extension in the SE portion of the Sierra Madre Occidental. The Eocene to Quaternary volcanic rocks associated to these structures range in composition either from subalkaline basalts to basanites or from basaltic andesite to rhyolites, and were emplaced during five magmatic events. New trace element analyses obtained by the ICP-QMS method show that the three oldest ones, ranging in age from middle Eocene to late Oligocene, emplaced potassic calc-alkaline intermediate to evolved lavas. These originated from subduction-related mafic magmas through open-system fractional cristallization coupled with assimilation and possibly melting of the continental crust. The two youngest volcanic phases (Miocene and Quaternary) emplaced intraplate subalkaline to alkaline basalt and basanites derived from variable melting degrees of enriched mantle.

Key words: volcanic fields, volcanic units, trace elements, ICP-QMS, San Luis Potosí, Mexico.

A. Aguillón-Robles*
M. Tristán-González
R. A. López-Doncel
Ma. E. García-Arreola
Instituto de Geología
Universidad Autónoma de San Luis Potosí
Av. Dr. Manuel Nava #5, Zona Universitaria
San Luis Potosí, S.L.P.
México
Corresponding author: aaguillonr@uaslp.mx
E-mail:mtristan@uaslp.mx
rlopez@uaslp.mx; maria.garcia@uaslp.mx

J. L. Almaguer-Rodríguez
Área Ciencias de la Tierra; DES Ingeniería
Universidad Autónoma de San Luis Potosí
Av. Dr. Manuel Nava #8
Zona Universitaria
San Luis Potosí, S.L.P.
México
E-mail: almaguerjocelyn@gmail.com

R. C. Maury
Université Européenne de Bretagne
Université de Brest
CNRS; UMR 6538 Domaines Océaniques
Institut Universitaire Européen de la Mer
Place N. Copernic
29280 Plouzané
France
E-mail: maury@univ-brest.fr

Introduction

Two main large volcanic structures are located in the southern portion of the San Luis Potosí State. The formation of the San Luis Potosí Volcanic Field (SLPVF) started during the Eocene with the eruption of andesitic lava flows (Labarthe-Hernández *et al*., 1982; Tristán-González *et al*., 2009a). Andesites, dacites and rhyolites were emplaced until late Oligocene (Labarthe-Hernández *et al*., 1982; Tristán-González, 1986; Aranda-Gómez *et al*., 1989; Labarthe-Hernández *et al*., 1991; 1992; Tristán-González *et al*., 2009a). They are either overlain or crosscut by basaltic intraplate lavas emitted sporadically from Miocene to Pleistocene. The building of the second structure, the Río Santa María Volcanic Field (RSMVF), was initiated by middle Eocene andesitic lava eruptions and followed by the emplacement of voluminous felsic volcanics during the Oligocene. These include a large volume of rhyolitic pyroclastic flows overlain by trachytic and andesitic lava flows. The pyroclastic eruptions were responsible of the Caldera Milpa Grande collapse (Grassel, 1979; Labarthe-Hernández *et al*., 1984; Tristán-González, 1987; Labarthe-Hernández *et al*., 1989). The RSMVF volcanism ended with sporadic andesitic lava flows interbedded with rhyodacites and basaltic andesites.

The previouslly mentioned volcanic fields are separated by the Villa de Reyes Graben volcano-tectonic structure (VRG) which shows a dominant NE-SW trend. The SLPVF and the western portion of the RSMVF were affected by high angle NW-SE normal faults and the blocks were tilted towards the NE (Figure 1). This system formed a complex pattern of domino faults and narrow tectonic grabens. In some of these grabens, the emplacement of rhyolitic pyroclastic flows, were alternated with basaltic lava flows, forming a typical bimodal volcanic association (Tristán-González, 1986; Aguirre-Díaz and Labarthe-Hernández, 2003; Torres-Aguilera, 2005; Torres-Hernández *et al*., 2006; Tristán-González *et al*., 2006; Tristán-González, 2008; Tristán-González *et al*., 2008; Rodríguez-Ríos and Torres-Aguilera, 2009).

These volcanic events occurred in the southern portion of the Mesa Central Physiographic Province (MC, Figure 1). This area is considered as belonging to the Magmatic Province of the Sierra Madre Occidental (SMOc), the origin of which has been discussed by several authors (Cameron *et al*., 1980; Cameron and Hanson, 1982; Graham *et al*., 1995; Smith *et al*., 1996; Ruiz *et al*., 1988; 1990; Bryan *et al*., 2000, 2002; Ferrari *et al*., 2002; 2005). Three alternative models have been proposed to explain the origin of the voluminous silicic volcanic cover of the SMOc. The first one involves partial melting of the continental crust (Cameron *et al*., 1980; Cameron and Hanson, 1982). It implies the uprise of large amounts of basaltic magmas from the mantle, which provided the heat necessary to melt the crust. The second hypothesis postulates that the felsic magmas, mainly rhyolitic, derived from the fractional crystallization of basaltic magmas generated in the mantle, with little or not contribution of the continental crust (Smith *et al*., 1996; Ruiz *et al*., 1988; 1990; Bryan *et al*., 2002). In the third (and the most complex) model, magmas originated by partial melting of the base of the lithosphere mixed whith existing magmas of felsic composition, and were extruded through faults and fissures associated to the cortical extension (Aranda-Gómez *et al*., 2007; Aguillón-Robles *et al*., 2009; Tristán-González *et al*., 2009b).

The volcanism associated to the formation of the SLPVF, intermediate to felsic in composition, is considered as a product of the partial melting of the Precambian lower continental crust (Ruiz *et al*., 1988; Aguillón-Robles *et al*., 1994; 1996; 1997; Orozco-Esquivel *et al*., 2002). Although fractional crystallization processes operated at a smaller scale, their influence was significant in the evolution of these magmas (Verma, 1984; Rodríguez-Ríos *et al*., 2007; Aguillón-Robles *et al*., 2009).

Given the existing controversy on the origin of the volcanism for this portion of the SMOc, we have used the ICP-QMS method recently developed in UASLP (Universidad Autónoma de San Luis Potosí) to obtain a set of new trace element data. The aim of this article is to show that these data allow us to constrain the various petrogenetic models discussed above, and to better understand the relationship between the activity of the volcanic fields and the volcano-tectonic structure of Villa de Reyes Graben.

Sampling of the geologic units

We sampled some representative volcanic units of the volcanic fields of SLP and Río Santa María, as well as volcanic units associated to the formation of Villa de Reyes Graben (Figure 1). The stratigraphy of this region was studied in detail by Labarthe-Hernández *et al*. (1982) and Tristán-González *et al*. (2009a); the names of the volcanic units were taken from the original work (Labarthe-Hernández, *et al.*, 1982), which was named by petrographic criteria; however, subsequently chemical analysis showed they have different composition, as in the case of units named as Casita Blanca andesite, Portezuelo latite and Ojo Caliente trachyte, which fall in the field from basaltic-andesite to rhyolite (Figure 2), to update their names would be necessary to reinterpret them, because this nomenclature has been used in this way throughout the past

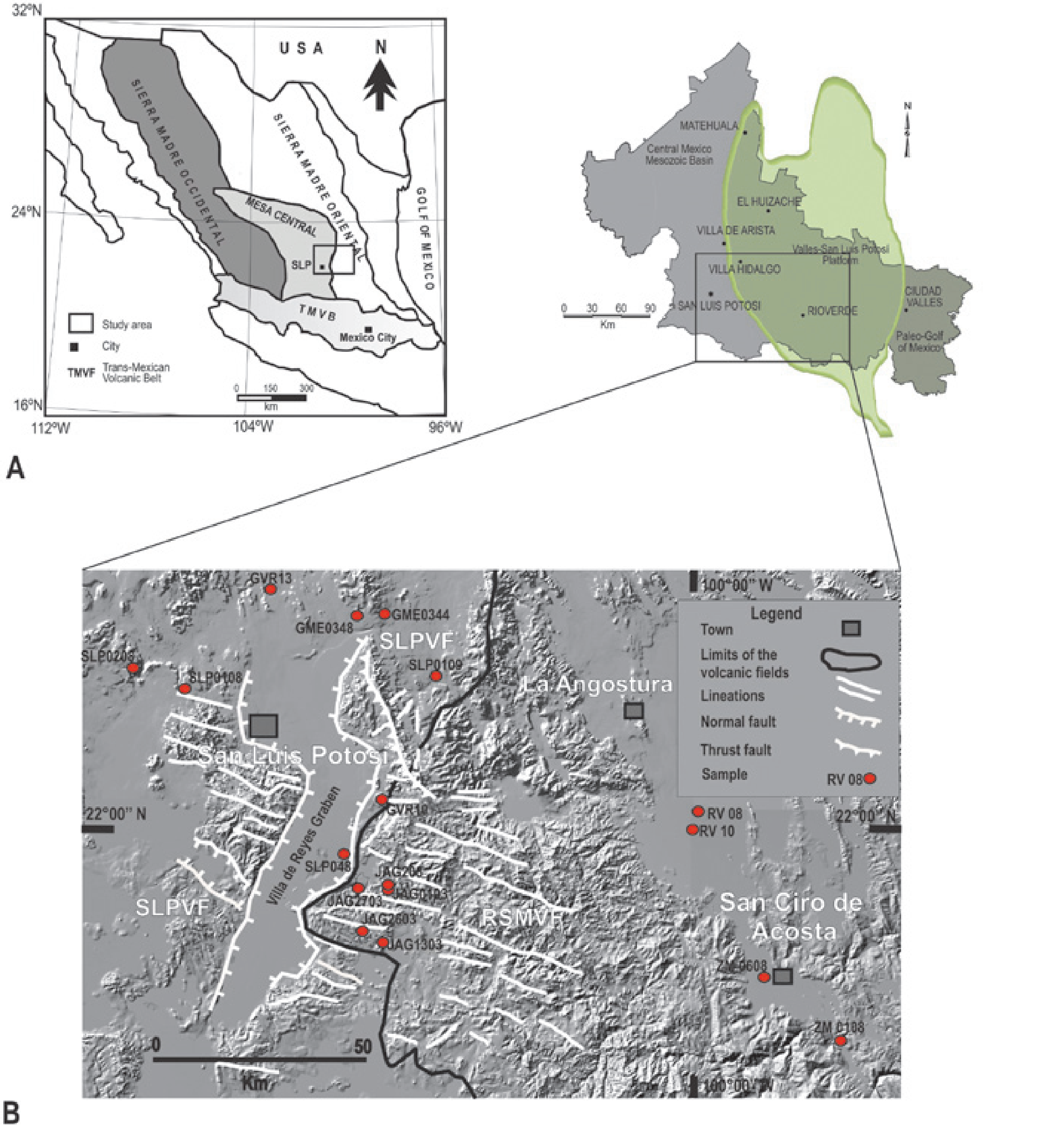

Figure 1. Location of San Luis Potosí (SLPVF) and Río Santa María Volcanic Fields (RSMVF). A: position and relationships with the main physiographic provinces (left) and paleogeographic structures (right) from northern Mexico (modified after Tristán *et al*., 2009b); B: location of the main volcano-tectonic structures of the southern part of San Luis Potosí state (modified after Tristán-González *et al*., 2009a).

literature. We collected 18 volcanic rock samples, which include: two basaltic-andesitic lava flows located in the SLPVF; three recent samples associated to "*maar*" type structures emplaced between 1.50 and 0.59 Ma (Tristán-González *et al*., 2009a); nine samples from the RSMVF, among which five are lava flows from Ojo Caliente unit (trachytic magma; Labarthe-Hernández *et al*., 1982) and four others are basaltic lava samples erupted along the regional faults and/or NW-SE trending fissures. The latter appeared event during the late Miocene (Barboza-Gudiño pers. com.), and are interpreted here for the first time as associated to the final volcanic events in this area. Finally, we sampled dacitic lavas associated to the VRG volcano-tectonic structure.

Casita Blanca andesite

Labarthe-Hernández *et al*. (1982) have termed Casita Blanca andesite a serie of andesitic to basaltic lava flows which mark the beginning of the SLPVF vulcanism. One of these lava flows crops out in the northwestern and northern parts of the volcanic field and in some stratigraphic windows located to the east of the SLPVF in

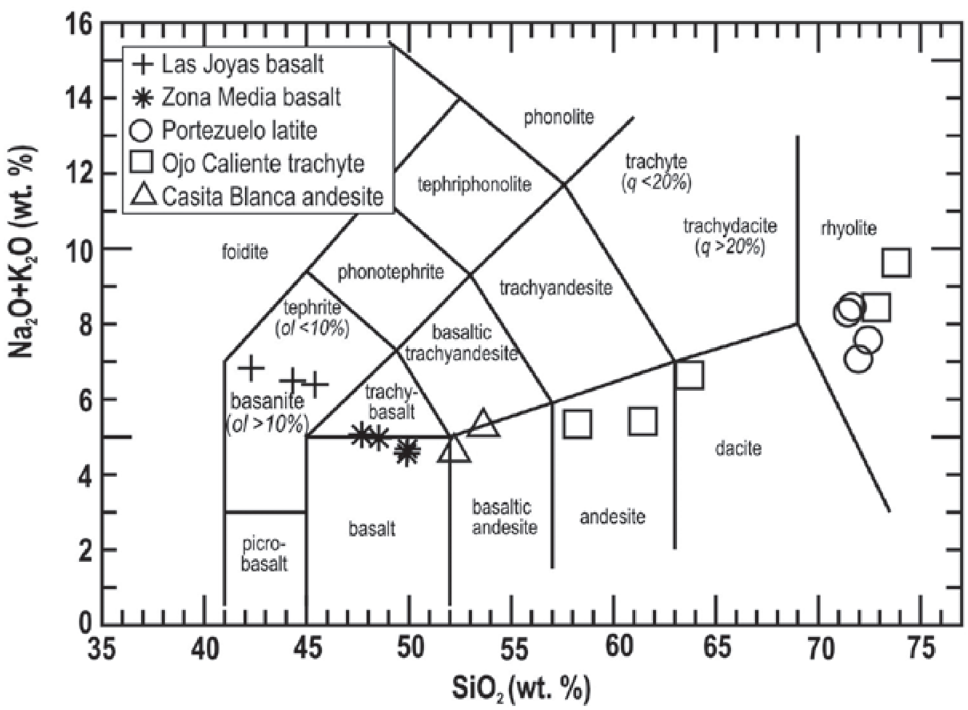

Figure 2. TAS (total alkalies *vs*. silica; Le Bas *et al*., 1986) diagram for San Luis Potosí, Río Santa María and Villa de Reyes Graben lava samples. Volatile-free analyses recalculated using the SINCLAS program (Verma *et al.*, 2002).

the vicinity of Cerro de San Pedro (Labarthe-Hernández *et al*., 1982; Tristán-González *et al*., 2009b). It is a moderately porphyritic rock of greenish dark gray color, with *ca.* 5 modal % of phenocrysts of biotite and plagioclase in an aphanitic microlitic matrix, composed of plagioclase and biotite. The top of this flow ranges from 20 to 80 m thick, which rests over Mesozoic marine rocks and continental lacustrine sediment, contains abundant vesicles, some of them filled up with chalcedony. Whole rock K-Ar ages of 45.5 ± 1.1; 44.4 ± 1.0, and 42.4 ± 1.0 (middle Eocene) have been reported (Tristán-González *et al*., 2009a).

Ojo Caliente trachyte

This name applies to a *ca.* 180 m thick pile of trachytic lava flows which crop out mainly in the western portion of the RSMVF (Labarthe-Hernández *et al*., 1982); although in the present study, the collected samples classify as andesite, dacites and rhyolites (Figure 2). This unit overlies rhyolitic pyroclastic flows, the emplacement of which marked the start of volcanic activity in this volcanic field around 32 Ma (Labarthe-Hernández *et al*., 1982; Tristán-González *et al*., 2009a). These light gray colored moderately porphyritic lava contains *ca.* 5 modal% phenocrysts of sanidine and clinopyroxenes sometimes altered to iron oxides, set in a devitrified groundmass. Corresponding whole rock isotopic ages are 31.8 ± 0.7 and 31.6 ± 0.7 Ma, *i.e.* early Oligocene (Tristán-González *et al*., 2009a).

Portezuelo latite

Although the volcanic unit referred to as Portezuelo latite outcrops are within the SLPVF; its emplacement was associated to the main extension event which formed the volcano-tectonic structure of the VRG. Thus, its main outcrops are located all along this graben (Labarthe-Hernandez *et al*., 1982; Tristán-González, 1986; 2008; Tristán-González *et al*., 2009b). This unit is associated to a *ca.* 440 m thick pile of porphyritic lava flow of rhyolitic composition. These light gray color porphyritic rocks contain 10 to 15 modal% phenocrysts of sanidine, plagioclase and subordinated quartz, set in a microlitic groundmass bearing plagioclase, magnetite, zircon and apatite (Labarthe-Hernandez *et al*., 1982); in this study all the samples were according to their geochemistry classificated as rhyolites. The corresponding whole rock ages range from 30.6 ± 1.5 to 31.0 ± 0.7 Ma, *i.e.* early Oligocene (Labarthe-Hernández *et al*., 1982; Tristán-González *et al*., 2009a).

Zona Media basalt

The unit known as Zona Media basalt is a pile of fissural lava flows of basaltic-andesitic composition which were emitted from scoria cones and of blocky lava flows extruded along NW-SE trending faults and/or fissures. These lava flowed within depressions dug into sediments associated to the Valles-San Luis Potosí Platform, near San Ciro and Angostura SLP (Figure 1). This volcanic unit, located at the NE border of the RSMVF, has

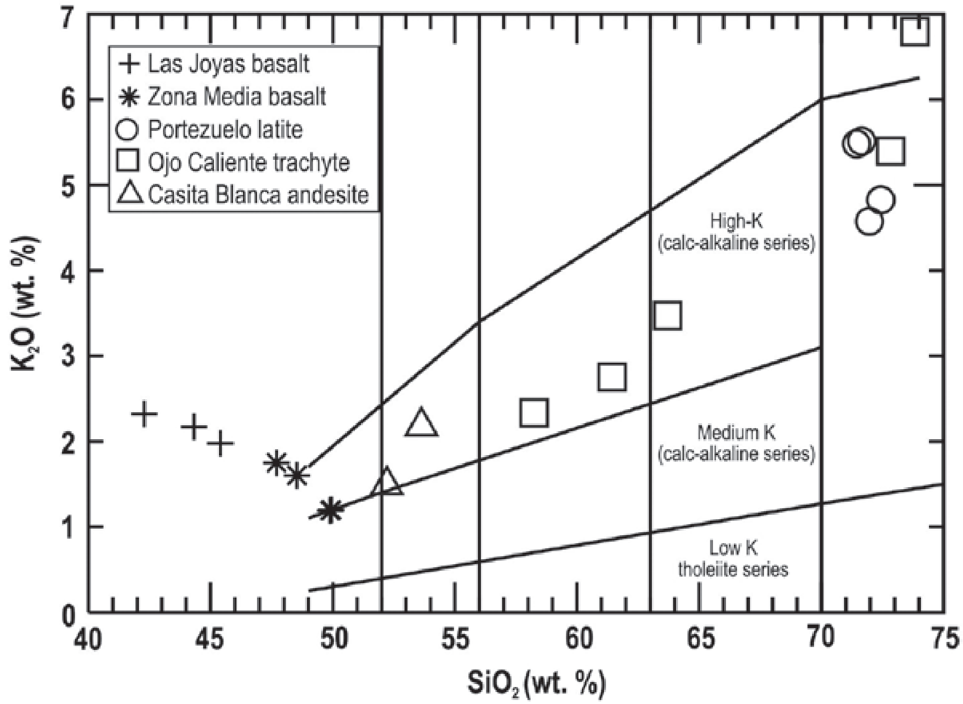

Figure 3. K_2O *vs*. SiO_2 diagram (Peccerillo and Taylor, 1976) of San Luis Potosí and Río Santa María lavas, showing the features of low-K, medium-K and high-K (potassic) calc-alkaline series.

been associated to a Miocene intraplate event subsequent to volcanism of the SLPVF. These porphyritic basalt and andesites contain *ca*. 20 modal% phenocrysts of plagioclase, olivine and augite, embedded in a fine-grained plagioclase- and augite-bearing microlitic groundmass (Sánchez-García, 2009).

Las Joyas basalt

The youngest volcanic event recognized in the southern portion of the SLP state emplaced the Las Joyas basalt, a set of Quaternary pyroclastic flows and lava flows associated to "*maar*" type volcanic structures (Labarthe-Hernández *et al*., 1982). These vesicular basaltic lava flows contain a few percent phenocrysts of olivine altered to iddingsite, set in a groundmass bearing calcic plagioclase together with pigeonite and/or augite. They filled up the depressions of the local rugged topography, and were only covered in some sites by recent alluvial deposits. The whole rock K-Ar isotopic ages obtained for this volcanic unit are 1.50 ± 0.8 Ma; 1.01 ± 0.08 Ma and 0.59 ± 0.06 Ma (Tristán-González *et al*., 2009a).

Analytical Methods

Major elements analyses (Table 1) were obtained by X-ray fluorescence at the Institute of Geology UNAM (Universidad Nacional Autónoma de México). The samples were finely powdered in an agate grinder. The details of the analytical method are reported by Lozano and Bernal (2005). The trace element analyses (Table 2) were performed at the Geochemical Laboratory in the Institute of Geology of the UASLP (LGIG), by the ICP-QMS (Thermo Scientific Serie X2, inducted coupled plasma- quadrupole mass spectrometer) method. The analytical techniques are described in Almaguer-Rodrígez (2010).

Major element data

The samples are rather fresh, with LOI values (loss of ignition at 1,000°C) ranging from slightly negative values up to 2.60 and exceptionally to 3.22 wt.% (Table 1). Samples from Casita Blanca, Ojo Caliente and Portezuelo units are silica-oversaturated basaltic andesites, andesites, dacites and rhyolites (Figure 2). All of them display the usual major element features of K-rich calc-alkaline series (Figure 3; Peccerillo and Taylor, 1976), with typically low Na_2O/K_2O ratios. The alumina saturation index $[Al_2O_3/(CaO+K_2O+Na_2O)]$ ratio range from 0.86 to 1.01 for the silica-rich units; a single sample (JAG27-03), has been determined as peralkaline $[(Na_2O+K_2O)/Al_2O_3>1]$. In Harker diagrams (not shown), TiO_2, Fe_2O_3*, MgO, MnO, and CaO display negative correlations with SiO_2, while K_2O (Figure 3) and to a lesser extent Na_2O (not shown) positive ones; the decrease of compatible elements and the increase of incompatible elements (mainly large ion lithophile elements) with SiO_2 are potentially consistent with assimilation, fractional crystallization or coupled (AFC) processes. The Differentiation Index (DI) of Thornton and Tuttle (1960), varies from 58.6 to 89.7 for felsic units (Portezuelo latite and Ojo

Table 1. Major element analyses of representative San Luis Potosí, Río Santa María and Villa de Reyes Graben lavas. Analytical method described in the text. Total iron as Fe_2O_3.

Sample	SLP0108	SLP0208	JAG0103	JAG0203	JAG1303	JAG2603	JAG2703	SLP0108A	GVR10
Rock*	BA	BA	A	A	R	D	R	R	R
GU**	Tcb	Tcb	Toc	Toc	Toc	Toc	Toc	Tlp	Tlp
Lat. N	22.2741º	22.2918º	21.8914º	21.8853º	21.7850º	21.8036º	21.8875º	22.2889º	22.0572º
Long W	101.1541º	101.1981º	100.7207º	100.7161º	100.7333º	100.7730º	100.7805º	101.2055º	100.7350º
Major elements (wt.%)									
SiO_2	53.32	51.82	59.30	56.50	70.40	61.00	72.79	70.65	70.50
TiO_2	3.41	1.59	1.46	2.04	0.31	0.92	0.28	0.56	0.34
Al_2O_3	14.11	16.27	14.65	14.32	13.24	15.10	12.67	13.69	13.15
Fe_2O_3	12.24	9.38	8.42	10.36	3.98	8.15	3.03	3.24	4.22
MnO	0.17	0.13	0.12	0.14	0.03	0.10	0.03	0.01	0.03
MgO	3.24	7.49	2.50	3.02	0.14	0.94	0.15	0.27	0.26
CaO	7.30	8.22	5.12	5.75	0.68	3.54	0.37	1.83	1.53
Na_2O	3.06	3.08	2.50	2.85	2.87	2.96	2.72	2.90	2.68
K_2O	2.16	1.47	2.60	2.21	5.16	3.27	6.64	5.43	4.70
P_2O_5	1.15	0.40	0.35	0.45	0.04	0.24	0.02	0.19	0.14
LOI	0.06	0.25	2.61	2.05	2.30	3.22	0.09	1.37	1.80
Total	100.22	100.10	99.63	99.69	99.15	99.44	99.66	100.14	99.35
Major elements to 100% free volatiles (calculated with SINCLAS program**)**									
SiO_2	53.635	52.216	61.439	58.241	72.835	63.701	73.83	71.643	72.427
TiO_2	3.430	1.599	1.513	2.103	0.321	0.961	0.286	0.569	0.349
Al_2O_3	14.197	16.388	15.178	14.761	13.698	15.768	12.858	13.885	13.509
Fe_2O_3	4.723	3.43	3.538	4.199	2.125	3.720	1.710	1.719	2.177
FeO	6.827	5.413	4.666	5.831	1.793	4.310	1.230	1.406	1.942
MnO	0.171	0.132	0.124	0.144	0.031	0.104	0.032	0.007	0.031
MgO	3.259	7.542	2.590	3.113	0.145	0.982	0.157	0.273	0.267
CaO	7.345	8.285	5.305	5.927	0.704	3.697	0.378	1.857	1.572
Na_2O	3.081	3.104	2.590	2.938	2.969	3.091	2.758	2.941	2.753
K_2O	2.176	1.484	2.694	2.278	5.338	3.415	6.738	5.512	4.824
P_2O_5	1.156	0.406	0.363	0.464	0.041	0.251	0.021	0.189	0.144
CIPW normative minerals (calculated from SINCLAS program)									
qz	10.801	1.088	20.778	15.863	33.042	22.404	60.079	29.481	34.007
or	12.859	8.77	15.92	13.462	31.546	20.181	0.136	32.574	28.532
ab	26.07	26.265	21.916	24.860	25.123	26.155	25.03	24.886	23.295
an	18.481	26.4	21.832	20.36	3.225	16.701	1.864	7.978	6.858
ne	---	---	---	---	---	---	---	---	---
c	---	---	---	---	1.854	0.866	8.216	0.156	1.24
di	8.377	9.599	1.715	4.873	---	---	---	---	---
hy	7.371	18.928	8.995	9.422	1.425	5.892	2.077	0.915	1.913
ol	---	---	---	---	---	---	---	---	---
mt	6.847	4.973	5.129	6.088	3.081	5.393	1.963	2.492	3.156
il	6.514	3.037	2.874	3.994	0.610	1.825	0.583	1.081	0.663
ap	2.678	0.941	0.841	1.075	0.095	0.582	0.053	0.438	0.334
Mg#	45.973	71.294	49.735	48.761	12.599	28.883	14.672	25.712	19.684
DI	49.73	36.123	58.614	54.185	89.711	68.740	85.245	86.941	85.834
ASI	0.804	0.917	1.010	0.940	1.015	1.073	0.860	0.980	0.996

Caliente trachyte) and from 36.1 to 49.7 for the old mafic unit (Casita Blanca andesite).

The young mafic samples Zona Media basalt and Las Joyas basalt units include silica-saturated subalkaline basalts and silica-undersaturated (ne-normative) alkaline basalts, basanites and trachy-basalt (Figure 2), which display high contents in incompatible major element oxides (TiO_2, Na_2O, K_2O; P_2O_5). Their FeO*/MgO ratios are rather low (less than 1.3) and their Mg numbers are scattered from 75.0 to 61.9. In contrast to the former group, they display relatively high Na_2O/K_2O ratios (from 1.8 to 2.8). In Harker diagrams (not shown), TiO_2, $Fe_2O_3^*$, MgO and P_2O_5 as well as K_2O and $K_2O + Na_2O$ (Figure 3) display negative correlations with SiO_2. The two latter ones are not consistent with differentiation- or assimilation-related processes, but could indicate variations in partial melting degrees of an ultramafic source.

Table 1A. Major element analyses (continued).

Sample	GVR13	SLP048	RV08	RV10	ZM0108	ZM0608	SLP0109	GME0344	GME0348
Rock*	R	R	B, subal	B, alk	B, subal	TB, pot	BSN, bsn	BSN, bsn	BSN, mnp
GU**	Tlp	Tlp	ZMb	ZMb	ZMb	ZMb	Qbj	Qbj	Qbj
Lat. N	22.4558º	21.9511º	22.0359	22.0066	21.5010º	21.6501º	22.2900º	22.4075º	22.4075º
Long W	100.9641º	100.8137º	100.0428	100.0985	99.6666º	99.7833º	100.6235º	100.7273º	100.7831º
Major elements (wt.%)									
SiO_2	69.85	70.81	49.40	47.60	49.619	46.937	43.354	44.80	41.90
TiO_2	0.46	0.454	1.94	2.04	1.835	2.04	3.233	2.30	2.96
Al_2O_3	13.29	13.723	15.60	13.98	15.239	14.391	13.364	14.00	11.85
Fe_2O_3	4.56	4.272	11.85	12.10	11.929	11.192	13.136	13.40	13.50
MnO	0.04	0.043	0.17	0.19	0.155	0.152	0.189	0.21	0.20
MgO	0.36	0.358	6.29	8.60	7.563	9.966	8.468	7.78	12.90
CaO	1.71	1.301	9.40	8.90	8.972	8.919	9.365	9.80	8.70
Na_2O	2.42	2.791	3.45	3.30	3.346	3.25	4.224	4.35	4.46
K_2O	4.44	5.431	1.18	1.57	1.181	1.721	2.121	1.95	2.30
P_2O_5	0.17	0.148	0.41	0.58	0.364	0.562	1.199	0.91	1.15
LOI	2.51	1.11	-0.09	0.03	-0.11	0.86	0.94	0.67	-0.38
Total	99.81	100.441	99.60	98.89	100.093	99.99	99.593	100.17	99.54
Major elements to 100% free volatiles (calculated with SINCLAS program*)**									
SiO_2	71.961	71.434	49.937	48.534	49.903	47.698	44.32	45.41	42.294
TiO_2	0.474	0.458	1.961	2.08	1.846	2.073	3.305	2.331	2.988
Al_2O_3	13.692	13.844	15.77	14.254	15.326	14.624	13.662	14.191	11.962
Fe_2O_3	2.292	2.25	4.25	4.35	4.241	4.004	4.926	5.05	5.039
FeO	2.165	1.854	6.954	7.187	6.979	6.631	7.651	7.678	7.728
MnO	0.041	0.043	0.172	0.194	0.156	0.154	0.193	0.213	0.202
MgO	0.371	0.361	6.358	8.769	7.606	10.128	8.657	7.886	13.021
CaO	1.762	1.312	9.502	9.075	9.023	9.064	9.574	9.933	8.782
Na_2O	2.493	2.816	3.488	3.365	3.365	3.303	4.318	4.409	4.502
K_2O	4.574	5.479	1.193	1.601	1.188	1.749	2.168	1.976	2.322
P_2O_5	0.175	0.149	0.414	0.591	0.366	0.571	1.226	0.922	1.161
CIPW normative minerals (calculated from SINCLAS program)									
qz	35.493	30.76	---	---	---	---	---	---	---
or	27.031	32.379	7.05	9.461	7.021	10.336	12.812	11.677	13.722
ab	21.095	23.828	29.514	27.204	28.474	22.338	13.209	14.228	3.206
an	7.598	5.536	23.849	19.06	23.204	19.91	11.492	13.094	5.573
ne	---	---	---	0.687	---	3.039	12.638	12.503	18.900
c	1.855	1.252	---	---	---	---	---	---	---
di	---	---	16.569	17.667	15.373	16.957	22.257	24.162	24.063
hy	2.299	1.768	6.921	---	8.506	---	---	---	---
ol	---	---	5.25	14.293	6.918	16.353	11.333	10.45	18.867
mt	3.323	3.262	6.162	6.306	6.148	5.805	7.142	7.321	7.305
il	0.90	0.87	3.724	3.95	3.506	3.937	6.277	4.427	5.675
ap	0.405	0.345	0.959	1.369	0.848	1.323	2.84	2.136	2.69
Mg#	23.399	25.766	61.974	68.503	66.017	73.137	66.854	64.675	75.021
DI	83.619	86.967	36.564	37.352	35.495	35.713	38.659	38.408	35.828
ASI	1.049	0.967	0.804	0.731	0.816	0.745	0.610	0.625	0.548

* Chemical classification of rock types are presented according to total alkalis vs. silica diagram (Le Bas *et al*., 1986); BA, basaltic-andesite; A, andesite; R, rhyolite; D, dacite; TB, trachy-basalt; BSN, basanite; mnp, melanephelinite; alk, alkali; subal, subalkali. ***Geologic Unit the stratigraphy of the volcanic fileds reported by Labarthe-Hernández *et al*. (1982); and Tristán-González *et al*. (2009a); Tcb, Casita Blanca andesite; Toc, Ojos Caliente trachyte; Tlp, Portezuelo latite; ZMb, Zona Media basalt; Qbj, Las Joyas basalt (see the text). ****SINCLAS Program by Verma *et al*. (2002). Mg#= $100(Mg^{2+}/Mg^{2+}+Fe^{2+})$; FeO= Fe_2O_3(total) x 0.85. DI, diferentiation index, DI= *qz* + *or* + *ab* + *ne* + *lc* (Thornton y Tuttle, 1960). ASI, alumina saturation index= $Al_2O_3/(K_2O + Na_2O + CaO)$.

Trace element data

The trace element data for the analyzed samples, combined with the major element features discussed above, allows us to distinguish two lava types. The first group corresponds to old calc-alkaline potassic lavas ranging in composition from Casita Blanca andesite to felsic lavas (Portezuelo latite and Ojo Caliente trachyte). It displays variable enrichment in Rb, Th, Yb and Ba, the contents of which increase together with SiO_2 contents during magmatic differentiation and/or assimilation and mixing (Figure 4). The second group corresponds to the young subalkaline/alkaline lavas (Zona Media basalt and Las Joyas basalt). These are less evolved than the calc-alkaline ones according to their rather high contents in Ni, Cr and Co (Table 2). They also display high contents in most incompatible elements and especially in Nb (Figure 4).

In the multielement plots normalized to the Primitive Mantle (Figure 5; Sun and McDonough, 1989), calc-alkaline lavas display highly fractionated patterns, with positive spikes for most large ion lithophile elements (LILE, especially Rb, K and Pb), and strong negative anomaly in high field strength elements (HFSE: Nb, Ta, P, Zr, Hf and Ti). These features, as well as their highly fractionated rare earth element (REE) patterns, are characteristic of subduction-related calc-alkaline magmas. In addition, negative anomalies in Sr and Eu can indicate plagioclase fractionation during differentiation, while similar negative anomalies in Ti and P can be due to iron oxides and apatite fractionation, respectively. The patterns of the young subalkaline/alkaline lavas are enriched in the most incompatible elements. The highest enrichments are observed for Ba, Nb and Ta, and the light REE (Figure 5). Such features are typical of intraplate alkali basalts and related "OIB-type" lavas (Sun and McDonough, 1989; Wilson, 1989).

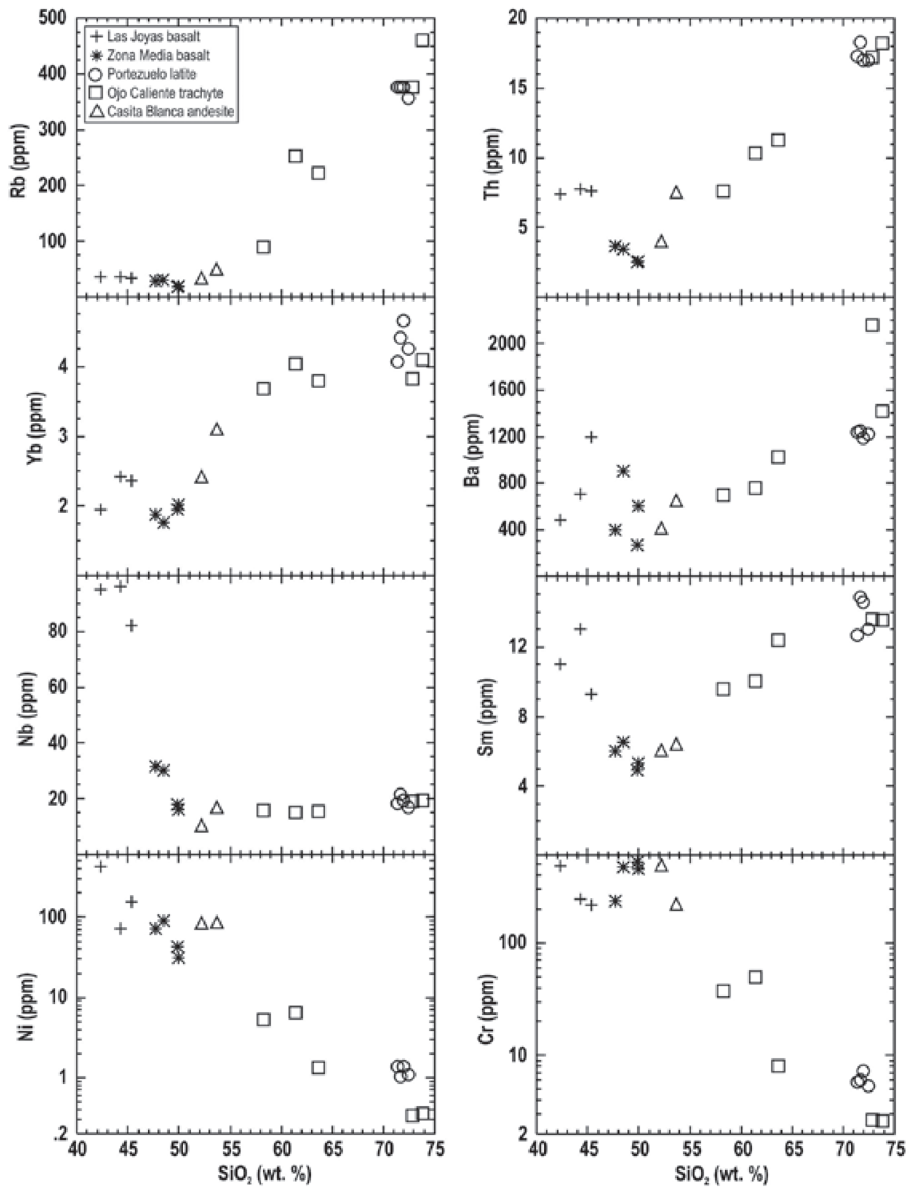

Figure 4. Plots of a selection of incompatible trace elements (ppm) *vs.* SiO_2 (wt.%). See text for explanations.

Table 2. Trace element analyses (ppm) of representative San Luis Potosí, Río Santa María and Villa de Reyes Graben volcanic rocks. Analytical method described in the text.

Sample	SLP0108	SLP0208	JAG0103	JAG0203	JAG1303	JAG2603	JAG2703	SLP0108A	GVR10
Rock*	BA	BA	A	A	R	D	R	R	R
GU**	Tcb	Tcb	Toc	Toc	Toc	Toc	Toc	Tlp	Tlp
Trace elements (ppm)									
Ba	658.39	410.52	757.25	699.77	2157.89	1022.22	1414.36	1243.65	1223.83
Rb	49.58	33.63	253.51	90.10	375.67	222.45	460.92	376.13	356.21
Sr	870.83	535.76	378.72	346.51	114.22	343.96	42.23	184.62	157.50
Y	36.75	15.67	28.16	26.20	29.11	29.42	30.98	33.49	33.73
Zr	238.67	233.01	421.57	425.64	433.29	464.87	295.18	121.73	135.82
Nb	16.46	10.43	15.24	15.67	19.20	15.55	19.46	21.38	16.97
Th	7.55	4.02	10.33	7.64	17.22	11.24	18.19	18.25	17.01
Pb	8.24	5.59	13.49	9.24	24.54	15.69	23.06	25.67	25.94
Ni	87.86	83.57	6.52	5.25	0.34	1.33	0.36	1.03	1.09
V	204.79	149.12	58.28	71.19	5.51	22.64	12.41	13.86	11.73
Cr	222.98	489.89	49.95	37.03	2.68	7.98	2.60	6.00	5.31
Hf	5.57	4.27	0.00	8.11	8.13	7.58	6.09	2.94	3.09
Cs	0.58	0.58	5.29	6.13	7.37	6.52	8.83	7.91	7.98
Ta	0.99	1.16	1.41	1.40	1.99	1.48	2.01	2.16	1.90
Co	30.75	35.72	26.27	26.29	0.79	11.32	0.55	3.15	3.10
U	0.22	1.02	2.55	1.75	3.12	3.40	4.88	3.56	2.89
Rare earth elements (ppm)									
La	30.96	24.40	42.43	59.01	117.58	86.17	104.49	111.94	94.14
Ce	71.85	52.84	90.56	83.94	125.76	111.55	129.29	141.44	121.19
Pr	10.35	5.44	9.39	8.71	14.40	12.41	14.62	15.24	13.01
Nd	36.39	28.08	48.12	44.61	66.83	59.27	68.70	75.15	64.40
Sm	6.88	6.08	10.06	9.59	13.58	12.39	13.54	14.84	13.03
Eu	2.39	1.52	1.93	1.93	1.78	2.15	1.38	1.86	1.67
Gd	6.93	5.49	8.98	8.47	11.03	10.32	10.69	12.35	10.84
Tb	1.06	0.75	1.24	1.16	1.44	1.37	1.44	1.64	1.48
Dy	6.11	4.31	7.02	6.55	7.74	7.40	7.79	8.87	8.20
Ho	1.27	0.84	1.36	1.29	1.41	1.38	1.45	1.65	1.54
Er	3.36	2.39	3.97	3.67	4.01	3.84	4.14	4.65	4.43
Tm	0.49	0.33	0.54	0.50	0.55	0.53	0.56	0.61	0.59
Yb	3.19	2.42	4.04	3.68	3.83	3.80	4.09	4.41	4.26
Lu	0.47	0.31	0.53	0.48	0.51	0.49	0.52	0.55	0.54

* Chemical classification of rock types are presented according to total alkalis vs. silica diagram (Le Bas *et al*., 1986); BA, basaltic-andesite; A, andesite; R, rhyolite; D, dacite; TB, trachy-basalt; BSN, basanite; mnp, melanephelinite; alk, alkali; subal, subalkali. ** Geologic Unit the stratigraphy of the volcanic fileds reported by Labarthe-Hernández *et al*. (1982); and Tristán-González *et al*. (2009a); Tcb, Casita Blanca andesite; Toc, Ojos Caliente trachyte; Tlp, Portezuelo latite; Qbj, Las Joyas basalt (see the text).

Discussion

It is important to obtain a large set of trace element data for the study of magmatic rocks because (i) they are much more numerous (*ca.* 80) than the major elements, (ii) they belong to several chemical groups with specific properties (e.g. the LILE, HFSE and REE), (iii) some of them, especially the HFSE, are relatively immobile during alteration, hydrothermalism and metamorphism, and therefore are good indicators of the nature of the protolith of old igneous rocks, and finally (iv) because of their concentrations, they vary considerably during magmatic processes such as partial melting, fractional crystallization, magma mixing and metasomatism. One of the most reliable analytical methods for them is the inducted coupled plasma – Quadrupole Mass Spectrometry (ICP-QMS, already implemented in the LGIG, UASLP). The method ICP-QMS used for this study (Almaguer-Rodríguez, 2010) is based on the combination of the procedures used for the ICP-AES at the Université de Bretagne Occidentale at Brest France (Cotten *et al*., 1985; inducted coupled plasma - atomic emission spectroscopy) and for the ICP-MS method at the University of Arizona (1997).

The volcanic units associated to the formation event of the San Luis Potosí Volcanic Field (Labarthe-Hernandez *et al*., 1982; Tristán-González *et al*., 2009a), have been emplaced simultaneously with other volcanic units that are associated either to the Río Santa María Volcanic Field (Labarthe-Hernandez *et al*., 1989; Tristán-González, 1987) or to the main extension event

Table 2A. Trace element analyses (continued).

Sample	GVR13	SLP048	RV08	RV10	ZM0108	ZM0608	SLP0109	GME0344	GME0348
Rock*	R	R	B, subal	B, alk	B, subal	TB, pot	BSN, bsn	BSN, bsn	BSN, mnp
GU**	Tlp	Tlp	ZMb	ZMb	ZMb	ZMb	Qbj	Qbj	Qbj
Trace elements (ppm)									
Ba	1185.24	1237.95	603.78	901.47	271.30	396.22	709.43	1200.00	485.00
Rb	376.57	376.24	19.25	30.12	17.86	28.45	35.60	34.50	36.50
Sr	156.91	141.71	610.49	862.84	524.28	774.81	1198.58	995.00	976.00
Y	39.84	32.21	22.80	15.95	14.34	14.33	22.78	32.50	30.00
Zr	82.92	118.20	165.38	198.64	166.31	210.68	387.53	265.00	335.00
Nb	19.28	18.33	16.29	30.32	18.08	31.41	95.93	82.00	95.00
Th	16.99	17.29	2.60	3.43	2.49	3.66	7.73	7.60	7.40
Pb	25.74	27.59	2.27	3.18	2.15	2.38	4.82	---	---
Ni	1.39	1.36	31.35	89.05	42.41	70.71	71.22	156.00	424.00
V	16.48	13.59	165.42	167.85	168.32	167.24	196.32	202.00	197.00
Cr	7.29	5.84	450.28	468.89	514.62	236.12	246.24	216.00	480.00
Hf	2.06	2.66	3.01	3.22	2.98	3.48	7.38	---	---
Cs	8.77	8.02	0.32	0.71	0.14	0.48	0.71	---	---
Ta	2.12	1.98	1.627	2.88	1.91	3.12	6.43	---	---
Co	2.24	2.65	45.86	59.58	52.30	56.53	58.26	44.00	57.00
U	3.66	3.98	0.75	1.10	0.75	1.28	2.40	---	---
Rare earth elements (ppm)									
La	102.95	95.12	21.98	33.04	19.19	28.47	102.20	60.00	60.00
Ce	134.37	121.13	42.10	59.59	39.34	55.22	124.66	105.00	114.00
Pr	14.19	12.94	4.38	6.14	3.98	5.65	12.71	---	---
Nd	71.40	64.36	22.37	31.71	20.90	29.34	66.25	40.00	57.50
Sm	14.58	12.66	5.34	6.57	4.93	6.05	12.99	9.30	11.00
Eu	1.68	1.60	1.61	1.88	1.45	1.72	3.52	2.94	3.38
Gd	12.51	10.54	5.23	5.81	4.76	5.44	10.93	8.10	9.10
Tb	1.71	1.42	0.73	0.75	0.66	0.71	1.34	---	---
Dy	9.53	7.82	4.14	3.95	3.86	3.92	6.68	6.10	6.20
Ho	1.81	1.48	0.79	0.73	0.74	0.73	1.14	---	---
Er	5.04	4.23	2.17	1.99	2.06	2.02	2.99	2.80	2.70
Tm	0.67	0.58	0.29	0.25	0.28	0.26	0.36	---	---
Yb	4.65	4.07	2.02	1.76	1.95	1.87	2.42	2.36	1.95
Lu	0.58	0.52	0.26	0.22	0.27	0.24	0.29	---	---

* Chemical classification of rock types are presented according to total alkalis vs. silica diagram (Le Bas *et al*., 1986); BA, basaltic-andesite; A, andesite; R, rhyolite; D, dacite; TB, trachy-basalt; BSN, basanite; mnp, melanephelinite; alk, alkali; subal, subalkali. ** Geologic Unit the stratigraphy of the volcanic fileds reported by Labarthe-Hernández *et al*. (1982); and Tristán-González *et al*. (2009a); Tcb, Casita Blanca andesite; Toc, Ojos Caliente trachyte; Tlp, Portezuelo latite; ZMb, Zona Media basalt; Qbj, Las Joyas basalt (see the text).

of the volcano-tectonic structure of Villa de Reyes Graben (Tristán-González, 1986; 2008). The corresponding structures have been identified in the southern portion of San Luis Potosí state (Figure 1), where five successive volcanic stages have been recognized (Tristán-González *et al*., 2009b).

Subalkaline and alkaline basalts, basanites and trachybasalts of intraplate type were emplaced during the two youngest stages, which occurred during the Miocene (23 to 21 Ma) in the RSMVF and the Quaternary in the SLPVF (Tristán-González *et al*., 2009a). Both Miocene and Quaternary lavas were considered as derived from a progressive partial melting of a peridotitic mantle (Aranda-Gómez *et al*., 2005). Our new data support this interpretation. Indeed, the REE and multielement patterns of these lavas (Figure 5) are rather smooth. They display no evidence of interaction with the continental crust, which would have resulted in positive LILE and negative HFSE anomalies, and more generally in a somewhat erratic behavior of incompatible trace elements. In addition, the variations observed in incompatible trace element plots (Figure 6) are consistent with variable partial melting degrees and limited fractional crystallization processes. The studied alkaline lavas are fairly similar to the Encinos Volcanic Field hawaiites located in the north of the San Luis Potosí state, which in addition have experienced some crustal contamination (Luhr *et al*., 1994).

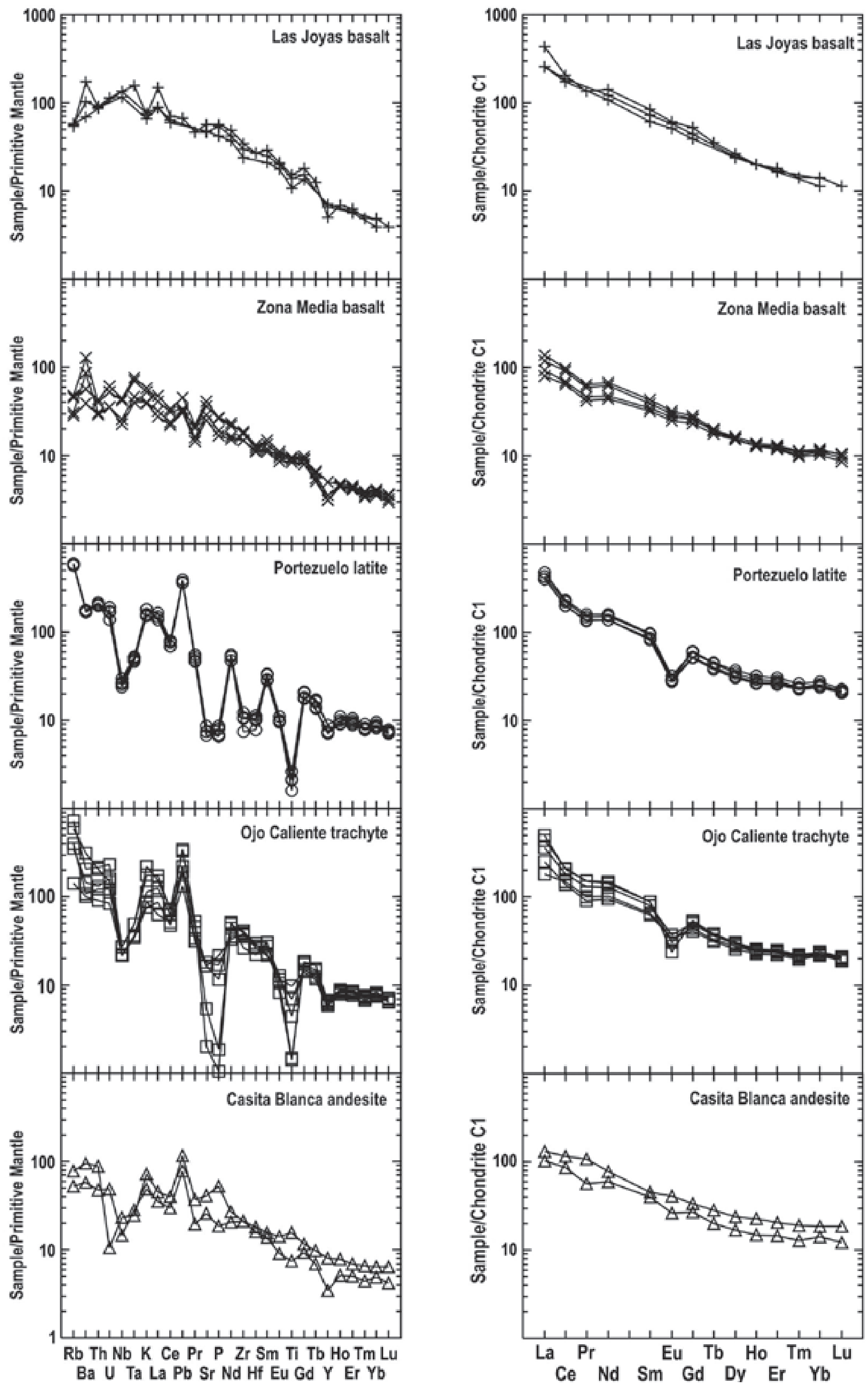

Figure 5. Primitive Mantle –normalized multielement plots and C1 chondrite-normalized rare earth element patterns. Normalization values from Sun and McDonough (1989).

The three older volcanic events emplaced successively (i) the Casita Blanca andesite (mid Eocene); (ii) dacitic to rhyolitic domes and pyroclastic deposits between 32 and 28 Ma in the SLPVF and contemporaneous trachytes and rhyolites in the RSMVF, such as the Ojo Caliente trachyte (Labarthe-Hernandez *et al*., 1982; Tristán-González *et al*., 2009a), and the Portezuelo latite associated to the main extension event that originated the VRG (Tristán-González, 1986); and finally (iii) rhyolitic magmas extruded between 28 and 26 Ma (Labarthe-Hernández *et al*., 1982; Tristán-González *et al*., 2009a), which belong to a bimodal volcanic series (Tristán-González, 2008; Tristán-González *et al*., 2009a; Rodríguez-Ríos and Torres-Aguilera, 2009). All these potassic calc-alkaline lavas display typical fractionated REE and multielement

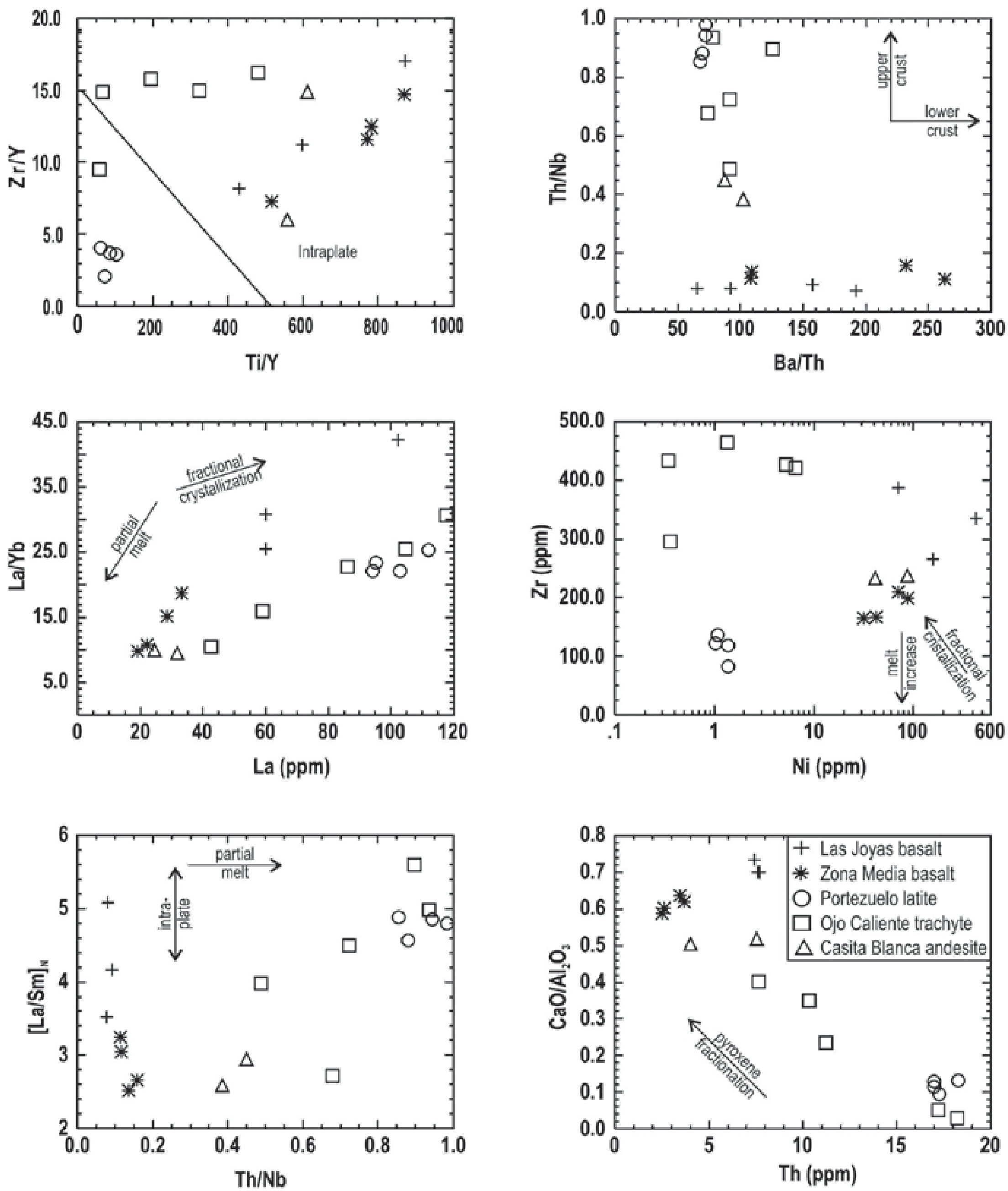

Figure 6. Rectangular plots for selected incompatible element concentrations and ratios; showing the features of intraplate volcanism (Zr/Y *vs*. Ti/Y; $[La/SM]_N$ *vs*. La diagrams); or magma generation by AFC in the lower or upper crust (La/Yb *vs*. La; Zr vs. Ni diagrams). The CaO/Al_2O_3 *vs*. Th diagram displays features associated to partial melting following clinopyroxene depletion in the source (Luhr *et al*., 1995).

patterns (Figure 5). These patterns are consistent with their derivation from a mantle source metasomatized by LILE- and LREE- rich hydrous fluids and/or magmas ascending from a subducted oceanic slab. The intermediate/evolved character of these lavas, their low MgO, Ni, Cr and Co contents, their negative Sr, Eu, Ti and P anomalies, as well as their trends in Figure 6 incompatible element plots, are consistent with their derivation from mafic magmas through fractionation of a plagioclase – olivine – pyroxene –titanomagnetite – apatite phenocryst assemblage (Aranda-Gómez *et al*., 2007; Aguillón-Robles *et al*., 2009). However, the displays in Figure 6 plots suggests that their evolution was controlled by more complex petrogenetic processes than closed-system fractional crystallization. Those can include assimilation coupled with fractional crystallization (AFC; DePaolo, 1981) or melting-assimilation-storage-homogeneization (MASH; Hildreth and Moorbath, 1988), both of them involving the chemical contribution of the lower or upper continental crust (Medina-Romero *et al*., 2005; Aguillón-Robles *et al*., 2009).

Conclusions

Combined major and trace element data allow us to divide the five magmatic events which emplaced the volcanic fields of San Luis Potosí and Río Santa María from Eocene to Pleistocene into two groups. The three oldest ones, ranging in age from middle Eocene to late Oligocene, emplaced potassic calc-alkaline intermediate (andesitic) to evolved (trachytic and rhyolitic) lavas. These originated from suduction-related mafic magmas through open-system fractional crystallization coupled with assimilation and possibly melting of the continental crust. In addition, mixing with the magma chamber may have contributed to the genesis of dacitic and trachytic lavas extruded along the SLPVF and RSMVF (Portezuelo latite and Ojo Caliente trachyte; Aguillón-Robles *et al*., 2009). Later, a fast extensional event formed a faulting pattern used for the ascent of magmas from the two youngest volcanic phases (Miocene and Quaternary). These emplaced mostly OIB-type subalkaline to alkaline basalt and basanites which derived from variable melting degrees of enriched mantle and experienced limited amounts of fractionation. The association between cortical extension and OIB-type intraplate magmatism is typical feature of the evolution of the Mesa Central of Mexico (Luhr et al., 1994; Tual, 2010; Rodríguez-León, 2012).

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