

## Geochemistry of the extensive peralkaline pyroclastic flow deposit of NW Mexico, based on conventional and handheld X-ray fluorescence. Implications in a regional context

Geoquímica del extenso depósito de flujo piroclástico hiperalcalino del NW de México, basada en fluorescencia de rayos X convencional y portátil. Implicaciones en un contexto regional

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### Abstract

Chemical analyses conducted on the surface of rock slabs under a combination of two X-ray spectrometry methods, wavelength dispersive XRF and energy dispersive XRF, are used to establish a geochemical correlation between the studied samples. This proves to be an excellent method for the characterization of volcanic glasses, particularly when particles of exotic origin are present, because the effect of these is not easily eliminated by conventional whole rock analysis. Analyses of glassy rhyolites (ignimbrites and lava flows) in northwestern Mexico establish a geochemical signature for the samples, providing criteria that allow us to: a) correlate them with a peralkaline volcanic event, previously reported, that occurred during Middle Miocene time; b) distinguish them from other metaluminous varieties in the region and, c) propose a correlation between all the peralkaline vitrophyres that crop out within the studied area, of at least 50.000 km<sup>2</sup>, validating the hypothesis that they are related to the same volcanic event. Finally, based on the results of this study and previous geological investigations, it is proposed that a distance of more than 100 km between the geographical location of the thickest peralkaline deposits in Sonora, is probably related to a displacement along transtensional dextral faults during the Late Miocene..

**Keywords:** Geochemical correlation, ignimbrites, peralkaline rhyolites, NW México

### Resumen

El análisis químico realizado en secciones de roca bajo la combinación de dos métodos de espectrometría de fluorescencia de rayos x, por dispersión de longitudes de onda y por dispersión de energías, permitió establecer una correlación geoquímica entre las muestras estudiadas, resultando ser un excelente método para la caracterización de vidrios volcánicos, en particular cuando contie-

nen partículas ajenas al magma que no pueden ser eliminadas por el análisis de roca total convencional. Los resultados obtenidos sobre las riolitas vítreas estudiadas (ignimbritas y coladas) del Noroeste de México permiten establecer una firma geoquímica de las muestras que proporciona criterios permitiendo: a) correlacionarlas con un evento volcánico, anteriormente descrito, de tipo hiperalkalino que ocurrió durante el Mioceno medio; b) diferenciarlas de las ignimbritas metaluminosas también presentes en la región y, c) proponer una correlación entre los vitrófros de la zona estudiada, de al menos 50000 km<sup>2</sup>, haciendo válida la hipótesis de que todos ellos provienen de una misma erupción. Finalmente, basados en los resultados de este estudio y de trabajos geológicos previos, se propone que una diferencia de hasta más de 100 km en la ubicación geográfica de los depósitos hiperalkalinos de mayor espesor, es probablemente relacionada con un desplazamiento a lo largo de fallas dextrales asociadas a un evento extensivo en transtensión ocurrido durante el Mioceno superior.

*Palabras clave:* Correlación geoquímica, ignimbritas, riolitas hiperalkalinas, NW de México

## 1. Introduction

In Northwestern Mexico, shortly after the Miocene Continental Volcanic Arc became inactive, a Middle Miocene magmatic event occurred, characterized by the eruption of anorogenic melts in a rift environment immediately prior to the Gulf of California opening. This volcanic event comprised some occurrences of mafic lavas with transitional signatures, but was dominated by peralkaline silicic volcanic rocks (Vidal-Solano, 2005). The peralkaline comenditic rocks crop out as lavas and pyroclastic flow deposits. Moreover, an ignimbritic sequence has been widely recognized on both sides of the Gulf of California (Fig. 1), in Baja California where it is known as the Tuff of San Felipe (Stock *et al.* 1999; Oskin *et al.* 2001; Bennett, 2009; Olguin-Villa, 2010; Olguin-Villa *et al.*, 2010), and in the state of Sonora where it is described as peralkaline ignimbrite (Vidal Solano *et al.*, 2005, 2007, 2008a; Barrera-Guerrero and Vidal-Solano, 2010; Gómez-Valencia and Vidal-Solano, 2010). This ignimbritic episode, whose outcrops span an area of at least 50.000 km<sup>2</sup>, has been attributed to a possible mega-eruption that occurred during Middle Miocene time (Vidal-Solano *et al.*, 2008b). In this paper we test a method of geochemical characterization of the peralkaline pyroclastic deposits recognized in NW Mexico (Vidal-Solano, 2012), with the aim to correlate major and trace element variations in the basal vitreous lithofacies by analyzing flat surfaces of rock slabs.

## 2. Methods

Geochemical methods are useful to correlate outcrops of ignimbrites that belong to the same event in different regions. However, it is important to check first that samples show no alteration and to use elements that have little mobility. Some immobile or slightly mobile trace elements can be determined by X-ray fluorescence (XRF) with great accuracy; this analytical technique is therefore useful to generate good results with low investment of

time and resources. The existence of an extensive ignimbrite unit (the Tuff of San Felipe in Baja California and Middle Miocene ignimbrites near Hermosillo), which crops out over an area of at least 50 000 Km<sup>2</sup> in NW Mexico, has been attributed to a possible mega-eruption during Middle Miocene time (Vidal-Solano *et al.*, 2008a). Until now, the correlations between the different outcrops located both in Sonora and Baja California were based on paleomagnetic studies (Oskin *et al.*, 2001; Hernandez-Mendez *et al.*, 2008, Stock *et al.*, 2008), which have shown similar magnetization and an unusual direction for Middle Miocene time (Olguin-Villa *et al.*, 2010). Geochemical analyses of pyroclastic flow deposits may show erratic variations in some elements, due to: 1) the use of whole rock samples that, in the case of ignimbrites, can contain fragments of alien or mixed liquids, and, 2) the poor representativeness of the samples with the required chemical data, because the cost of these analytical techniques restricts the number of analyses (Vidal-Solano and Meza-Figueroa, 2009).

In this work we have used both WD-XRF and ED-XRF techniques to obtain the geochemical data on the surface of rock chips remaining after preparation of thin sections. The analytical method is carried out in a specific point of small size and well located on the surface rock. This method is highly useful, because it allows us to determine original compositions of magmas by analyses of the rock surface which is free from exotic fragments. In addition, such a method represents a very low cost investment in sample collection and preparation for the analysis, because the hand specimen can be re-used and only requires minimal preparation. Furthermore, the time needed on the analytical equipment is minimal; the procedure is very efficient and yields results that are useful complements to the initial petrographic study.

## 3. Analytical Techniques

Analyses reported in this study were carried out at the X-ray Fluorescence Laboratory and the Environmental

Geochemistry Laboratory of the *Universidad Nacional Autónoma de México*, using a Siemens SRS 3000 WD-XRF sequential spectrometer and a Thermo Scientific portable analyzer ED-XRF Niton XL3T. The SRS 3000 spectrometer was used to measure the trace elements Rb, Sr, Ba, Y, Zr, Nb, V, Cr, Co, Ni, Cu, Zn, Th and Pb, under the analytical and reference materials used in the construction of calibration curves reported in Lozano and Bernal (2005). To shorten the total measurement time, an adjustment was made spending only 20 seconds per point, reducing therefore the time per sample to ca. 15 min. With the Niton XL3T spectrometer we measured Rb, Sr, Zr, Zn and Pb, but also some major elements like Mn, Ti, Fe, Ca and K on three different areas of one square centimeter on each rock slab. All these values were corrected using standard analysis of the IGL series (IGLSY, IGLA-1 and IGLS-1) and RGM-1. The total measurement time per sample was 3 minutes, and the variables of the analysis are reported in Zamora *et al.* (2008). IGLA-1 and RGM-1

were analyzed by both techniques under the same conditions in order to assure that analytical results were well calibrated. Trace elements measured with the SRS3000 showed an excellent agreement between measured and certified values with a mean accuracy of 93.4%. Values for IGLA-1 reported by Niton showed for Fe, Ca and K a mean accuracy of 88% calculated by  $A=100-Abs[(True\ value-Meas\ value)/Meas\ value]*100$ ].

*Sample preparation*

The sample preparation consists in smoothing, cleaning and drying the surface of each slab to expose the flat side to the x-ray. This is not difficult because after the preparation of thin sections the slabs already had a flat surface, as well as a suitable size to adjust them on the sample loader of the SRS 3000 spectrometer (Fig. 2). Samples smaller than 34 mm were mounted on a plastic film inert to X-rays (mylar) prior to the analysis.

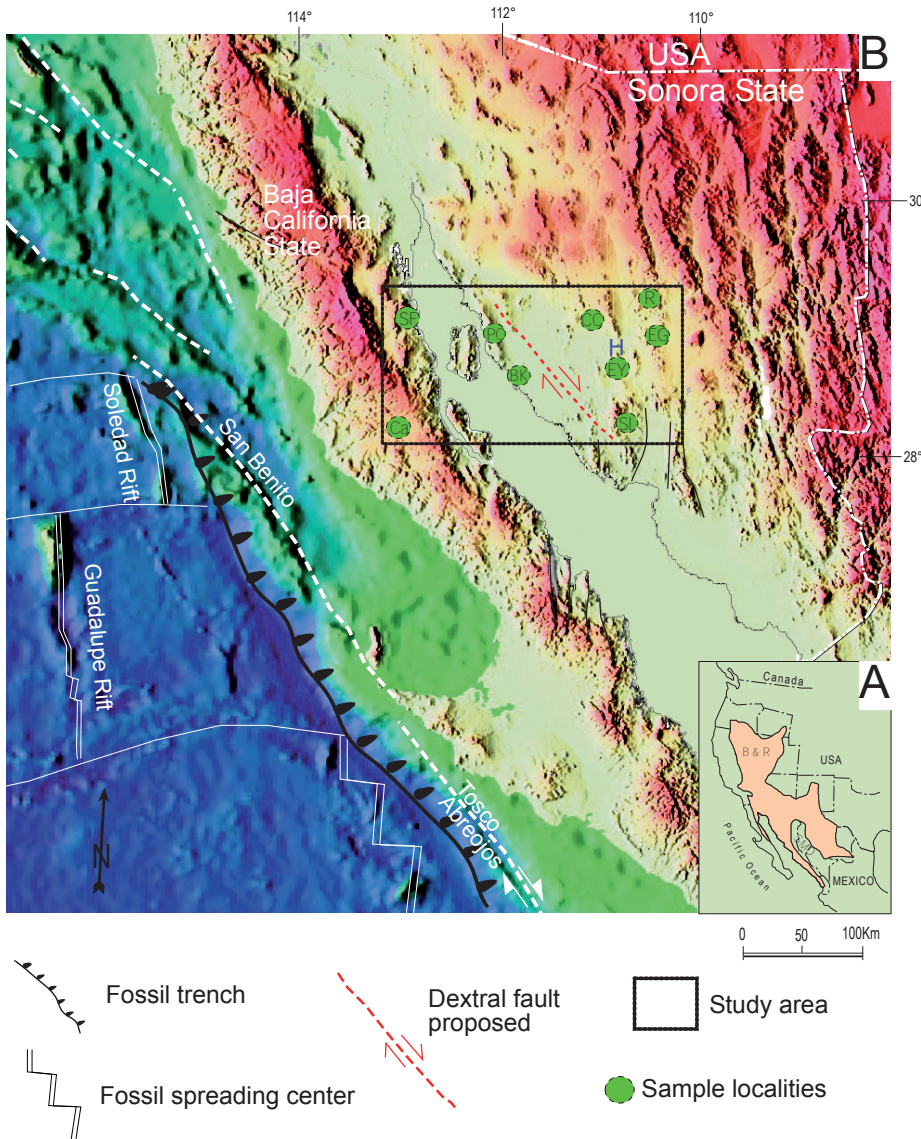


Fig. 1.- A: Geographical location of the NW of Mexico showing the province of the Sierra Madre Occidental (SMO) and the areas affected by Miocene extensional tectonics (Basin and Range). B: Tectonic reconstruction for Middle Miocene time (12 Ma) showing the initial position of the northern part of the Baja California peninsula relative to Sonora, modified from Vidal-Solano *et al.* (2008a). Location of the proposed system of dextral faults that displace sites of Kino Bay and Punta Chueca is illustrated. SF, San Felipe; Ca, Cataviña; PC, Punta Chueca; BK, Bahía de Kino; SL, Sierra Libre; CC, Cerro La Ceja; H, Hermosillo; EY, Cerro El Yeso; R, Rayón; EG, El Gavilán.

Fig. 1.- A: Localización geográfica del NW de México mostrando la provincia de la Sierra Madre Occidental (SMO) y las zonas afectadas por la tectónica extensional del Mioceno (Basin and Range). B: Reconstrucción tectónica para el Mioceno medio (12 Ma) de la posición inicial de la parte norte de la Península de Baja California con respecto a Sonora, modificado de Vidal-Solano *et al.* (2008a). Se representa la ubicación del sistema propuesto de fallas dextrales que desplazan los sitios de Bahía Kino y Punta Chueca. SF, San Felipe; Ca, Cataviña; PC, Punta Chueca; BK, Bahía de Kino; SL, Sierra Libre; CC, Cerro La Ceja; H, Hermosillo; EY, Cerro El Yeso; R, Rayón; EG, El Gavilán.



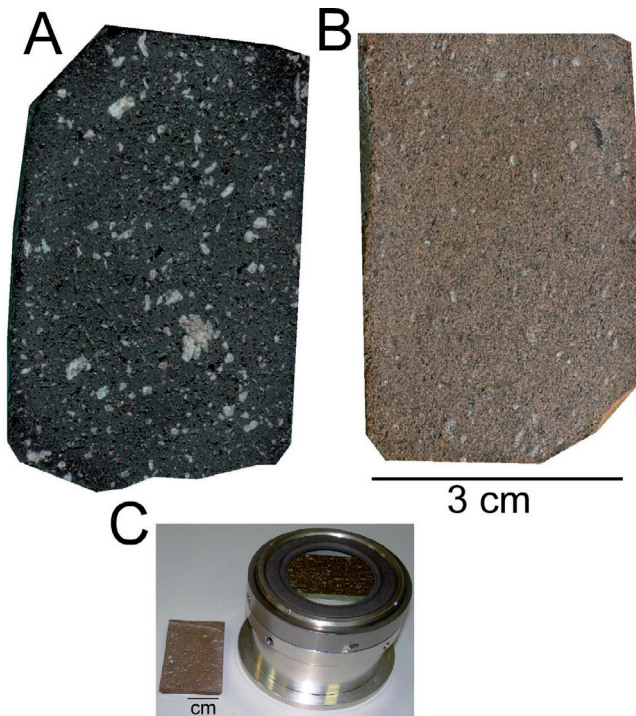


Fig. 2.-Example of rock slabs studied. A: black eutaxitic vitrophyre with porphyritic texture (5% alkali feldspar), B: brown vitroclastic, almost aphanitic, vitrophyre. C: sample loader used for WD-XRF spectrometer.

Fig. 2.-Ejemplo de las secciones de roca estudiadas, A: vitrófiro negro eutaxítico porfírico de Feldespato alcalino (5%), B: vitrófiro café vitroclástico casi afanítico. C: porta-muestra utilizado para el análisis por WD-FRX en el espectrómetro WD-FRX.

#### 4. Studied material

We studied 35 slabs of peralkaline rocks: 22 samples of vitrophyre facies of the ignimbritic deposits and 13 samples of glassy facies of porphyritic rhyolitic lava flows having the same chemical affinity. One sample of a metaluminous rhyolite was also analyzed for reference. The ignimbritic samples are slightly porphyritic (<15% phenocrysts), with different degrees of welding yielding vitroclastic to eutaxitic textures (Fig. 2). Their mineralogical association is characterized by the presence, in order of abundance, of Na-sanidine, greenish iron-rich ferrohedenbergite and fayalite. Plagioclase and hydrous minerals such as biotite or amphibole are never present in these lavas. This distinctive mineral association characterizes comendite-type high-silica rhyolites (Vidal-Solano *et al.*, 2007). Chemically, these rocks have, unlike the metaluminous rhyolites, high  $\text{SiO}_2$  (> 72%) and alkali values (7-9 %), but low alumina (< 12 %) giving rise to their peralkaline affinity, and relatively high iron contents (Table 1, Vidal-Solano *et al.*, 2005, 2007, 2008b). Another

important feature is their high concentration in Rb and Zr, and very low values in Sr and Ba.

#### 5. Results

The peralkaline rhyolitic lavas and the metaluminous rhyolite were used as references for the geochemical discrimination. The results are reported in Tables 1 and 2. Zr, Sr, Rb, Pb, Zn, Ba, Nb, Th, determined by WD-XRF sequential spectrometry, and Zr, Sr, Rb, Pb, Zn, Mn, Ti, Ba,  $\text{Fe}_2\text{O}_3$ , CaO and  $\text{K}_2\text{O}$ , determined by ED-XRF spectrometry, show concentrations and ratios consistent with the values obtained by ICP-MS analyses on whole rock samples (Vidal-Solano *et al.*, 2005, 2007, 2008b, Olguin-Villa, 2010). The concentrations of these elements were reported on binary, ternary and multi-element diagrams to better visualize the relationships and variations among the different samples (Fig. 3 and 4).

All the samples of the peralkaline rhyolite (ignimbrites and lavas) retain similar element ratios (Fig. 3A): low Sr and Ba, high Rb and Th, and moderate concentrations in Nb and Zr compared to the metaluminous rhyolite. Parallelism of the spectra in this diagram indicates a genetic link for all the peralkaline samples. However, a difference does exist between the concentrations in the ignimbrites and those in the lavas. This is best illustrated on the diagram of Figure 3B, which shows the clustering of the ignimbrite samples, suggesting a good correlation between ignimbrite outcrops, and a wide dispersion of the points representing the rhyolite lava flows. The ratios between Rb,  $\text{K}_2\text{O}$ , Sr, and  $\text{Fe}_2\text{O}_3$  concentrations for each ignimbrite sample are plotted in Figure 4A, which allowed the distinction of different data sets. Three groups with similar chemical signature can be defined, suggesting a common source for samples from different outcrops; this in turn leads to a more precise correlation of the different units.

##### 5.1. Geochemistry

The major element analyses show that the ignimbrite samples have high but variable concentrations in  $\text{K}_2\text{O}$  (2 to 5%) and low CaO contents (<1%). Total  $\text{Fe}_2\text{O}_3$  values are generally higher than 1% and increase when Mn and Ti increase. This is also a criterion that differentiates peralkaline rhyolites from metaluminous ones (Vidal-Solano, 2005).

The trace element characteristics are best visualized on a multi-element diagram (Fig. 3). Incompatible multi-element patterns, normalized to N-MORB (Pearce, 1983), of the peralkaline ignimbrites exhibit an overall parallelism of the spectra (Fig. 3A), with irregular patterns character-

Sample	Rhyolite type	UTM East	UTM North	Locality	Zr ppm	Sr ppm	Rb ppm	Pb ppm	Zn ppm	Ba ppm	Nb ppm	Th ppm	SiO <sub>2</sub> * %	TiO <sub>2</sub> * %	Al <sub>2</sub> O <sub>3</sub> * %	Fe <sub>2</sub> O <sub>3</sub> * %	MgO* %	CaO* %	Na <sub>2</sub> O* %	K <sub>2</sub> O* %	
EP071A SLAB	Ignimbrite	12R 517371	3165548	Sierra Libre Son.	357	69	462	34	347	47	33	37									
EPV10-01A SLAB	Lava	12R 289107	3526447	El Pinacate Son.	798	7	146	26	141	90	57	19	74.25	0.46	11.41	1.91	0.08	0.42	5.35	4.70	
SLE007A SLAB	Lava	12R 512172	3168291	Sierra Libre Son.	636	1	147	29	139	111	34	14									
SLEG19 SLAB	Lava	12R 511341	3167978	Sierra Libre Son.	763	0	162	29	166	13	39	16									
SLEG17A SLAB	Lava	12R 511511	3167685	Sierra Libre Son.	619	1	156	26	147	92	34	15									
SLEG17B SLAB	Lava	12R 511512	3167686	Sierra Libre Son.	611	2	152	28	140	98	34	14									
EPV010B SLAB	Lava	12R 289107	3526447	El Pinacate Son.	802	6	151	25	145	89	58	19	75.89	0.20	11.23	2.11	0.08	0.45	3.78	3.65	
EPV01A SLAB	Lava	12R 289107	3526447	El Pinacate Son.	794	6	148	24	142	79	58	20									
EH1001 SLAB	Lava	12R 482091	3208159	Hermosillo Son.	652	2	179	17	137	9	45	18									
SLE07B SLAB	Lava	12R 512172	3168291	Sierra Libre Son.	512	1	114	17	108	83	27	11									
EG073 SLAB	Ignimbrite	12R 544361	3243156	El Gavilán Son.	340	24	219	31	119	31	31	27	72.77	0.12	12.01	1.05	0.07	0.05	3.46	4.73	
MCR1001A SLAB	Ignimbrite	12R 530160	3276607	Rayón Son.	349	35	214	36	105	84	31	23									
CEI071 SLAB	Ignimbrite	12R 484989	3287559	C. La Ceja Son.	336	28	219	31	99	67	30	24									
PAR1002A SLAB	Ignimbrite	12R 530632	3275303	Rayón Son.	316	33	219	33	106	57	30	24									
EG075 SLAB	Ignimbrite	12R 544361	3243156	El Gavilán Son.	314	11	225	33	119	33	30	24									
DEL0802D SLAB	Ignimbrite	11R 708533	3402097	San Felipe B.C.	317	17	220	30	98	46	29	21	72.20	0.10	12.30	1.70	0.10	0.60	4.60	3.30	
DEL0802B SLAB	Ignimbrite	11R 708534	3402098	San Felipe B.C.	327	13	224	29	101	47	30	25	71.90	0.10	12.30	1.70	0.10	0.60	4.40	3.50	
SA0911B SLAB	Ignimbrite	11R 689374	3311426	Cataviña B.C.	319	102	192	27	82	144	26	20	71.70	0.16	11.80	1.98	0.67	1.32	3.24	4.31	
MEC092A1 SLAB	Ignimbrite	11R 707505	3305646	Cataviña B.C.	298	91	182	35	103	124	28	22									
MEC092A SLAB	Ignimbrite	11R 707505	3305646	Cataviña B.C.	287	88	182	36	101	89	27	23									
MEC091A SLAB	Ignimbrite	11R 707505	3305646	Cataviña B.C.	333	60	196	30	99	105	29	22									
CEU091B SLAB	Ignimbrite	12R 401865	3195911	B. Kino Son.	365	146	261	35	283	59	29	34									
CEU091B1 SLAB	Ignimbrite	12R 401866	3195912	B. Kino Son.	361	130	257	33	257	62	29	32									
LPSL093 SLAB	Lava	12R 503562	3162260	Sierra Libre Son.	580	1	322	28	152	25	39	13									
LMCR093A SLAB	Ignimbrite	11R 526131	3291842	Rayón Son.	314	34	207	31	89	72	31	22									
MCD094A SLAB	Ignimbrite	12R 527679	3284565	Rayón Son.	368	99	186	39	114	71	33	26									
MEC0901B SLAB	Ignimbrite	11R 707505	3305646	Cataviña B.C.	306	82	187	34	93	327	29	21	75.80	0.13	11.40	1.78	0.24	1.22	3.10	4.80	
SA0911A SLAB	Ignimbrite	11R 689374	3311426	Cataviña B.C.	289	113	186	29	82	160	28	21	74.20	0.16	12.35	2.12	0.26	1.00	3.72	4.54	
PP0906 SLAB	Lava	12R 394164	3206028	Punta Chueca Son.	208	553	80	14	57	654	9	5									
EP0703 SLAB	Lava	12R 517475	3165442	Sierra Libre Son.	824	58	507	29	422	27	41	25									
PP0909 SLAB	Ignimbrite	12R 394166	3206030	Punta Chueca Son.	305	20	198	35	82	49	27	21									
SA0912F SLAB	Ignimbrite	11R 689375	3311427	Cataviña B.C.	297	70	197	35	100	72	28	21	72.00	0.14	11.75	1.88	0.43	0.84	2.92	4.83	
PP0901 SLAB	Lava	12R 394164	3206028	Punta Chueca Son.	247	215	232	24	79	565	16	24									
CEY0902 SLAB	Ignimbrite	12R 500727	3204376	Hermosillo Son.	343	110	234	28	118	56	29	26	72.88	0.15	12.20	0.77	0.13	0.52	5.23	4.53	

Table 1.- Trace element concentrations determined in the rhyolite slabs studied by WD-XRF spectrometer. (\*) Major element concentrations determined in whole rock by ICP-AES (Vidal-Solano, 2005; Vidal-Solano et al., 2005; Vidal-Solano et al., 2008a, 2008b; Olguin-Villa 2010). Sample locations are given in WGS84.

Tabla 1.- Concentraciones de elementos traza determinadas en las secciones de las riolitas estudiadas bajo un espectrómetro WD-FRX. (\*) Concentraciones de elementos mayores determinados en roca total por ICP-AES (Vidal-Solano, 2005; Vidal-Solano et al., 2005; Vidal-Solano et al., 2008a, 2008b; Olguin-Villa 2010). Coordenadas de las muestras en el datum WGS-84.



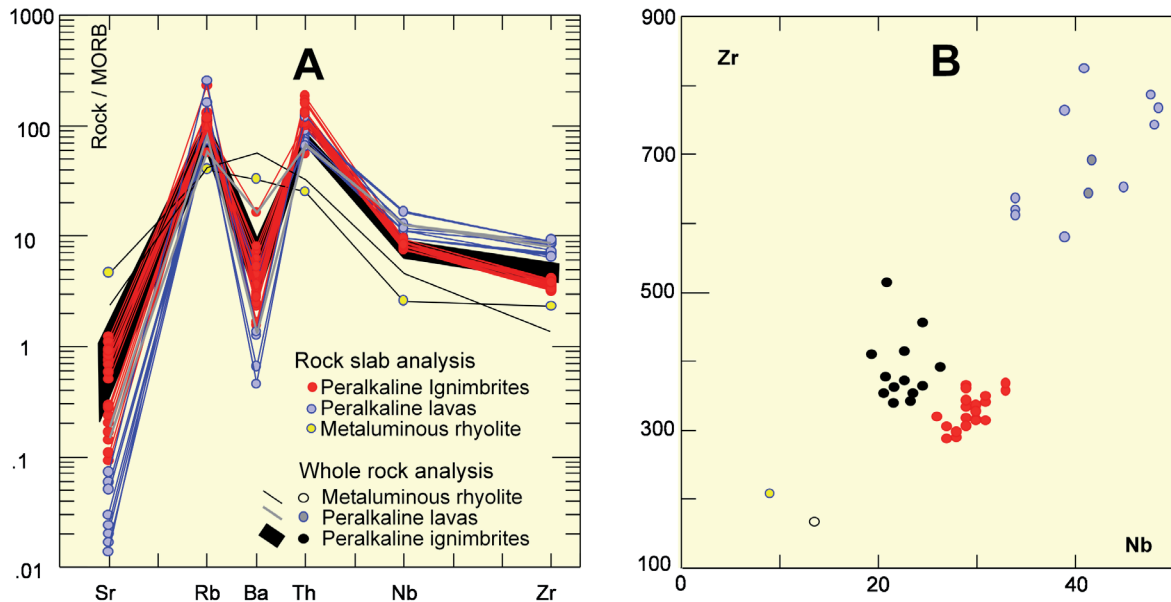


Fig. 3.- Diagrams illustrating the chemical identity of the samples analyzed: A, MORB normalized multi-element diagram of Pearce (1983); B, variation diagram of Nb vs Zr. See discussion in text. Values previously determined by analysis of whole-rock samples by ICP (Vidal-Solano, 2005; Vidal-Solano et al., 2005; Vidal-Solano et al., 2008a, 2008b; Olguin-Villa 2010) are included in these and subsequent diagrams to illustrate the good correlation values obtained by the rock slab analysis techniques.

Fig. 3.- Diagramas que ilustran la identidad química de las muestras analizadas: A, diagrama multielemental normalizado a MORB de Pearce (1983); B, diagrama de variación Zr vs Nb. Ver discusión en el texto. Valores previamente obtenidos por medio de análisis de roca total (Vidal-Solano, 2005; Vidal-Solano et al., 2005; Vidal-Solano et al., 2008a, 2008b; Olguin-Villa 2010) están incluidos aquí y en las figuras siguientes para mostrar la buena correlación de los valores obtenidos con las técnicas de análisis de las secciones de roca.

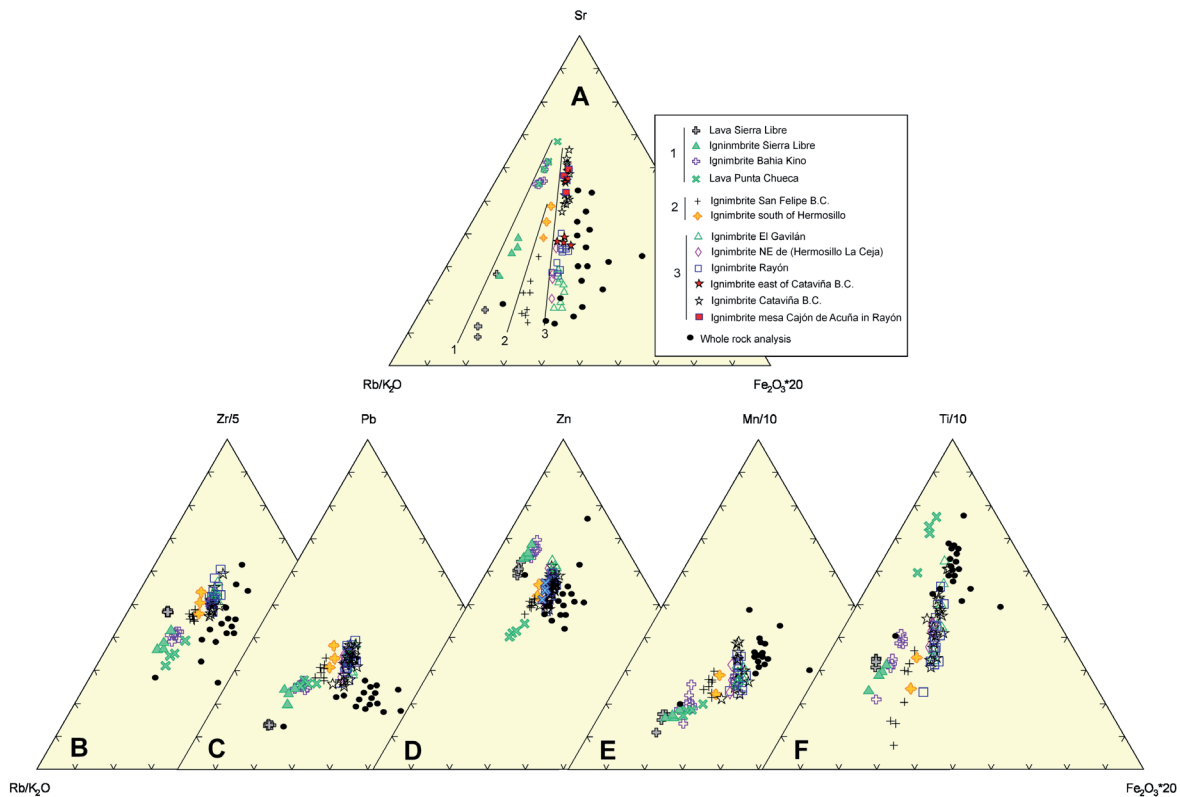


Fig. 4.- Ternary diagrams used in chemical discrimination and correlation of the ignimbrite deposits studied, built with the major and trace elements that are best represented in these rocks. The combination of these elements distinguishes three chemical groups probably derived from magma differentiation processes.

Fig. 4.- Diagramas ternarios utilizados en la discriminación química y la correlación entre los depósitos ignimbríticos estudiados, construidos con los elementos mayores y traza mejor representados en estas rocas. La combinación de estos elementos permite reconocer tres grupos químicos probablemente derivados de los procesos de diferenciación de los magmas.



ized by pronounced peaks in Rb and Th, moderate peaks in Nb and Zr, and negative anomalies in Ba and Sr, due to feldspar fractionation. The rhyolitic lavas present similar patterns, but more pronounced negative anomalies and a higher degree of enrichment in Nb and Zr. The parallelism of the spectra of ignimbrites and rhyolites supports a common source for all the peralkaline samples. It is also noted that it is possible to differentiate between the concentrations of the rhyolitic ignimbrite and lava flow samples. The ratio between concentrations of elements in the peralkaline rhyolites, which is visibly different from one of the metaluminous rhyolites analyzed, imparts in these lavas a unique geochemical identity (Fig. 3A).

Concentrations of incompatible and immobile elements Nb, Zr and Th, called HFSE (High Field Strength Elements), are highly variable for the rhyolitic samples, while the points representing the ignimbrite samples plot in a limited area (Fig. 3B) illustrating a good correlation between all the studied ignimbrite outcrops.

For a better chemical discrimination we plot on ternary diagrams trace and major elements with sufficient abundance in these rocks (Fig. 4). On the Rb/K<sub>2</sub>O-Sr-Fe<sub>2</sub>O<sub>3</sub> diagram (Fig. 4A), we can discriminate 3 different trends: a) one corresponding to the ignimbrite and lavas from Sierra Libre, Bahía de Kino and Punta Chueca; b) a second trend corresponding to samples from Hermosillo and those from San Felipe in Baja California and finally, c) a third trend that brings together most of the Sonora and Baja California outcrops. Each group shows a strong variation in Sr contents, which can be attributed to different percentages of alkali feldspar fractionation. The distal ignimbritic deposits from Cataviña (Baja California) and Rayón (Sonora), which are separated by more than 500 km, plot in the same trend. Most particularly, the vitrophyre samples from Mesa Cajón de Acuña in Rayón (Sonora) fall in the same group (with higher Sr content) as the Cataviña samples (Olguin-Villa, 2010; Olguin-Villa et al., 2010, Gomez-Valencia and Vidal-Solano, 2010; Olguin-Villa et al., 2013).

## 6. Discussion

### 6.1. Reliability of the approach

Several factors can influence the reproducibility of the chemical signature of the studied samples: a) the percentage of glass and phenocrysts, b) the presence of xenocrysts and, c) the presence of xenoliths or lithic clasts. Xenoliths can be easily detected because a petrographic study is conducted at the same time on the analyzed samples. Some porphyritic samples can contain phenocrysts that come from a different liquid; these xenocrysts are not

in equilibrium with the peralkaline liquid and therefore introduce discrepancies in the data. This factor is however negligible as all the vitreous samples studied in this work have more than 85% glass.

The greatest difference in composition was observed in rock slabs of Cataviña pyroclastic outcrops in Baja California (Table 1 and 2, group 3 in Fig. 4A), where the same ignimbrite unit shows variations in xenocryst contents ranging from 5 to 15%. These crystals such as plagioclase, biotite, hornblende and orthopyroxene are easily identified as phenocrysts because they do not correspond to the mineral phase association observed in peralkaline magmatism. In accord with previous analysis, results obtained by this approach on obsidians at the base of some peralkaline rhyolitic lava flows show also low Sr values that can be related to different percentages of alkali feldspar fractionation. Excellent geochemical correlations as well as characterization of major and trace element variations in the peralkaline pyroclastic deposits were obtained by analyzing flat surfaces of rock slabs, giving evidence of the reliability of this approach.

### 6.2. Regional implications

The variations of the concentrations in Zr, Pb, Zn, Mn and Ti (Figs. 4B, C, D, E and F) established that ignimbrite samples range from low values (except for Zn which has a reverse behavior) in thicker deposits such as those of Sierra Libre or Kino Bay, up to higher values in the distal deposits of reduced thickness that correspond to the boundary of the ignimbrite exposures, such as those of the Rayón and Cataviña areas (Fig. 1). During a sustained large-volume eruption, successive asymmetric lobes of an ignimbrite may develop in different locations (Branney and Kokelaar, 2002). Sequentially developed regional lobes may be difficult to distinguish within an extensive ignimbrite sheet, but can be revealed by detailed fieldwork coupled with petrographic analysis in cases where the composition of the eruption or included lithic clasts changed with time (e.g. Bishop Tuff; Wilson & Hildreth 1997). Such a distribution of the thickness and chemical variations suggest that all of these peralkaline pyroclastic flow deposits in NW Mexico are directly associated and related to a unique and large event (mega-eruption). Oskin (2002) and Oskin and Stock (2003) proposed that the vent area of the Tuff of San Felipe was located at Punta Chueca, north of Kino Bay, because of the unusual characteristics of the base of the deposit. In that location the ignimbrite does not have a defined base, with a vitrophyre, but rather appears to continue downward into fluidal rhyolites, suggesting that the ignimbrite corresponds to an intracaldera facies rather than an outflow



sheet. Although the ignimbrite does have a basal vitrophyre in one part of the Sierra Libre, we consider Sierra Libre as a more appropriate vent location, because great volumes of peralkaline rhyolite lavas have been found there in clear stratigraphic relationship with peralkaline ignimbrites (Barrera-Guerrero and Vidal-Solano, 2010; Barrera-Guerrero, 2012). The chemical variations and the geographic distribution of ignimbrite deposits may suggest that they are related to a zoned magma reservoir. The detailed relationships of the lavas with the ignimbrite at Punta Chueca and at Sierra Libre, and the interpretation of the basal relationships of the ignimbrite in the vicinity of these two locations, remain to be determined. Nevertheless, we propose that both of these regions were originally adjacent and part of the same vent system or at least the same volcanic field. Our proposal is based on stratigraphic and geochemical correlation of the peralkaline units in the volcanic sequence of both regions.

An excellent correlation is observed for group 1 ignimbrites (Fig. 4) that comprise the Sierra Libre and Kino Bay outcrops, which are separated by more than 100 km. Recently, Bennett (2009) has proposed the existence of a rapid Late Miocene west-northwest-directed transtensional displacement across the Kino Bay area, which could represent some of the Pacific-North America (PAC-NAM) plate boundary deformation. However, this dextral shear zone localized within the Kino Bay area is not sufficient to successfully accommodate the ~150 km missing after the paleo-tectonic restoration of the post-6.1 Ma PAC-NAM plate boundary position (Oskin *et al.*, 2001). On the basis of the chemical correlations, and our existing understanding of the basal characteristics of the ignimbrite, we propose the existence of dextral faults between Kino Bay and Sierra Libre, which may have displaced crustal blocks during a period of strong tectonic activity (12-6 Ma) related to a proto-Gulf transtensional episode (Fig. 1). The outcrop distribution of the Sonora samples suggests a displacement of at least 100 km that affected the ignimbrites of coastal Sonora, during a Late Miocene transtensional event prior to the opening of the Gulf of California. This major structure would now be buried by the large amount of sediment that has been deposited in recent deltas on the Sonora coast.

## 7. Conclusions

The combination of analytical methods applied in this work lead to several main conclusions [i] WD-XRF and ED-XRF analyses of surfaces of rock slabs are an excellent complement to the petrological characterization of vitreous samples, particularly those from pyroclastic density current deposits in which the lithic influence on

whole rock analysis cannot be ignored. [ii] This kind of analysis allows us to determine the peralkaline character of the Middle Miocene anorogenic rhyolites (ignimbrites and lava flows) and to discriminate them from the meta-luminous rhyolites. [iii] By applying this method to the regional ignimbrites, we are able to correlate localities separated by hundreds of kilometers, supporting the hypothesis that all the studied ignimbrite vitrophyres stem from a unique mega-eruption. [iv] Our regional correlations suggest displacement (up to more than 100 Km) between some of the thickest ignimbrite deposits, which we attribute to now-buried dextral faults related to the proto-Gulf of California opening during Middle-Late Miocene time.

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