

Volatile elements in alkaline and calc-alkaline rocks from the Colima graben, Mexico: Constrains on their genesis and evolution

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RESUMEN

Tomando esencialmente como base la composición química de los elementos mayores, tres diferentes grupos de rocas fueron reconocidos en el graben de Colima: El grupo alcalino, calcialcalino y calcialcalino rico en potasio. Dichos grupos fueron originados a partir de diferentes magmas primitivos. El primero de ellos está compuesto por traquibasaltos y de todas las muestras estudiadas, es el que cuenta con las más altas concentraciones en elementos compatibles, elementos incompatibles, potasio y fluor. De los tres grupos, el grupo calcialcalino representado por andesitas y dacitas es el que tiene el más amplio rango en composición debido probablemente a procesos evolutivos de baja presión. El último grupo reconocido (calcialcalino rico en potasio) está formado por andesitas y dacitas ricas en potasio y yace entre los grupos alcalino y calcialcalino. En los grupos calcialcalino y calcialcalino rico en potasio no se encontraron rocas primitivas. Los elementos hidromagmatófilos tienen patrones similares en todas las muestras estudiadas con valores altos de LILE/HFSE. El análisis de los elementos volátiles (F, Cl, S, y C) muestra que C y S se encuentran en bajas concentraciones en las rocas básicas de los tres grupos y no presentan tendencias evolutivas significativas; Cl y F son inicialmente bajos en las rocas básicas de los grupos calcialcalino y calcialcalino rico en potasio y tienden a incrementarse con el grado de evolución. Sin embargo, debido a exsolución en la cámara magmática a poca profundidad algunas muestras perdieron estos dos halógenos. Es importante hacer notar que las rocas alcalinas tienen concentraciones iniciales de F y K₂O muy superiores a las encontradas en las rocas primitivas de los otros dos grupos. Puede asumirse que un manto rico en micas probablemente flogopita, afectado por diferentes grados de fusión parcial, dio origen a los diferentes grupos de rocas encontrados en el área de Colima. Sin embargo esta es sólo una hipótesis de trabajo. Para poder entender los diferentes procesos evolutivos que dieron lugar a las rocas estudiadas, un mayor número de estudios mineralógicos, petrológicos y geoquímicos necesitan ser realizados.

PALABRAS CLAVE: Elementos volátiles, fluor, Colima graben, México.

ABSTRACT

Based on major element chemical composition, three groups of rocks having different parental magmas can be recognized in the Colima graben region. The most mafic rocks belong to the alkaline group, which display the highest incompatible and compatible element contents among the rocks studied. The second group, the calc-alkaline volcanics have the largest compositional range among the rocks studied due probably to low pressure evolutionary processes. A third group straddles the subalkaline-alkaline field boundary, and has K₂O abundances intermediate between alkaline and calc-alkaline volcanics. Primitive rocks were neither found in calc-alkaline nor in high potassium calc-alkaline rocks. All the rocks studied have similar hydromagmaphile patterns with high LILE/HFSE values. Halogens (F and Cl), S and C analyses have been performed on the majority of the samples from the three groups of rocks of the Colima region. All the most primitive rocks of the three groups are characterized by comparable low abundances of C and S. Cl is initially relatively low, but tends to increase with the degree of evolution. On the contrary, the most primitive rocks of the three groups have distinctly different F contents. Alkaline rocks have the highest values and calc-alkaline the lowest F contents. Fluorine, as well as chlorine, tends to increase with the degree of evolution in calc-alkaline and high potassium calc-alkaline rocks, although some samples seem to have lost halogens by exsolution in a shallow level magmatic reservoir. The fluorine and potassium abundances seem to indicate phlogopite as one of the mineral phases in the Colima sub-arc mantle. A mica-bearing mantle source affected by different degrees of partial melting can be hypothesized for the genesis of alkaline and calc-alkaline parental magma. Nevertheless, this has to be still considered as a working hypothesis, and further mineralogical, geochemical and petrological studies must be performed to better constrain the role of evolution in the genesis of studied rocks.

KEY WORDS: Volatile elements, fluorine, Colima graben, Mexico.

INTRODUCTION

The time-space relationships between calc-alkaline and alkaline volcanism in the Colima graben region, western Mexico, has been the topic of several magmatological investigations. Calc-alkaline magmatism is believed to be related to subduction of the Cocos and Rivera plates beneath Mexico, whereas rifting processes were responsible for the coeval alkaline magmatism (Luhr *et*

al., 1989). Presently a large set of geochemical and petrological data are available on these rocks (e.g. Luhr and Carmichael, 1980, 1981, 1982; Luhr *et al.*, 1985; Allan and Carmichael, 1984; Luhr and Carmichael, 1992).

Although the role played by volatile elements is important and especially halogens, in the genesis and evolution of magmas, no data on these elements have been reported on the products of both calc-alkaline and alka-

line magmatism in the Colima region. Recent studies indicate the importance of volatiles such as F, C, H, etc. in the control of partial melting and in the polymerization of silicate liquids (Kogarko, 1974; Holloway, 1981; Manning, 1981; Foley *et al.*, 1986a, b). Thus, the distribution of volatile elements is paramount in the knowledge of how magma generated, and their evolution after segregation from their source.

In order to fill this gap, analyses of F, Cl, C and S on a large set of samples from the Colima region have been performed. The data presented here are discussed together with major and trace element geochemistry with the aim of understanding the role of volatiles in the genesis and evolution of the rocks.

REGIONAL TECTONIC SETTING AND VOLCANOLOGICAL BACKGROUND

The Trans-Mexican Volcanic Belt (TMVB) is a calc-alkaline continental arc that runs across the central part of Mexico. The TMVB is broadly accepted to be the result of the Cocos and Rivera plates subduction beneath the North American plate; moreover, there exist other theories that proposed the TMVB to represent a crustal fracture. These theories were broadly discussed by Verma (1984, 1987). The Central America Volcanic Arc (CAVA) formed by the subduction of the Cocos plate beneath the Caribbean plate and North American plate in Central America forms a volcanic trench-gap narrow and almost parallel to the Middle American Trench (MAT). Beyond the Guatemalan-Mexican border the volcanic arc (TMVB) becomes discontinuous and far from the trench forms an angle of 15 to 20° respects MAT (Thorpe, 1977; Moorbatte *et al.*, 1978). In fact, the TMVB is just 80 to 200 km away from the trench in the Colima region and 350 to 400 km away from the trench at its eastern end (Robin, 1982). These volcanic arc-trench distances are directly associated to the Benioff Zone angles beneath Mexico. The Benioff Zone in the vicinity of the Colima volcano is about 30°, as little as 20° beneath Toluca in central Mexico and San Andrés Tuxtla (Nixon, 1982), and about 30° beneath El Chichón volcano (Stoiber and Carr, 1973).

The western TMVB is characterized by the superposition of two tectonic regimes, the subduction of the Rivera plate beneath Mexico and the rifting process taking place at the Colima graben site. This complex tectonic environment has generated alkaline and calc-alkaline coeval volcanism the last 4.6 m.y. in the Colima graben area (Allan, 1986), and the last 3 m.y., outside the Colima graben but within the Jalisco Block (Wallace and Carmichael, 1989; Lange and Carmichael, 1991).

The western TMVB is formed by three regional structures: the Colima graben, the Chapala graben and the Zacoalco right-lateral fault zone. They intersect about 50 km south-southwest of Guadalajara city and are disposed at counterclockwise angles of 100°, 115°, and 145° from the Colima graben (Luhr *et al.*, 1985).

More recently a lamprophyric volcanic belt located about 40 to 50 km trenchward from the TMVB has been described near the towns of Mascota, Los Volcanes and San Sebastian (Lange and Carmichael, 1991). These authors suggest that the potassic lavas emplaced in the Jalisco Block are the direct consequence of extension in the Tepic-Zacoalco and Colima rifts (Figure 1).

Volcanism is represented in the Zacoalco graben by six composite volcanoes with products having calc-alkaline affinity besides two small cinder cones characterized by alkaline products (Nelson and Carmichael, 1984; Luhr *et al.*, 1985). According to Delgado (1991), volcanism in the Chapala graben has only been of calc-alkaline affinity.

The Colima graben is the southern arm of the Colima-Zacoalco-Chapala triple junction system. It is bordered by N-S normal faults running from the junction with the Chapala and Zacoalco grabens, at north, to the Pacific Ocean coast, on the south. It is almost 130 km long, and it can be divided in two parts by the Mazamitla normal fault, which has a NE-SW direction and is characterized by hot thermal water springs (Garduño and Tibaldi, 1990).

In the Colima graben both calc-alkaline and alkaline volcanics were coevally produced. The first calc-alkaline volcanics erupted in the Colima graben region have ages of 10 m.y., and they were emitted by small centers located along the N-S faults that border the graben. Only in the last million years has the magmatism concentrated in the central part of the graben built up three large stratovolcanoes: the Volcan de Fuego, Nevado de Colima and the Cantaro Complex volcanoes. The Volcan de Fuego is the youngest volcano among the three large volcanoes in the Colima region and the most active volcano in Mexico. All alkaline volcanism is related in space and time with calc-alkaline igneous activity. The early alkaline volcanites (4.7 m.y., Allan and Carmichael, 1984) were emplaced along N-S fractures delimitating the graben, similar to the oldest calc-alkaline products. Furthermore, several recent monogenetic cinder cones (1 m.y., Luhr and Carmichael, 1981) characterized by alkaline volcanics are scattered at the base and on the flanks of the large stratovolcanoes.

ANALYTICAL PROCEDURES

Fifty samples of lava and scoria belonging to alkaline and calc-alkaline volcanic centers were collected during two field campaigns (Figure 2). Particular care was taken to collect unaltered samples. Major and volatile elements analyses were performed at the Dipartimento di Scienze della Terra in Florence. Major element abundances were determined using XRF (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, CaO, and K₂O), employing the correction procedure suggested by Franzini *et al.* (1972), AAS (CaO, MgO, Na₂O and K₂O), titration (FeO), and colorimetry (P₂O₅). Wet chemical analyses were performed after digestion of 200 mg of rock powder by pure HClO₄+HF+HCl. F and Cl were de-

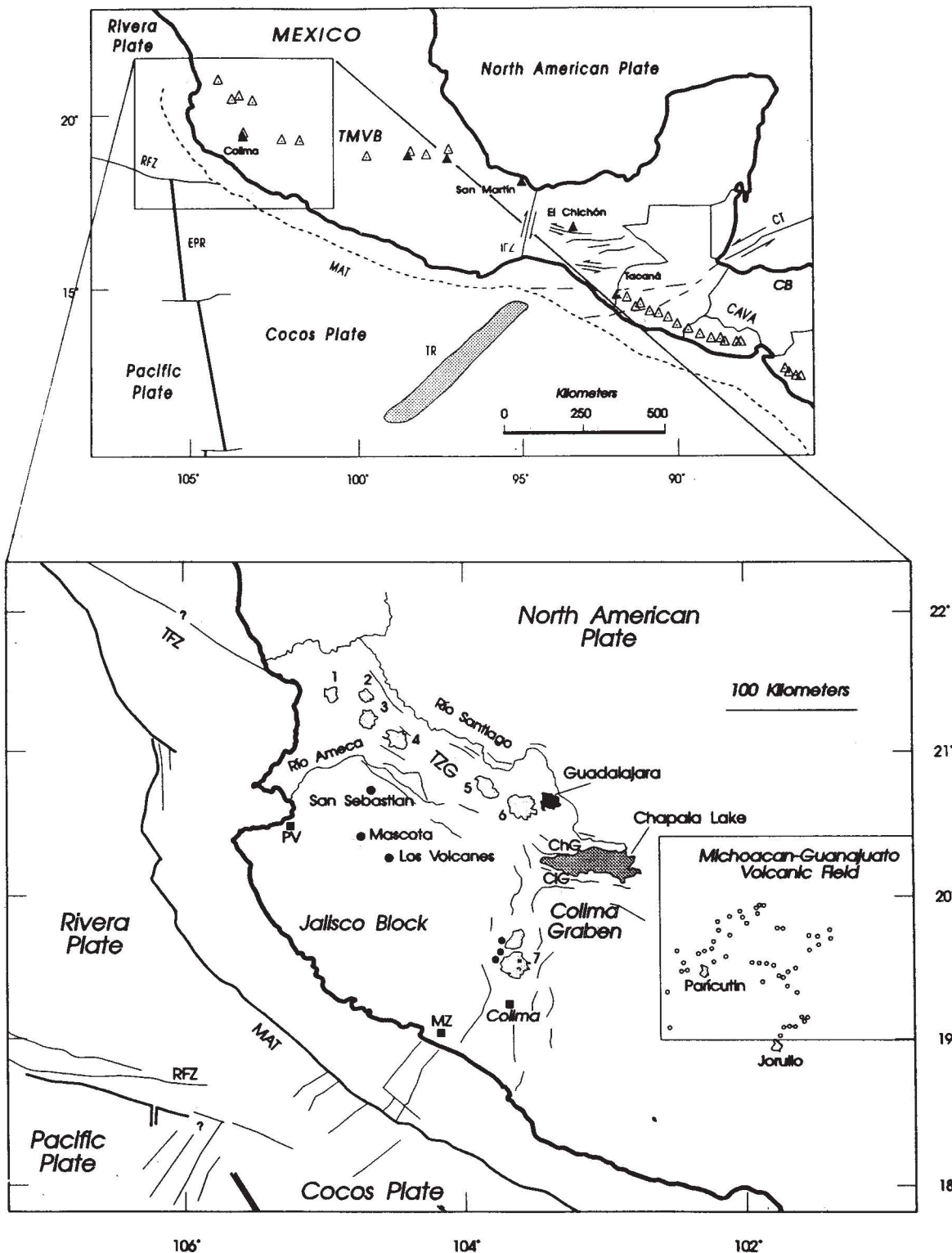


Fig. 1. Small scale map shows the Trans-Mexican Volcanic Belt, the large scale map shows the Western Trans-Mexican Volcanic Belt after Burbach *et al.*, (1984), Duffield *et al.* (1984), DeMets and Stein (1991), Lange and Carmichael (1991), Luhr *et al.* (1989) and Sheridan and Macías (1992). Solid triangles represent active volcanoes, open triangles are extinct volcanoes in Mexico and volcanoes in Central America. Shaded region indicates major bathymetric features. Andesitic volcanoes are: 1) San Juan, 2) Sanganguey, 3) Tepetitlic, 4) Ceboruco, 5) Tequila, and 7) Colima Volcanic Complex (Cantaro, Nevado de Colima and Volcan de Colima). La Primavera Caldera is numbered 6. Potassic centers related to the Jalisco Block are large solid circles. Abbreviated capital letters are: TMVB= Trans-Mexican Volcanic Belt, CAVA= Central America Volcanic Arc, CB=Caribbean Plate, EPR=Eeast Pacific Rise, CT=Cayman Trench, IFZ=Isthmus Fault Zone, TZG=Tepic-Zacoalco Rift, ChG=Chápala Graben, RFZ=Rivera Fracture Zone, MAT=Middle American Trench, TFZ=Tamayo Fracture Zone, and PV=Puerto Vallarta.

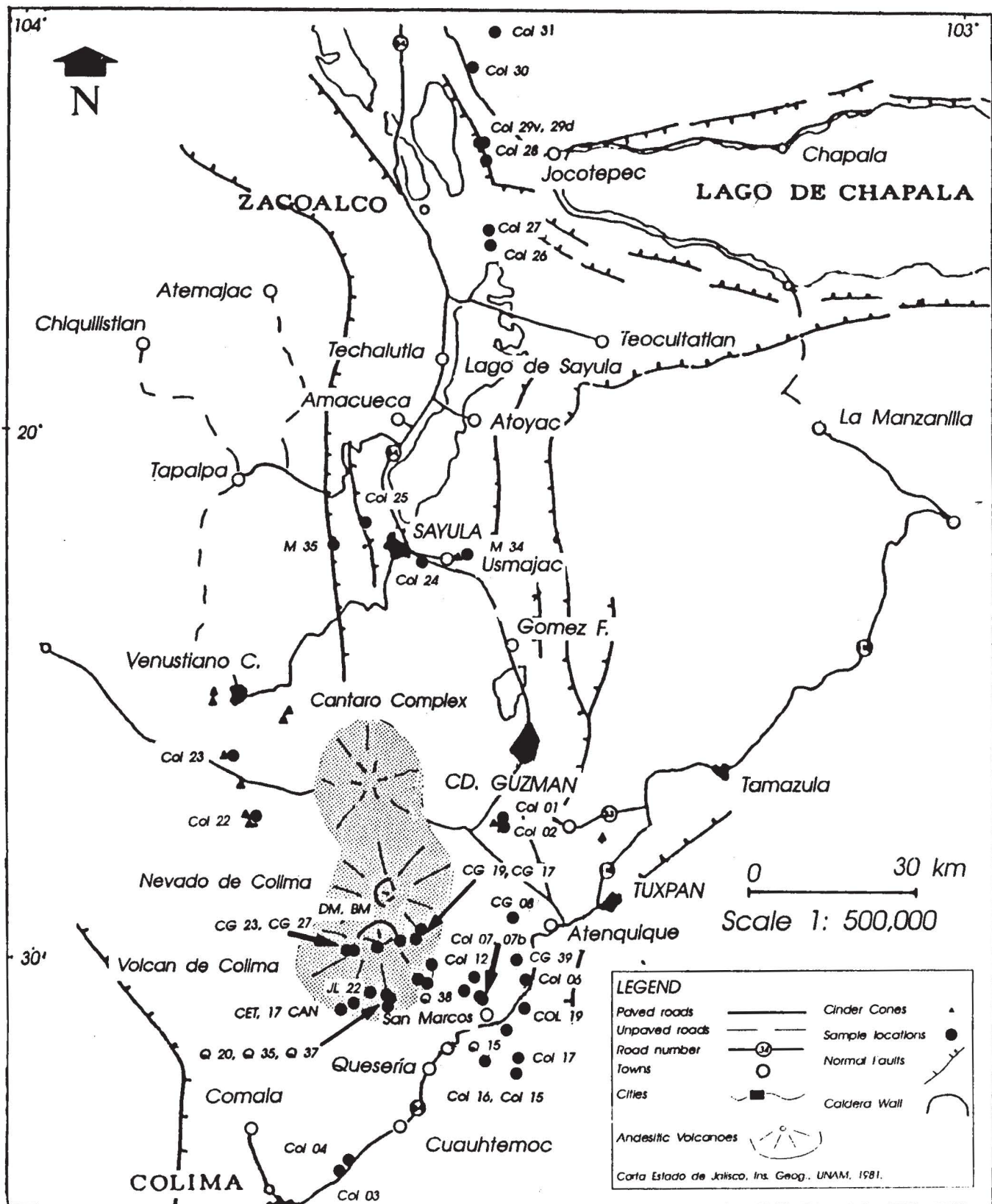


Fig. 2. Sketch map of the studied area, with sample locations. Shaded area represents the Colima Volcanic Complex (Cántaro, Nevado de Colima and Colima Volcano).

terminated using potentiometric techniques (Coradossi and Martini, 1981). S and C were measured with a "LECO CS-125" Carbon-Sulfur determinator, in which samples are ignited in a high-frequency induction furnace and successively determined in the form of SO₃ and CO₂ in an infrared cell. Trace elements were determined by XRF using the methods described by Hower (1959) and ICP at the C.N.R.S., Centre de Recherches Pétrographiques et Géochimiques, C.R.P.G.-UPRA 6821 at Vandœuvre-les-Nancy, France.

RESULTS

Some major elements, F, Cl, S and C determined on the studied samples are reported in Table 1. In Figure 3 a chemical classification diagram (TAS, Le Bas *et al.*, 1986) is shown. It is clear from Figures 3 and 4 that the studied samples can be divided in two main groups, an alkaline and a calc-alkaline set. Members of the alkaline group show a narrow range in SiO₂ (47-50 wt.%), relatively lower Al₂O₃ (12-16 wt.%) and Na₂O (2.9-3.9 wt.%), and higher TiO₂ (1.1-2.4 wt.%), MgO (7.1-12.8 wt.%), CaO (7.8-8.5 wt.%), K₂O (2.1-4.1 wt.%) and P₂O₅ (1.4-3.7 wt.%) contents than calc-alkaline volcanics as a whole (Figure 4). The lack of a primitive member that could represent a primary liquid is a general feature of calc-alkaline rocks in general and of the studied rocks in particular as remarked by Luhr *et al.* (1989). However, continuous compositional variation from basaltic andesites (BA) to dacites (D) through andesites (A) is observed in the studied calc-alkaline rocks (Figure 4). It is worth noting the slightly higher alkaline contents of some of the studied rocks compared with calc-alkaline volcanics from elsewhere (Gill, 1981). Thus a high-K calc-alkaline series (HKCA) can be recognized. Allan and Carmichael (1984) and Allan *et al.* (1988), also identified high-K andesites in the Colima region. However, our samples do not only represent high-K andesites but a wider spectrum of rocks from basaltic andesites to dacites. These HKCA rocks were originated from the Colima graben walls and from some minor older volcanic centers located N-NW from the Colima graben. The typical calc-alkaline rocks come from the three large volcanoes Volcán de Fuego, Nevado de Colima and Cántaro Complex. However, intimate mixing of alkaline and calc-alkaline rocks was observed in some tephra deposits from the Colima volcano (Luhr and Carmichael, 1982).

Trace element distribution in alkaline and calc-alkaline rocks is quite different. The most primitive alkaline volcanics (trachybasalts=TB) have much higher Cr (TB≥500 ppm; BA≤100 ppm), V (TB≥190 pp; BA≤150 ppm), Ni (TB≥300 ppm; BA≥60 ppm), Cu (TB≥100 ppm; BA≤50 ppm), Rb (TB≥50 ppm; BA≤30 ppm), Sr (TB≥1500 ppm; BA≤700 ppm), Zr (TB≥400 ppm; BA≤200 ppm), Ba (TB≥1500 ppm; BA≤650 ppm) and REE, and lower Ga (TB≥25 ppm; BA≤40 ppm), Y (TB≥20 ppm; BA≤25 ppm), Yb (TB≥1.8 ppm; BA≤2.4 ppm) and Th (TB≥10 ppm; BA≤20 ppm) than the most mafic basaltic andesites (author's unpublished data). Nevertheless trachybasalts and basaltic andesites have similar abundan-

ces of Nb (≈10 ppm) and Ta (≈1 ppm). Rare Earth Elements (REE) patterns of trachybasalts and basaltic andesites (Figure 5) display significant differences between the two groups. In contrast, the diagram of hydromagmaphile elements, normalized to the primordial mantle (Figure 6) shows that in spite of the different absolute abundances no large differences are present among the large-ion lithophile elements (LILE) and high field strength elements (HFSE) distribution in the two groups of rocks.

Trachybasalts show the highest volatile element abundances among the studied rocks (Capaccioni *et al.*, 1990). They are richer in F and S than basaltic andesites, whereas no general distribution rule is observed between the two groups for C and Cl (Figure 7). Allan and Carmichael (1984) conducted microprobe analyses in some alkaline Colima rocks, where they determined fluorine concentrations in the ground mass, apatite, and phlogopite mineral phases as the only phases containing F in the rock. We obtain F concentrations varying from 480 to 2,200 ppm in the alkaline rocks. This range of concentrations falls well within our F determinations. Fluorine enrichments have been also detected in apatite and phlogopite minerals from Los Volcanes potassic center rocks by Lange and Carmichael (1991).

Due to the narrow compositional range shown by the alkaline studied rocks, no large variation in volatile contents is observed among them. On the other hand, calc-alkaline rocks show a very large range in volatile abundances (Figure 8), and roughly correlate with SiO₂ and other incompatible elements. C has low abundances both in calc-alkaline and alkaline rocks. In contrast the HKCA group has a wide range in C contents. S has consistently low values for all the studied rocks except two samples of monogenetic cinder cones (San Isidro and Telcampana) located at the foot of Colima volcano.

BEHAVIOR OF VOLATILES DURING MAGMATIC EVOLUTION

The distribution of volatile elements in magmatic rocks is influenced either by differentiation and evolution processes or by degassing of magmas. Different volatile element compositions are related to primary basaltic magmas generated by partial melting of mantle sources (Holloway, 1981; Foley *et al.*, 1896a, b). The same may be true for magmas in equilibrium with a crustal source (Manning, 1981). Thus, different initial volatile element abundances found in the most primitive magmas of different series may be inherited directly either from their mantle source or from fractionation during the partial melting processes. Subsequent to magma genesis, the process of evolution generally would enrich the residual liquids in volatile elements (Martini and Peccerillo, 1981; Metrich, 1990). However, fractionation of volatile elements may occur during ascent to the surface or subaerial emplacement of magmas. In fact, exsolution and degassing of volatiles from the silicate melt may occur in response to the variations of physical conditions between source region and the surface. Observations directed toward magma degassing during different stages of volca-

TABLE 1

Analyses of some major (wt%), trace (ppm), and volatile (ppm) elements of selected samples from the Colima Region.

Sample	SiO ₂	TiO ₂	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Mg-V	F	S	C	Cl	K/Al	La/Nb
COL 22	47.70	1.80	7.80	3.08	3.68	1.28	75.9	1496	693	140	915	0.306	4.92
COL 02	48.80	1.79	8.46	3.07	4.03	0.91	71.2	856	25	114	1145	0.284	2.33
COL 23	48.81	1.05	7.89	3.45	2.04	0.87	79.4	800	363	78	930	0.144	n.d.
COL 01	50.11	1.78	8.13	2.94	3.62	0.87	65.9	890	18	85	1000	0.224	n.d.
CG 23	54.62	0.67	7.03	3.87	1.00	0.13	65.2	165	n.d.	n.d.	110	0.060	n.d.
M 34	55.07	1.53	7.33	3.90	1.61	0.34	54.4	251	n.d.	n.d.	80	0.097	n.d.
COL 27	52.22	1.33	7.18	3.85	1.52	0.30	52.4	318	24	206	1000	0.087	2.25
COL 31	55.82	1.30	7.14	4.15	1.66	0.26	48.3	140	37	227	140	0.092	n.d.
COL 26	56.36	1.29	7.21	3.88	1.65	0.39	52.1	140	67	595	160	0.101	n.d.
COL 15	57.32	1.14	5.48	4.68	1.52	0.27	54.3	402	23	619	1355	0.104	n.d.
COL 25	57.71	0.58	6.28	4.40	1.67	0.29	68.5	272	41	795	n.d.	0.100	2.25
Q 45	58.75	0.67	6.63	4.18	1.23	0.14	61.6	145	n.d.	n.d.	90	0.068	n.d.
COL 06	58.94	0.66	6.28	4.53	1.36	0.16	60.2	100	18	65	950	0.074	n.d.
CG 27	59.05	0.66	6.67	4.34	1.21	0.13	58.8	160	n.d.	n.d.	120	0.068	n.d.
DM	59.05	0.64	6.70	4.32	1.24	0.15	58.7	475	n.d.	n.d.	1436	0.069	n.d.
CR	59.11	0.62	6.74	4.18	1.27	0.15	58.7	90	n.d.	n.d.	85	0.070	n.d.
CG 28	59.27	0.72	6.33	4.55	1.19	0.16	52.7	260	n.d.	n.d.	80	0.066	n.d.
Q 34	59.46	0.74	6.36	4.51	1.55	0.26	51.4	528	n.d.	n.d.	1159	0.085	n.d.
COL 03	59.68	0.55	5.82	4.52	1.32	0.11	64.3	176	n.d.	n.d.	1070	0.075	n.d.
COL 17	59.90	0.65	6.14	4.32	1.50	0.16	57.2	354	14	67	1230	0.083	n.d.
Q 38	60.07	0.66	6.46	4.49	1.38	0.15	54.6	633	n.d.	n.d.	1228	0.073	n.d.
Q 37	60.54	0.67	6.33	4.58	1.46	0.18	51.1	105	n.d.	n.d.	150	0.078	n.d.
COL 16	60.62	0.62	5.99	4.43	1.56	0.17	56.1	406	14	150	950	0.088	6.33
CG 12	60.73	0.63	5.90	4.68	1.71	0.18	53.5	230	n.d.	n.d.	120	0.099	n.d.
CG 08	60.76	0.53	4.41	4.36	1.80	0.21	49.2	350	n.d.	n.d.	85	0.093	n.d.
M 35	60.85	0.48	4.11	3.56	1.88	0.08	55.5	125	n.d.	n.d.	110	0.113	n.d.
COL 24	60.87	0.71	5.59	4.09	1.77	0.21	70.3	374	49	305	1050	0.114	n.d.
CG 19	61.04	0.55	6.05	4.48	1.45	0.15	52.4	135	n.d.	n.d.	115	0.082	n.d.
CG 17	61.06	0.66	5.84	4.36	1.51	0.17	51.2	213	n.d.	n.d.	70	0.085	n.d.
COL 18	61.06	0.70	4.33	4.00	2.63	0.26	53.5	358	20	363	930	0.169	n.d.
Q 35	61.08	0.57	5.99	4.53	1.39	0.16	54.9	352	n.d.	n.d.	1498	0.078	n.d.
CG 04	61.14	0.68	5.83	4.51	1.67	0.19	50.9	167	n.d.	n.d.	110	0.096	n.d.
BM	61.38	0.56	5.96	4.45	1.49	0.15	56.6	170	n.d.	n.d.	175	0.082	n.d.
COL 04	61.44	0.57	5.51	4.57	1.34	0.12	63.4	78	11	173	1015	0.079	n.d.
Q 20	61.61	0.52	5.96	4.30	1.40	0.15	59.1	559	n.d.	n.d.	1043	0.079	n.d.
CG 07	61.86	0.61	5.43	4.58	1.79	0.18	49.2	151	n.d.	n.d.	100	0.102	n.d.
COL 07b	62.32	0.50	5.27	4.42	1.28	0.10	63.4	234	28	153	1215	0.080	n.d.
CG 06	62.36	0.62	5.26	4.64	1.81	0.18	48.6	72	n.d.	n.d.	110	0.106	n.d.
JL 22	62.42	0.57	5.59	4.76	1.45	0.12	52.5	594	n.d.	n.d.	1404	0.086	n.d.
COL 30	62.51	0.66	5.35	3.80	2.27	0.12	53.4	280	5	3	1180	0.138	n.d.
17 CAN	62.94	0.58	5.53	4.41	1.41	0.17	50.6	679	n.d.	n.d.	1186	0.085	n.d.
COL 07	63.18	0.44	4.83	4.57	1.93	0.18	48.4	112	53	11	1035	0.113	n.d.
COL 28	63.42	0.62	4.96	3.74	2.82	0.14	54.1	286	19	93	880	0.176	n.d.
COL 29v	63.69	0.61	4.93	3.89	2.28	0.12	53.1	330	12	192	1420	0.141	n.d.
CG 03	63.90	0.47	5.18	4.76	1.49	0.16	43.5	125	n.d.	n.d.	90	0.086	n.d.
PIC	64.05	0.63	5.15	4.45	1.59	0.15	54.9	225	n.d.	n.d.	1095	0.094	n.d.
COL 29d	64.45	0.59	4.93	3.97	2.33	0.12	53.1	270	19	118	205	0.143	n.d.
CET	65.27	0.59	4.37	4.14	2.37	0.14	60.2	826	n.d.	n.d.	1568	0.147	n.d.
COL 12	65.80	0.35	4.66	4.92	1.51	0.16	51.3	234	30	150	69	0.089	n.d.
QB 42	67.15	0.27	4.24	4.76	1.91	0.17	48.3	790	n.d.	1523	n.d.	0.114	n.d.

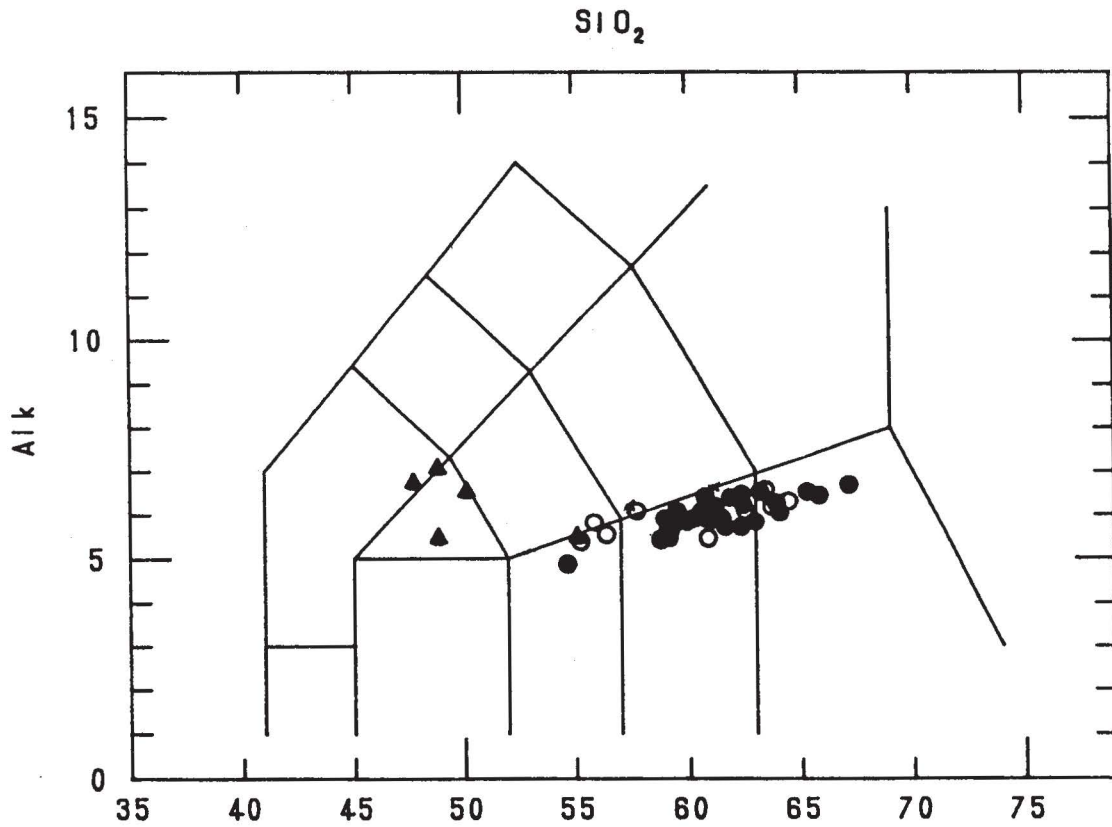


Fig. 3. Alkali-silica classification diagram (TAS, after Le Bas *et al.*, 1986). Filled triangles = alkaline rocks; Open circles = HKCA rocks; Filled circles = Calc-alkaline rocks.

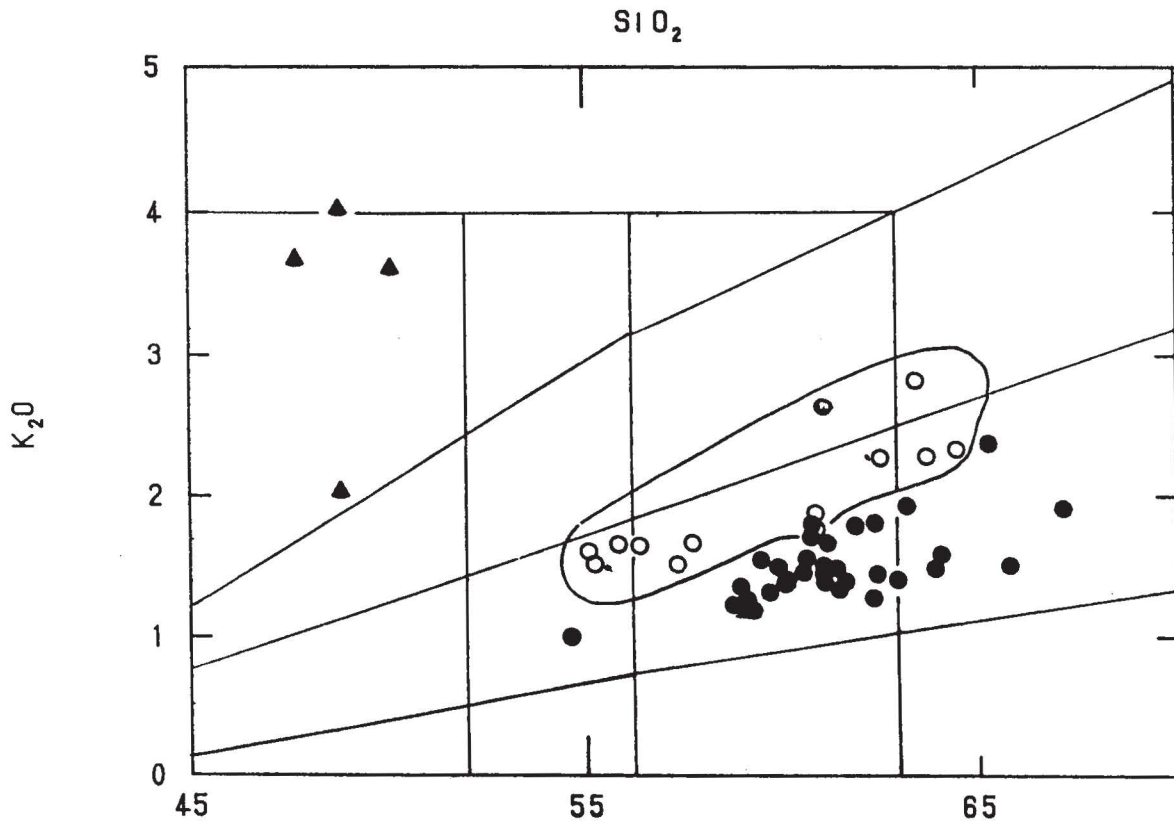


Fig. 4. K₂O-silica classification diagram (after Peccerillo and Taylor, 1976). Filled triangles = alkaline rocks; Open circles = HKCA rocks; Filled circles = Calc-alkaline rocks. The High-K Calc-alkaline rocks enclosed by an open area.

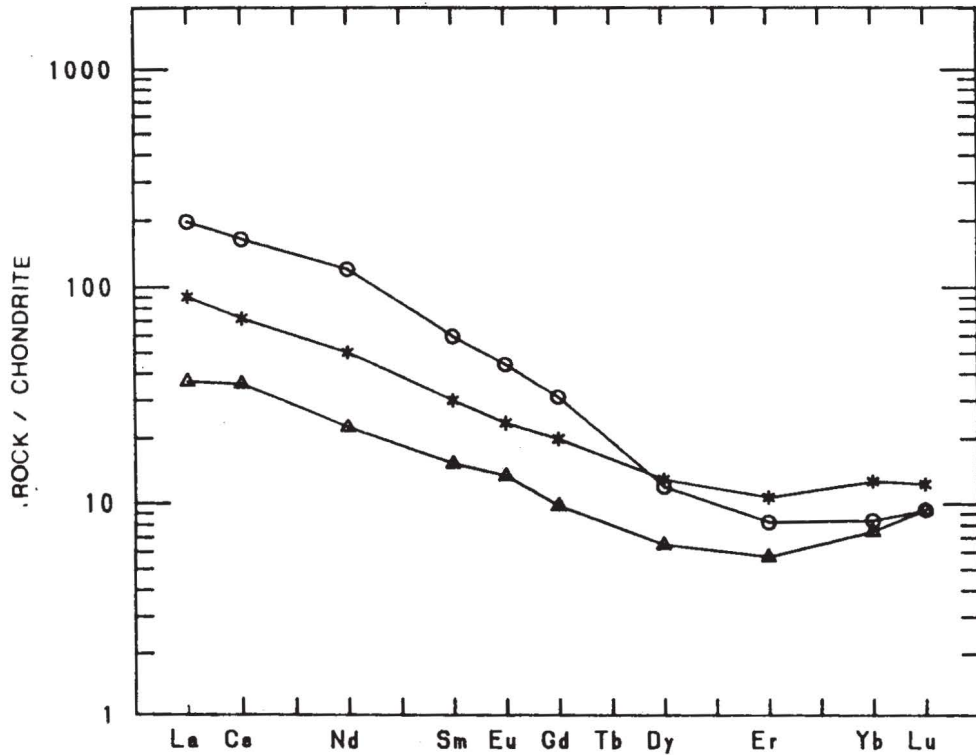


Fig. 5. Rare Earth Element chondritic patterns normalized to the values of Haskins *et al.* (1966). Circles: Alkaline rocks (Col 22); Asterisk: HKCA rocks (Col 27); Triangle: Calc-alkaline rocks (Col 25).

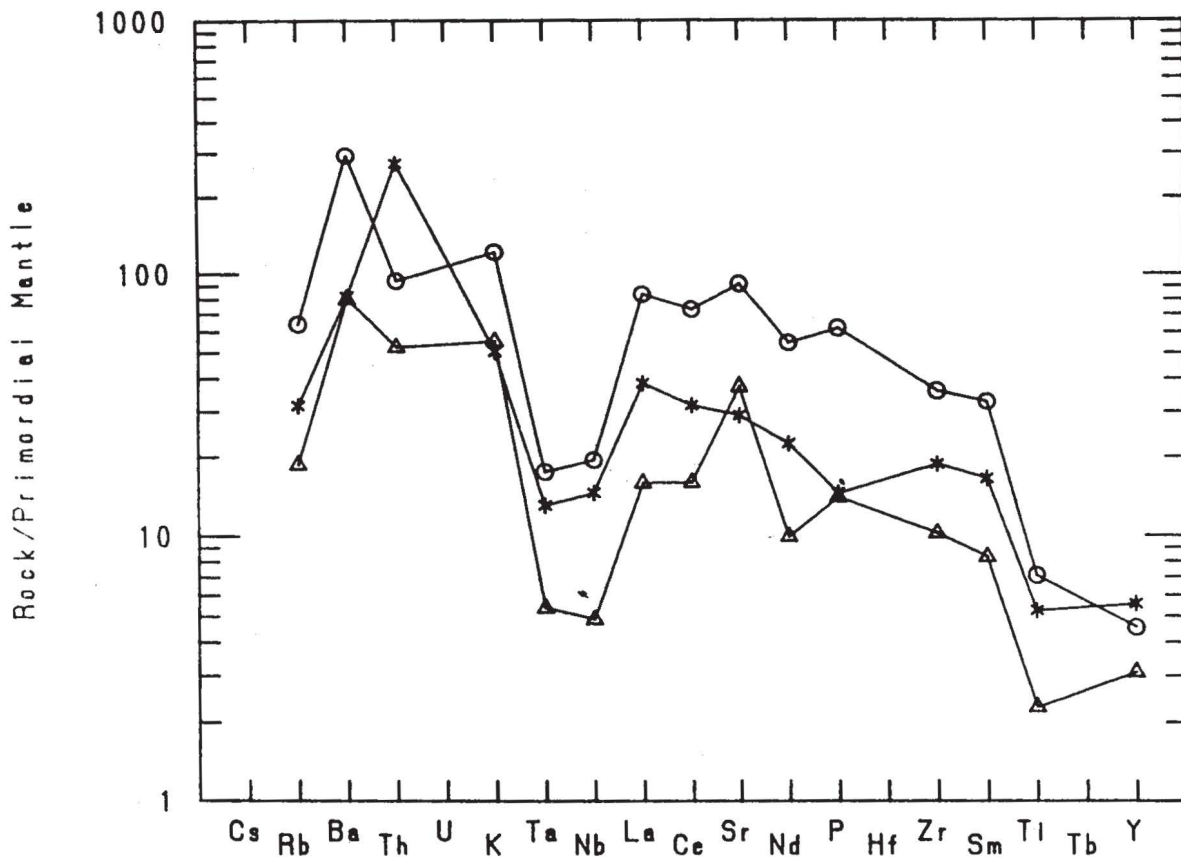


Fig. 6. Spider diagram showing hydromagmaphile elements normalized to primordial mantle (Wood, 1979). Filled triangles = alkaline rocks; Open circles = HKCA rocks; Filled circles = Calc-alkaline rocks.

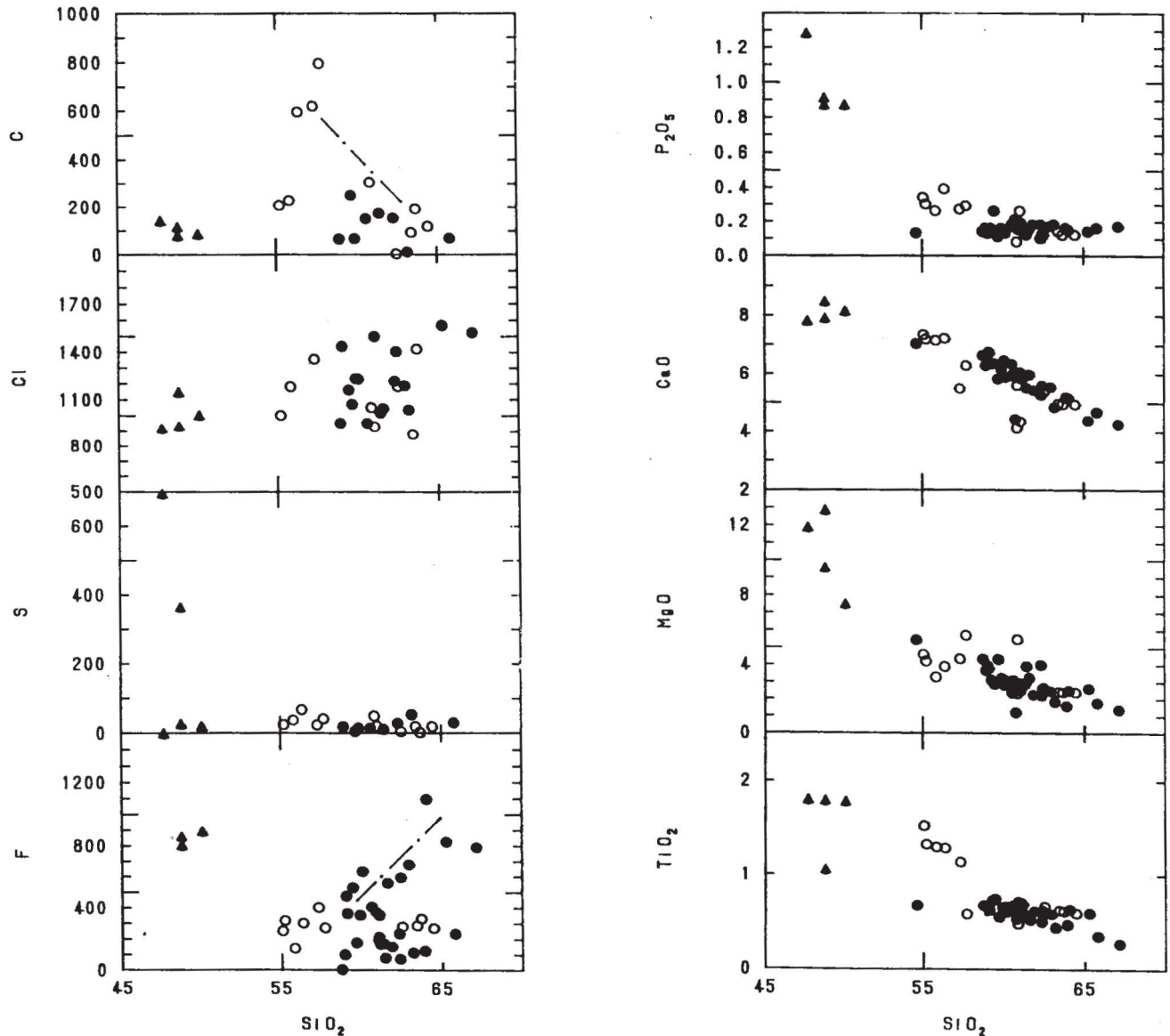


Fig. 7. Variation diagrams for some major (A) and volatile elements (B) Filled triangles = Alkaline rocks; Open circles = HKCA rocks; Filled circles = Calc-alkaline rocks.

nic activity, together with experimental results on solubilities of volatiles in silicate melts, suggest that volatile elements have different solubilities, increasing from C to F as follows: $CO_2 < SO_2-SO_3 < HCl < HF$ (Iwasaki and Katsura, 1967; Stoiber and Rose, 1971; Kilinc and Burnham, 1972; Menyailov, 1975). Nevertheless, large loss of chlorine by degassing may occur only during the final stage of differentiation; while fluorine degassing is negligible (Anderson, 1974; Schilling *et al.*, 1980; Metrich, 1990). The same cannot be true for C and S.

In the light of the above discussion, fluorine and chlorine variations observed in the studied rocks may be a general effect of magmatic processes. Therefore, it may be noteworthy to point out the different initial contents in the primary melts in volatile elements of the different

groups studied. Alkaline rocks have the highest values whereas calc-alkaline rocks have the lowest abundances in halogens among the three groups of rocks recognized. Furthermore, a twofold increase was observed with evolution. The general correlation of F with SiO_2 for the HKCA is the same for most of the evolved calc-alkaline volcanics (field 1 in Figure 9); it may be due to a passive enrichment in F contents due to its strong residual character. Enrichment in fluorine and chlorine during magmatic low pressure evolution has also been found in other calc-alkaline and alkaline suites (e.g. South Italy: Martini and Peccerillo, 1981; Metrich, 1990). In contrast a second group of calc-alkaline rocks seems to be depleted in F and Cl at high SiO_2 contents (Figure 5 and field 2 in Figure 9c). This may be explained by either degassing or crystallization and separation from the magma of a F- and Cl-rich mineral. F-rich apatite has been claimed as

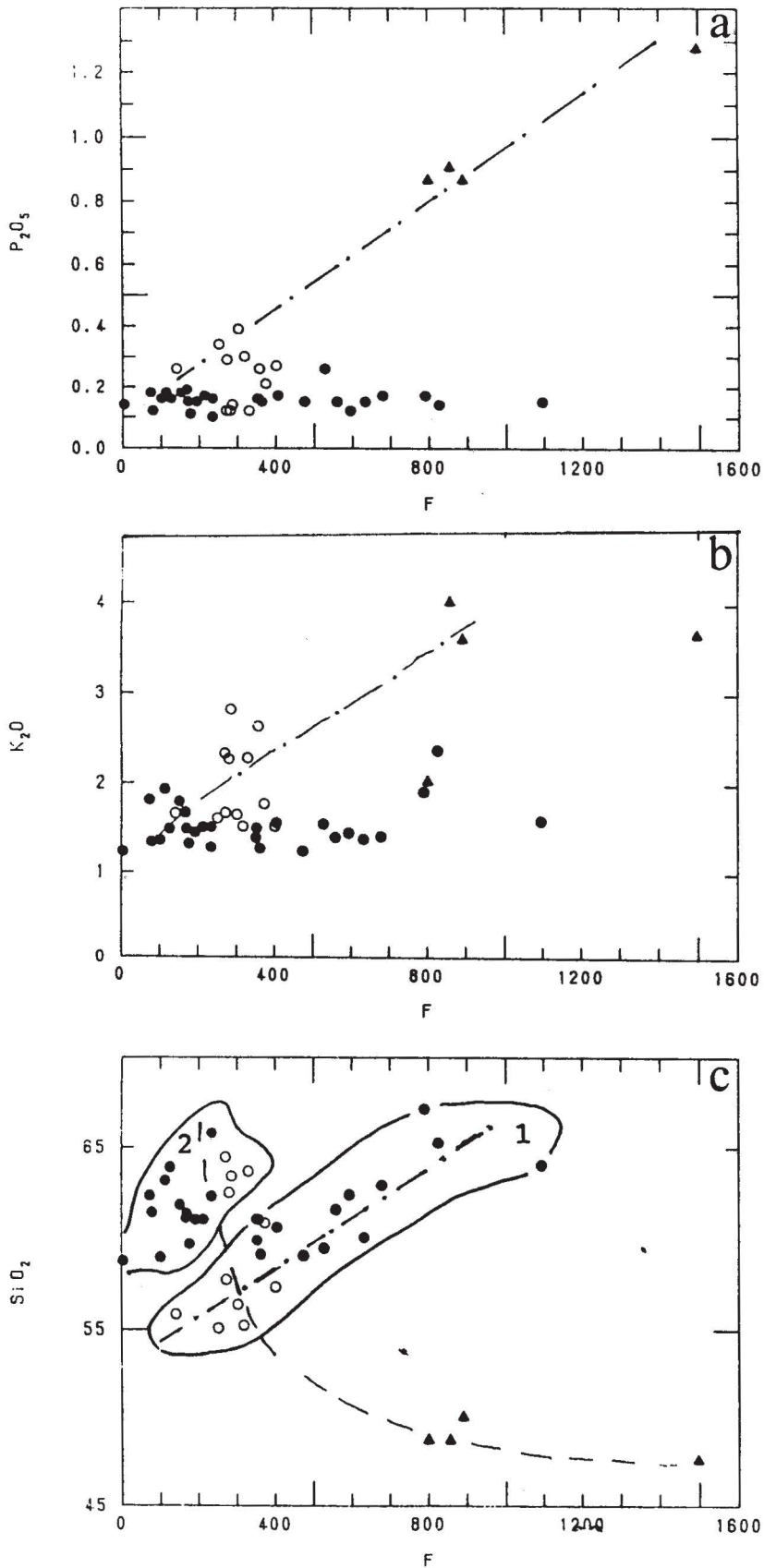


Fig. 8. SiO_2 , P_2O_5 and K_2O vs. fluorine in the Colima rocks. Filled triangles = alkaline rocks; Open circles = HKCA rocks; Filled circles = Calc-alkaline rocks. Fields 1 and 2 in Figure 8c are rocks with diverse degrees of fluorine enrichment (see text).

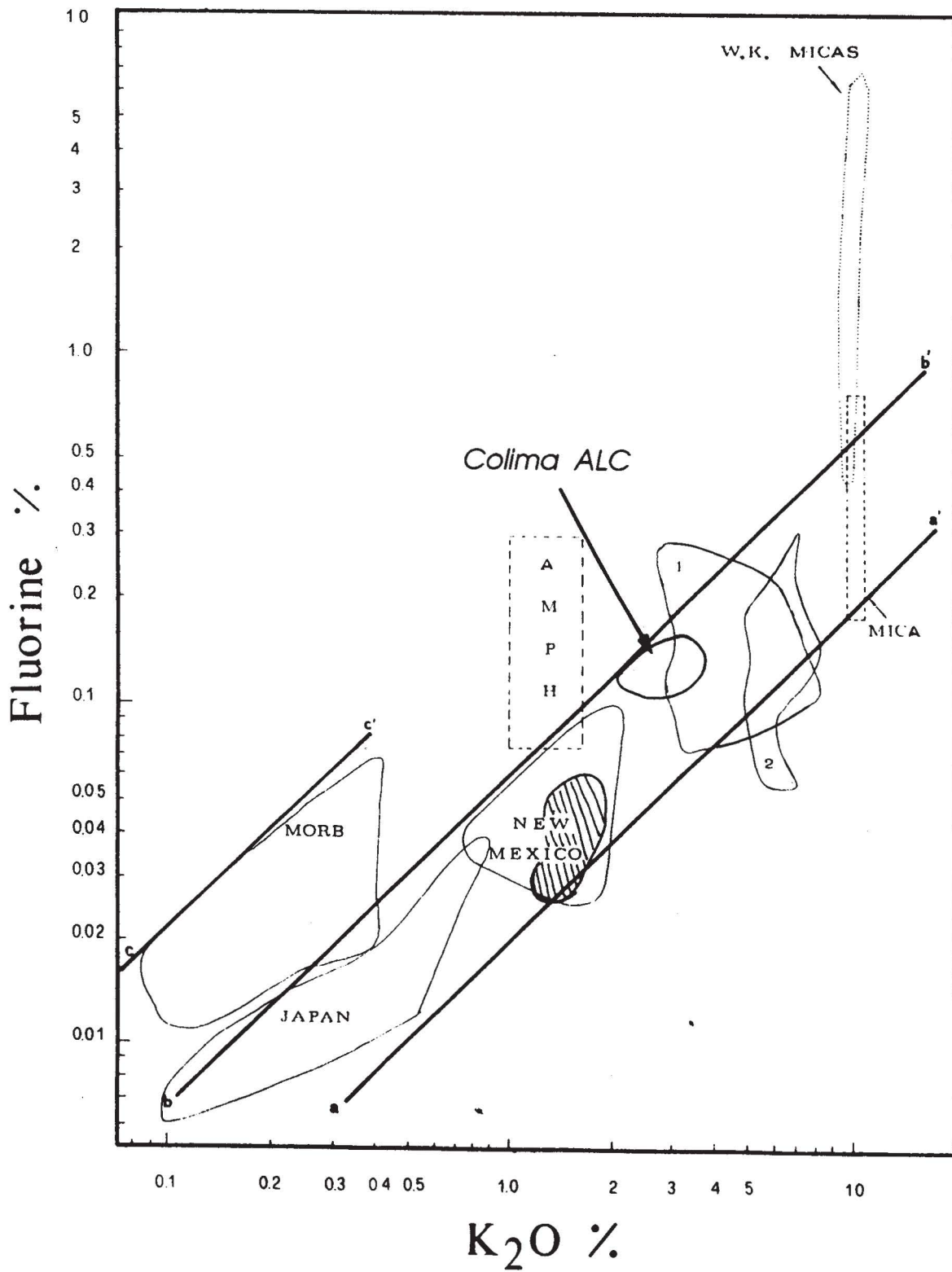


Fig. 9. Logarithmic plot of fluorine vs. K₂O comparing worldwide basalt, mica and amphibole compositions (after Foley, 1989). Dashed area represent the field of calc-alkaline and HKCA rocks from Colima region. "Colima ALC" is the field of alkaline members. Areas numbered 1 and 2 are rocks from the African Rift and ultrapotassic rocks from Italy respectively.

an important magmatic phase able to fractionate halogens in magmatic systems (Metrich, 1990). However, a poor correlation is observed between F and P_2O_5 for the studied rocks (Figure 9a). Phlogopite may be an alternative phase for halogens fractionation in magmatic systems (e.g. Capaccioni and Martini, 1986; Foley, 1989, 1990). According, micas from pumice of Vesuvius (Italy) have F and Cl abundances of 2670 and 2640 ppm respectively, with K^F solid/liquid=2.68 and K^{Cl} solid/liquid=0.60 distribution coefficients (Capaccioni and Martini, 1986). Diverse mineral phases have been proposed to constitute the sub-arc mantle in the Colima region. phlogopite (Luhr *et al.*, 1984); and apatite, phlogopite and amphibole in western Mexico (Wallace and Carmichael 1989).

The lack of correlation between K_2O and F also helps to rule out a role of mica in halogen depletion in some calc-alkaline dacites and rhyolites. Hence, strong degassing processes may be invoked.

Consistently low C and S abundances are observed in all studied rocks. This may be due to the fact that both alkaline and calc-alkaline magmas were originally poor in these elements. Possible incorporation of carbon in crystalline phases, mainly as carbonates, practically is restricted to carbonatitic and some foiditic magmas. Its solubility in silicate melt appears well controlled by alkali and alkaline-earth metal concentration (Kogarko, 1974). The behavior of sulfur during magmatic processes is at present very poorly known. Holloway (1981) suggested two main types of ionic forms when dissolved in silicate melts: as SO_4^{2-} and as $(SO_4)^{2-}$. Its incorporation in magmatic mineral phases practically is limited to some metal sulphide which rarely occurs as opaque minerals. Thus, the lack of any increase in S and C with degree of evolution may be ascribed only to exsolution and degassing from magmas in pre-eruption stages, probably in shallow level magmatic reservoirs.

THE ROLE OF VOLATILES IN THE GENESIS OF MAGMAS

In Figure 9 the studied rocks plotted in a K_2O vs. F diagram are compared with composition of basaltic rocks worldwide, and those of F-bearing mantle minerals (i.e. mica and amphibole) (Aoki *et al.*, 1981; Foley, 1989). The studied alkaline rocks plot close to the F composition of Potassic rocks from elsewhere, especially they plot close to the African Rift rocks (field 1 in Figure 9). Calc-alkaline volcanics on the other hand overlap partially the field of New Mexico rocks. The most peculiar feature is that both calc-alkaline and alkaline rocks from the Colima region plot in the array, defined by Foley (1989), of magmas in equilibrium with a phlogopite mantle source. Hence, mantle sources of both calc-alkaline and alkaline rocks from the Colima region appear to have been mineralogically similar as pointed out by Luhr *et al.* (1989). Furthermore, the distribution of hydromag-

maphile elements (Figure 7) confirms this similarity. However, the observed HFS elements negative anomalies, and the high LILE/HFSE values for both calc-alkaline and alkaline Colima volcanics are typical of worldwide calc-alkaline and alkaline magmas erupted at destructive plate boundaries, as mentioned by Wallace *et al.* (1992). Interpretation of HFS elements depletion observed in magmas from convergent plate boundaries is still a matter of debate and is beyond the scope of the present paper.

F and K_2O/Al_2O_3 correlations among the most primitive Colima region volcanics may suggest an increasing role of mica during partial melting from alkaline to calc-alkaline magma genesis (Figure 10). Moreover, no variations in the K_2O/Al_2O_3 value are observed with evolution.

CONCLUSIONS

Three diverse groups of rocks were identified in the Colima region. An alkaline suite is composed of trachy-basalts with high abundances of REE, LILE, IE, K_2O and F. The calc-alkaline suite has a wide compositional range and is represented by andesites and dacites with low-concentrations of REE, LILE, IE and F. The high-K calc-alkaline suite is composed of andesites and dacites, and has intermediate concentrations between the first two groups. The most primitive rocks of the calc-alkaline and high-K calc-alkaline suites are characterized by low fluorine and chlorine abundances; however, both elements tend to increase with the degree of evolution. Because mafic alkaline Colima rocks are enriched in fluorine and potassium, it seems probable that alkaline primary melts may be the result of a lower degree of partial melting than calc-alkaline melts under similar C-O-H conditions from a mantle bearing phlogopite in the Colima region. The latter melts were probably buffered at low X_{CO_2} by the hydrous environment of a mantle wedge typical of active subduction zones. At the present, this may be considered only as a working hypothesis because geochemical and petrological details are still missing. The relative wide spectrum of rocks in the Colima region is probably due to heterogeneity of the sub-arc mantle as claimed for other regions of the Jalisco Block, which seems to be enriched in mineral phases such as phlogopite and amphibole.

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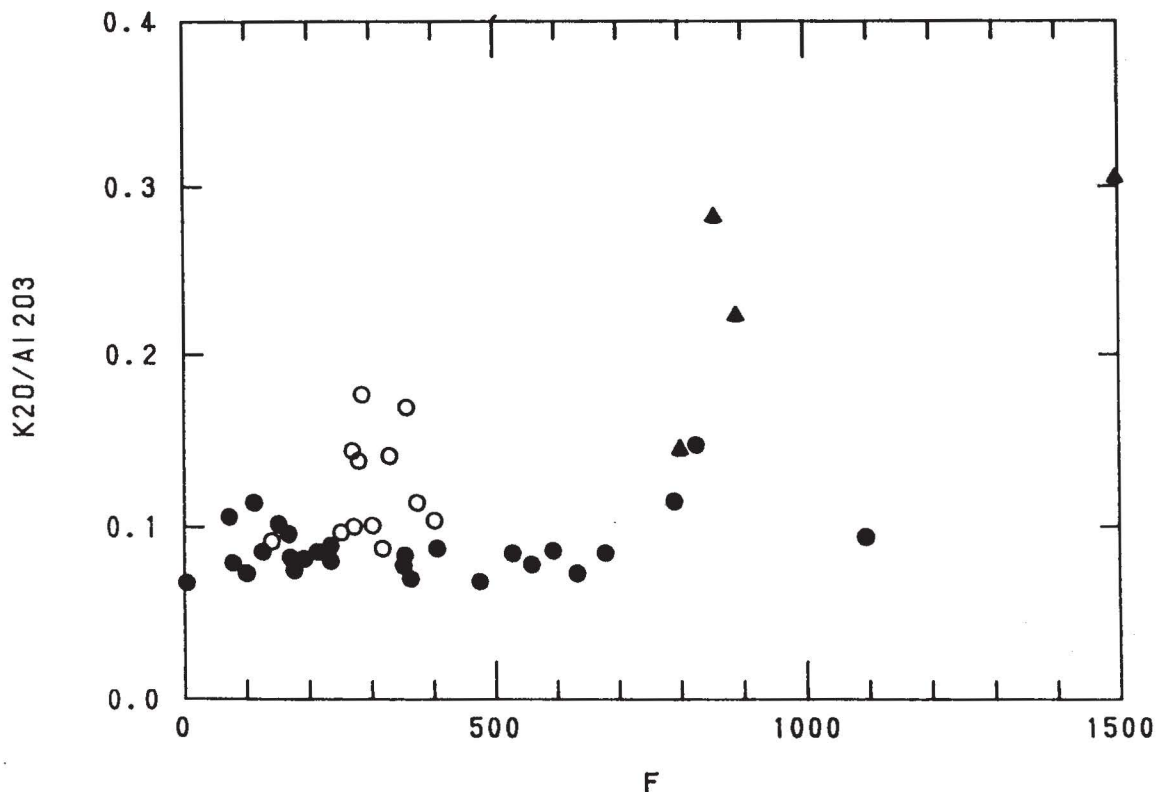


Fig. 10. K_2O/Al_2O_3 vs. fluorine diagram. Filled triangles = Alkaline rocks; Open circles = HKCA rocks; Filled circles = Calc-alkaline rocks.

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