CRUSTAL CONTAMINATION OF CARBONATITES INDICATED BY δ^{34}S-δ^{13}C CORRELATIONS (FUERTEVENTURA, CANARY ISLANDS)

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Abstract: The magmatic activity of Fuerteventura (Canary Islands) has had an extended history. Initial submarine alkaline basaltic series and simultaneous pyroxenite, gabbro and syenite intrusions were followed by later syenite-carbonatites complexes. Based on a δ^{13}C-δ^{18}O-δD study, Demény et al. (1998) have proposed a model in which the carbonatite-bearing syenite magma suffered sediment contamination during storage in shallow magma chambers. The degree of contamination shows areal variation. The syenite-carbonatite complexes contains Fe-sulfides and Ba- and Sr-sulfates as disseminated grains. A δ^{34}S study of these sulfur minerals has been undertaken to provide information on the mantle fluids on one hand, and to serve as a test of the contamination model on the other. For the least-contaminated complex (Ajui-Solapa), igneous sulfide has a δ^{34}S value of -2.5 ‰, whereas the sulfate δ^{34}S value is +4.5 ‰. The presumed most contaminated carbonatite (Esquinzo) contains only sulfate with δ^{34}S values from +10.1 to +12.4 ‰. This positive shift cannot be related to differences in T and fO$_2$, but it correlates well with the δ^{13}C data of the carbonatites. The observed δ^{13}C-δ^{34}S correlation fits well with possible carbonatite-sediment mixing model curves.

Keywords: Canary Islands, Basal Complex, carbonatite, crustal contamination, stable isotope, sulfur, carbon.

Resumen: La actividad magmática de la isla de Fuerteventura (Islas Canarias) ha sido muy dilatada. La formación volcánica submarina y las intrusiones plutónicas más antiguas formadas por piroxenitas, gabros y sienitas están atravesadas por diversos complejos sienítico-carbonatíticos. Basándose en un estudio de δ^{13}C-δ^{18}O-δD, Demény et al. (1998) han propuesto un modelo en el que el magma sienítico-carbonatítico se contaminó con sedimentos durante su almacenamiento en cámaras magmáticas someras. Esta contaminación cortical muestra una intensidad variable en cada Complejo. Sienitas y carbonatitas contienen granos diseminados de sulfuros de Fe y sulfatos de Ba y Sr. En este trabajo se ha realizado un estudio del δ^{34}S de estos minerales con el fin de obtener información sobre los fluidos de origen mantélico y para comprobar el modelo de contaminación cortical. En el Complejo sienitico-carbonatítico menos contaminado (Ajui-Solapa) los sulfuros de origen ígneo presentan un valor de ^{34}S de -2.5 ‰, mientras que los sulfatos tienen un valor de δ^{34}S de +4.5 ‰. En las carbonatitas en las que se presume un mayor grado de contaminación (Esquinzo) sólo hay sulfatos con valores de δ^{34}S que oscilan entre +10.1 y +12.4 ‰. Esta variación no puede ser explicada mediante variaciones de T y fO2 pero se relaciona bien con los valores de δ^{13}C de las carbonatitas. Las relaciones entre δ^{13}C y δ^{34}S coinciden con las curvas teóricas de mezcla calculadas entre sedimentos y carbonatita.

Palabras clave: Islas Canarias, Complejo Basal, carbonatita, contaminación cortical,isótopos estables, azufre, carbono.

Ohmoto & Rye (1979) and Ohmoto (1986) have summarised our knowledge on the fractionations of sulfur isotopes in magmatic and hydrothermal systems. Using average sulfur contents and isotope compositions of sulfur reservoirs, Ohmoto (1986) and Jambon (1994) have modelled the geochemical cycling of sulfur. However, recent debates on S characteristics of mantle-derived rocks (Ionov et al., 1992; Ionov et al., 1993; Lorand, 1993) elucidated the uncertainties of average sulfur contents and isotopic compositions of one of the most important reservoirs, the mantle. Meteorites have S isotopic compositions around 0 ‰ (Nielsen, 1978), whereas the primary mantle composition seems to be slightly more positive (0 to +2 ‰, Sakai et al., 1982; Sakai et al., 1984; Chaussidon et al., 1989; Ionov et al., 1992; Eldridge et al., 1991). Mass balance would
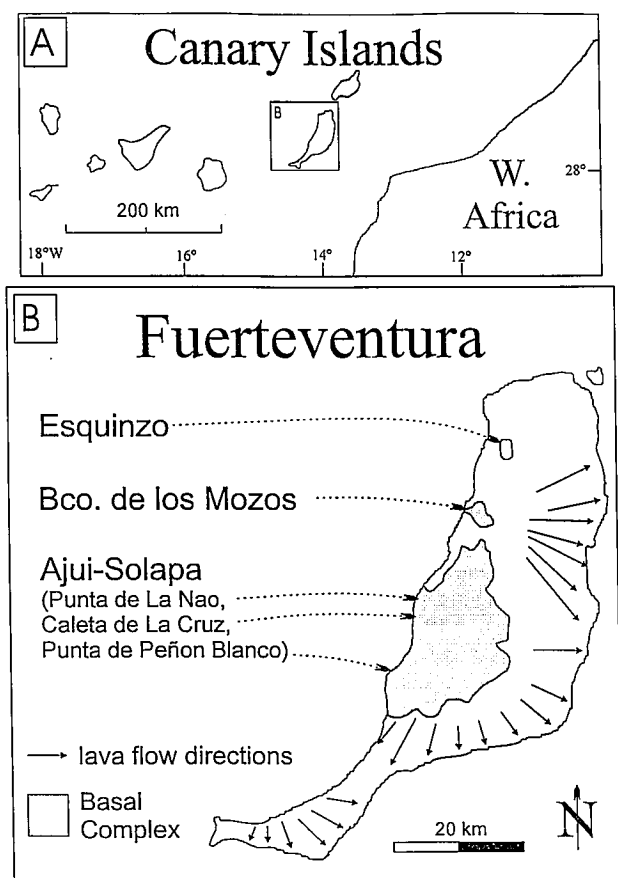
Figure 1.- A) Location of the study area. B) Sampling localities and Basal Complex exposures in Fuerteventura, Canary Islands. Directions of Miocene lava flows are from Ancochea et al. (1996).

require the existence of a reservoir with negative $\delta^{34}S$ values. Negative $\delta^{34}S$ values have been found in mantle-derived massive peridotites and xenoliths (Chaussidon & Lorand, 1990; Ionov et al., 1992) and have been interpreted by modifications after partial melting that results in preferential removal of ^{32}S into the liquid (Chaussidon et al., 1989; Ionov et al., 1992). Significantly more positive $\delta^{34}S$ values (up to +20.7 ‰) are found in arc volcanic rocks (Woodhead et al., 1987; Alt et al., 1993); these have been explained by invoking sediment recycling (Woodhead et al., 1987; Eldridge et al., 1991) and mixing of mantle-derived S and metasomatic seawater (Alt et al., 1993).

Carbonatite magma is produced during extraction of fluids from a mantle volume 1000 -10000 times the volume of the carbonatite magma (Deines, 1989); thus, it might represent an average of the respective mantle region. However, taking the low crystallization temperature of the carbonatite magma (Krafft & Keller, 1989; Dawson et al., 1990) into consideration, the $\delta^{34}S$ data of carbonatites may not only reflect mantle compositions, but perhaps also sulfur isotope fractionation at the T-fO_2-pH conditions of the related fluids (Mitchell & Krouse, 1975). The S isotope compositions of primary, high temperature carbonatites are close to the meteoritic value (0 ± 2 ‰, Grinenko et

al., 1970). The $\delta^{34}S$ data of sulfides in later stage carbonatites show a negative shift (Grinenko et al., 1970; Mäkelä & Vartiainen, 1978). The reason is that with falling temperature and rising fO_2 the sulfate/sulfide ratio increases and the $\delta^{34}S$ value of sulfate approaches the bulk sulfur isotope composition. Thus, the $\delta^{34}S$ (sulfide) value must be negative as a result of the sulfate-sulfide isotope fractionation (Ohmoto & Rye, 1979).

The carbonatites of Fuerteventura belong to the plume-related ocean island system of the Canary Islands (Hoernle & Tilton, 1991). Since carbonatites concentrate volatiles within the magmatic complex, stable isotope studies can provide essential information on primary compositions and evolution of mantle-derived fluids. In this respect, the carbonatites of Fuerteventura are especially interesting, since only two oceanic carbonatite occurrences are known so far providing insight into the volatile characteristics of oceanic island systems.

Beside the above considerations, these carbonatites are thought to have suffered variable degrees of sediment contamination (Demény et al., 1998). Thus, a $\delta^{34}S$ study of sulfides and sulfates in these rocks might not only provide information on the genetics of mantle fluids, but could also help to test the contamination model. In this paper we present S isotope data of sulfides and sulfates in carbonatites and related rocks and, on the basis of $\delta^{13}C$-$\delta^{34}S$ correlations, investigate the effect of mixing of carbonatite and crustal material.

Geological background

Two major geological units can be distinguished in Fuerteventura: the Basal Complex, and younger subaerial volcanic series of Miocene and Pliocene-Quaternary age (Fúster et al., 1968; Ancochea et al., 1996). In Fuerteventura the Basal Complex is exposed in the western part of the island (Fig. 1), and consists of a group of sedimentary materials, submarine volcanic rocks, plutonic intrusions and dike swarms generated mainly during the stage of submarine growth of the island (Fúster et al., 1968; Stillman et al., 1975; Fúster et al., 1980; Le Bas et al., 1986; Stillman, 1987).

The geological history of Fuerteventura started with deposition of Mesozoic sediments (Early-Middle Jurassic-Late Cretaceous) in a deep sea fan (Robertson & Stillman, 1979; Robertson & Bernoulli, 1982; Steiner et al., 1998). During the Late Cretaceous to Early Paleocene magmatic activity commenced with submarine alkaline basaltic lavas and simultaneous series of alkali pyroxenites, gabbros and syenites (Le Bas et al., 1986; Stillman, 1987; Balogh et al., 1999). These plutonic rocks were later intruded by carbonatite and syenite dikes of Oligocene to Lower Miocene age (Cantagrel et al., 1993; Balogh et al., 1999). The plutons of these two earlier events were intruded by gabbro-pyroxenite and gabbro-syenite bodies (Muñoz, 1969; Fúster et al., 1980; Muñoz & Sagredo, 1975;

Muñoz & Sagredo, 1989; Muñoz *et al.*, 1996). The dense basaltic dike swarm which traverses these lithologies may be considered as feeder conduits to the volcanic systems that form the submarine and subaerial complexes of Fuerteventura (Stillman, 1987).

Carbonatite dikes associated with syenites are found in outcrops at Punta del Peñon Blanco, Caleta de La Cruz, Punta de La Nao (in the so called Ajui-Solapa complex) and in relation with syenites and ijolites in the Esquinzo area (Barrera *et al.*, 1981) (Fig. 1). The emplacement of carbonatite-syenite dikes is related to extensional tectonics and shear zones resulting in ductile deformation at some localities (Punta del Peñon Blanco and Caleta de La Cruz: Casillas *et al.*, 1994; Fernández *et al.*, 1997). The carbonatites are sövites with sanidine, aegirine-augite, phlogopite/biotite, apatite, pyrochlore and magnetite. The nepheline-syenite associated with the carbonatite is mainly composed of sanidine, aegirine-augite and nepheline.

In the outcrops of Punta del Peñon Blanco and Caleta de La Cruz 20-30 cm thick pyrite-magnetite masses appear related to late stage fluid movements and skarn development in the carbonatite-syenite dikes (Fernández *et al.*, 1997; Ahijado, 1999). Sulfides formed in metasomatized pyroxenite (sample 97/40-A) and syenite (sample 97/40-B) are also regarded to belong to the skarn development. Partially resorbed pyrite grains (~0.1 mm) were found in a carbonatite dike (sample 96/35) that contains igneous biotite that has preserved primary isotopic compositions and water contents in spite of the intense deformation in the surrounding rocks. Thus, other minerals also sensitive to late-stage fluid influence, such as pyrite, might have also been preserved. Hence this pyrite is considered to be primary. Disseminated Sr-sulfate grains (0.1-0.5 mm) were found in a similar carbonatite at Caleta de La Cruz (sample 96/28). In the outcrop of Punta de La Nao sulfide is subordinate. Disseminated pyrite grains regarded as primary crystals were found in a carbonatite dike that preserved igneous textures and show no signs of deformation and alteration (sample 96/2). Other carbonatite dikes of the outcrop contain disseminated sulfate (mainly Ba-, less frequently Sr-sulfate) grains (0.01-0.1mm). In the carbonatites of Esquinzo only disseminated Ba-sulfate grains have been found. The submarine alkaline basalts studied contain disseminated pyrite grains. Adjacent basalt dikes contain carbonate xenoliths whose $\delta^{13}C$ values (-2.9 to -1.6 ‰ to PDB) indicate their likely sedimentary origin (Demény *et al.*, 1998).

Analytical methods

Carbonatite samples that contained carbonate were treated with 10 % HCl. Since most carbonatites are sövites with >95% $CaCO_3$, the insoluble concentrated sulfides and sulfates making the very low bulk sulfur content measurable. Sulfides and sulfates were oxidized at 1050°C and 1120°C, respectively, in the
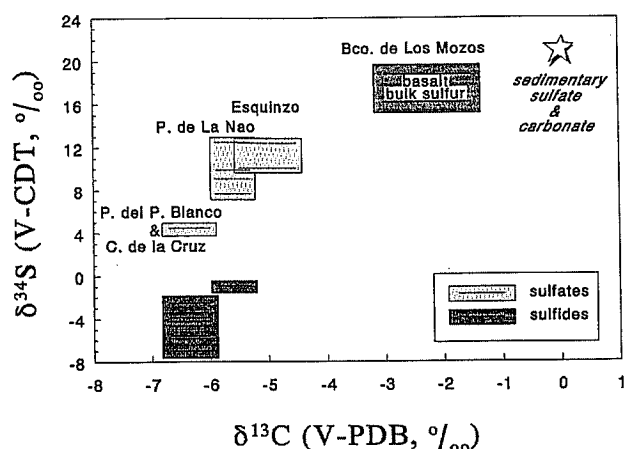

$$\delta^{13}C \ (V\text{-}PDB, \ ^\circ\!/_{\circ\circ})$$

Figure 2.- Sulfur isotope compositions of sulfides and sulfates *vs.* carbon isotope compositions of the carbonatites of Fuerteventura (Canary Islands, Spain). Horizontal lines represent measured $\delta^{34}S$ values and $\delta^{13}C$ ranges found in the respective outcrops (from Demény *et al.*, 1998). $\delta^{34}S$ data obtained on sulfides and sulfates are marked by dark and light shaded envelopes, respectively. See text for further details. Sedimentary compositions reflect recent seawater and are from Hoefs (1987).

presence of O_2 as described by Coleman & Moore (1978). The $^{34}S/^{32}S$ ratios were determined on SO_2 gas using a VG SIRA II mass spectrometer at Scottish Universities Research and Reactor Centre. Carbon isotope compositions of carbonates were determined using the conventional H_3PO_4 digestion method (McCrea, 1950). $^{13}C/^{12}C$ ratios were determined on CO_2 using a Finnigan MAT delta S mass spectrometer at the Laboratory for Geochemical Research (Hungarian Academy of Sciecnces, Budapest). Results are expressed in the δ notation as ‰ relative to V-PDB (for $\delta^{13}C$) and V-CDT ($\delta^{34}S$). Reproducibilities are better than ±0.2 ‰ for $\delta^{13}C$ and better than ±0.25 ‰ for $\delta^{34}S$.

Results and discussion

The $\delta^{34}S$ data of sulfides and sulfates and sulfur contents of whole rocks are listed in Table I. The areal distribution and the $\delta^{13}C$ ranges of the studied localities (Demény *et al.*, 1998) are shown in figure 2. Taking the frequencies of sulfides and sulfates into consideration, the bulk compositions vary significantly in the outcrops of Punta del Peñon Blanco ($\delta^{34}S_{avg}$~ -4 ‰), Punta de La Nao ($\delta^{34}S_{avg}$~ +8 ‰) and Esquinzo ($\delta^{34}S_{avg}$~ +11 ‰). The most positive $\delta^{34}S$ values are found in the submarine alkaline basalts (+16.2 and +18.8 ‰). Although only pyrite was identified in the basalts by the electron microprobe, the high $\delta^{34}S$ values would suggest the presence of sulfate as well.

Geothermometry

Although sulfate-sulfide pairs coexisting in the same samples were not available, the spatial proximity of the sulfide- and sulfate-bearing samples within one outcrop allows us to estimate the sulfate-sulfide

sample	locality	rock type	δ³⁴S ‰	S(ppm)
sulfides				
96/35	Punta de Peñon Blanco	carbonatite		-2.5
97/39	Punta de Peñon Blanco	sulfide+magnetite mass		-6.9
97/40-A	Punta de Peñon Blanco	pyroxenite		-5.8
97/40-B	Punta de Peñon Blanco	syenite		-5.5
97/1	Caleta de La Cruz	sulfide+magnetite mass		-3.8
97/1-A	Caleta de La Cruz	sulfide+magnetite mass		-4.6
97/1-A mass	Caleta de La Cruz	sulfide+magnetite mass		-4.2
96/2	Punta de La Nao	carbonatite		-0.9
96/54	Barranco de Los Mozos	alkaline basalt		+18.8
96/62	Barranco de Los Mozos	alkaline basalt		+16.2
sulfates				
96/28	Caleta de La Cruz	carbonatite		+4.5
96/16	Punta de La Nao	carbonatite		+7.7
96/19	Punta de La Nao	carbonatite		+9.1
96/20	Punta de La Nao	carbonatite		+12.5
96/25	Punta de La Nao	carbonatite		+9.9
96/48	Esquinzo	carbonatite		+12.4
96/51	Esquinzo	carbonatite		+10.1

Table I.- Stable sulfur isotope compositions of sulfides and sulfates from carbonatites and related rocks in Fuerteventura, Canary Islands, Spain. The data are in ‰ relative to CDT. Sulfur contents (in ppm) were determined on whole rocks. Other samples were hand-picked mineral grains.

Figure 3.- Sulfur isotope compositions of sulfides and sulfates (in ‰ relative to V-CDT) in the carbonatites of Fuerteventura (Canary Islands, Spain). Fractionation relationships and compositions of submarine basalts are from Ohmoto & Rye (1979) and Sakai et al. (1984), respectively. Data in shaded and open envelopes are from primary and secondary assemblages, respectively. $T(\Delta^{18}O)$ denote temperatures calculated on the basis of oxygen isotope compositions of silicate minerals (Demény et al., in preparation, see also text).

isotope fractionation with the assumption of sulfur isotope equilibrium. The $\delta^{34}S$ data of sulfates and sulfides from Punta del Peñon Blanco and Punta de La Nao are plotted in figure 3. Since the sulfide-magnetite masses are considered to be secondary, these are not included in the discussion of thermometry, but their $\delta^{34}S$ values are shown for comparison. The data distributions reflect sampling; thus, the sulfate-sulfide fractionation likely falls into the field between the sample envelopes. Isotope fractionation relationships at different temperatures are also shown in figure 3 using the sulfate-pyrite fractionation equation of Ohmoto & Rye (1979). The field indicates a formation temperature between 500 and 800°C, which is in agreement with the measured temperature of carbonatite magma at Oldoinyo Lengai (495 to 593°C, Krafft & Keller, 1989; Dawson et al., 1990). Preliminary investigations on oxygen isotope compositions of silicate minerals of the carbonatites (Demény et al., unpublished data) give temperatures from 560 to 1200°C (see insert of figure 3). This range might represent crystallization sequence, or reflect differences in closure temperatures. Nevertheless, the estimated sulfur isotope temperatures are not inconsistent with the oxygen isotope ones. Additionally, sulfate-sulfide isotopic fractionations in submarine basalts from (diferent oceanic islands (i.e: Galapagos, Juan de Fuca, Kilauea) (after Sakai et al., 1984) have also been indicated in figure 3. The data indicate higher isotope exchange temperatures which is in compliance with the higher crystallization temperature of the basaltic magma.

Negative $\delta^{34}S$ values

The $\delta^{34}S$ values of the sulfides of Punta del Peñon Blanco and Caleta de La Cruz are significantly more negative than mantle compositions (0 to +2 ‰, see Introduction). However, most of the data derive from the
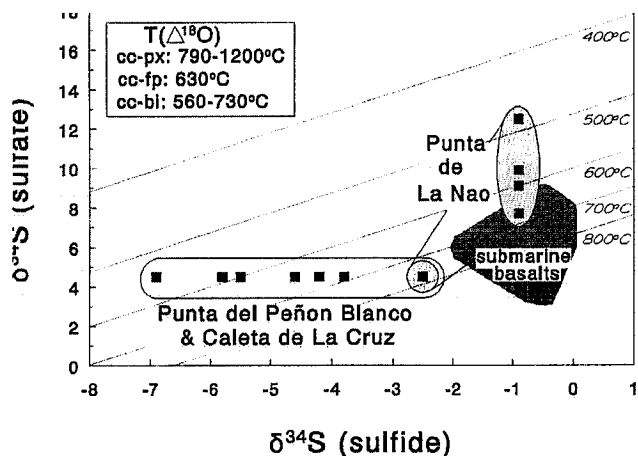
skarn-related sulfide+magnetite masses. The skarn-related origin of sulfide in metasomatized silicate rocks (samples 97/40-A and B) is supported by the similarity of $\delta^{34}S$ data in these rocks (Table I). If the sulfide and sulfate of samples 96/35 and 96/28 whose igneous biotites have preserved primary magmatic H and O isotope compositions (Demény et al.1998), respectively, are regarded as primary, then the bulk magmatic composition might be in between them, i.e. about 0 ‰, that agrees well with the mantle range. On the other hand, the skarn-related fluids might be derived from the carbonatitic magma, and, thus, their compositions should also be taken into consideration, shifting the inferred magma composition toward negative values.

A possible explanation for negative $\delta^{34}S$ values was given by Chaussidon et al. (1989) and Ionov et al. (1992), who suggested that low-$\delta^{34}S$ magma can be produced by partial melting. Since the carbonatite magma has likely been produced by partial melting of a carbonatitic silicate rock (Wallace & Green, 1988; Gittings, 1989; Wyllie et al. 1990; Yaxley et al. 1991; Kogarko et al. 1995), this process might have resulted inlow $\delta^{34}S$ values in the carbonatite. Another possibility is SO_2 degassing that would remove ^{34}S from the magma (Sakai et al. 1982; Alt, 1995). However, this process would produce SO_2-bearing fluids and in this case traces of ^{34}S-rich sulfate should appear beside the pyrite. Low-temperature sulfide-fluid fractionation might also cause ^{32}S-enrichment in the sulfide if the fluid has a high fO_2 (supported by the presence of magnetite) and is sulfate-dominated. Since those outcrops that contain the sulfide-magnetite masses do not contain sulfate this process can probably be neglected.

Positive $\delta^{34}S$ values

Following the approach of Mitchell & Krouse (1975), presuming a bulk composition of 0 ‰, sulfates

with $\delta^{34}S$ values up to +12.5 ‰ would be formed from a sulfide-dominated system. Such sulfide, however, has not been observed at Punta de La Nao and Esquinzo where sulfates with $\delta^{34}S$ values from +7.7 ‰ to +12.5 ‰ are formed. Thus, another explanation for the observed $\delta^{34}S$ differences must be found. In order to explain the areal $\delta^{34}S$ variation the following factors should be considered:

Temperature. Based on oxygen isotope fractionations between silicate minerals (Demény *et al.*, in preparation), no significant formation temperature difference has been found in the rocks of the occurrences studied.

Chemical composition. As has been shown in the Introduction, changing fO_2 and pH can affect the sulfate/sulfide ratio and, thus, the sulfur isotope compositions of precipitating sulfides and sulfates. However the relative abundances of sulfate and sulfide (i.e. few sulfate at Punta del Peñon Blanco and no sulfide at Esquinzo) are just the opposite to what would be required for the observed $\delta^{34}S$ variation.

Degassing of H_2S. Positive $\delta^{34}S$ values have been found in Oldoinyo Lengai carbonatites by Dawson *et al.* (1995) who attributed these values to H_2S degassing. However, they chose the degassing hypothesis because the $\delta^{13}C$ data showed no deviations, in contrast to what is observed for the Fuerteventura carbonatites. If degassing is considered to be responsible for the positive $\delta^{34}S$ shift, it should have been associated with a negative $\delta^{13}C$ shift, as CO_2 is enriched in ^{13}C relative to the remaining carbonate melt (Javoy *et al.*, 1978; Mattey, 1991; Scheele & Hoefs, 1992). The opposite is observed for the studied carbonatites, thus, degassing is not considered to be responsible for the $\delta^{34}S$ variation.

Admixing of external sulfur. Based on a $\delta^{13}C$-$\delta^{18}O$-δD study, Demény *et al.* (1998) have proposed a model in which the carbonatitic syenite magma assimilated sedimentary material during its storage in shallow magma chambers. The $\delta^{13}C$ data indicate that the degree of contamination varies between the localities studied. The difference in $\delta^{34}S$ values of sedimentary sulfate and mantle-derived sulfur is so large (Holser & Kaplan, 1966; Sakai *et al.*, 1982; Sakai *et al.*, 1984; Chaussidon *et al.*, 1989; Ionov *et al.*, 1992; Eldridge *et al.*, 1991) that sediment contamination should also affect the $\delta^{34}S$ values. Vollmer (1976) established a numerical mixing model in which two end-members with two components of different amounts are mixed. In a plot showing relationships between variables of the two components (e.g. $\delta^{34}S$ for sulfur *vs.* $\delta^{13}C$ for carbon) mixing trajectories define curves whose shapes depend on the amounts of the studied components in the end-members. For example, admixing of sulfur-rich sediment to sulfur-poor magma would result in a significant sulfur contamination (i.e. $\delta^{34}S$ change) even at low degrees of sediment assimilation (i.e. small $\delta^{13}C$ change). In this case the relative amount effect is expressed by the $r=(S/C)_{sediment}/(S/C)_{magma}$ ratio. If $r>1$,
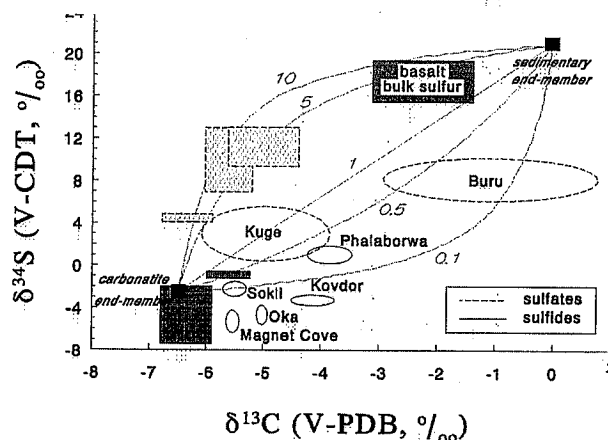

Figure 4.- Sulfur isotope compositions of sulfides and sulfates *vs.* carbon isotope compositions of the carbonatites studied and other carbonatite occurrences (after Deines, 1989). See also figure 2 and text for explanation of mixing curves.

sediment contains more sulfur relative to carbon compared with the magma. Mixing model curves with end-member compositions of $\delta^{13}C_{carbonatite}=-6.5$ ‰, $\delta^{34}S_{carbonatite}=-2.5$ ‰, $\delta^{13}C_{sediment}=0$ ‰, $\delta^{34}S_{sediment}=+21$ ‰ (Holser & Kaplan, 1966) and varying $r=(S/C)_{sediment}/(S/C)_{carbonatite}$ ratios are shown in a $\delta^{34}S$-$\delta^{13}C$ plot of the data (Fig. 4). The data of the present study can be explained with mixing of carbonatitic magma and sediment at r values between 5. The sulfur contents of the carbonatites studied are between 7 and 870 ppm (Table I). Since samples with the highest sulfur mineral content were selected for $\delta^{34}S$ analyses, the sulfur content of the original carbonated silicate magma might not exceed several tens of ppm. This S content agrees well with the mantle sulfur content proposed by Ionov *et al.* (1992) and is much less than the average crustal concentration (~800 ppm, Holser & Kaplan, 1966). Thus, these sulfur contents are in compliance with the high r values proposed for the mixing relationship.

The high $\delta^{34}S$ values (the highest of our data set) obtained in submarine alkaline basalts may indicate that the basalts have suffered the most extensive contamination. Their $\delta^{34}S$ data alone can be explained by seawater infiltration during or after their eruption, but the presence of sedimentary carbonate xenoliths in these rocks indicates sediment assimilation, and further supports the contamination model.

For the sake of comparison, $\delta^{34}S$ and $\delta^{13}C$ ranges of other carbonatite complexes are also shown in figure 4. The $\delta^{34}S$-$\delta^{13}C$ correlation described by Deines (1989) can be explained by crustal contamination at varying r values and/or starting compositions.

Conclusions

The areal $\delta^{13}C$ variations in the carbonatites of Fuerteventura (Canary Islands) indicate sediment assimilation that took place during magma storage in

shallow chambers (Demény *et al.*, 1998). Sulfur isotope compositions of sulfides and sulfates of carbonatites and related rocks have been studied in order to test this hypothesis and to gain information on the mantle fluids. Sulfur isotope fractionations between sulfates and sulfides within the same outcrop indicate formation temperatures between 500 and 800°C, which is in compliance with preliminary oxygen isotope thermometry calculations and well known carbonatite crystallization temperatures.

The sulfur isotope compositions found in the presumed least-contaminated complex are significantly more negative than the meteoritic composition (down to -6.9 ‰), which is explained by partial melting that enriches the light S isotope in the melt and/or SO_2 degassing. Much more positive $\delta^{34}S$ values (up to +12.5 ‰) are found in those localities where the $\delta^{13}C$ data indicate higher degrees of sedimentary contamination. The data obtained show $\delta^{34}S$-$\delta^{13}C$ correlation that can be modelled with mixing of carbonatite magma and sedimentary material. Thus, the sulfur isotope compositions of sulfides and sulfates support the contamination model.

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