

SULPHUR ISOTOPE SYSTEMATICS OF GRANITOIDS AND ASSOCIATED ROCKS FROM THE AVILA - LA ALBERCA AREA (WESTERN SISTEMA CENTRAL, SPAIN)

C.Recio (1), A.E.Fallick (2) and J.M.Ugidos (3)

- (1) Servicio General de Análisis de Isótopos Estables (SGAIE). Facultad de Ciencias. Universidad de Salamanca. 37008-SALAMANCA (Spain).
(2) Scottish Universities Research and Reactor Centre (SURRC). East Kilbride. Glasgow, G75 0QU. SCOTLAND (U.K.)
(3) Departamento de Geología. Facultad de Ciencias. Universidad de Salamanca. 37008-SALAMANCA (Spain).

ABSTRACT

A reconnaissance sulphur isotopic study has been carried out on acid-soluble and non acid-soluble sulphides separated from late Hercynian granites and their host-rocks in the western area of the Sistema Central Español. Of the different rocks studied (amphibole-bearing biotite granites, biotite granites, cordierite-bearing biotite granites, nebulites and Complejo Esquisto Grauváquico host-rocks) only the Complejo Esquisto Grauváquico shales, the nebulites and the cordierite-bearing granites (and their enclaves) have yielded enough sulphur for analysis. Petrographic examination, in polished thin sections, of the samples analyzed identified the acid-soluble sulphide as pyrrhotite, and the non acid-soluble sulphide as pyrite, with minor contributions from chalcopyrite. Mass-balance corrected $\delta^{34}\text{S}$ values range between -3.9 and +4.8‰ (average: -0.8 ± 3.8 ; 1σ , $n=4$) for cordierite-bearing granites. The nebulites with which these granites are sometimes in gradual contact yielded exclusively positive values between $\delta^{34}\text{S} = +1.1$ and +10.6‰ (av.: $+4.1 \pm 3.4$; 1σ , $n=6$). The Complejo Esquisto Grauváquico shale-type rocks gave both positive and negative $\delta^{34}\text{S}$ values of +7‰ and around -5‰. Intermediate to basic enclaves gave $\delta^{34}\text{S}$ values mainly close to 0‰, except for one anomalous acid-soluble sulphide in a quartzdioritic enclave that has a value of $\delta^{34}\text{S} = +13.4$ ‰.

Most of the acid-soluble / non acid-soluble pairs follow a straight line, whose slope approaches 1, in a $\delta^{34}\text{S}_{\text{acid-soluble}}$ vs $\delta^{34}\text{S}_{\text{non acid-soluble}}$ plot, and this is interpreted to indicate reequilibration at high T; therefore an origin for the sulphur in the granites is suggested to be external to the granite magma system, consistent with assimilation of country-rocks by the granite magma.

Key words: Stable isotopes, Granites, Hercynian, Sistema Central Español, $\delta^{34}\text{S}$, Sulphides.

RESUMEN

Se han determinado las relaciones isotópicas $^{34}\text{S}/^{32}\text{S}$ en sulfuros separados de granitoides hercínicos tardíos y su encajante en el área occidental del Sistema Central Español. En cada muestra se han analizado dos tipos de sulfuros, en función de que sean solubles o insolubles en ácidos. Los tipos de rocas estudiados han sido granitos biotítico-anfibólicos, granitos biotítico-cordieríticos, nebulitas y rocas del Complejo Esquisto Grauváquico. Sólo las rocas del Complejo Esquisto Grauváquico, las nebulitas y los granitos biotítico-cordieríticos (y sus enclaves) contienen sulfuros en cantidad suficiente como para permitir su recuperación por el método empleado. El estudio petrográfico en lámina delgada pulida de las muestras analizadas permitió la identificación del sulfuro soluble en ácidos como pirrotita, y de aquellos no solubles en ácidos como pirita, con cantidades menores de calcopirita. Los valores medios de $\delta^{34}\text{S}$ obtenidos, ponderados teniendo en cuenta el balance de masas, oscilan entre -3.9 y +4.8‰ (media: -0.8 ± 3.8 ‰; 1σ , $n=4$) para los granitos biotítico-cordieríticos. Las nebulitas, con las cuales estos granitos están a veces en contacto gradual, presentan exclusivamente valores positivos, entre $\delta^{34}\text{S} = +1.1$ y +10.6‰ (media: $+4.1 \pm 3.4$ ‰; 1σ , $n=6$). Las rocas del Complejo Esquisto Grauváquico muestran tanto valores positivos como negativos de +7‰ y alrededor de -5‰. Enclaves de composición intermedia a básica presentan en su mayoría valores de $\delta^{34}\text{S}$ próximos a 0‰, excepto un sulfuro soluble en ácidos, separado de un enclave cuarzodiorítico, para el cual se obtuvo un valor de $\delta^{34}\text{S} = +13.4$ ‰.

Palabras clave: Isótopos estables, Granitos, Hercínico, Sistema Central Español, $\delta^{34}\text{S}$, Sulfuros.

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1. INTRODUCTION

Petrographic examination in polished thin section of samples collected in the western area of the Sistema Central Español as part of a wider reaching geochemical and isotopic study revealed the presence of some minor sulphide minerals, mainly as pyrrhotite, and in lesser amounts, pyrite and chalcopyrite. This relative order of sulphide abundance is considered by Whalen and Chappell (1988) as typical of S-type granites, as opposed to I-types, in which they find the sulphide mineral assemblage to be dominated by pyrite. According to these authors, sulphides in S-type Lachlan fold belt granites are texturally early phases.

Magmas formed by partial melting of the mantle, and the rocks and fluids that may evolve from them, should have $\delta^{34}\text{S}$ values close to their mantle protolith (Ohmoto, 1986). If this protolith is as homogeneous as it would appear mostly to be for sulphur, their $\delta^{34}\text{S}$ values should be close to zero (the reference standard used for sulphur isotopes is the troilite found in the Cañon del Diablo meteorite). Chaussidon *et al.* (1989) have discussed the validity of meteorites as indicators of mantle sulphur $\delta^{34}\text{S}$, sulphur isotope fractionation between mantle and silicate-melt, and $\delta^{34}\text{S}$ homogeneity/heterogeneity of the mantle.

However, igneous rocks present variable values (Coleman, 1979; Kubilius, 1983, in Ohmoto, 1986; Ishihara and Sasaki, 1989; Laouar *et al.*, 1990), and this is interpreted by Ohmoto (1986) as the result of assimilation of upper crustal rocks by magmas of mantle or lower crustal derivation: the sulphur content of granites and granodiorites frequently exceeds the amount that would be expected purely as a result of the solubility of sulphide sulphur in the pertinent magmas, and this, coupled with the fact that frequently the $\delta^{34}\text{S}$ values of sulphides in the granites and their country rocks are very similar, suggests that most of the sulphur was actually acquired during emplacement (see Ohmoto, 1986).

Possible outgassing processes should also be considered, particularly at low sulphur contents. ^{34}S is fractionated towards the species with the highest oxidation state of S. The effects degassing will have on the resultant $\delta^{34}\text{S}$ of a granite will depend on whether the degassed species was in an oxidised or reduced form.

As much as 10% of total crustal sulphur may be in the form of dissolved sulphate in seawater. Present day average $\delta^{34}\text{S}$ value of dissolved sulphate is about 21‰ (Rees *et al.*, 1978), but studies of evaporites indicate that this value has varied with geological time (see Ohmoto and Rye, 1979; Claypool *et al.*, 1980; Ohmoto, 1986), although no age inferences should be made employing sulphur isotopes (Laouar *et al.*, 1990).

Bacterial reduction of seawater sulphate results in an average fractionation of about -35‰ (Fisher and Hudson, 1987), although this varies depending on the particular conditions of each environment. Non-bacterial reduction of sulphates involves kinetic fractionation effects that are essentially negligible provided reduction is complete and the system is closed to sulphur exchange.

phur exchange.

Different sulphur reservoirs therefore have distinctive signatures that might be possible to trace when sulphur becomes part of geological processes, such that well defined patterns of sulphur isotope variations can be identified in granitic rocks (Laouar *et al.*, 1990).

2. GEOLOGICAL SETTING OF THE GRANITOIDS OF THE WESTERN AREA OF THE SISTEMA CENTRAL ESPAÑOL

The Sistema Central is part of the "Central Iberian Zone" of the Hesperian Massif (Lotze, 1945; modified by Julivert *et al.*, 1974), and is characterized by abundant granitoids and high-grade metamorphic rocks formed during the Hercynian orogeny.

A broad first order subdivision of the granitic rocks could be made into early to syn-tectonic granites, that were deformed by the Hercynian orogeny, and late to post-tectonic granites, that are undeformed (López-Plaza and Martínez-Catalán, 1988). It is these late Hercynian granites (fig. 1) that will be the subject of this work.

The Complejo Esquisto Grauváquico materials are the country-rocks into which the granites were emplaced, and correspond mainly to Upper-Precambrian / Lower-Cambrian shales and greywackes, with intercalations of conglomerates, limestones, quartzites and volcanoclastic materials (see for example Rodríguez-Alonso, 1985). These rocks were affected by two or three (depending on the area and the level considered) main deformation phases (Diez-Balda, 1986), and by the Hercynian metamorphism, that evolved from intermediate pressure conditions to low-pressure, high temperature conditions towards late stages (Ugidos, 1990, and references therein).

Nebulites are the most evolved migmatitic types found in the zone, where they have been developed from Complejo Esquisto Grauváquico metasedimentary rocks. Gradual transitions from the cordierite-bearing nebulites, to less evolved migmatitic types, and these to lower metamorphic-grade country-rocks can be observed.

Mineralogically, the nebulites are composed of quartz, oligoclase, cordierite, alkali feldspar and minor biotite, sillimanite (usually fibrolite), apatite, occasional andalusite, and ore minerals. The high content (15-20%) of fresh, euhedral to subhedral cordierite is characteristic of these rocks.

In some areas, the nebulites are in apparent gradual transition to cordierite-bearing granites, or as enclaves within them. In no case have intrusive relations of nebulites into any other rocks been observed.

Cordierite-bearing biotite granite is the most typical granitic type in marginal zones of the western part of the study area, where it is characterized by the frequent presence of prisms of cordierite. The amount of cordierite decreases towards internal areas of the ba-

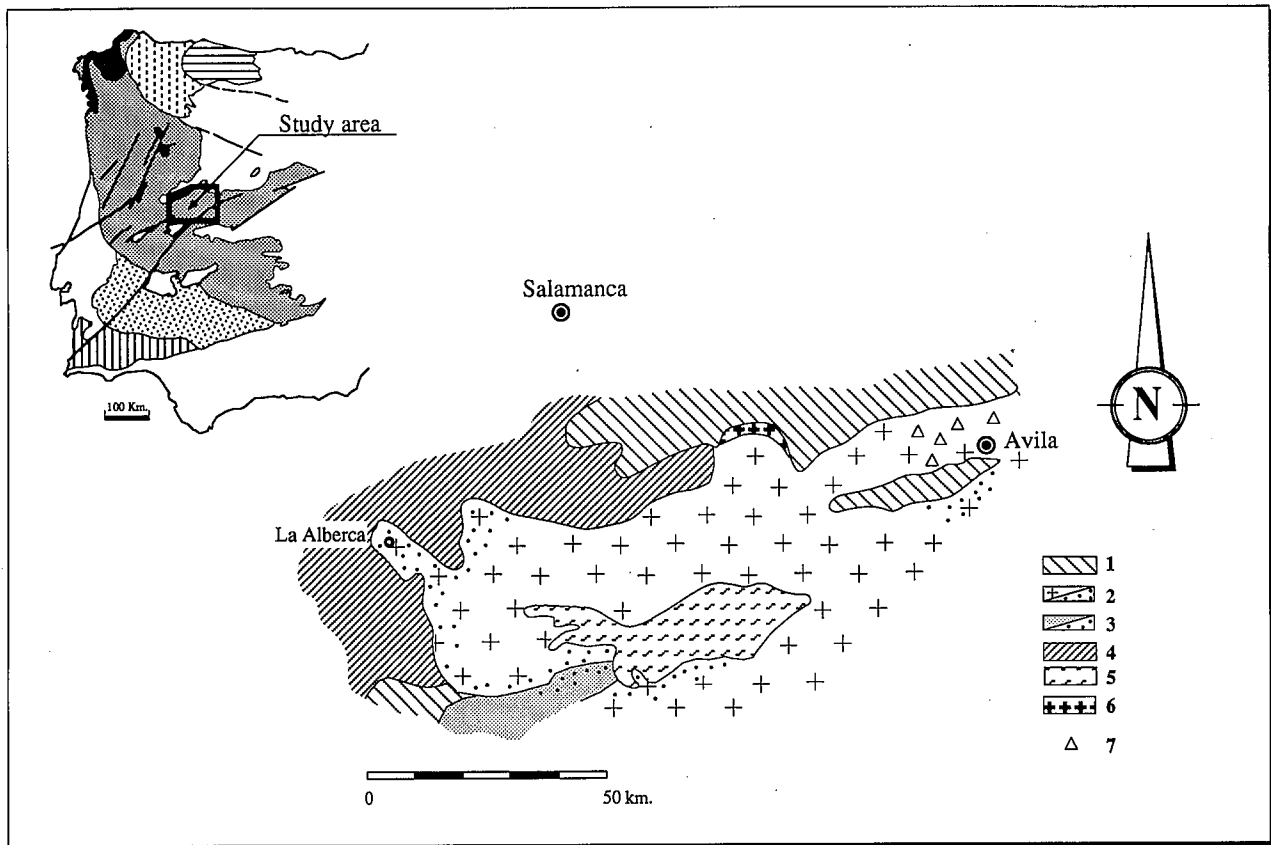


Fig. 1.-Geological scheme of the granites in the western area of the Sistema Central Español. Based on Aparicio *et al.* (1975), López Ruiz *et al.* (1975) and Department of Petrology, University of Salamanca (1983). 1.- Post-Palaeozoic sediments; 2.- Biotite granites \pm cordierite (dots); 3.- Biotite \pm sillimanite \pm muscovite \pm andalusite granites, \pm cordierite (dots); 4.- Metamorphic rocks; 5.- Cordierite migmatites; 6.- Leucogranites; 7.- Amphibole-bearing biotite granites.

Fig. 1.-Esquema geológico de los granitos del área occidental del Sistema Central Español. Basado en Aparicio *et al.* (1975), López Ruiz *et al.* (1975) y Department of Petrology, University of Salamanca (1983). 1.- Sedimentos post-Paleozoicos; 2.- Granitos biotíticos \pm cordierita (puntos); 3.- Granitos biotíticos \pm sillimanita \pm moscovita \pm andalucita, \pm cordierita (puntos); 4.- Rocas metamórficas; 5.- Migmatitas cordieríticas; 6.- Leucogranitos; 7.- Granitos biotítico-anfibólicos.

tholith and when the cordierite disappears altogether, the rock changes into a biotite granite.

Other than almost invariably pinitized cordierite, these granites are composed of quartz, plagioclase (mostly oligoclase; rarely andesine), alkali feldspar, \pm muscovite, and very rare sillimanite. Other accessory minerals are apatite, zircon and ore minerals.

Microgranular enclaves of tonalitic to quartzdioritic nature and with sizes of several centimetres can be frequently found, as well as the already mentioned nebulites. Decametric gabbroic enclaves have also been reported (Ugidos *et al.*, 1988). Enclaves of migmatite and hornfels, also found, are related to the type of host-rock (Ugidos, 1987).

The biotite granites are in gradual transition to cordierite-bearing biotite granites to the west, and to amphibole-bearing biotite granites to the northeast. The biotite granites are formed by quartz, plagioclase (andesine-oligoclase), alkali feldspar and biotite. Accessory minerals are as for the cordierite-bearing granites, except for the occasional presence of titanite in the biotite granites. No muscovite has been found.

Microgranular, biotitic to biotitic-amphibolitic,

centimetre-sized enclaves are frequent, but much bigger enclaves (8 to 10 metres visible) of quartzdioritic nature have also been found (Ugidos and Recio, 1985; personal observation). A macroenclave (tens of metres big) of cordierite has been reported inside the biotite granite (Ugidos, 1988).

The presence of amphibole, either as isolated prisms or as polycrystalline aggregates, as well as allanite, and more frequent titanite, differentiates the amphibole-bearing granites from the biotite granites, to which they are always related, showing gradual transitions. In no case have intrusive relations between both types of granites been observed.

Microgranular tonalitic to quartzdioritic enclaves, biotitic or biotitic-amphibolitic (in which case allanite and titanite are also present) are frequent. These enclaves show typically magmatic textures, and it is frequent to find apatite needles included in crystals of other minerals, as well as single needles that are enclosed within two or more different crystals. Metamorphic enclaves of hornfels are rare and restricted to the contacts with the host-rock.

Amphibole-bearing biotite granites and biotite gra-

nites have been considered to derive from a mixed deep crustal source on the basis of $\delta^{18}\text{O}$ data (Ugidos *et al.*, 1989; Recio, 1990), with cordierite-bearing biotite granites resulting from assimilation processes that involved the interaction of high-grade metamorphic host-rocks and nebulites with biotite granites (more petrographic details and assimilation model in Ugidos, 1990).

Opaque mineralogy is dominated by ilmenite in both the cordierite-bearing granites and the nebulites, although magnetite may also be present, mostly in the nebulites. Ilmenite contents in the enclaves tend to be less important than in the granites relative to sulphides.

Ilmenite in the granites appears mostly as euhedral to subhedral, texturally early crystals, sometimes twinned. It can occasionally show pleochroism in plane polarized light, and is distinctively anisotropic when observed under crossed polars. Although crystals up to 1 mm big have been observed, these are infrequent. Grains a few tens of microns across predominate. In the nebulites ilmenites tend to be more irregularly shaped and smaller, and the optical characteristics are not so well developed.

Magnetites are rare in the granites, and much less abundant than ilmenites in the nebulites, where they appear as smaller, subhedral to anhedral, isotropic crystals. Magnetite is most abundant in UHR-28, the gabbro macroenclave, where the quantities of ilmenite and magnetite are similar.

Amongst the sulphides, in nebulites and granites pyrrhotite is always the most abundant, sometimes as much as about ten times the abundance of pyrite, the next sulphide in importance. This tendency is however reversed in the Complejo Esquisto Grauváquico shales, where pyrite is the most abundant sulphide or even the only one present.

The pyrrhotite appears as irregular, anhedral grains, usually not more than a few microns to tens of microns across. It can be either occupying intergranular spaces or infilling small cracks in silicates. Occasionally it can be found along cleavage lines of phyllosilicates. It is not unusual to find pyrrhotites that include very small, rounded chalcopyrites.

Pyrite is generally smaller and less abundant than pyrrhotite, although its mode of occurrence is similar. Occasionally pyrite and pyrrhotite appear together, as if one was being transformed into another.

Chalcopyrite is the last sulphide common to all samples studied. It appears mostly as small, rounded grains; frequently as an inclusion within pyrrhotite, but also isolated within silicate minerals. Volumetrically it is unimportant.

A single grain of what appears to be galena has been observed in one single cordierite-bearing granite sample, although its determination is by no means certain.

Only in nebulites have galena and sphalerite been determined. They are usually small, anhedral, volumetrically unimportant isolated grains, either as inclusions within silicates or as infillings of intergranular spaces. Also in nebulites what are likely to be copper sulpho-

salts have been observed, although its exact mineralogical nature could not be determined. In any case, the amount of the aforementioned materials is minimal.

The quantity of opaque minerals is variable; small in the granites (from nearly absent to not more than wgt.%, and with ilmenite more abundant than the sulphides), and more important in the nebulites, where it can reach over 5 wgt.% in some occasions, and where the sulphides dominate over the oxides. The maximum ore mineral content is in the gabbro macroenclave UHR-28, where sulphide and oxide contents are similar, and add to well over 5 wgt.%.

The Complejo Esquisto Grauváquico shales, where most of the ore minerals are sulphides, have higher opaque mineral contents than the granites, but noticeably smaller than the nebulites.

3. ANALYTICAL METHODS

The amount of sulphides found in the granitoid samples from the Sistema Central, and their grain size (see above), are small enough to make physical separation (magnetic separation; heavy liquids, ...) impractical, not only to separate between different sulphide minerals, but also to separate the sulphides from the silicates. To be able to recover the sulphur for isotopic analysis, we have used a chemical extraction technique that is based in the works of Zhabina and Volkov (1978), Canfield *et al.*, (1986) and Hall *et al.*, (1988), but with modifications as appropriate.

Our technique uses a digestion apparatus based on that designed by Canfield *et al.* (1986) to measure the amount of reduced inorganic sulphur in a powdered sample, and the principles described by Hall *et al.* (1988) for sample preparation for isotopic analysis. The method has been in use at the Isotope Geology Unit at SURRC since 1988, and successful separations of sulphides other than those mentioned here are routinely performed. Briefly, and when applied to our samples that contained only pyrrhotite and pyrite, with minor chalcopyrite, the procedure is as follows:

Between 1 and 25 g (depending on the abundance of sulphides observed during the petrographic study) of powdered sample are placed in a reaction vessel (similar to that depicted in fig. 1 of Canfield *et al.*, 1986); ethanol (about 10 ml for the weights of sample normally used) is added (this will help the mixture to reach its boiling point earlier when heated) and the different parts of the reaction equipment are attached together. The system is then flushed with dry, oxygen-free nitrogen and the liquid heated to boiling point. When all the air has been expelled, the appropriate reagents (see below) are added by means of a syringe. In about two hours (Canfield *et al.*, 1986) the reaction should have been completed. Successive use of HCl and CrCl_2 allowed us to separate the sulphur (as H_2S) derived from acid soluble sulphides (in this case pyrrhotite) from that derived from non acid soluble sulphides (in our case, mainly pyrite, with a minor contribution from chalcopy-

rite). During the time to complete the reaction, the evolved H_2S is collected in another vessel containing a zinc acetate plus NH_4 solution. The H_2S will react with the ZnAc to form ZnS . Addition of AgNO_3 facilitates the recovery of sulphur in the form of precipitated Ag_2S . The Ag_2S is preferred for isotopic analysis because it gives higher and more consistent yields than the ZnS , as well as being more easily recoverable from solution (Hall *et al.*, 1988, and our own analytical experience).

Isotopic analyses were performed at the IGU of SURRC, employing a method similar to that described by Robinson and Kusakabe (1975). Briefly, a few milligrams of sample are thoroughly mixed with cuprous oxide (Cu_2O) and combusted under vacuum at 1075°C . Any SO_3 produced is converted to SO_2 by means of a copper furnace at 750°C . The sulphur, in the form of SO_2 , is passed through a slush trap (a mixture of acetone and solid CO_2) to remove water and collected in a n-pentane trap cooled by liquid nitrogen, where any remaining impurities (mainly as CO_2) are removed by fractional distillation. The yield of clean SO_2 is then measured manometrically and collected for isotopic analysis.

$^{34}\text{S}/^{32}\text{S}$ ratios were determined in an ISOSPEC-64 mass spectrometer. Duplicate analyses, including chemistry, of several reference standards gave an average

reproducibility of $\pm 0.27\text{‰}$. Results are reported in the familiar δ notation, relative to CDT (the Cañón del Diablo troilite) in table 1.

During chemical extraction of sulphur as Ag_2S , a black film floating on top of the reagents was observed in some cases. Since such material could not be attributed to any form of contamination, it was assumed to be carbon and collected for isotopic analysis. Given its colour and general appearance, this material had to be an organic compound. It could not be a carbonate, since sulphur extraction involved attack with hot concentrated acids, that would have resulted in carbon being released as CO_2 and lost, and it was unlikely to be graphite, since test-runs of artificial samples of known composition, that included graphite in several occasions, never released anything similar.

Sample preparation followed the method of Sofer (1980). Very briefly, the sample was loaded into a quartz tube containing copper oxide in wire form, and the tube was evacuated and sealed. Tubes are then placed into an oven and heated to 850°C for three hours, and left to cool slowly. The evolved CO_2 was purified in a vacuum line by means of a slush trap (a mixture of CO_2 and acetone); manometrically measured, and collected. $^{13}\text{C}/^{12}\text{C}$ isotopic ratios were determined in a triple-collector VG SIRA-10TM mass spectrometer, and

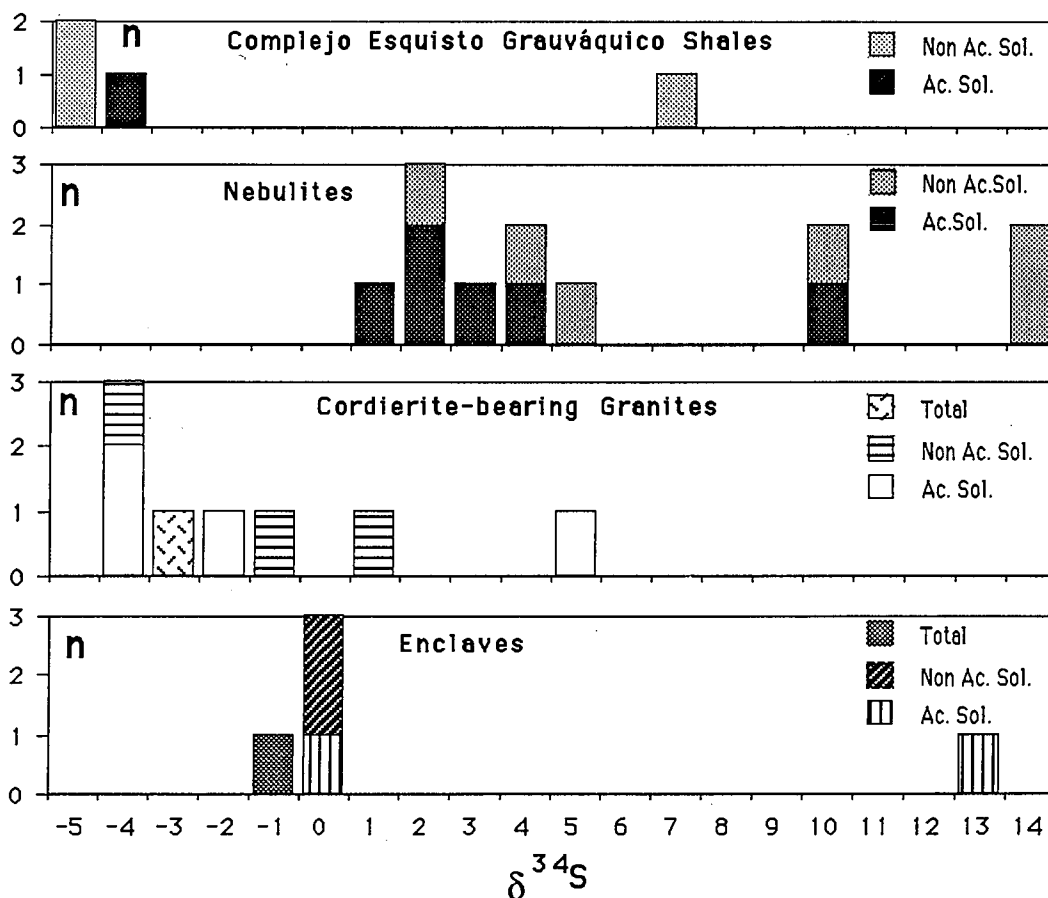


Fig. 2.-Histogram of $\delta^{34}\text{S}$ values of samples from the Sistema Central Español, separated by type of rock from which the sulphur was extracted.

Fig. 2.-Histograma de valores de $\delta^{34}\text{S}$ en las muestras del Sistema Central Español analizadas, separadas según el tipo de roca del cual se extrajo el azufre.

Sample	Acid soluble		Non-acid soluble		Total	
	M ₁	δ ³⁴ S ₁	M ₂	δ ³⁴ S ₂	M _T	δ ³⁴ S _T
	(mg/g)	‰	(mg/g)	‰	(mg/g)	‰
NEBULITES						
JAM-2	0,9	10,0	0,2	13,9	1,1	10,6
ABE-4	15,5	4,0	2,8	5,2	18,3	4,2
XSA-3	6,2	2,1	1,3	9,8	7,5	3,4
PHU-2	8,1	0,9	1,9	2,1	10,0	1,1
I-30	27,2	2,1	6,2	2,8	33,3	2,2
XSA-1	20,4	2,8	3,2	3,6	23,5	2,9
Av. ±1σ	13±9.8	3.7±3.3	2.6±2.1	6.2±4.7	15.6±11.8	4.1±3.4
CORDIERITE-BEARING GRANITES						
MC-12	2,5	-3,9	1,1	-3,9	3,6	-3,9
XSA-10	0,4	-4,2	0,2	0,5	0,6	-2,4
XSA-9	0,2	4,8			0,2	4,8
BEU-15	1,1	-2,0	0,9	-0,8	2,0	-1,5
Av. ±1σ	1.1±1.0	-1.3±4.2	0.7±0.5	-1.4±2.3	1.6±1.5	-0.8±3.8
ENCLAVES						
GU-13.A					0,3	-0,9
BEU-18.A	0,5	13,4	0,8	0,2	1,4	5,5
UHR-28	8,0	-0,3	12,0	0,4	20,0	0,1
COMPLEJO ESQUISTO GRAUVAQUICO SAMPLES						
GU-21			0,9	-5,0	0,9	-5,0
HR-41	2,0	-4,3	8,5	-4,8	10,5	-4,7
HR-42			14,6	7,2	14,6	7,2

Table 1.- δ³⁴S values of those samples from the Sistema Central Español found to have sulphide minerals. M₁ and M₂ represent milligrams of Ag₂S obtained per gram of whole rock sample reacted. M_T is the total amount of Ag₂S obtained (both from acid soluble and non acid soluble sulphides). δ³⁴S_T is the sulphur isotopic value of the sample as calculated by mass balance. When only "TOTAL" values are reported, it indicates that no separation between acid and non acid soluble sulphides was possible, and only the bulk value for the sample is given.

Table 1.- Valores de δ³⁴S de aquellas muestras del Sistema Central Español en las cuales se han podido separar sulfuros. M₁ y M₂ son mgr de Ag₂S obtenidos por cada gr de roca total utilizado. M_T es la cantidad total de Ag₂S obtenida (suma de sulfuros solubles e insolubles en ácidos). δ³⁴S_T es el valor isotópico obtenido por balance de masas. En aquellas muestras en las que se indica un solo valor bajo la columna "TOTAL" no fue posible separar entre sulfuros solubles e insolubles en ácidos, y solo se da el valor correspondiente al azufre total.

are reported as δ¹³C values relative to the PDB reference standard. The exact chemical nature of the material, however, has not been determined, since the amount of sample available was not enough to do both isotopic and chemical analysis. Results are reported in table 3.

4. RESULTS AND DISCUSSION

Sulphur isotopic results are reported in table 1 and fig. 2. From table 1 it can be seen that the sulphide content of nebulites, between 1.1 and 33.3 mg/g; average 15.6 ±11.8 (1s, n=6) is generally several times higher than sulphide content of cordierite-bearing granites,

that ranges between 0.2 and 3.6 mg/g; average 1.6 ±1.5 (1s, n=4). In the biotite and amphibole-bearing granites sulphur content was below the lower recoverable limit of 0.06% sulphide content. Contents in the enclaves vary with petrological nature, such that it is higher in the gabbro (UHR-28, 20 mg/g) and lower in progressively more acidic samples (as BEU-18.A, 1.4 mg/g and GU-13.A, 0.3 mg/g). The Complejo Esquisto Grauváquico samples (values between 0.9 and 14.6 mg/g; average 8.7±7.0 (1s, n=3)) have higher sulphur content than the granites, but lower (in general) than the nebulites.

In fig. 2 the δ³⁴S values corresponding to different groups of samples have been separately plotted. Nebu-

lites show exclusively positive values, mainly between $\delta^{34}\text{S} = +1$ to $+5\text{‰}$, whereas in the cordierite-bearing granites, negative values between -1 and -4 predominate. The Complejo Esquisto Grauváquico shales have mainly negative values, around $\delta^{34}\text{S} = -5\text{‰}$, but positive ones can also be found. The enclaves plot mainly close to zero. This is consistent with the nature of the enclaves (gabbros and tonalites-quartzdiorites), and coincides with values close to zero reported for mantle and lower crustal rocks (Thode *et al.*, 1961; Smitheringale and Jensen, 1963; Sasaki, 1973; Sasaki and Ishihara, 1979; Ohmoto, 1986). A source of isotopically enriched sulphur ($\delta^{34}\text{S} = +13$ to $+14\text{‰}$), evident in the nebulites and in one enclave, but not found in the granites or the Complejo Esquisto Grauváquico shales, has a so far uncertain origin.

In fig. 3, the sulphide isotopic composition has been plotted against the sulphide content of the samples analyzed. The lower the sulphide content of the sample, the wider is the scatter in the isotopic values. Part of this could be attributed to the difficulties inherent in analyzing small samples. It can be seen in fig. 3 that the nebulites plot at fairly homogeneous $\delta^{34}\text{S}$ values. The only nebulite that deviates appreciably has a higher $\delta^{34}\text{S}$. The cordierite-bearing granites plot towards lower $\delta^{34}\text{S}$ values. This is an argument favouring the isotopic values measured in the granites not being an artifact of the analytical procedure, since the values measured in the nebulites would indicate that possible errors would be towards heavier isotopic ratios. Since the granites yield lighter isotopic ratios, it is inferred that the measured values are real ones. Kubilius (1983; in Ohmoto, 1986) found a very similar relationship between the $\delta^{34}\text{S}$ value and the total sulphide content (see fig. 24 of Ohmoto, 1986) for sulphide-derived sulphur of granitoids from Nova Scotia, where the average $\delta^{34}\text{S}$ of granitoids and their hosts is essentially identical. Note however that the sulphide contents reported by this author are much lower than those found in the Sistema Central rocks studied for this work. The similarities in $\delta^{34}\text{S}$ values between granite and their hosts in the Sistema Central are also evident in fig. 2.

In fig. 4, the $\delta^{34}\text{S}$ values of sulphur extracted as acid-soluble and as non acid-soluble fractions have been plotted against each other. The majority of the samples plot very close to a straight line through the origin (0,0), although three samples do not. Even acknowledging that this line is not a proper isotherm, since its slope is different than 1 (see Gregory and Criss, 1986), it is very close to it. Accepting the best fit line defined by the nine other data points to be a good enough approximation to the isotherm, would mean that the original isotopic compositions of the different samples have been modified. Since the samples plot close to the isotherm with $\Delta=0$ (i. e., the one that passes through the origin), it is assumed that the samples analyzed from the igneous rocks established their isotopic signature at high temperature, at which small Δ values are to be expected. If this is true, it means that the sulphides were already in the original rocks before these were dis-

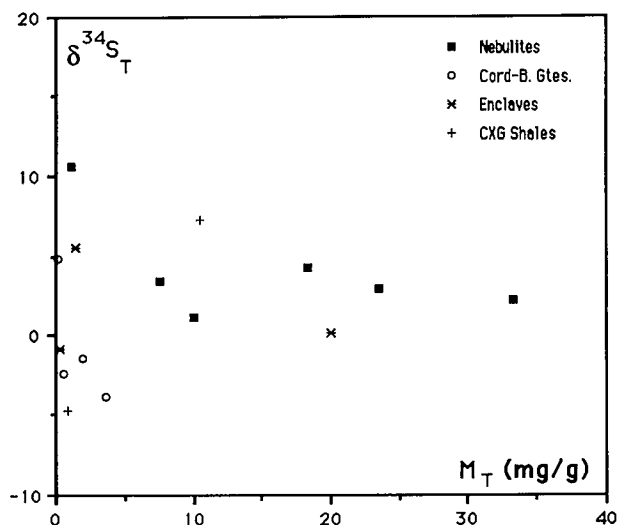


Fig. 3.- $\delta^{34}\text{S}_T$ values versus sulphide content of samples from the Sistema Central Español. Mris mg of Ag_2S (acid-soluble + non acid-soluble) per g of whole rock sample used. $\delta^{34}\text{S}_T$ is the sulphur isotopic composition of the rock as calculated by mass balance, from the isotopic composition of the acid soluble and non acid soluble fractions.

Fig. 3.-Representación de $\delta^{34}\text{S}_T$ frente al contenido en sulfuro de las muestras del Sistema Central Español analizadas. Mrson mgr de Ag_2S (soluble en ácidos + no soluble en ácidos) por gr de roca total empleado. $\delta^{34}\text{S}_T$ es la composición isotópica del azufre total, calculado por balance de masas, a partir de los valores correspondientes a los sulfuros solubles y no solubles en ácidos.

turbed by later events, and have subsequently been modified during magmatic processes. This can explain amounts of sulphur well above the expected solubility for this element in granite magmas (about 200-300 ppm; in Ohmoto, 1986) in the cordierite-bearing granites. This is also consistent with UHR-28, a gabbro enclave, whose sulphur might be expected to be of magmatic derivation, plotting in line with the rest of the samples, but it conflicts with HR-41, a low-grade metamorphism Complejo Esquisto Grauváquico host-rock sample, plotting in the same line.

In a diagenetic environment, the sulphide mineral that precipitates is conditioned both by the sulphur and the metal available. Supposing that the sulphur derives from bacteriogenic reduction of sulphate, the metals will probably be mostly Fe, and perhaps Cu, Zn, Pb, ... If precipitation of diagenetic sulphides is taking place at the same time that reduced sulphur is being generated, on encountering the metal, the sulphide will precipitate. If two different metals are present, two sulphides will precipitate, and the sulphur in them will be nearly the same, with only a small isotopic fractionation conditioned by the nature of the mineral precipitating: pyrite (the non acid-soluble sulphide) will tend to concentrate ^{34}S , whereas pyrrhotite (the acid-soluble sulphide) would be slightly depleted in the heavy isotope relative to pyrite (see for example Ohmoto and Rye, 1979). This can be an explanation of why the fractionation between the acid-soluble and non-acid-soluble sulphide is

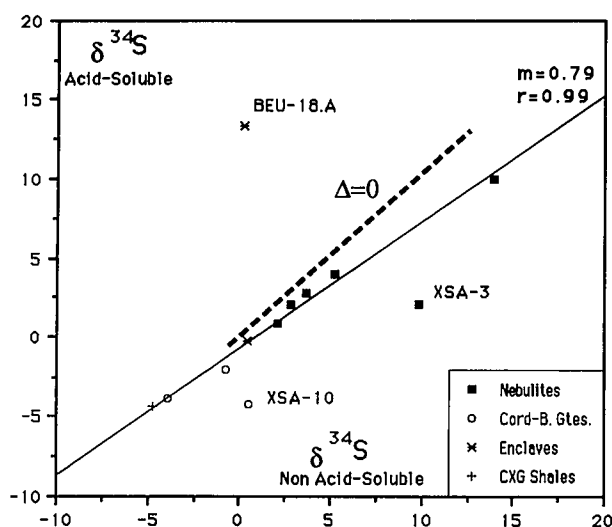


Fig. 4.- $\delta^{34}\text{S}$ measured in acid-soluble sulphides plotted versus values measured in non acid-soluble ones. Dotted line is best fit to nine sample points. Note the near perfect correlation ($r = 0.99$) despite the different petrological nature of the samples analyzed. Slope of this line ($m = 0.79$) is not very far away from the slope of the isotherm of $\Delta = 0$ (the thick, dashed line).

Fig. 4.- Valores de $\delta^{34}\text{S}$ medidos en sulfuros solubles en ácidos representados frente a los valores correspondientes a sulfuros insolubles en ácidos. La línea de puntos es la de mejor ajuste a nueve de los datos. Nótese la casi perfecta correlación ($r = 0.99$) a pesar de la muy diferente naturaleza petrológica de las muestras consideradas. La pendiente de esta línea ($m = 0.79$) no es muy diferente de la pendiente de la isoterma de $\Delta = 0$ (la línea gruesa de trazos).

close to the $\Delta = 0$ line, even having been formed at low (diagenetic) temperatures.

In any case, the hypothesis offered requires sulphur derived from a source external to the granite and explains the reason for the Complejo Esquisto Grauváquico shale plotting close to the $\Delta = 0$ line. An anatectic (S-type) origin for the granite cannot be sustained on view of the sulphur isotopic results. At the high temperatures involved in anatectic melting, both pyrite (the non acid-soluble sulphide) and pyrrhotite (the acid-soluble sulphide) should be open to isotopic exchange, and therefore no isotopic differences would be expected between the different granite samples, considering that a melt phase would have been available to reequilibrate the different sulphide minerals, according to those authors that postulate anatectic melting of metasediments as the origin of the granites (see for example Fúster *et al.*, 1974; Franco, 1980; Bea, 1982; Aparicio *et al.*, 1983; Bea and Moreno-Ventas, 1985; Franco and García de Figuerola, 1986). The cordierite-bearing granite is intrusive into higher levels. This implies that the amount of melt is likely to have been around 40% at least (van der Molen and Paterson, 1979; Wickham, 1987). On the other hand, the presence of ilmenite and organic carbon in some samples (see below) is an indication of the likely reducing redox state of the magma. In those conditions, the sulphur dissolved in the mag-

ma should be as H_2S or HS^- (in Ohmoto, 1986). The presence of a volatile sulphur-bearing species in an intruding, probably convecting magma would be expected to result in homogenization of the sulphur isotopic composition of the different sulphides, even considering that some of them might be restitic from the source-rock. Also, if this was to be true, a magmatic isotopic temperature might be expected from the pyrite-pyrrhotite pair in the granites. According to the temperatures shown in table 2, however, only two geologically reasonable isotopic temperatures are obtained for the granites, but that for BEU-15 is out of the experimentally calibrated range for the pyrite-pyrrhotite isotope geothermometer (200-600°C; Ohmoto and Rye, 1979), and therefore not reliable, and XSA-10 cannot be used, since it plots away from the straight line defined by nine other samples in fig. 4. The case for this sample being out of isotopic equilibrium is argued below. The nebulites, however, are obviously anatectic rocks, but they also show inhomogeneous or geologically meaningless temperatures, indicative of lack of isotopic equilibrium. The amount of melt in the nebulites, has not been enough for the magma to intrude, and is unlikely to have been any higher than 20-25% (van der Molen and Paterson, 1979; Vielzeuf and Holloway, 1988; Le Breton and Thompson, 1988). In this situation, even if temperatures high enough for reequilibrium taking place have been reached, the different sulphides have not been reequilibrated because they probably never were in contact with each other, and in the case of the nebulites, there was no volatile phase able to "connect" them. Ugidos (1990) indicates that cordierites in the granite are systematically pinitized, whereas they are mostly fresh in the nebulite. Recio (1990) attributes this to the presence, in the cordierite-bearing granite, of a fluid that did not exist in the nebulite.

What happens, then, with the samples that deviate from such straight line? BEU-18. A is a quartzdioritic macroenclave inside the granite, and the proportion of the acid soluble sulphide sulphide is about half the amount of the non acid soluble sulphide. The less abundant, acid soluble sulphur would have been more easily exchanged should any secondary process (whatever its nature) have been active. The existence of a deuteric fluid operating in the granite has been discussed by Recio (1990) employing textural, geochemical and isotopic data. Should this fluid have disturbed the sulphur isotopic equilibrium, it might be expected to be in the sense of enriching the less abundant sulphide in the sample in the heavy isotope, since the lighter one is more reactive, and thus more easily scavenged.

Alternatively, and given the large size of this enclave, together with evidence of its having been relatively unaffected by possible late deuteric fluids (Recio, 1990), the possibility of the measured values being primary, or retrograde processes having been active, must be taken into account. Since the δ values obtained from acid-soluble and non acid-soluble sulphides are obviously disequilibrium values (pyrrhotite is isotopically heavier than pyrite, when the opposite should be the

	$\delta^{34}\text{S}$ Pyrrhotite	$\delta^{34}\text{S}$ Pyrite	Calculated T °C
CORDIERITE-BEARING GRANITES			
MC-12	-3,9	-3,9	-
XSA-10	-4,2	0,5	527
BEU-15	-2,0	-0,8	775*
NEBULITES			
JAM-2	10,0	13,9	552
ABE-4	4,0	5,2	775*
XSA-3	2,1	9,8	471
PHU-2	0,9	2,1	775*
I-30	2,1	2,8	930*
XSA-1	2,8	3,6	888*
ENCLAVES			
BEU-18.A	13,4	0,2	-
UHR-28	-0,3	0,4	930*

Table 2.- Calculated isotopic temperatures obtained from the acid-soluble and non acid-soluble pairs separated from the nebulites, the cordierite-bearing granites and their enclaves. Calculations have been performed employing the A, B and C constants of table 10.1 and the equations of table 10.3 of Ohmoto and Rye (1979). It was considered for calculation that all acid-soluble sulphide was pyrrhotite and all non acid-soluble sulphide was pyrite. Values marked with an asterisk (*) are geologically meaningless because they are outside the 200-600°C range within which the py-po geothermometer is calibrated.

Tabla 2.- Temperaturas isotópicas calculadas a partir de los pares de sulfuros soluble e insoluble en ácidos separados de nebulitas, granitos biotítico-cordieríticos y sus enclaves. Para los cálculos se han empleado las constantes A, B y C de la tabla 10.1 y las ecuaciones de la tabla 10.3 de Ohmoto y Rye (1979). A efecto de cálculo se consideró todo el sulfuro soluble en ácidos como pirrotita, y el no soluble como pirita. Las temperaturas marcadas con un asterisco (*) no tienen sentido geológico dado que están fuera de los límites 200-600°C dentro de los cuales está calibrado el geotermómetro py-po.

case), some sort of post-formation process has to be admitted. In support of this last possibility is the fact that pyroxene relicts, retrograded to amphibole, have been identified in this sample during microprobe analyses (Recio, 1990). This might be an explanation of why this sample plots alone: its sulphur isotopic composition was conditioned by processes different from those that affected all other samples, and its size prevented reequilibration taking place.

The anomalous character of XSA-10 can similarly be attributed to fluid activity. Again, sulphide content is low, and this particular sample shows a completely pinitized cordierite, as well as KFd megacrysts, both consistent with strong fluid activity towards late magmatic stages. In any case, if the sample originally plotted closer to the straight line, and assuming that fluid activity results, as it is reasonable to think, in enrichment in the heavy isotope, it would have been the non acid-soluble sulphide the one more strongly modified in this sample. From table 1, the non acid-soluble sulphide is clearly less abundant in this sample than the acid soluble sulphide.

Such arguments are not applicable to XSA-3. The amount of sulphur in this sample is high enough to require an explanation different from the above. The ano-

malous character of XSA-3 respect to other isotopic systems has been discussed earlier by Recio (1990; mineral separates $\delta^{18}\text{O}$ values all plot within a few tenths of a permil unit, whereas a wider spread was to be expected), as has the fact that true nebulitic material coexists with schistose material in which the reactions that generated the cordierite nebulite have not been completed (i. e., biotite + sillimanite can still be found). The lack of sulphur isotopic equilibrium in this sample is therefore no surprise.

Carbon compounds have only been found in sediments (Complejo Esquisto Grauváquico samples) or sediment-related samples (as cordierite bearing granites and nebulites). This is a first indication that the carbon bearing compounds had a surficial origin, probably as organic matter trapped in the sediments. This is clearly corroborated by the HR samples, whose $\delta^{13}\text{C}$ values (-24.0; -27.0‰) are quite typical of organic matter in sedimentary rocks (see for example Leventhal *et al.*, 1987; Eakin, 1989, or Schwarcz, 1969, in Ohmoto and Rye, 1979). The $\delta^{13}\text{C}$ value of -37.0‰ for the third Complejo Esquisto Grauváquico sample, although not as typical, is also acceptable as indicator of an origin after organic matter. The cordierite bearing granite and the nebulite sample, however, cannot represent simply trapped organic matter, and therefore require a different explanation. Whatever their origin, it is remarkable that the isotopic composition is the same in both samples, so that it is logical to think of a common origin for the carbon in both the nebulite and the cordierite-bearing granite. Identical $\delta^{13}\text{C}$ values have been reported by Leventhal *et al.* (1987) in organic matter associated to pegmatites in Canada.

Because of the very limited data-set, the discussion will not be taken further here, although the C isotopic signature is considered important enough as to deserve proper attention, such that it will be one of the priorities of future research efforts. It is however relevant, in the absence of other type of data, to note that the presence of reduced organic carbon in the granites is an indicator of the reduced redox state of the granitic magma.

5. CONCLUSIONS

Sulphur isotopic ratios measured in acid- and non

Sample	$\delta^{13}\text{C}$	Type of sample
I-30	-44.2	Nebulite
BEU-15	-44.2	Cordierite-bearing Granite
HR-44	-24.0	Complejo Esquisto Grauváquico Sample
HR-42	-27.0	Complejo Esquisto Grauváquico Sample
GU-21	-37.0	Complejo Esquisto Grauváquico Sample

Table 3.- $\delta^{13}\text{C}$ results obtained by analysis of organic materials extracted from granitoid and sediment samples from the Sistema Central Español.

Tabla 3.- Valores de $\delta^{13}\text{C}$ obtenidos por análisis de materiales orgánicos extraídos de granitoides y sedimentos del Sistema Central Español.

acid-soluble sulphides separated from granitoids, their enclaves and their host-rocks in the western area of the Sistema Central indicate that the sulphur found in the granites is most probably derived from a source external to the granite. That source is likely to be the nebulites, and ultimately the Complejo Esquisto Grauváquico host-rocks. A minor part of the sulphur, however, may be of igneous derivation, as indicated by its presence in basic to intermediate enclaves, but this has been volumetrically unimportant, as proved by its absence (or its presence in quantities below detection limit) in biotite and amphibole-bearing granites. Even if isotopically distinct sulphur was originally present, this may have suffered a thermal event that reequilibrated it with the externally derived sulphur and masked its nature.

Carbon isotopic ratios are distinctive of sedimentary organic carbon in the Complejo Esquisto Grauváquico samples, but their significance remains enigmatic in the nebulite and the cordierite-bearing granite. It

is intriguing, however, to note that identical values have been reported by Leventhal *et al.* (1987) for carbon in pegmatites found in similar granitic areas in Canada.

The derivation of sulphur from sources external to the granites is consistent with those hypotheses that indicate assimilation processes as responsible for the generation of the Sistema Central cordierite-bearing granites, as indicated for example by Ugidos (1988, 1990), Ugidos *et al.* (1989) or Recio (1990).

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