

# Application of specific extraction chromatographic methods to the Rb-Sr, Sm-Nd isotope study of geological samples: The Hombreiro-Santa Eulalia Granite (Lugo, NW Spain)

*Aplicación de métodos de cromatografía de extracción específica al estudio isotópico de Rb-Sr, Sm-Nd en muestras geológicas: el granito de Hombreiro-Santa Eulalia (Lugo, NW de España)*

J. F. Santos Zalduegui (\*), C. Pin (\*\*), A. Aranguren (\*\*\*) and J. I. Gil Iburguchi (\*)

(\*) Dpto. Mineralogía y Petrología, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, 48080 BILBAO

(\*\*) Département de Géologie Université Blaise Pascal, URA 10,5 Rue Kessler, 63038 Clermont-Ferrand Cedex

(\*\*\*) Dpto. de Geodinámica, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, 48080 BILBAO

## ABSTRACT

The analytical application to geological samples of three new chromatographic resins, TRU-Spec<sup>®</sup>, Sr-Spec<sup>®</sup> and LN-Spec<sup>®</sup> has been investigated. Seven samples of the Hombreiro massif (Lugo, NW Spain) have been studied, that yield a Rb-Sr age of  $298 \pm 5$  Ma ( $Sr_o = 0.7086$ , MSWD = 1.64) for the magma crystallization. Sm-Nd data results for the same massif give  $\epsilon_{Nd}$  values close to -2 at 300 Ma. This suggests that the origin of the magma might be related to the partial melting of immature sediments, likely involving volcanoclastic sequences.

## RESUMEN

Se han investigado las posibilidades analíticas, en muestras geológicas, de tres nuevos tipos de resinas cromatográficas, TRU-Spec<sup>®</sup>, Sr-Spec<sup>®</sup> y LN-Spec<sup>®</sup>. A partir de siete muestras estudiadas, pertenecientes al macizo de Hombreiro (Lugo, NW de España), se ha obtenido una una edad Rb-Sr, para la cristalización del magma, de  $298 \pm 5$  Ma ( $Sr_o = 0.7086$ , MSWD = 1.64). Los resultados de Sm-Nd, indican un valor de  $\epsilon_{Nd}$  cercano a -2 para una edad de 300 Ma. Todo ello sugiere que el origen de dicho magma se puede relacionar con la fusión parcial de sedimentos poco evolucionados, posiblemente asociados a secuencias volcanoclásticas.

**Key words:** Chromatographic methods, Rb-Sr age, Sm-Nd, Hombreiro-Santa Eulalia, Hercynides

Geogaceta, 20 (2) (1996), 495-497

ISSN: 0213683X

## Introduction

The use of cationic and anionic resins in isotope analyses of geological samples is a well-established procedure. However, the employment of these resins is often exceedingly time consuming and/or requires the use of great amounts of reagents. A new generation of extraction chromatographic materials have been developed recently at the Argonne National Laboratory (USA). These include TRU-Spec<sup>®</sup>, Sr-Spec<sup>®</sup> and LN-Spec<sup>®</sup>. Pin and Bassin (1992) and Pin *et al.*, (1994) have demonstrated the usefulness of these new resins for separation of Sr and Sm-Nd on geological standard reference materials.

In this study we present an improved procedure for the separation of Sm, Nd and Sr from geological samples of granitic composition. The method uses

a combination of two columns, partially superposed, that contain TRU-Spec<sup>®</sup> and LN-Spec<sup>®</sup> for Sm-Nd separation. A third column with Sr-Spec<sup>®</sup> is used for Sr separation.

This method of separation has been applied to the geochemical and geochronological (Sr and Sm-Nd) study of the Hombreiro and Santa Eulalia de Pena granite pluton. Sr data are used in combination with Rb data to determine the age of emplacement of the igneous body. Moreover, they are used in combination with Sm-Nd data to obtain information on the materials that participated in the genesis of the granite magma.

## Experimental procedure

TRU-Spec<sup>®</sup> and Sr-Spec<sup>®</sup> show great affinity for transuranids and Sr, respectively (Chiarizia *et al.*, 1992; Horwitz *et al.*,

1992, 1993). While LN-Spec<sup>®</sup> is a more classical extraction chromatographic material based on the properties of di-ethyl-hexyl phosphoric acid (HDEHP). The scheme for separating Sm, Nd and Sr from silicate rocks is as follows:

TRU-Spec	LN-Spec
Conditioning	
Sample introduction	
Rinsing of major elements	Conditioning
Coupling of two columns	
REE elution	Receiving elution
Decoupling of columns	
	La-Ce-Pr elution
	Nd elution
	Sm elution

The procedure is to be used on the same solution and differs from published schemes in the coupling/decoupling step allowing for full separation in a single experiment. Further details on reagents used, dimension of silica-glass columns, quantity of resin,

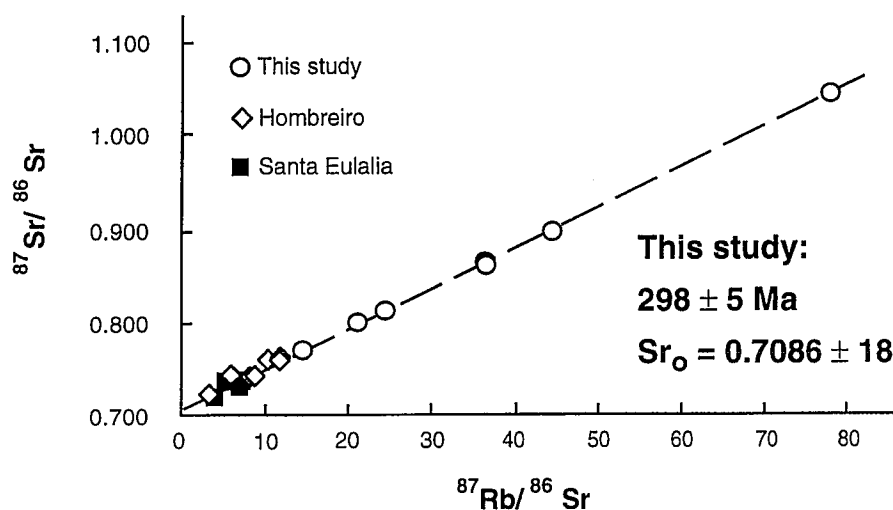


Fig. 1.- Rb-Sr whole-rock isochron diagram for samples from the Hombreiro granite massif. Circles: this study; square and rhombs: previous data (see text for details).

Fig. 1.- Isocrona Rb-Sr para muestras del macizo granítico de Hombreiro. Círculos: este estudio; cuadrados y rombos: datos previos (ver texto para detalles).

memory effects, etc. are given elsewhere (Pin and Bassin, 1992; Pin *et al.*, 1994; Pin *et al.*, in prep.).

#### Geological application

The Hombreiro-Santa Eulalia granite massif is located in the western sector of the West-Asturian Leonese Zone, near the boundary with the Central Iberian Zone. It forms part of the Lugo dome mega-structure in the inner part of the Mondoñedo thrust nappe (Bastida *et al.*, 1986). The granite intruded Precambrian micaschists of the Villalba Series and is affected by thrust tectonics of the Mondoñedo nappe (D2) and by the Vivero normal fault (post-D2 extensional normal fault) compatible with a bulk E-W directed crustal shortening (Pérez-Estaún *et al.*, 1991; Aranguren and Tubía, 1992, Martínez *et al.*, 1996).

Published whole rock Rb-Sr data (5 analyses) for the heterogranular facies of the Hombreiro massif (Bellido *et al.*, 1992) show considerable dispersion and high analytical errors that result in a poorly constrained age estimate of  $295 \pm 58$  Ma ( $Sr_0 = 0.70147$ ). Additional data have been presented by Cocherie (1978, 1 analysis) and Peucat *et al.*, (in prep., 1 analysis) that do not allow for a better geochronological result. As for the Santa Eulalia de Pena granite, three whole rock Rb-Sr analyses obtained by Peucat *et al.*, (in prep.) fit to a value of  $318 \pm 14$  Ma ( $Sr_0 = 0.70406$ ).

Seven new samples from the Hombreiro granite have been analyzed. Samples JF1, JF6, JF7 and JF3 are from deformed outer areas of the granite. The remaining samples (JF2, JF4, JF5) are either from inner or from external undeformed zones of the granite (cf. Aranguren, 1994). All samples analyzed in this work present  $^{87}\text{Rb}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  values higher than those previously published (Fig. 1, Table 1). The age obtained for the seven point isochron is  $298 \pm 5$  Ma (MSWD = 1.64) with and  $Sr_0 = 0.7086 \pm 0.0018$ . Inclusion of results presented by Bellido *et al.*, (1992, excluding sample 4232 of doubtful assignment to this massif), Cocherie (1987) and Peucat *et al.*, (in prep), yields the following values:  $302 \pm 12$  Ma,  $Sr_0 = 0.707245$  and MSWD = 2.37.

The same samples of the Hombreiro granite have been analyzed for Sm-Nd (cf. results in Table 1). The data obtained do not yield an isochron. Samples JF1 and JF6 show relatively high Sm-Nd concentrations by comparison with those of the other five samples. The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios, reported as  $\epsilon_{\text{Nd}}$ , range from -1.8 to -3.5 at 300 Ma. CHUR ages vary from 0.7 to 1 Ga, except for sample JF3 that yielded a too high 4.3 Ga age. This most likely reflects fractionation of Sm/Nd at the time of granitic magma genesis, and/or crystallization (ex: monazite fractionation), and violates basic assumptions of model ages calculation. No correlation between

the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio ( $\epsilon_{\text{Nd}}$ ) and the 1/Sm content or  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio could be established.

#### Discussion and conclusions

The new method for the concomitant extraction of Sr and Sm-Nd from the same sample solutions employed is based on the specificity of Sr-Spect<sup>®</sup> and TRU-Spec<sup>®</sup>. The coupling of TRU and LN-Spec<sup>®</sup> columns permits a direct extraction of Sm and Nd considerably reducing the time of manipulation compared to previous methods which involved a two-step procedure, with a first separation of the REE followed by the isolation of Sm and Nd.

Nd data presented for the Hombreiro granite show relatively high  $\epsilon_{\text{Nd}}$  values at 300 Ma (ca. -2). This suggests that the origin of the magma might be related to the partial melting of immature sediments, likely involving volcanoclastic sequences, or the participation of igneous mafic magmas in the process of crustal melting. The first hypothesis is preferred here in view of the generalized absence of mafic enclaves within the granite (Aranguren, 1994). A CHUR model age between 0.7 to 1 Ga suggests that a relatively young crustal sequence was involved in the origin of the granite magma. Tectonic models for this sector of the Hercynides involve development of a thickened pile in relation to thrust-nappe stacking during the Hercynian collision (Pérez Estaún *et al.*, 1991; Aranguren and Tubía, 1992). The present data would be in agreement with the generation of granite magmas in such a tectonic setting.

The age of  $298 \pm 5$  Ma provided by the Rb-Sr data for the crystallization of the magma may be considered as a minimum age for the regional Hercynian deformation (D2). Similar ages have been reported for granitic plutons elsewhere within the NW Iberian massif, though these were generally not so well constrained from the structural point of view (e. g. Serrano and Gil Ibarguchi 1987, Bellido *et al.*, 1992).

#### Acknowledgements

This study was carried out during the post-doctoral stage at the University of Clermont-Ferrand of JFSZ. Financial support was provided essentially by grants EX94.15372041 of Spanish DGICYT and the Spanish-French Collaboration 1996 (81B). Additional support

Sample	Concentration (ppm) <sup>a</sup>		(per mil 1σ)		ε <sub>Chur</sub> <sup>b</sup>	CHUR age
	Sm	Nd	<sup>143</sup> Sm/ <sup>144</sup> Nd	<sup>143</sup> Nd/ <sup>144</sup> Nd		
JF-1	2.49	9.04	0.1665	0.512474 ± 0.007	-2.1	0.8
JF-2	1.54	5.48	0.1702	0.512496 ± 0.012	-1.8	0.8
JF-3	1.23	3.93	0.1899	0.512447 ± 0.017	-3.5	4.3
JF-4	1.40	5.20	0.1633	0.512430 ± 0.008	-2.8	1.0
JF-5	1.53	5.61	0.1652	0.512488 ± 0.011	-1.8	0.7
JF-6	3.43	12.6	0.1654	0.512461 ± 0.009	-2.3	0.9
JF-7	1.72	5.98	0.1741	0.512447 ± 0.006	-2.9	1.3

Sample	Concentration (ppm) <sup>c</sup>		(per mil 1σ)	
	Rb	Sr	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr
JF-1	354	28.6	36.4	0.86481 ± 0.014
JF-2	205	41.6	14.3	0.76897 ± 0.016
JF-3	256	30.7	24.4	0.81249 ± 0.015
JF-4	290	23.3	36.6	0.86053 ± 0.014
JF-5	424	16.2	78.2	1.04232 ± 0.012
JF-6	286	40.0	20.90	0.79823 ± 0.009
JF-7	307	20.3	44.60	0.89676 ± 0.010

<sup>a</sup> Measured with spiked samples

<sup>b</sup> Calculated at 0.3 Ga

<sup>c</sup> Measured by WD-XRF at Ecole Nationale des Mines d'Alès (Francia) following methods outlined by Pin (1989). <sup>87</sup>Rb/<sup>86</sup>Sr ratio given with an error of 2 %

Table 1.- Sm-Nd and Rb-Sr analytical results for seven samples of the Hombreiro granite massif.

Tabla 1.- Resultados analíticos para siete muestras del macizo granítico de Hombreiro

came from grants PB92.470 (DGICIT) and EB033.93 (UPV).

#### References

- Aranguren, A. (1994). *Lab. Xeol. Laxe* "Serie Nova Terra" N° 10, 237 pp
- Aranguren, A. and Tubía, J.M. (1992). *Jour. Struct. Geol.*, 14, 10, 1229-1237.
- Bastida, F.; Martínez Catalán, J.R. and Pulgar, J.A. (1986). *Jour. Struct. Geol.*, 3/4, 8, 415-430.
- Bellido, F., Brandle, J.L., Lasala, M. and Reyes, J. (1992). *Cuad. Lab. Xeol. Laxe*, 17, 241-261.
- Chiarizia, R.; Horwitz, E.P. and Dietz, M.L. (1992). *Solvent Extr. Ion. Exch.*, 10: 337
- Cocherie, A. (1978) *These Univ. Rennes*, 210 pp.
- Horwitz, E.P.; Chiarizia, R. and Dietz, M.L. (1992). *Solvent Extr. Ion. Exch.*, 10: 313
- Horwitz, E.P.; Chiarizia, R.; Dietz, M.L.; Diamond, H. and Nelson D.M. (1993): *Anal. Chem Acta*, 281: 361
- Martínez, F.J.; Carreras, J. and Arboleya, M.L. (1996). *Jour. Struct. Geol.*, 18, 1, 61-73
- Perez-Estaún, A., Martínez Catalán, J.R. and Bastida, F. (1991). *Tectonophysics.*, 191, 243-253.
- Pin (1989). *These Univ. Clermont-Ferrand II*, 500 pp.
- Pin, C. and Bassin, C. (1992). *Anal Chem Acta*, 269: 249
- Pin, C.; Briot, D.; Bassin, C. and Poitrasson, F. (1994). *Anal. Chim Acta*, 298: 209-217
- Serrano Pinto and Gil Ibarguchi (1987). *Mem. Mus. Labor. Miner. Geol.*, Fac. Ciencias do Porto N°1: 171-186