

# Nd isotopic heterogeneity in late-Hercynian granitic plutons from Central Spain

*Heterogeneidades isotópicas de Nd en plutones graníticos tardi-hercínicos de la Región Central Española*

C. Villaseca (\*), L. Barbero (\*\*), G. Rogers (\*\*\*), J. Reyes (\*\*\*\*), and J. F. Santos Zalduegui (\*\*\*\*\*)

(\*) Dpto. Petrología y Geoquímica, Facultad C. C. Geológicas, Universidad Complutense, 28040 Madrid

(\*\*) Dpto. Geología, Facultad C. C. del Mar, Universidad de Cádiz, 11510 Puerto Real, Cádiz

(\*\*\*) SURRC, Isotope Geosciences Unit, East Kilbride, Glasgow, G75 0QF, Reino Unido

(\*\*\*\*) ITGE, Ríos Rosas, 23, 28003 Madrid

(\*\*\*\*\*) CAI Geocronología y Geoquímica Isotópica, Universidad Complutense, 28040 Madrid

## ABSTRACT

Some Hercynian granitic plutons from Central Spain show variation in initial Nd isotopic ratios defining different trends with increasing silica content. There is a decoupling between the Sr and Nd isotopic systems as these plutons present homogeneous initial Sr ratios. Magmatic processes could explain this Nd isotopic disequilibrium; it is suggested that Nd-bearing restitic or early precipitating accessory phases could control the Nd isotopic heterogeneity of the granites.

**Key words:** Sr and Nd isotopes, Hercynian granites, open/closed magnetic processes.

## RESUMEN

Algunos plutones graníticos hercínicos muestran diversas pautas de heterogeneidad en isótopos de Nd según sea la acidez de la roca. Como en relaciones isotópicas de Sr son homogéneos, hay un desacoplamiento entre ambos sistemas isotópicos. Se discuten las posibilidades de generar disequilibrios isotópicos de Nd en diversos procesos magmáticos y el papel dominante de los minerales accesorios, principales portadores de Nd, que pueden ser de origen restítico o de cristalización precoz.

Geogaceta 23 (1998), 165-168

ISSN: 0213683X

## Introduction

With the increasing availability of isotopic data, it is becoming progressively clear that certain plutons show variable degrees of Nd isotopic heterogeneity, even in cases where they show Sr isotopic homogeneity, thus indicating a decoupling between both isotopic systems (Ben Othman *et al.*, 1984; Siebel *et al.*, 1995).

In the European Hercynides, several plutons such as those from the Pyrenees (Ben Othman *et al.*, 1995), Corsica (Poitrasson *et al.*, 1994), French Massif Central (Downes *et al.*, 1997) or Bohemia (Siebel *et al.*, 1995) show heterogeneity in the initial Nd isotopic signature. Also, in felsic magmatic systems of recent age, this heterogeneity has been also observed (Halliday *et al.*, 1989).

In the present work, Sr-Nd isotopic data from three granitic plutons from the Spanish Central Region (including Montes de Toledo and Sierra de Guadarrama) are presented. Different types of initial Nd isotopic variations observed in the

considered granitic plutons are described and several hypotheses for the origin of this Nd isotopic disequilibrium are discussed.

## Granitic types from the Spanish Central Region

The three granitic massifs considered in this study are located in the axial part of the Hercynian Central Iberian zone. They were intruded during late Hercynian times, post-dating the metamorphic climax, and generated contact aureoles in the surrounding metamorphic country rocks. The Mora pluton is the biggest ( $> 500 \text{ km}^2$ ) and oldest ( $320 \pm 8 \text{ Ma}$ , Rb-Sr whole-rock age from Andonaegui, 1990) of the studied massifs. It is a typical peraluminous pluton with accessory amounts of cordierite in all the petrographic varieties. The Mora pluton is a PS type following the nomenclature of Villaseca *et al.* (1993). La Cabrera pluton ( $\approx 160 \text{ km}^2$ ) has an Rb-Sr whole-rock age of  $310 \pm 14 \text{ Ma}$  (Vialeto *et al.*, 1981). Finally, La Atalaya Real pluton is the smallest ( $\approx 18 \text{ km}^2$ ) and youngest ( $284 \pm 13 \text{ Ma}$ , Villaseca

*et al.*, 1995) of the three massifs. The latter two plutons have variable amounts of accessory amphibole and allanite and are less peraluminous than the Mora pluton; they are included in the PI typology of Villaseca *et al.* (1993). Petrographic and geochemical characteristics of these granite types are described in previous works (Villaseca *et al.*, 1993; Villaseca and Barbero, 1994; Villaseca *et al.*, *in press*). Samples for this work have been collected from the different petrographic facies of the plutons, including the dominant granodioritic - monzogranitic lithologies and the more leucocratic varieties, which are normally interpreted as representing fractionated liquids from monzogranitic parental magmas (Bellido, 1979; Andonaegui and Villaseca, *in press*).

## Analytical techniques

Isotopic analyses were performed at SURRC (East Kilbride, U. K.) (11 samples) and at the Isotope Geochemistry laboratory of the CAI of the Complutense University

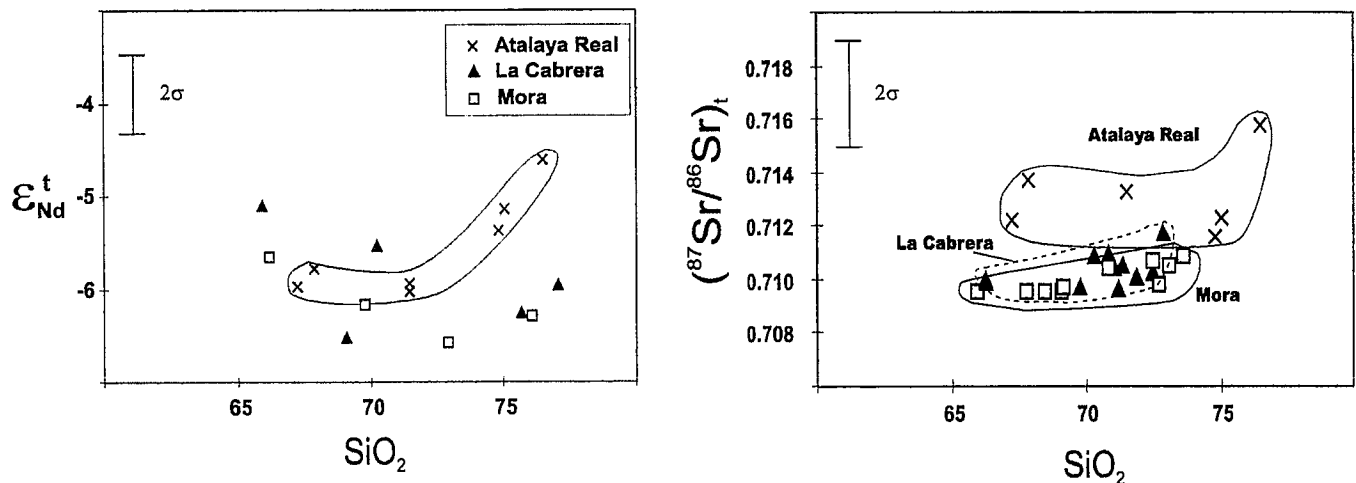


Fig. 1.-  $\epsilon_{Nd}^t$  and  $(^{87}Sr/^{86}Sr)_t$  vs.  $SiO_2$  at the time of the emplacement of the different plutons. Analytical error bars ( $2\sigma$ ) are also shown in the diagrams.

Fig. 1.- Diagramas de  $\epsilon_{Nd}^t$  y  $(^{87}Sr/^{86}Sr)_t$  vs.  $SiO_2$  calculados para la edad de emplazamiento de cada plutón. Se muestran las barras de errores analíticos ( $2\sigma$ ).

(Madrid, Spain) (6 samples). In both laboratories dissolution, concentration and separation techniques for Sm and Nd were similar, following the methods described in Barbero *et al.* (1995) and Reyes *et al.* (1997). Sm and Nd contents were determined by ICP-MS techniques in the laboratories of CNRS (Nancy, France). At both SURRC and Madrid Nd isotopic ratios were measured using a VG SECTOR 54 thermal ionisation mass spectrometer. Consistency of the analysed samples is

demonstrated by the almost total coincidence in Nd isotopic ratios of three samples that were measured in both laboratories (see table 2 in Reyes *et al.*, 1997).

Nd isotope geochemistry

On figures 1 and 2 initial Sr and Nd isotopic ratios are plotted against  $SiO_2$  and Nd contents. In both figures initial Nd isotopic heterogeneity is evident. Two types

of patterns with respect to the initial Nd ratio can be distinguished. The first is defined by an increase in the initial Nd isotopic ratio with increasing  $SiO_2$  content and decreasing Nd concentration; that is, an increase in the initial Nd isotopic ratio towards the more evolved and felsic varieties. This trend is exemplified by La Atalaya Real pluton. The second type of pattern is defined by the other two studied granitic plutons, and is characterised by slightly decreasing initial  $^{143}Nd/^{144}Nd$  with increasing silica content of the rock (Fig. 1). In general, evolution of initial Nd isotopic ratios is more poorly constrained in this second type of trend, especially in the case of the Mora pluton where the range of variability in the Nd data is close to the range of analytical error (Fig. 1). Trends of decreasing initial  $^{143}Nd/^{144}Nd$  ratio with increasing  $SiO_2$  content of the granite, have been noticed in certain Hercynian granites from France (Massif Central: Downes *et al.*, 1997 or Pyrenees: Ben Othman *et al.*, 1984).

It is important to note that not all the granitoids from the Spanish Central Region show significant Nd isotopic heterogeneity, for example, the Ventosilla pluton (Villaseca *et al.*, this volume) is isotopically homogeneous in terms of Sr and Nd. Also, it is important to note that in these three plutons, the heterogeneity is much more marked in Nd than in Sr isotopes (Fig. 1) which is highlighted by the fact that in the three cases Rb-Sr whole-rock isochrons have been fitted to the data (Viale *et al.*, 1981; Andonaegui, 1990; Villaseca *et al.*, 1995). We caution that for high Rb/Sr rocks, such as these felsic granites, a small error in Rb/Sr determination change significantly the calculated initial  $^{87}Sr/^{86}Sr$ . For example, assuming a rock with  $^{87}Rb/^{86}Sr = 30$  and  $T = 300$  Ma, a change of 2% in  $^{87}Rb/^{86}Sr$  ratio,

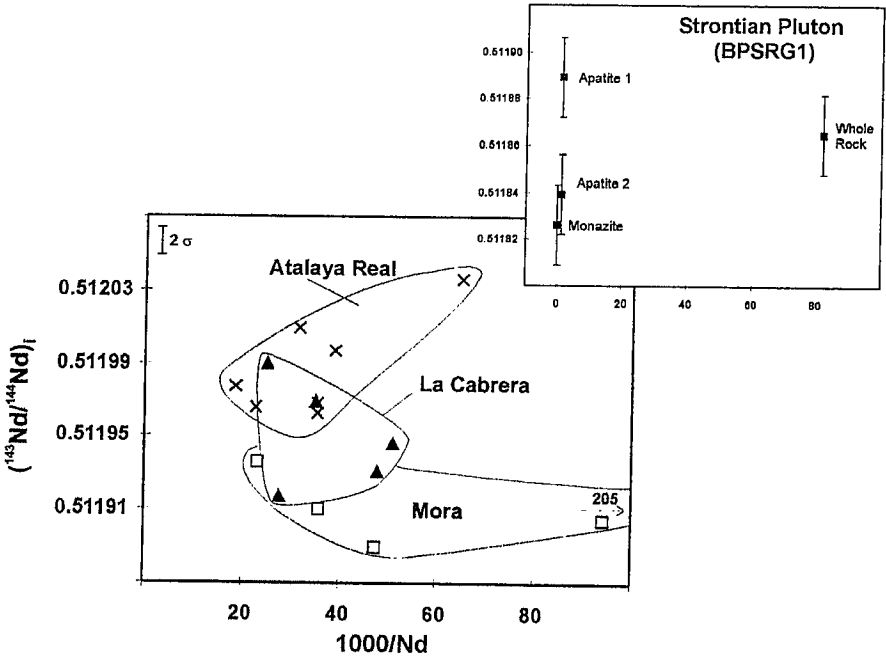


Fig. 2.-  $(^{143}Nd/^{144}Nd)_i$  ratio vs.  $1000/Nd$  calculated at the time of plutonic emplacement. Analytical error bar  $\pm 2\sigma$  in the  $^{143}Nd/^{144}Nd$  ratio is also shown in the diagram. The inset shows data for mineral separates and the whole-rock from sample BPSRG1 from the Strontian Pluton (Paterson *et al.*, 1992).

Fig. 2.- Diagrama de relaciones iniciales  $(^{143}Nd/^{144}Nd)_i$  vs.  $1000/Nd$ , calculadas para la edad de emplazamiento plutónico. Se muestra la variación debida a los errores analíticos ( $2\sigma$ ) en el cálculo de la relación  $^{143}Nd/^{144}Nd$ . También se muestra un diagrama con datos de roca total y minerales separados de la muestra BPSRG1 del plutón de Strontian (Paterson *et al.*, 1992).

which is considered to be around our analytical error (Villaseca *et al.*, 1995), would introduce a shift in the age-corrected  $^{87}\text{Sr}/^{86}\text{Sr}$  by 0.004. So, by considering such analytical errors, no Sr isotopic heterogeneities are found in these plutons (Fig. 1). In contrast, the variation shown by initial Nd isotopic ratios of the studied granites are clearly bigger than the errors attained during analysis (Fig. 1 and 2). Furthermore, the Sm/Nd ratio of granites may be subjected to only minor changes in geological processes due to their limited fractionation during magmatic evolution and the general immobility of REE during metamorphism and alteration (Rollinson, 1993). With our data it is not possible to define clear linear correlations in  $^{143}\text{Nd}/^{144}\text{Nd}$  vs.  $^{147}\text{Sm}/^{144}\text{Nd}$  diagrams.

### Discussion

The presence of initial Nd isotopic heterogeneity has been usually interpreted in the light of an open magmatic system whose duration was short enough to preclude re-equilibration of the different magma batches. As magma mixing and crustal contamination processes have not been described as being the mechanism producing the chemical variability in the studied plutons (Bellido, 1979; Andonaegui, 1990; Eugercios *et al.*, 1995), in the next section the possibility of creating Nd isotopic heterogeneities in magmatic closed systems undergoing fractional crystallization processes is also considered.

#### a) Isotopic disequilibrium related to open magmatic systems (mixing, contamination, source heterogeneity...)

It is sometimes sometimes accepted that differences in the initial Nd isotopic composition, specially those showing linear trends in chemical diagrams as that of figure 2, (La Atalaya Real pluton) are suggestive of mixing between melts that do not reach complete Nd isotopic equilibrium (Siebel *et al.*, 1995). In certain cases like that of the Gueret pluton (Downes *et al.*, 1997), in which there is also a linear variation in the initial Sr isotopic ratios, the mixing hypothesis seems plausible. In other cases there is a clear decoupling between the Sr and Nd isotopic systems with Sr isotopes showing more homogeneity (Bohemian plutons, Siebel *et al.*, 1995).

Nd and Sr decoupling can be certainly explained by the fact that diffusion rates for rare earth elements are much lower than those for Sr (Cherniak and Ryerson, 1993), as has also been stated concerning the petrogenesis of mafic microgranular enclaves (Holden *et al.*, 1987). Also, early precipitation of REE-rich accessory phases

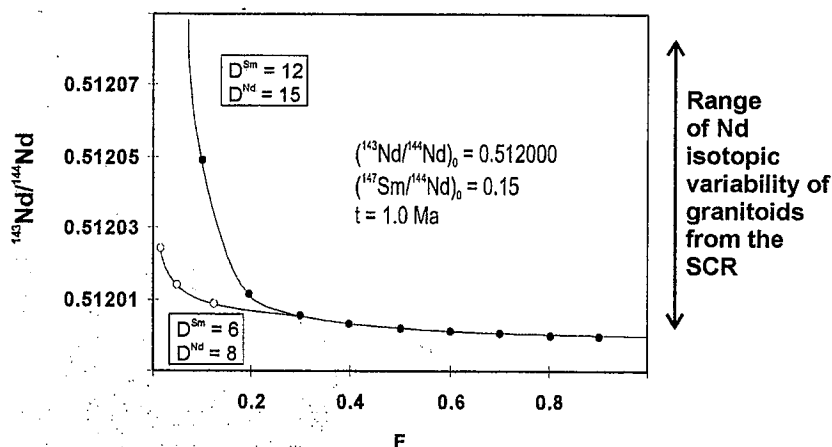


Fig. 3.- Evolution of the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio in a residual liquid of a magma evolving through fractional crystallisation as a function of the fraction of residual liquid remaining (F). Black points have been calculated for  $D^{\text{Sm}}$  and  $D^{\text{Nd}}$  of 12 and 15 respectively. Open dots represent a two step model in which at  $F=0.3$  a change in the bulk partition coefficient to values of  $D^{\text{Sm}} = 6$  and  $D^{\text{Nd}} = 8$  has been produced.

Fig. 3.- Evolución de la relación inicial de  $^{143}\text{Nd}/^{144}\text{Nd}$  en el líquido residual de un sistema magmático que evoluciona por fraccionamiento cristalino, en función de la fracción remanente del mismo (F). Los puntos negros son cálculos con  $D^{\text{Sm}}$  y  $D^{\text{Nd}}$  de 12 y 15, respectivamente. Los puntos huecos representan un modelo con una segunda etapa a partir de  $F=0.3$ , donde hay un cambio en los coeficientes globales de partición:  $D^{\text{Sm}} = 6$  y  $D^{\text{Nd}} = 8$ .

could partially retain the Nd isotopic composition of the first melts, which due to the low diffusion rate of the REE could prevent total re-equilibration of the Nd isotopic signature during the mixing process. In granites, the presence of accessory minerals which have initial Nd isotopic ratios out of equilibrium with respect to the whole-rock and other accessory phases is normally interpreted in terms of the accessory phases being restitic (zircons in von Blanckenburg, 1992; zircons in Paterson *et al.*, 1992; monazites in Edwards and Harrison, 1997).

There are two main objections arise against this kind of processes as the explanation for the Nd isotopic heterogeneities found in the studied plutons. First, the studied granitic plutons show a chemical variation that is well explained by common fractional crystallization mechanisms. The well defined decrease in some major (Fe, Mg, Ti, Ca, Al) and trace (Sc, V, Ba, Sr, Eu, Zr, LREE) elements shown by the granites is interpreted as progressive crystallization of major and minor phases typical in acidic magmas (Andonaegui, 1990; Eugercios, 1995). Moreover, numerical modelling reproduces the chemical trends of those plutons (Andonaegui and Villaseca, in press; Villaseca *et al.*, submitted), supporting the geological lack of important magmatic mixing or contamination evidence.

A second objection is the nature of the theoretical mixing (or contaminant) poles. This is exemplified by the Atalaya Real

trend, which has the best defined initial Nd isotopic heterogeneity. The two components that may explain this trend are two crustal components ranging between a Sr-poor, metasedimentary-derived melt (pole A, with  $\text{ENd}_i = -6$  and  $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.710$  to  $0.712$ ) and a highly evolved crustal source (pole B, with  $\text{ENd}_i = -4$  to  $-3$  and  $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.716$ ). The best fit to the trend of Atalaya Real pluton would be a mixing hyperbola with a value of  $K_{\text{Sr/Nd}} = (\text{Sr/Nd})_A / ((\text{Sr/Nd})_B)$  much less than 1. Crustal materials of the Spanish Central Region usually do not show significant differences in Sr/Nd ratios (i.e. Fig. 6 of Villaseca *et al.*, 1993).

#### b) Generation of Nd isotopic disequilibrium in a closed magmatic system

Nd isotopic ratios increase with time depending on the Sm/Nd ratio of the melt following the classic equation: (1)

$$^{143}\text{Nd}/^{144}\text{Nd} = (^{143}\text{Nd}/^{144}\text{Nd})_0 + ^{147}\text{Sm}/^{144}\text{Nd}(e^{\lambda t} - 1)$$

As magmatic systems are generally short lived ( $< 10^6$  years), and the Sm/Nd ratio of the majority of magmas is low and fairly uniform, the possibility of changing the  $^{143}\text{Nd}/^{144}\text{Nd}$  during the crystallisation of a magma is highly unlikely. For example, in 1 Ma, for an average  $^{147}\text{Sm}/^{144}\text{Nd} = 0.15$ , an initial  $^{143}\text{Nd}/^{144}\text{Nd}$  of 0.512000 would change to 0.512001, which is insufficient to explain the variations found in the Spanish Central System plutons. We can modify equation (1) for introducing the effect of fractionation, i. e. the change in the Sm/Nd ratio as the magma evolves, in the same way as Cavazzini (1994) does for the Rb-Sr

system (equation 7 of Cavazzini, 1994), obtaining: (2)

$$^{143}\text{Nd}/^{144}\text{Nd} = (^{143}\text{Nd}/^{144}\text{Nd})_0 + \lambda t \text{ Sm}/^{144}\text{Nd} f$$

where  $f = (1 - F^{b+1})/(b+1)$ ,  $b = D^{\text{Sm}} - D^{\text{Nd}}$  (bulk partition coefficients) and  $F$  is the fraction of residual liquid.

Equation 2 gives similar results to equation 1 for all cases except if the REE behaves in the magmatic system as highly compatible elements. In this way, if we consider the crystallisation of accessory amounts ( $\leq 0.25\%$  vol.) of allanite ( $K_d^{\text{Nd}} = 1620$  and  $K_d^{\text{Sm}} = 867$ , Mahood and Hildreth, 1983) and/or monazite ( $K_d^{\text{Nd}} = 4500$  and  $K_d^{\text{Sm}} = 3830$ , Cocherie *et al.*, 1994), the bulk partition coefficients ( $D$ ) could reach values of 15 and 12 for Nd and Sm respectively. With these  $D$  values, the  $f$  parameter in equation (2) can be high even for high degrees of fractionation ( $F = 0.1$ ) and, if the duration of the magmatic system is  $10^6$  years, the Nd isotopic ratios would change from an initial value of 0.512000 to 0.512049 (Fig. 3). If we consider a shorter magmatic system of  $10^5$  to  $5 \cdot 10^5$  years, as seems more realistic, the change from an initial Nd isotopic ratio of 0.512000 would be to 0.512005 or 0.512025 respectively.

Such highly compatible behaviour for the REE could be only possible at certain moments and places in the system where the crystallisation of monazite or allanite were taking place. If the bulk partition coefficients for the REE during the crystallisation of the granitic magma were as high as mentioned above (15 for Nd and 12 for Sm), the residual granitic liquid would be totally exhausted in REE even at low degrees of fractionation ( $F = 0.8$ ), which is not observed in the granites of the area. Lower bulk distribution coefficients would produce variations in the initial Nd isotopic ratios much lower than those observed. In summary, crystal fractionation using geologically reasonable values for the bulk partition coefficients and other parameters of the process cannot produce sufficient variation in the initial Nd isotopes ratios to explain the observed Nd isotopic heterogeneity.

At this point, it is important to remember that Paterson *et al.* (1992) in their study of accessory minerals from the Strontian pluton (Scotland) found slight differences in initial Nd ratios between the monazite and the whole rock of the same magnitude to that observed in the Spanish Central Region granites (see inset in Fig. 2). Nevertheless, the errors attained in that

analytical work overlap much of the isotopic variation (Fig. 2) indicating that the degree of disequilibrium (if any) is insignificant (Paterson *et al.*, 1992). Monazite in the Strontian pluton does not present important zoning, neither residual nucleus, and, coupled with the initial Nd isotopic equilibrium with the whole-rock and co-existing apatite, interpreted as being of magmatic origin (Paterson *et al.*, 1992).

## Conclusions

The presence of initial Nd isotopic disequilibrium in Hercynian granitoid intrusions in central Spain may be due to a lack of homogenization between the several components (liquids, solids) involved in the petrogenesis of the whole pluton. Nd isotopic heterogeneity is the only indication of open magmatic processes in their genesis, but problems arise in explaining in a trend where higher initial Nd and Sr isotopic ratios, and lower Sr and Nd total contents in the more felsic granitic facies occurs. In the Spanish Central Region, we do not know of any crustal material which has high Nd and Sr isotopic ratios and high Sr/Nd ratios, that could explain this kind of trend. It also does not seem possible to explain the range of Nd isotopic disequilibrium found in certain plutons as a consequence of simple crystal fractionation, although such a process certainly could slightly increase the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio. The abundance of REE-rich accessory minerals in La Atalaya Real pluton (monazite, allanite, xenotime, ...), their variable restitic character in felsic magmas together to their high mineral partition coefficients ( $K_d$ ) for Sm and Nd might have played an important role for the development of local Nd isotopic disequilibrium. Much work needs to be performed on mineral fraction separates of these granite plutons in order to explain these problems.

## Acknowledgements

This work is included in the objectives of the project DGICYT PB93-0295-CO2 of the Spanish Ministerio de Educación y Cultura. SURRC is supported by the Scottish Universities.

## References

Andonaegui, P. (1990): *Tesis doctoral*, Universidad Complutense de Madrid,

- 365 pp.  
 Andonaegui, P. and Villaseca, C. (1997): *Bol. R. Soc. Esp. Hist. Nat.* (in press).  
 Barbero, L., Villaseca, C., Rogers, G. and Brown, P.E. (1995): *J. Geophys. Res.*, 100, B8, 15745-15765.  
 Bellido, F. (1979): *Tesis doctoral*, Universidad Complutense de Madrid, 331 pp.  
 Ben Othman, D., Fourcade, S. and Allègre, C. (1984): *Earth Planet. Sci. Lett.*, 69, 290-300.  
 Cavazzini, G. (1994): *Chem. Geol.*, 118, 321-326.  
 Cherniak, D.J. and Ryerson, F.J. (1993): *Geochim. Cosmochim. Acta*, 57, 4653-4662.  
 Cocherie, A., Rossi, Ph., Fouillac, A. M. and Vidal, Ph. (1994): *Chem. Geol.*, 115, 173-211.  
 Downes, H., Shaw, A., Williamson, B.J. and Thirlwall, M.F. (1997): *Chem. Geol.*, 136, 99-122.  
 Eugercios, L., Villaseca, C. and Huertas, M.J. (1995): *VI Congr. Geoquim. España*, 1057-1066.  
 Edwards, M.A. and Harrison, T.M. (1997): *Geology*, 25, 543-546.  
 Halliday, A.N., Mahood, G.A., Holden, P., Metz, J.M., Dempster, T.J. and Davidson, J.P. (1989): *Earth Planet. Sci. Lett.*, 94, 274-290.  
 Holden, P., Halliday, A.N. and Stephens, W.E. (1987): *Nature*, 330, 53-56.  
 Mahood, G. and Hildreth, W. (1983): *Geochim. Cosmochim. Acta*, 47, 11-30.  
 Paterson, B.A., Rogers, G. and Stephens, W.E. (1992): *Contrib. Mineral. Petrol.*, 111, 378-390.  
 Poitrasson, F., Pin, C., Duthou, J.L. and Platouvet, B. (1994): *Chem. Geol.*, 112, 199-219.  
 Reyes, J., Villaseca, C., Barbero, L., Quejido, A. and Santos, J.F. (1997): *VII Congr. Geol. España*, (in press). 46-55.  
 Rollinson, H. R. (1993): *Longman Scientific & Technical*, 352 pp.  
 Siebel, W., Höhndorf, A. and Wendt, I. (1995): *Chem. Geol.*, 125, 249-270.  
 Vialette, Y., Bellido, F., Fúster, J.M. and Ibarrola, E. (1981): *Cuad. Geol. Iber.*, 7, 327-335.  
 Villaseca, C. and Barbero, L. (1994): *Eur. J. Mineral.*, 6, 691-710.  
 Villaseca, C., Barbero, L. and Rogers, G. *Lithos*, (in press).  
 Villaseca, C., Barbero, L., Huertas, M.J., Andonaegui, P. and Bellido, F. (1993): *Servicios Publicaciones CSIC*, 122 pp.  
 Villaseca, C., Barbero, L., Reyes, J. and Santos, J.F. (1997): *Geogaceta*, this volume.  
 Villaseca, C., Eugercios, L., Snelling, N.J., Huertas, M.J. and Castellón, T. (1995): *Rev. Soc. Geol. España*, 8, 137-148.  
 von Blanckenburg, F. (1992): *Chem. Geol.*, 100, 19-40.