Geochemical characteristics of the Cadalso-Casillas de Flores Complex (Sierra de Gata). A late Hercynian peraluminous high phosphorus granite

Características geoquímicas del complejo de Cadalso-Casillas de Flores (Sierra de Gata). Un granito tardi-hercínico peralumínico y rico en fósforo

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ABSTRACT

The Cadalso-Casillas de Flores granitic complex is a peraluminous, phosphorus rich, late-hercynian epizonal granite. It is composed of six major units representing two different intrusions, where four of the units belong to the first intrusion. Concentrations of MgO, Al_2O_3, CaO, TiO_2, Fe_2O_3t, Sr, Y, Zr, Ba, REE and Th decrease with the evolution in the units of the first intrusion. Nevertheless, in the second, there is no observable evolutionary trend and only Rb, Nb and LREE clearly increase from one unit to the other. Moreover, the contents of Na_2O, Al_2O_3, P_2O_5, K_2O, Rb, Nb and U are higher in the units of the second intrusion and that of MgO, SiO_2, CaO, TiO_2, Fe_2O_3t, Sr, Y, Ba, REE and Th are lower. High normative corundum and the presence of muscovite and andalusite, both of magmatic origin may indicate the peraluminous character of the generating magma. Early crystallization of uraninite, presence of ilmenite, absence of magnetite and the magmatic crystallization of accessory sulphides, is typical of peraluminous granites generated and crystallized under low fO2.

RESUMEN

El complejo granítico de Cadalso-Casillas de Flores es peralumínico, rico en fósforo, epizonal y tardi-hercínico. Está compuesto de seis unidades mayores representantes de dos intrusiones distintas, cuatro de las cuales pertenecen a la primera intrusión. Las concentraciones de MgO, Al_2O_3, CaO, TiO_2, Fe_2O_3t, Sr, Y, Zr, Ba, REE y Th decrecen con la evolución en las unidades de la primera intrusión. Sin embargo, en la segunda, no se observa trend evolutivo alguno, y solamente Rb, Nb and TRL aumentan claramente desde una unidad a la otra. Además, los contenidos de Na_2O, Al_2O_3, P_2O_5, K_2O, Rb, Nb and U son más altos en las unidades de la segunda intrusión y los de MgO, SiO_2, CaO, TiO_2, Fe_2O_3t, Sr, Y, Ba, REE and Th más bajos. El corindón normativo alto, y la presencia de moscovita y andalucita, ambos de origen magmático, podrian indicar el carácter peralumínico del magma generador. La cristalización temprana de uraninita, presencia de ilmenita, ausencia de magnetita y la cristalización magmática de sulfuros accesorios, es típico de granitos peralumínicos generados y cristalizados bajo fO2 baja.

Key words: *geochemistry, major and trace elements, peraluminous granite, Hercynian Iberian Belt.*

Introduction and geological setting

The Cadalso-Casillas de Flores complex (Salamanca-Cáceres, Sierra de Gata), is a late Hercynian granitic massif located in the most western end of the Spanish Central System, in the so-called «Sierra de Gata». It intruded a low grade regionally metamorphosed metasedimentary rocks of the Schist-Graywacke Complex. This granitic complex is composed of a main body of six major units (Fig. 1), four of which (G1-G4), belong to a first intrusion, while the remaining two (G5-G6) pertain to a second and later intrusion. In addition, there are at least 10 fine grained small outcrops associated with the main complex. These small outcrops were grouped in G7, irrespective of their origin and spatial distribution. The units of the first intrusion are NW-SE oriented, generally porphyritic medium-coarse grained granites. They range in composition from biotite rich granites to muscovite dominant leucogranites and are related by fractional crystallization of mainly biotite, plagioclase and accessory minerals such as monazite, xenotime, ilmenite and zircon (Hassan, 1996). These were later intruded by spatially unrelated NE-SW oriented, medium-fine grained two minor units (Hassan, 1996). The units of the second intrusion, though comagmatic, seem vaguely related by fractional crystallization. The most distinctive chemical characteristic common to both intrusions is their exceptionally high phosphorus content (>0.24%wt), while lower $SiO_2 \leq 70\%$ and $CaO \leq 0.45\%$ characterizes the units of the second intrusion.

Furthermore, concentrations of some major elements (Na, Al, Si, K and Ca) and the behaviour of REE and Nb, mark the most conspicuos chemical differences between the two granitic intrusions. In this paper, we present data on the major and trace-element chemistry of the units of the two intrusions,
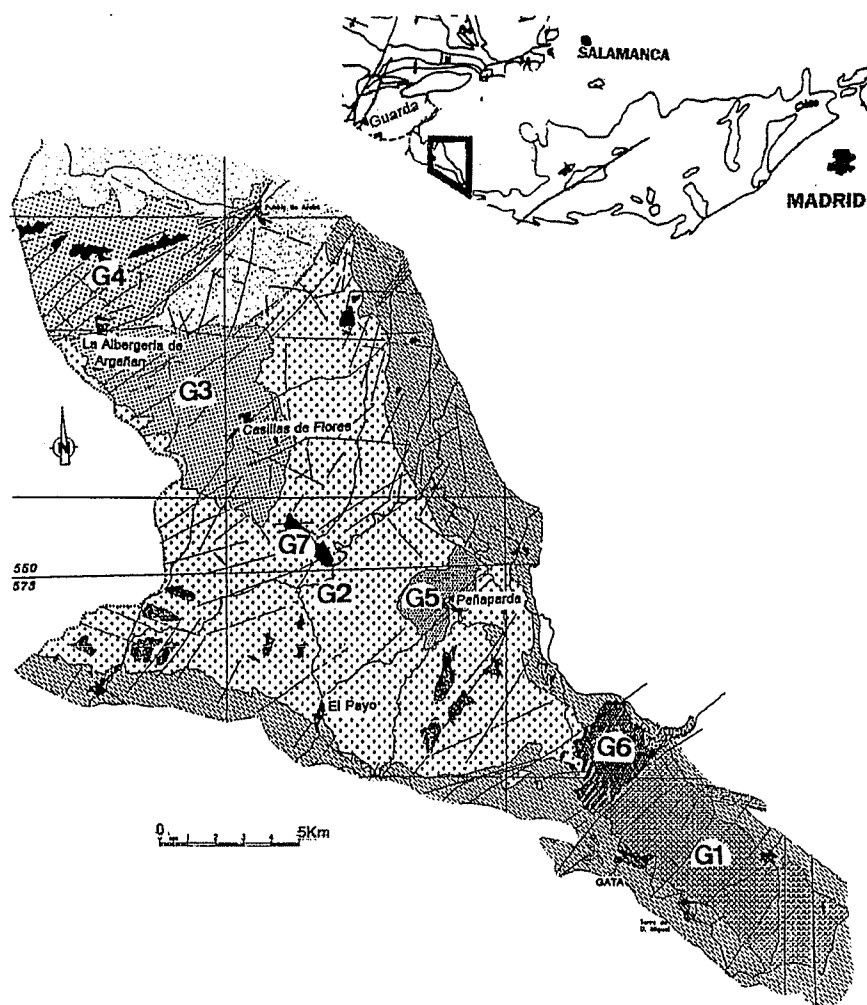
Fig. 1.- Geological map of Cadalso-Casillas de Flores complex.

Fig. 1.- Mapa geológico de complejo de Cadalso-Casillas de Flores

This highly reducing conditions are consistent with a sedimentary source with high concentrations of carbonaceous material. Furthermore, in contrary to other P_2O_5 rich S-type peraluminous granites, in the Cadalso-Casillas de Flores granite, phosphorus is fractionated in accessory phosphates (apatite, monazite and xenotime) and no phosphorus was detected in alkali feldespars.

Geochemistry

Sixty eight samples were selected for whole-rock chemical analysis. All samples contain 65-74.8 wt. % SiO_2, have high normative corundum (2.62-5.75%), and A/CNK > 1.5 (A/CNK = molar Al_2O_3/CaO+Na_2O+K_2O) after adjusting CaO for the formation of apatite. Another important feature of Cadalso-Casillas de Flores granitic complex is its high P_2O_5 content (0.25-0.58%). High P_2O_5 content is considered to be a general characteristic of S-type peraluminous granites (London et al., 1989 and Bea et al., 1992). It also has major element chemical characteristics typical of S-type granites (Chappell and White, 1974) and belongs to the ilmenite series according to the opaque mineral classification of Ishihara (1977). The most important chemical differences in major elements between the two intrusions are manifiested in the concentrations of Na_2O, Al_2O_3, P_2O_5 and K_2O which are higher in G5 and G6 and those of MgO, SiO_2, CaO, TiO_2, and Fe_2O_3t, which are lower. In G1-G4, MgO, Al_2O_3, CaO, TiO_2, and Fe_2O_3t are negatively correlated with SiO_2, while Na_2O, and K_2O are poorly correlated. P_2O_5 is the only oxide which is negatively correlated with SiO_2 in the most primitive units (G1 and G2) and inverts this tendency in the most fractionated units (G3 and G4). This behaviour of phosphorus is due to the depolymerization and low CaO content of the magma in the final stages (Hassan, 1996). In G5 and G6 in turn, neither correlations nor variations are observed as far as major elements are concerned (Fig. 2).

In general, the chemistry of the granites of the first intrusion is marked by slight enrichment in SiO_2 and Rb and a concomitant depletion in CaO, MgO, TiO_2, Fe_2O_3t, Al_2O_3, Sr, Ba, Zr, Th, Y and REE from G1-G4 during evolution (Fig. 2 and 3). This behaviour can be explained by fractional removal of early crystallized phases such as plagioclase, biotite, zircon, ilmenite, monazite and xenotime. In the units of the second intrusion, only Rb, Nb and LREE increase from G5-G6 (Fig. 3). This behaviour may at least suggest that monazite and rutile were not intensely fractionated until the late stages of the evolution of the magma of G5 and G6 and is consistent with the presence of these minerals as inclusions in

briefly describe their distinctive chemical characteristics and the chemical differences between them.

Petrography

In the six major units of Cadalso-Casillas de Flores granite, constituting essential minerals besides quartz are: plagioclase (maximum An% 30 in G1 and <An4% in G4, G5 and G6) which occurs as partly zoned megacrystals in the less evolved units and as mainly unzoned fine grains in the most evolved units. K-feldespar occurs as 1-8 cm euhedral megacrysts, though grain size is generally <1cm in the most fractionated units. Biotite is present either as large flakes rich in inclusions of plagioclase and accessory minerals or as smaller intersticial generally chloritized, fibrous or tabular crystals poor in inclusions. It is also found as anhedral clots that host inclusions of ilmenite, monazite and zircon, interpreted to be either relicts of partly digested metamorphic enclaves or early crystallized magmatic material (Hassan, 1996). Muscovite is present as euhedral-

subhedral flakes similar in size to adjacent biotites and with abundante inclusions of ilmenite, apatite, monazite and zircon. Such muscovites were interpreted to be of magmatic origin (Hassan, 1996). Muscovite was also interpreted to be magmatic in many low pressure 2.5-1 Kb, ocassionally H_2O rich peraluminous granites (Swanson, 1978: Anderson and Rowley, 1981; Miller *et al.*, 1981). The epizonal nature of Cadalso-Casillas de Flores granitic complex is also shown by the abundance of miarolitic cavities, presence of roof pendants and contact effects.

Identified accessory minerals are; zircon, monazite, apatite, ilmenite, pyrite, xenotime, loellingite, chalcopyrite, arsenopyrite, sphalerite, cobaltite, allanite, andalusite, uraninite, tourmaline and rutile. The majority of these accessory minerals are included in biotite in the units of the first intrusion. In G5 and G6 in turn, accessory minerals are mainly found as inclusions in albite, muscovite and quartz. Magmatic crystallization of ilmenite and accessory sulphides indicate low fO2. Similarly, early fractionation of uraninite imply fO2 below Ni-NiO (Farges *et al.*, 1992).

albite, muscovite and quartz.

Ba, Sr and Rb

These three elements exhibit variations that are typical of the influence of feldespars and biotite during crystal fractionation. Crystal fracionation of plagioclase, K-feldspar and biotite might be responsible of the revealed inverse trends of these elements marked by decrease of Ba and Sr with the evolution as a function of rising levels of Rb, though the effect of crystal fractionation is less evident in G5 and G6 (Hassan, 1996). Moreover, Rb content is higher in G5 and G6 and Sr and Ba contents are lower. This is consistent with the higher K_2O and lower CaO of the units of the second intrusion.

Y, Zr, Nb, Th and U

Concentrations of Y are moderately low in the units of the first intrusion and decrease from G1-G4. This decreasing tendency with the evolution is due to crystal fracionation of xenotime, as Y is an essential constituent of xenotime. Y contents in the second intrusion are very low if compared with the former and the two units have similar values, though there is a slight increase from G5-G6 (Fig. 3).

Zr presents moderate concentrations in both granitic groups. However, the behaviour of Zr is slightly different in the two granitic magmas. Zr contents decrease with magmatic differentiation from G1-G4 and vaguely increase from G5-G6 (Fig. 3). The progressive depletion of Zr denotes early fractionation of zircon in the less evolved units (G1 and G2) due to its low solubility in peraluminous magmas (Watson, 1979, Watson and Harrison, 1983) and the consequent removal of much of Zr from the residual melt that generated G3 and G4. By the other hand, increasing Zr concentrations may indicate higher solubility of zircon due to the high fluor concentrations of the magma that generated G5 and G6.

Nb is one of the trace elements that discriminate between the two granitic groups, for Nb mean values show no variations with the evolution from G1-G4, are much lower than that of the second and very similar to the Nb average in the crust (Taylor and McLennan, 1985). Nevertheless, Nb concentrations of the second intrusion increase from G5-G6 and are higher than the Nb average in the crust. So, because Nb is fractionated principally in rutile, its behaviour may reflect that of rutile in either intrusive group.

Although Th is generally considered to be compatible in peraluminous granitic magmas, in the Cadalso-Casillas de Flores granitic complex this element exhibits identical behaviour to that of REE in either granitic group. This is because more than 80% of Th concentration in the studed granites is fractionated in monazite (Hassan, 1996).
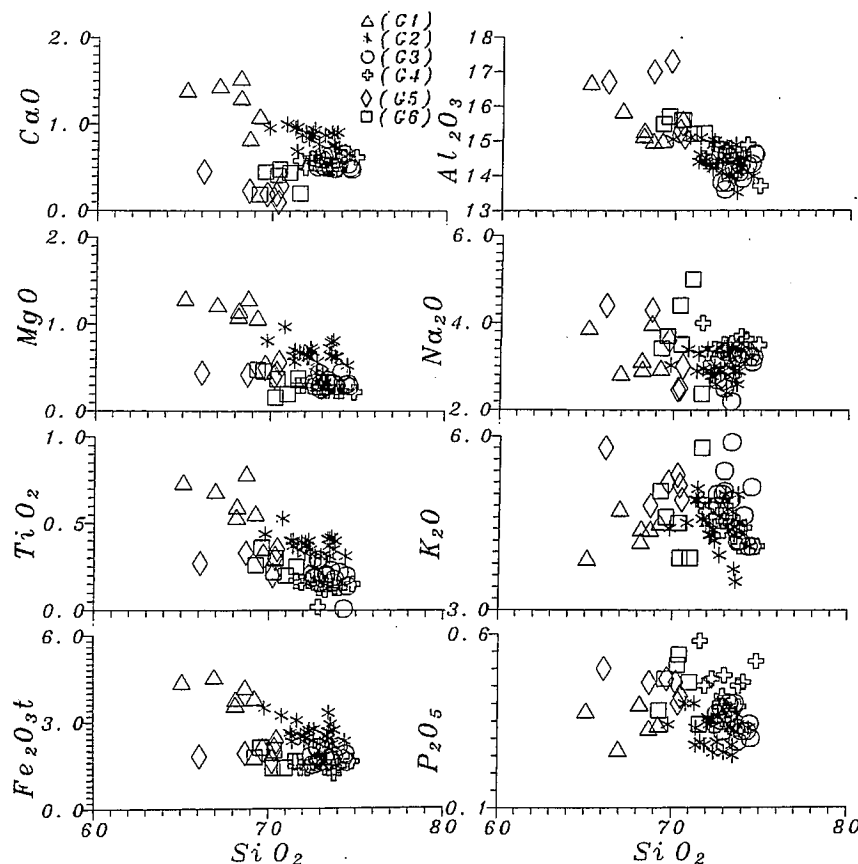
During the differentiation of peraluminous

Fig. 2.- Major element variation diagram.

Fig. 2.- Diagrama de variación de elementos mayores.

granitic magmas, uranium can be fractionated in many early crystallizing U-bearing accessory minerals such as zircon, monazite, xenotime and apatite. In addition, the low fO2 that characterizes the magma of the Cadalso-Casillas de Flores granitic complex, may cause early fractionation of uraninite and consequent depletion of U contents with the evolution. Nevertheless, though the original trend as in many other elements is partly masked by hydrothermal alteration processes, the concentration of U increases with the evolution and the most felsic members of these granites are enriched in U. This is because, uranium solubility in the magmatic stage depends principally on: (a) fO2 (Calas, 1979); (b) H_2O content of the magma (Chantal et al., 1994) and (c) concentration of viscosity reducing elements such as F (Keppler, 1993). So, though the fO2 was low, as evidenced by the presence of ilmenite, uraninite and magmatic sulphides. The high F content determined in samples of highly evolved units and the increasing H_2O content, due to the fractionation of anhydrous minerals, might be responsible of the observed U behaviour. Moreover, 62% of the total U of G5 and G6 are concentrated in zircon (Hassan, 1996). Thus, besides the mentioned factors, the behaviour of zircon plays a major role in that of U in the units of the second intrusion.

REE

Fourteen samples representing all the identified units were analysed for REE. Obtained results show different REE behaviour as a result of different behaviour of REE-bearing accessory minerals. Those of the four major units of the first intrusion (G1-G4) show a relatively high total REE in the less evolved units decreasing with the evolution, nearly flat REE patterns and a small negative Eu anomaly (Fig. 4a). REE concentrations of G5 and G6 have relatively lower total concentrations, lower HREE contents, slightly negative Eu anomaly and their LREE increase from G5 to G6 (Fig. 4b). Despite this opposite behaviour, especially in LREE, normalized REE patterns of both groups are characterized by flat to moderately fractionated curves and small negative Eu anomaly similar to those of other S-type peraluminous granites (Muecke and Clarke, 1981; Mittlefehldt and Miller, 1983; Holtz, 1989; Holtz and Barbey, 1991; Barbero and Villaseca, 1992 and Zhao and Cooper, 1993). Furthermore, as REE are fractionated principally in monazite and xenotime in both granitic groups (Hassan, 1996), gradual decreasing of REE concentrations from G1-G4 (G1= 190 ppm, G2= 145 ppm, G3= 70 ppm and G4= 45 ppm) imply continued crystal fractionation of monazite
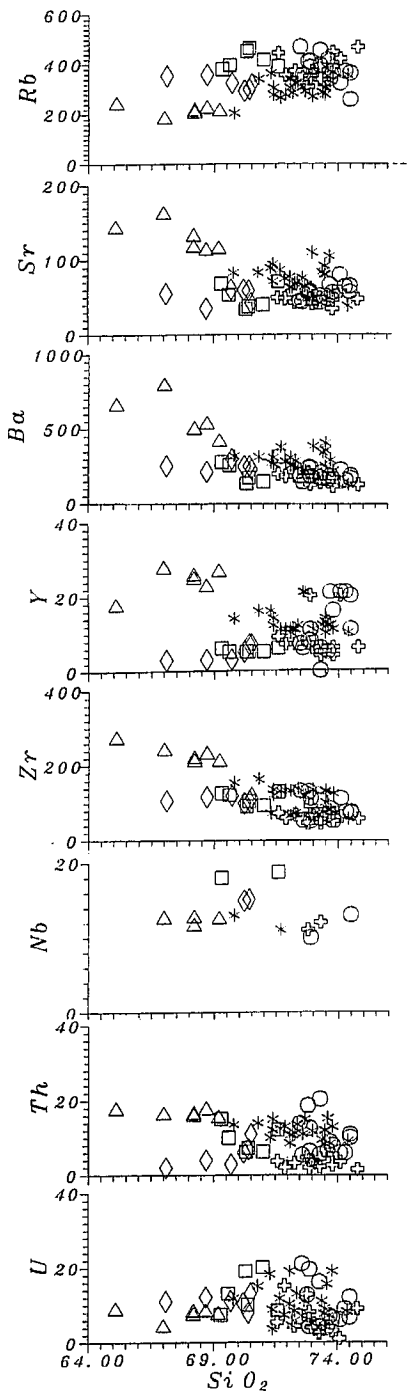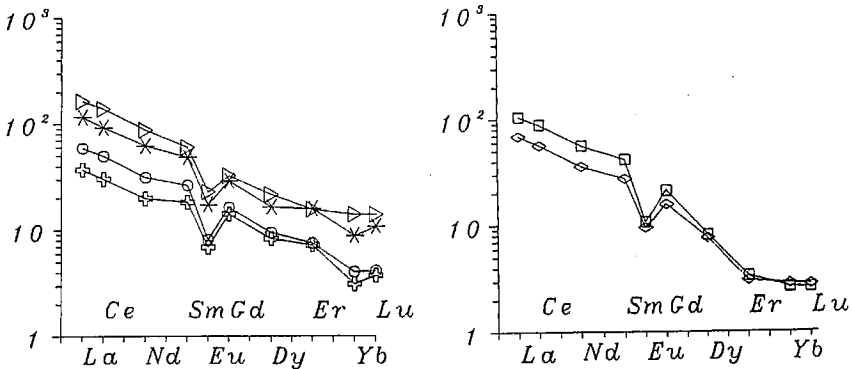
Fig. 4.- a) Mean values of normalized REE patterns of the first intrusion (G1-G4). Symbols as in fig. 2; b) Mean values of normalized REE patterns of the second intrusion (G5-G6). Symbols as in fig. 2.

Fig. 4.- a) Valores medios de los espectros normalizados de TR de la primera intrusión (G1-G4). Igual leyenda que la Fig. 2; b) Valores medios de los espectros normalizados de TR de la segunda intrusión (G5-G6). Igual leyenda que la Fig. 2.

Fig. 3.- Trace element variation diagram. Symbols as in figure 2.

Fig. 3.- Diagrama de variación de elementos traza. Igual leyenda que la figura 2.

and xenotime in this group. Meanwhile, increasing REE content from G5-G6 (G5= 77 ppm and G6= 118 ppm) may indicate higher solubility of monazite and probably xenotime in the magma of the second intrusion.

Conclusions

Cadalso-Casillas de Flores granitic complex, is a highly peraluminous, perphosphoric and epizonal granite, composed of two different granitic groups. Nevertheless, though both granitic groups share many chemical and mineralogical characteristics, there are conspicuos differences in the behaviour and content of certain chemical elements. These are probably due to small differences in crystal fractionation processes. Thus, the concentrations of Na_2O, Al_2O_3, P_2O_5, K_2O, Rb, Nb and U are higher in G5 and G6, while those of MgO, SiO_2, CaO, TiO_2, Fe_2O_3t, Sr, Y, Ba, REE and Th are lower. In addition, Nb and LREE have converse trends, as they decrease with the evolution from G1-G4 and increase from G5-G6 due to the different behaviour of rutile and monazite in the two intrusions.

Aknowledgements

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