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Magnetic susceptibility of Variscan granite-types of the Spanish Central System and the redox state of magma

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ABSTRACT

Magnetic susceptibility (MS) has been measured in Variscan granites from central Spain. They yield values in the order of 15 to 180µSI units for S- and I-type granites, indicating that both types belong to the ilmenite series. Only samples from magnetite-bearing leucogranites from the I-type La Pedriza massif show high MS values, in the order of 500-1400µSI, reflecting the presence of this ferromagnetic mineral. Mineral chemistry of magmatic Fe-rich minerals (mainly biotite) suggests similar oxidation values for both granite types. MS values change in highly fractionated granites accordingly either with the presence of rare new Fe-oxide phases (some I-type leucogranites) or with the marked modal amount decrease of Fe-rich minerals (I- and S-type leucogranites). The redox state in highly fractionated granite melts is mostly controlled by magmatic processes that modify redox conditions inherited from the source region. Thus, the occurrence of magnetite or ilmenite in granites is primarily controlled by the oxidation state of the source material but also by the differentiation degree of the granite melt. The presence of magnetite in some Variscan I-type leucogranites might be a consequence of crystal fractionation processes in a more limited mafic mineral assemblage than in S-type granite melts.

KEYWORDS **Magnetic susceptibility. Granite type. Biotite chemistry. Oxygen fugacity.**

INTRODUCTION

Magnetic susceptibility (MS) of granitic rocks is highly variable. It may range from low values of the order of 10^{-6} SI units in leucogranites, to the order of 10^{-1} in some granodiorites or tonalites. The magnitude of the bulk magnetic susceptibility of a rock (K, *i.e.* the ratio between induced magnetization M and the external applied field H, as it is defined by $M=KH$, and therefore dimensionless in SI units) reflects the cumulative contribution of its constituent magnetic minerals and hence the abundance, nature and chemical composition of magmatic minerals. Since the diamagnetic and antiferromagnetic contributions are very weak, MS is mainly carried by paramagnetic (iron-bearing silicates) and ferromagnetic (magnetite, along with accessory monoclinic pyrrhotite) minerals. Ferromagnetic minerals having much higher intrinsic magnetic susceptibility (about three orders of magnitude) than the paramagnetic matrix, the MS of a granite depends critically on the content or absence of magnetite. Therefore, the magnetic susceptibility has the potential to track petrographic and geochemical variations across granite batholiths (*e.g.* Ishihara *et al.*, 1984; 2000).

Magnetic susceptibility of granites is mainly controlled by the type and amount of magnetic minerals (paramagnetic major mafic silicates *vs.* ferromagnetic accessories such as iron oxides or sulphides), and their abundances have been explained by differences in the oxygen fugacity of magmas (*e.g.* Ishihara, 1977; Sant'Ovaia *et al.*, 2013). Consequently, MS has been used to discriminate granitic rocks of the magnetite- and ilmenite-bearing series (Ishihara, 1977), and to discuss the tectonic setting of granite-types considering that magnetic granites roughly correspond to the I- and/or A-types, while the weakly magnetic granites coincide with the S-types, being the susceptibility an indicator of granite origin (*e.g.* Ellwood and Wenner, 1981).

The redox condition of crustal sources during magma generation is a main factor to determine the magnetite occurrence in I-type series, as has also been shown in Variscan metaluminous granites (*e.g.* Gregorová *et al.*, 2003). Nevertheless, the direct correlation between granite type and magnetic series is questionable as the occurrence of magnetite instead of ilmenite is not only primarily controlled by the oxygen fugacity in the source but also by magmatic differentiation and late magmatic processes that can modify crystallization conditions (*e.g.* Pichavant *et al.*, 1996). Redox states of felsic magmas are initially constrained by its source region but are lately controlled by magmatic processes occurring during their evolution (fractional crystallization, volatile exsolution, magma immiscibility, etc.) (Czamanske and Wones, 1973).

In this paper we show magnetic susceptibility values of the two dominant (S- and I-type) granites of the Spanish Central System along with values from the associated scarce basic rocks, and from country rocks (metasedimentary and metaigneous) and lower crustal granulites. These results provide data for the discussion on the origin and processes operating during granite batholith construction.

GEOLOGICAL SETTING

The Spanish Central System (SCS) batholith is one of the largest exposures of granitic intrusions in the European Variscan Belt (*e.g.* Bea *et al.*, 1999). It outcrops in the innermost part of the Iberian belt, the so called Central Iberian Zone (CIZ) (Fig. 1). These felsic magmas were emplaced into an Upper Neoproterozoic to Lower Palaeozoic sequence of metasedimentary and metaigneous rocks. Granite plutons can be classified mainly as monzogranites, with minor proportions of leucogranites and granodiorites (*e.g.* Villaseca *et al.*, 1998). Most granites are peraluminous and display silica contents mainly from 67 to 76 wt.% (Villaseca and Herreros, 2000). Variations in their mineralogy and degree of Al saturation led to their subdivision into several series: i) S-type peraluminous cordierite-bearing granitoids (average A/CNK values from 1.07 to 1.20, from granodiorite to leucogranite), ii) I-type metaluminous amphibole-bearing granitoids (A/CNK from 1.01 to 1.10), and iii) transitional biotite granitoids of intermediate peraluminous affinity (A/CNK from 1.03 to 1.13) (Villaseca and Herreros, 2000). Scarce (< 1% in volume) basic to intermediate magmas, represented by small gabbroic to quartzdioritic plutons, are coeval with the granite intrusions (*e.g.* Orejana *et al.*, 2009).

Petrographical and geochemical data of I- and S-type granites from the SCS have been widely described in literature (*e.g.* Casillas, 1989; Villaseca *et al.*, 1998; Bea *et al.*, 1999), but some general features are included here. The S-type granitoids exhibit a compositional range from minor granodiorite, dominant monzogranite to less abundant leucogranite bodies (around 5-10%, 70-75%, 15-20%, respectively, of the overall abundance in outcrop). They are composed of quartz, K-feldspar, plagioclase and biotite, with minor amounts of local cordierite; whereas muscovite, tourmaline, and occasional andalusite, appear in leucogranites. Apatite, zircon, monazite, xenotime and ilmenite are the main accessory minerals. I-type granitoids show a similar compositional range (and relative petrographic abundances than S-type) having quartz, K-feldspar, plagioclase and biotite as the main rock-forming minerals; whereas amphibole, apatite, zircon, monazite, allanite and ilmenite are common accessories. In the SCS, accessory magnetite appears only in the evolved I-type La Pedriza leucogranite massif (Pérez-Soba and Villaseca, 2010). Magnetite has been described in other I-type granite plutons of the CIZ: Traba, El Pindo and Caldas de Rey in Galicia (Ortega and Gil-Ibarguchi, 1990; Cuesta, 1991); Manteigas, Lavadores and Gêres in Portugal (Silva and Neiva, 1998; Martins *et al.*, 2011; Sant'Ovaia *et al.*, 2013).

The main chemical differences between SCS S- and I-type granites are the peraluminosity degree, higher in S-type (mostly for their lower CaO content) than in I-types, and the contrasted compositional evolution of their respectively highly fractionated granites for some trace elements (*e.g.* Y, HREE, Th) at 74-76 wt.% SiO_2 (Villaseca *et al.*, 1998). Moreover, geochemical data on these granites show crystal fractionation trends which rarely connect I-type granites with more differentiated S-type leucogranites (Villaseca *et al.*, 1998). However, the broad similar isotopic (Sr, Nd, O, Pb, Hf) composition between these S- and I-type granites reflects the participation of similar source components (Villaseca *et al.*, 1998; 2012). The occurrence of mafic microgranular enclaves and the absence of mica-rich restites (or globular quartz) in both granite types also suggest similar protoliths. Therefore, differences in granite peraluminosity between these granite types might be related to variable partial melting conditions of similar crustal sources (Villaseca *et al.*, 2012).

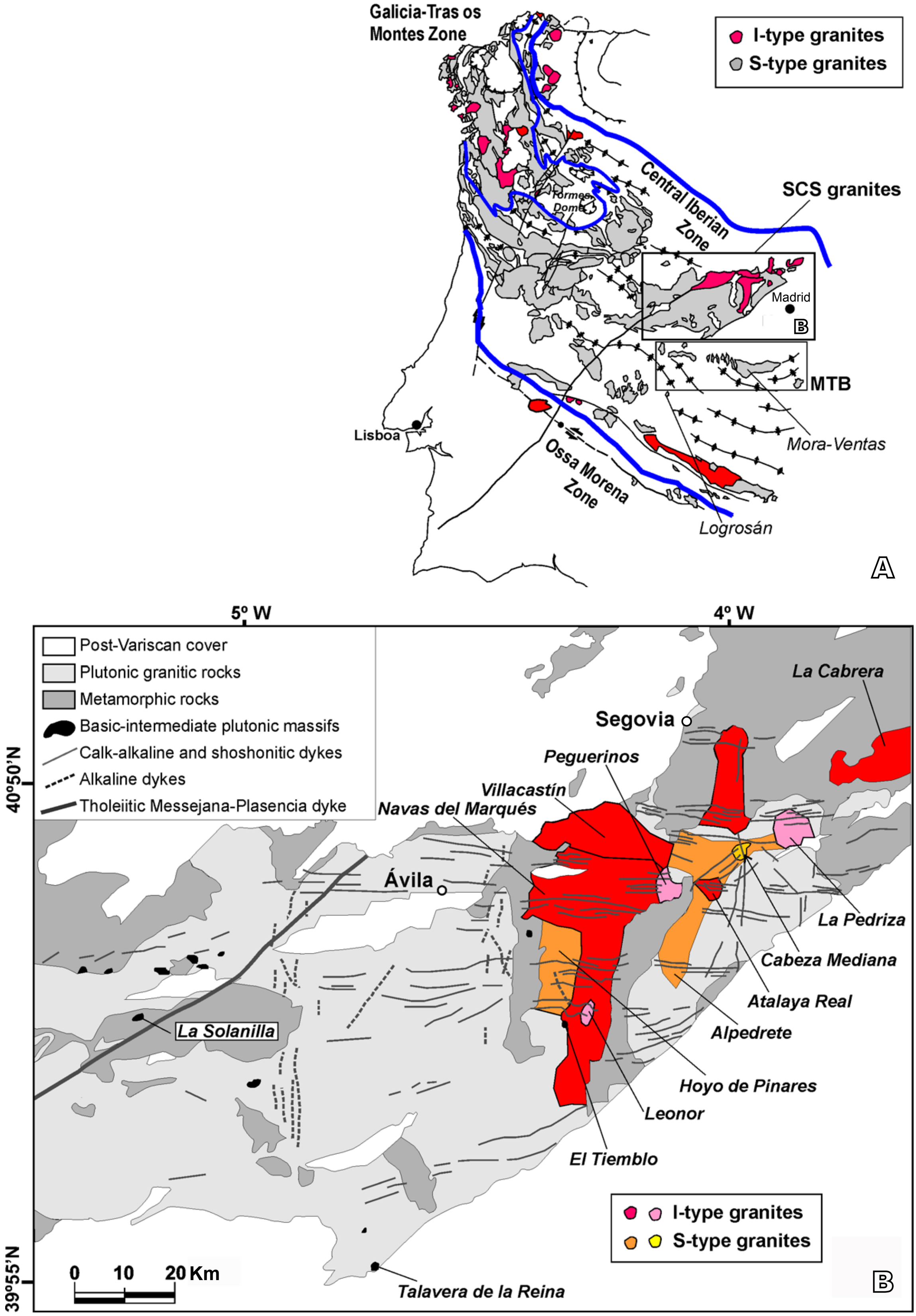

FIGURE 1. A) Geological map of Variscan granites from the Iberian Belt. SCS = Spanish Central System, MTB = Montes de Toledo Batholith. B) Geological sketch of the SCS showing location of some plutons mentioned in the text.

The origin of the SCS Variscan granites has been related to melting of the lower crust on the basis of bulk geochemistry and Sr-Nd-O-Pb isotope composition of deep-seated granulitic xenoliths (Villaseca *et al.*, 1999; Villaseca *et al.*, 2007). Recent studies on U-Pb geochronology of SCS granulites reinforce this idea, showing an abundant population of granulitic zircon formed in the range 320-283Ma, overlapping the age of the SCS batholith construction (Orejana *et al.*, 2011). Hf isotope zircon compositions also show a good overlap in chemical data between S- and I-type SCS granites and the meta-igneous granulite xenoliths from the SCS lower crust (Villaseca *et al.*, 2012). Nevertheless, other hypothesis regarding the origin of the SCS granitic batholith have been suggested: a) hybridization of crustal melts and mantle-derived magmas (*e.g.* Moreno-Ventas *et al.*, 1995); b) crustal assimilation by mantle-derived magmas (*e.g.* Castro *et al.*, 1999); and c) partial melting of metasedimentary crustal sources from mid-crustal levels (*e.g.* Bea *et al.*, 2003).

Most of the granitoids from the SCS batholith intruded after the main Variscan phases of ductile deformation, which are coeval with migmatization and low-pressure/high temperature M2 metamorphism, after an initial M1 Barrovian metamorphic event (*e.g.* Escuder-Viruete *et al.*, 1998). Peak metamorphism is poorly constrained at around 340Ma (Villaseca *et al.*, 2015), and the M2 metamorphism is constrained at 330Ma (Escuder-Viruete *et al.*, 1998; Castiñeiras *et al.*, 2008). Granites intruded producing a contact metamorphism in the high-grade gneisses, indicating that the country rock in the eastern sector of the SCS batholith was already cold at the time of intrusion. Recent U-Pb SHRIMP analyses on zircon from granites of western SCS yield ages concentrated in the range 308-303Ma (Zeck *et al.*, 2007; Díaz-Alvarado *et al.*, 2011), similar to those obtained in the eastern side (306-298Ma, Orejana *et al.*, 2012).

MATERIAL AND METHODS

A total of 76 granitic rock samples, 14 associated basic-intermediate rocks (gabbro to tonalite), 16 Neoproterozoic metasedimentary rocks from the S-CIZ

TABLE 1. Magnetic susceptibility (*K*) data for central Spain Variscan plutonic rocks

				Magnetic susceptibility (*K* x μSI)		SiO$_2$ (wt.%)	
Pluton	Granite-type	Mineralogy	nº	Mean	Range	Mean	Range
Talavera de la Reina	Gabbro	Ol-Cpx-Opx-bearing gabbro	2	5345	1770-8920	48.4	48.0 - 48.8
La Solanilla		Ol-Cpx-Opx-bearing gabbro	2	6470	3770-9170	48.3	47.9 - 48.6
Ventosilla	Intermediate rock	Amph-Bt-bearing tonalite (rim)	3	650	374-839	60.1	57.8 - 62.0
		Bt-bearing granite (core)	2	91	87-94	70.0	69.6 - 70.5
La Jarosa		Amph-bearing qtz-diorite	1	234		57.9	
El Tiemblo		Amph-bearing qtz-diorite	3	301	247-356	54.4	52.1 - 58.4
La Cañada		Amph-bearing qtz-diorite	1	377		52.6	
El Tiemblo	S-type granite	Bt-bearing granodiorite	2	161	139-186	64.7	63.6 - 65.7
La Carrascosa		Bt-Crd-bearing granite	2	55	55	74.1	74.0 - 74.3
Alpedrete		Bt-Crd-bearing granite	7	120	94-145	69.3	68.7 - 69.9
Cabeza Mediana		Bt-Ms-Crd-bearing leucogranite	7	45	21-67	75.2	73.3 - 76.9
Hoyo de Pinares		Bt-Ms-Crd-bearing leucogranite	5	16	0.29-35	75.2	74.5 - 77.0
Sierra del Francés		Bt-bearing granite	1	139		71.1	
Logrosán (Cáceres)[1]		Bt-Ms-bearing leucogranite	7	56	20-117	72.5	72.2 - 73.9
Atalaya Real	I-type granite	Amph-Bt-bearing granite	3	179	166-189	68.1	67.3 - 69.2
		Amph-Bt-bearing leucogranite	5	66	41-102	74.1	71.5 - 76.5
La Cabrera		Bt-bearing granite	3	107	103-113	69.7	68.1 - 71.2
Leonor		Bt-bearing leucogranite	4	33	17-59	74.3	73.9 - 75.9
Peguerinos		Bt-bearing leucogranite	7	65	23-130	76.0	75.8 - 76.4
La Pedriza		Bt-bearing leucogranite	13	48	19-148	75.3	74.0 - 76.1
G3 unit[2]		Bt-bearing leucogranite (acc. Mt)	10	853	484-1360	76.5	75.9 - 77.5

[1](see location in Fig.1A), [2] (Pérez-Soba and Villaseca, 2010), nº = number of samples

Schist Greywacke Complex, 10 Cambro-Ordovician orthogneisses and 12 lower crustal granulite xenoliths were analysed for low-field bulk magnetic susceptibility at the Paleomagnetic Laboratory (Faculty of Physics) in the Universidad Complutense of Madrid using an AGICO KLY-4S Kappabridge high-sensitivity apparatus (0.03µSI particularly well adapted to the study of low-MS rocks such as paramagnetic granites). Laboratory measurements were made at room temperature applying a field intensity of 300A/m (in the range where MS may be assumed as constant) at 875Hz operating frequency. Magnetic susceptibilities are given in SI units (Tables 1 and 2).

Mineral (biotite, ilmenite and magnetite) compositions were analysed at the *Centro Nacional de Microscopía Electrónica "Luis Bru"* (Universidad Complutense de Madrid) using a Jeol JXA-8900 M electron microprobe with five wavelength dispersive spectrometers. Analytical conditions were an accelerating voltage of 15kV and an electron beam current of 20nA, with a beam diameter of 5µm. Elements were counted for 10s on the peak and 5s on each background position. Corrections were made using the ZAF method.

Normalization of the microprobe analysis of biotite to a chemical formula is difficult because vacancies may occur and this analytical method cannot distinguish oxidation states. The ferrous-iron content of biotite may be proxy by an empirical formulae proposed by Bruiyn *et al.* (1983). They applied a multiple linear regression to a total of 272 biotite analyses, with FeO and Fe_2O_3 concentration from literature, to obtain a statistical formula:

$$FeO = -10.7325 + 0.0705 \times SiO_2 + 0.4598 \times TiO_2 + 0.3067 \times Al_2O_3 + 0.8433 \times FeO_{total} + 0.288 \times MnO - 0.0581 \times MgO - 0.0765 \times CaO - 1.1294 \times Na_2O + 0.4172 \times K_2O$$

The Fe_2O_3 is calculated by difference to the total FeO. When this proxy is applied to biotite composition from literature (Guidotti and Dyar, 1991; Shabani *et al.*, 2003; Bónová *et al.*, 2010), where the Fe_2O_3 content was obtained via Mössbauer spectroscopy (considered more reliable than those obtained by other analytical techniques), a systematic minor Fe_2O_3 subestimation is obtained (see Electronic Appendix I, Fig. I). Using Fe_2O_3 contents in biotite determined by Mössbauer spectroscopy, a new multiple linear regression was calculated. The new equation proposed to estimate the biotite Fe_2O_3 content is:

$$Fe_2O_3 = -0.5038 - 0.0243 \times SiO_2 + 0.4320 \times TiO_2 - 0.0145 \times Al_2O_3 + 0.2094 \times FeO_{total} + 1.5305 \times MnO + 0.2332 \times MgO - 2.0156 \times CaO - 0.7333 \times Na_2O - 0.3547 \times K_2O$$

Figure I (Electronic Appendix I) shows the correlation between FeO and Fe_2O_3 obtained via Mössbauer techniques with the contents calculated by Bruiyn's formula and with the equation here proposed, respectively. This new formula improves the Fe_2O_3 estimation in biotite composition, and is considered suitable for the purpose of this study.

Biotite composition of different I- and S-type Variscan granites from central Spain has been compiled (Casillas, 1989; Andonaegui, 1990; Pérez-Soba, 1991; Eugercios, 1994; Villaseca and Barbero, 1994; Castellón, 1995; Merino *et al.*, 2013; Merino, 2014; Chicharro, 2015). In addition, new analyses, mostly from La Pedriza and Hoyo de Pinares plutons, were performed to complete the biotite compositional range. Biotite cation proportions are normalized to a total positive charge of 22, and cations are assigned to crystallographic sites for the stoichiometry $(Na,Ca,K)_2(Fe,Mg,Mn,Al,Ti)_{4-6,}$ $(Al,Si)_8O_{20}(OH)_4$ in which the vacancies are determined by difference. Ca and Na occur in amounts that are generally below the detection limit of the microprobe.

MAGNETIC SUSCEPTIBILITY RESULTS

Most of the samples from S- and I-type granites of the SCS batholith show a similar range of low magnetic susceptibility *K* values, in the order of 10 to 10^2µSI units (Table 1), which are typical of the ilmenite–series group (*e.g.* Aydin *et al.*, 2007). Only samples from magnetite-bearing leucogranites from the La Pedriza massif reflect the presence of ferromagnetic minerals having higher values, in the order of 10^3µSI (from 480 to 1360µSI). In contrast, some extremely felsic S-type leucogranites, with almost only diamagnetic minerals (quartz and feldspars, with negative, low *K* values competing against the weak paramagnetic contribution), display the lowest values of our sampling (0.3µSI units, Table 1). Gabbro samples show higher magnetic values than granites (1770 to 9170µSI units), while quartzdiorite to tonalite samples are only slightly higher than granites (from 234 to 839µSI units).

Metasedimentary and metaigneous country rocks show a similar range of magnetic values to those of granites, the most similar being the orthogneisses (Fig. 2). In contrast, samples of granulite xenoliths from the lower crust are much more magnetic, showing a wide range of *MS* values (from 209 to 21250µSI) (Table 2, Fig. 2). The extreme restitic nature of some of these granulite xenoliths, rich in mafic minerals, such as orthopyroxene, garnet, rutile and spinel (Villaseca *et al.*, 1999), explains their high *K* values. Among granulite xenoliths, the highest *MS* is reached in samples of metapelitic character (Table 2).

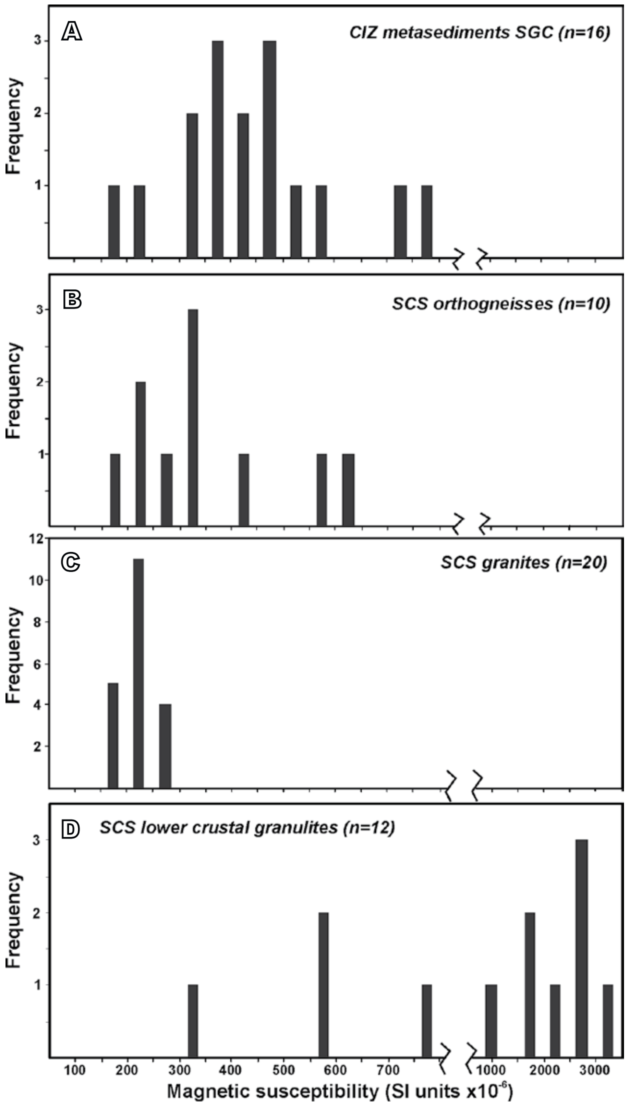

FIGURE 2. Histograms of magnetic susceptibility (MS) of central Spain Variscan plutonic and metamorphic rocks. In C) only granites with ≤72 wt.% of SiO_2 have been plotted to avoid MS variance of highly fractionated leucogranites, for better comparison with crustal lithotypes. SGC = Schist Greywacke Complex, SCS = Spanish Central System.

Geochemical features of plutonic rocks

Whole rock

Magnetite and ilmenite series of Japanese plutonic rocks were separated empirically by a boundary line close to the Fe_2O_3/FeO ratio of 0.5 at SiO_2 70 wt.% (Ishihara *et al.*, 2000). According to this criterion some samples from highly fractionated SCS I-type granites are classified as magnetite-series as they display a trend towards higher ferric/ferrous ratios, but some S-type leucogranites also show this trend (Fig. 3). However, most of the SCS I-type granites showing this increase in Fe_2O_3/FeO values are free of magnetite (*e.g.* La Cabrera: Bellido, 1979: Navas del Marqués: Casillas, 1989). In general, the two SCS granite series display similar chemical evolution and ranges of FeO_t content and FeO/(FeO+MgO) ratios.

In a SiO_2 *vs.* bulk magnetic susceptibility plot (Fig. 4), the studied SCS granites define a common trend of evolution which diverges for the highly fractionated leucogranites if magnetite appears. This is the case of the I-type magnetite-bearing leucogranites of La Pedriza pluton that show a strong enrichment in MS values. These high MS values are also shown by other felsic I-type magnetite-bearing felsic plutons of the Central Iberian Zone (*e.g.* Gerês pluton in Portugal, Sant'Ovaia *et al.*, 2013) (Fig. 4). In this plot it is remarkable to note: i) the divergent trend of MS values in highly fractionated leucogranites between both granite series when magnetite appears, and ii) the data connection of the Iberian Variscan magnetite-bearing leucogranites with the typical trend of evolution of cordilleran I-type granites (Ishihara, 1990). The only Variscan pluton from the CIZ which shows similar magnetic features to those of Cordilleran I-type granites is the magnetite-bearing Lavadores pluton from Portugal (Martins *et al.*, 2011; Sant'Ovaia, 2013). Moreover, the overlapping in MS values of some intermediate rocks (tonalites) with the granites suggests a mainly crustal derivation of these SCS Variscan plutonic rocks (Fig. 4).

Biotite

Biotite is the main and most frequent mafic silicate in I-type granites, with minor amphibole, whereas in S-type granites other Fe-bearing silicate minerals (such as cordierite, muscovite, tourmaline and minor garnet) may also occur. In most of the granitoids, biotite is found as small subhedral flakes of red brown colour, usually clustered with opaque minerals and other accessory phases (zircon, apatite, monazite, xenotime or allanite). Only in the most evolved I-type leucogranites, biotite is variably green to brownish. Accessory magnetite is associated with this last group of biotite.

All the studied mica consists of biotite in the sense of Deer *et al.* (1962) (*i.e.* Fe/(Fe+Mg)≥0.33) and shows low total sum of cations. This deficiency is explained by vacancies in the octahedral position (ranging from 4.84 to 6 atoms per formula unit, apfu) and deficient interlayer occupancy. The total Al content ranges from 2.36 to 4.73 apfu. Therefore, there is enough Al^{3+} both to complete the tetrahedral position along with Si and to enter in the octahedral position along with Fe, Mg, Ti and Mn. Some compositional differences between biotite from I- and S-type granites are shown in the octahedral position, clearly conditioned by the magmatic differentiation of the

TABLE 2. Magnetic susceptibility (*K*) data for central Iberian Variscan metamorphic rocks

				Magnetic susceptibility (K x μSI)		SiO_2 (wt.%)	
Formation	Lithology	Mineralogy	nº	Mean	Range	Mean	Range
Schist-Greywacke Complex	Metapelite	Chl-ms-bt-bearing slate	4	279	75-434	59.5	58.1 - 64.8
	Spotted slate	Bt-crd-ms-bearing slate	1	300		-	
	Hornfels	Bt-crd-and-kfs-bearing pelite	10	396	147-740	61.6	59.2 - 67.2
	Metagreywacke	Qtz-pl-bt-ms-bearing slate	1	208		71.5	
Orthogneisses	Augen gneiss	Grt-crd-bt-bearing metagranite	9	270	145-530	64.4	61.5 - 67.2
	Leucogneiss	Bt-bearing metagranite	1	100		72.6	
Lower crustal xenoliths	Pelitic restite	Grt-sill-restite	1	21250		35.9	
	Pelitic granulite	Grt-sill-qtz-kfs-pl granulite	3	17333	11100-21000	49.5	46.7 - 55.0
	Granulite	Grt-qtz-kfs-pl-sill granulite	3	1362	997-2050	-	
	Felsic granulite	Kfs-pl-qtz-grt granulite	5	1958	209-7720	62.5	58.6 - 68.4

selected rock types but also according to the I- or S-type granitoid affinity. In Figure 5 selected plots show that biotite composition defines different trends for S- or I-type granites according to the increasing Fe/(Fe+Mg) ratio, a good parameter of biotite differentiation in the studied samples. In general, I-type biotite shows higher Si and Fe and lower Al^{VI} contents than in S-type granites (see also Villaseca and Barbero, 1994) (Fig. 5D). The Ti content in biotite decreases in both granite types (Fig. 5A), whereas the Mn content clearly increases in the more evolved biotite from leucogranites, reaching high values (up to 2.5 wt.% MnO in green biotite from La Pedriza) (Fig. 5B). Remarkably, the green biotite associated with magnetite (from La Pedriza pluton) shows similar Ti and Fe (FeO and Fe_2O_3) contents to that of green biotite associated with ilmenite (from La Atalaya Real pluton) (Fig. 5A; C).

Wones and Eugster (1965) studied the stability of biotite composition under particular buffered conditions of fO_2. When plotted in the Fe^{2+}-Fe^{3+}-Mg diagram (Fig. 6A), the studied biotites of both granite types overlap in compositional fields following the Ni-NiO buffer. Nevertheless, biotite from the studied S-type granites plot slightly below the line separating mica from magnetite- and ilmenite-series granites (Buda *et al.*, 2004) (Fig. 6A), suggesting slightly lower redox conditions than those from I-type granites. The new Fe^{3+} estimation used in this work is in agreement with biotite chemistry of similar S-type granites from northern Portugal, where FeO and Fe_2O_3 were analysed separately by classical wet techniques, also plotting above the Ni-NiO buffer (Neiva, 1998).

If we assume that biotite equilibrated at different temperature during granite magma evolution (about 850-675 ºC, in most studied granites: Casillas, 1989; Pérez-Soba, 1991; Eugercios, 1994) it is possible to estimate roughly their fO_2 conditions. When using the Wones and Eugster (1965) approach, biotites from both studied granite types show a similar trend in this diagram (Fig. 6B). Only slightly different oxidation conditions are detected for these two granite types including the most evolved I-type leucogranites. Interestingly, green biotite (mainly from La Pedriza pluton), whether or not associated with magnetite, displays transversal trends in the Fe^{2+}-Fe^{3+}-Mg diagram (Fig. 6A) indicating an apparent reducing trend. These results would suggest that fO_2 has remained mostly buffered during magma evolution in the most evolved I-type granites, where the latest Fe-rich biotite crystallizes with accessory magnetite. This will be discussed in a section below.

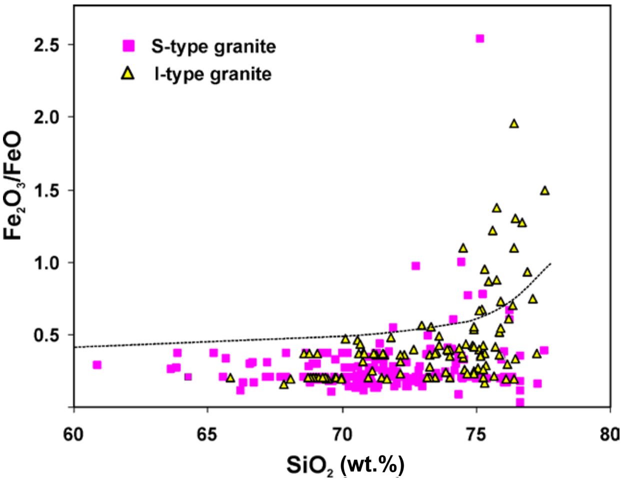

FIGURE 3. SiO_2 *versus* ferric/ferrous ratio of SCS granites. Whole-rock granite chemical data with ferrous iron determined by titration with a standardised potassium permangate solution are from Bellido (1979), Casillas (1989), Andonaegui (1990) and Pérez-Soba (1991). Broken line is the separation line between magnetite- and ilmenite-series (Ishihara *et al.*, 2000).

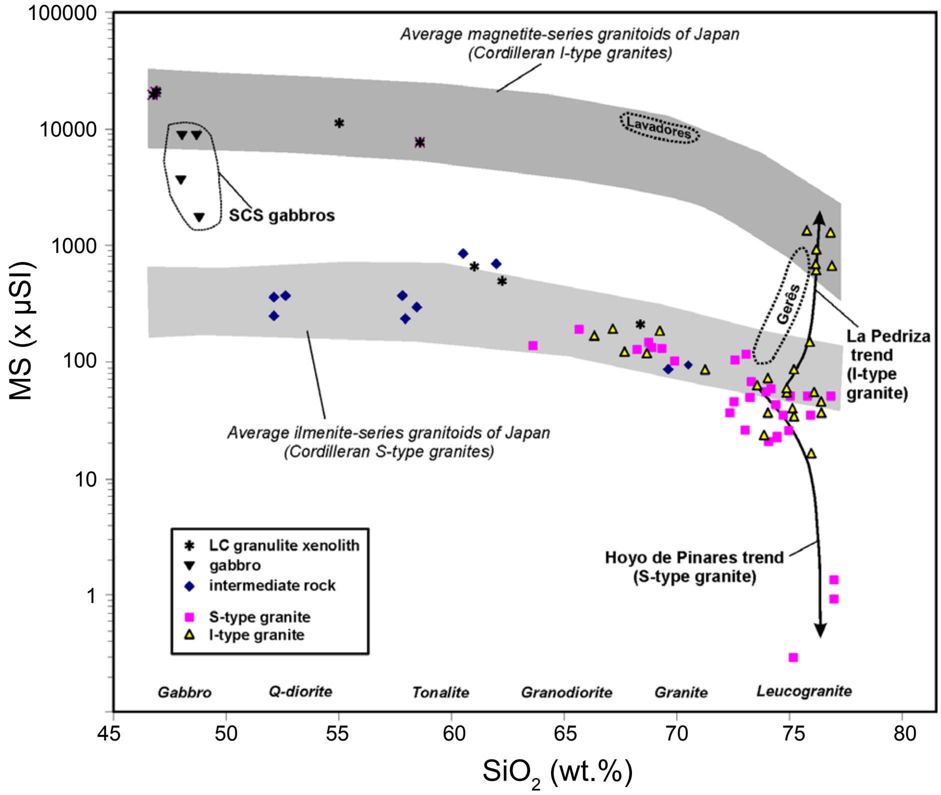

FIGURE 4. SiO_2 *versus* magnetic susceptibility (MS) for studied Variscan plutonic rocks. For comparison purposes SiO_2 compositional ranges of Lavadores (Silva, 2001) and Gerês (Mendes and Dias, 2004) plutons are included with their corresponding MS data (Sant'Ovaia *et al.*, 2013). Averaged ilmenite and magnetite series granitoids of Japan is taken from Ishihara (1990).

Fe-Ti oxides

Ilmenite ((Fe, Mn, Mg) TiO_3) is the only accessory Fe-Ti oxide mineral in S-types granitoids and is also dominant in I-type granites of the CIZ. Ilmenite with magmatic appearance is scarce and occurs as discrete and small anhedral crystals, frequently associated with mafic silicate minerals. Ilmenite abundance decreases in the most evolved granites, and it is absent in most of the SCS leucogranites at thin section scale. Tiny crystals also appear associated with chlorite alteration, but this secondary ilmenite has not been considered in this study. Ilmenite from the S- and I-type granites does not show chemical differences. Ilmenite composition defines a relatively extent solid solution towards the end member pyrophanite, which is shown by a MnO increase (up to 14.0 wt.%) within the more evolved granitoids, well negatively correlated with the FeO content (Villaseca and Barbero, 1994). This strong preference of Mn to occupy the Fe site is favoured by decreasing temperature (Neumann, 1974). The Fe_2O_3 content (calculated according to charge balance) is negligible.

Magnetite has been found exclusively in one of the most evolved (G3) units of the I-type La Pedriza leucogranite pluton and in its marginal aplite-pegmatite bodies (Pérez-Soba and Villaseca, 2010). It occurs mainly associated to green biotite and to other accessory minerals (fluorite and zircon), as suhedral to euhedral crystals. Associated secondary ilmenite occurs as lamellae, rims or within microcracks of magnetite crystals. Magnetite shows almost pure Fe_3O_4 composition, with minor and not significant Si, Ti, Al and Mn contents (Pérez-Soba, 1991).

DISCUSSION

Oxidation trends in Variscan granite magmas

It is known that iron content is the main geochemical control of the magnetic susceptibility in granitic rocks, and as FeO_t decreases during magmatic differentiation, the magnetic susceptibility decreases (*e.g.* Aydin *et al.*, 2007). Iron can be distributed between Fe^{2+} and Fe^{3+}, and ferric to ferrous iron ratios increase in the highly

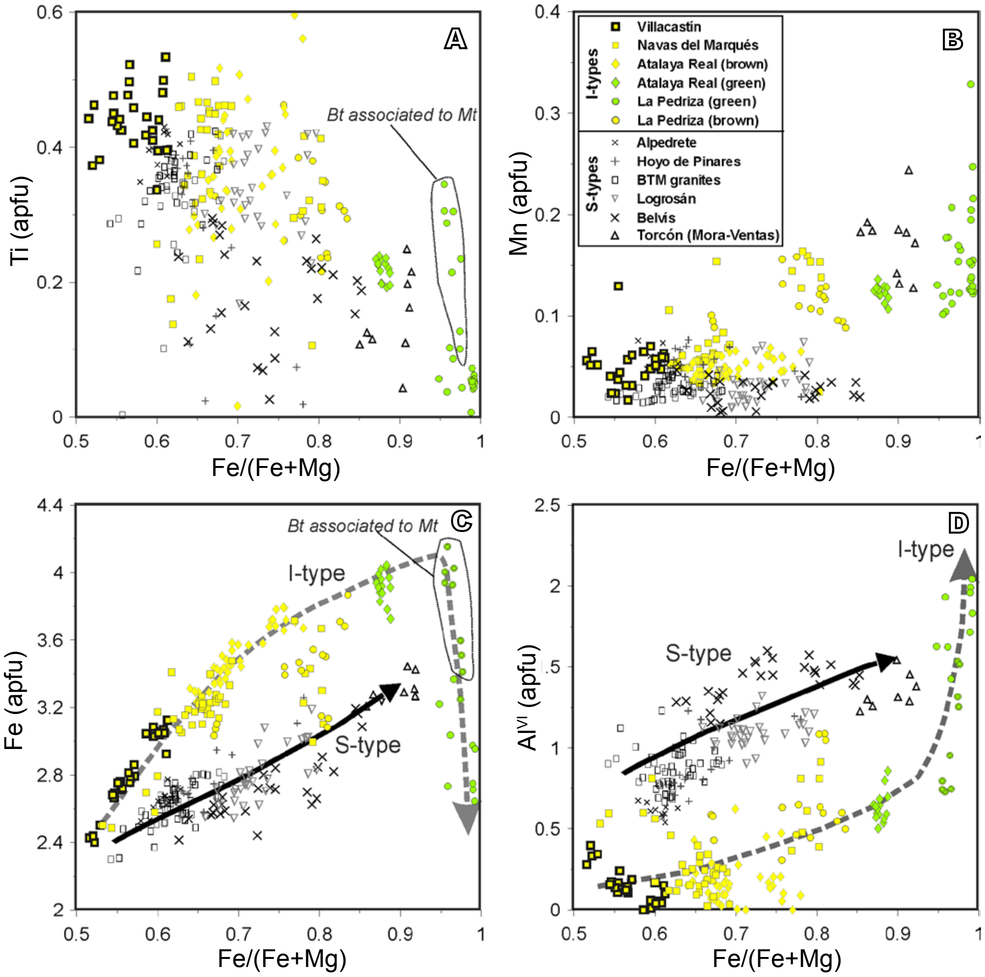

FIGURE 5. Biotite chemistry of central Iberian Variscan granites. Data from Casillas (1989), Andonaegui (1990), Pérez-Soba (1991), Eugercios (1994), Villaseca and Barbero (1994), Castellón (1995), Merino (2014), Chicharro (2015), and this work.

fractionated I-type granites, as well as in equivalent S-type leucogranites (Fig. 3) (Ishihara *et al.*, 2000). In consequence, redox magmatic conditions in late stage leucogranites of both granite types slightly change to more oxidizing values. This is reflected in the whole-rock geochemistry, but not so clearly in the mineral chemistry of Fe-rich minerals (biotite, Fe-oxides) of these peraluminous granites (Fig. 6).

In previous works, where Fe^{3+} content was estimated by Bruyin *et al.* (1983) equation, biotite analyses from the SCS S-type granites plotted mostly below the Ni-NiO buffer on Wones and Eugster (1965) Fe^{2+} – Fe^{3+} – Mg diagram for biotite (*e.g.* Casillas, 1989; Eugercios, 1994), in contrast with I-type granites that plotted within or slightly above this buffer, suggesting slightly higher oxidation conditions. Nevertheless, when using Fe^{3+} content of granite biotite with our empirical equation (as explained in analytical methods), T-fO_2 estimates for the SCS granites indicate crystallization conditions near the Ni-NiO buffer for all the granite types (Fig. 6B). Thus, similar oxidation conditions are estimated for all the studied granites. Nevertheless, in the most felsic I-type leucogranites (*e.g.* La Pedriza pluton), some late green biotites plotted clearly below the Ni-NiO buffer (Fig. 6), mostly those not related to the accessory magnetite. Thus, the Fe-richest biotites from the highly fractionated I-type leucogranites show a trend towards slightly lower oxidizing conditions (Fig. 6), in contradiction with the whole-rock chemistry. This is not a question of the Fe^{3+} estimation used for biotite chemistry because previous works drew the same evolution towards lower fO_2 values (*e.g.* Casillas, 1989; Neiva, 1998). Thus, granite biotite chemistry is not a good indicator of the redox state of the magma.

The change in the oxidation state during magmatic crystallization has been attributed to interaction with external sources either by contamination from wall-rocks

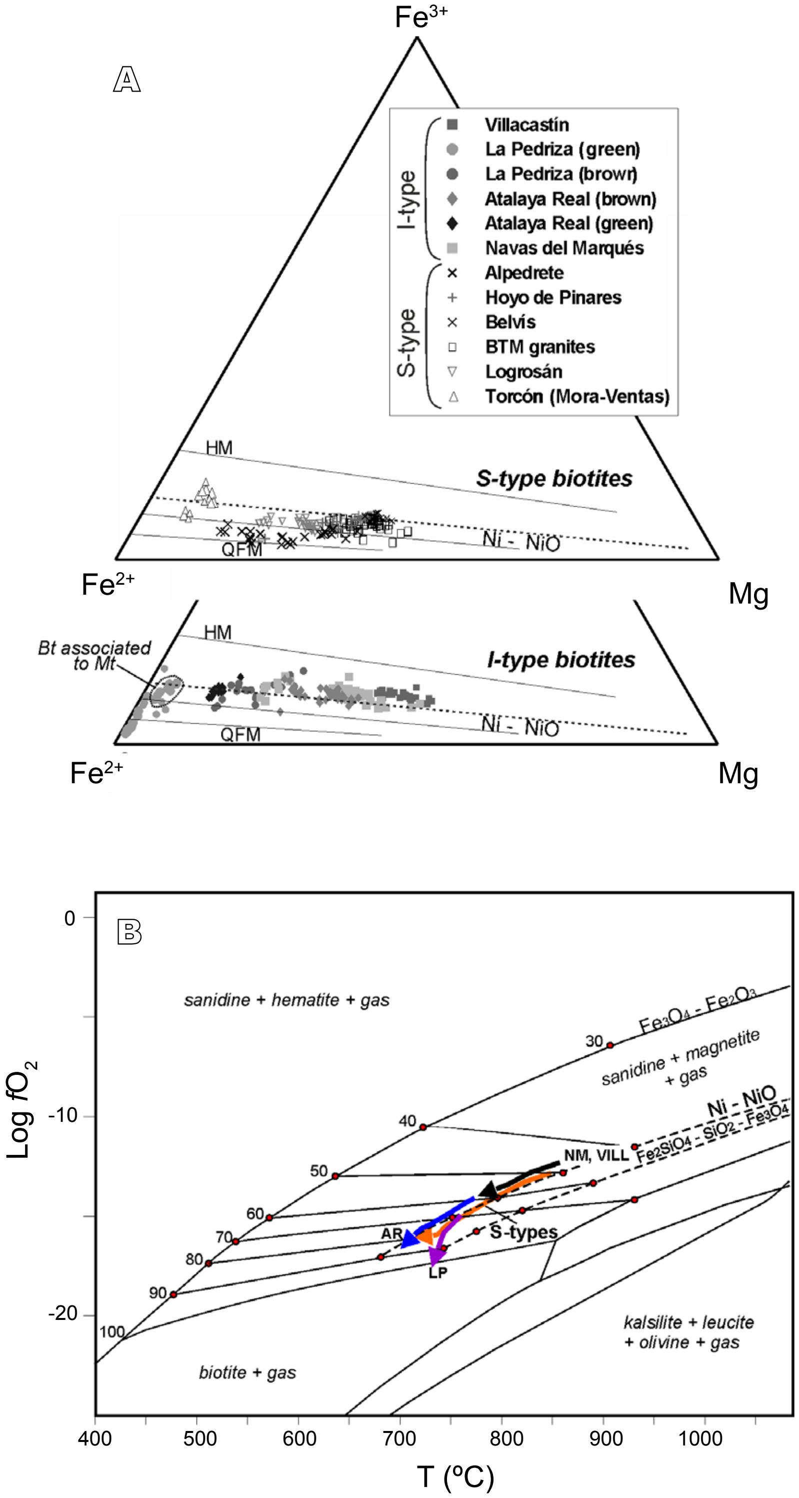

FIGURE 6. A) Fe^{2+}-Fe^{3+}-Mg diagram of biotite of Variscan granites. Lines represent composition of common fO_2 buffers for biotite: quartz-fayalite-magnetite (QFM), nickel-nickel oxide (NNO), and hematite-magnetite (HM) by Wones and Eugster (1965). The broken line separates biotite from magnetite- and ilmenite-series granite after Buda *et al.* (2004). B) Log fO_2-T diagram based in biotite chemistry (after Wones and Eugster, 1965) illustrating the redox conditions (at P= 2kb) of studied Variscan granites. Lines with numbers illustrate Fe/(Fe+Mg) isopleths. Green and brown biotite (from Atalaya Real –AR- and La Pedriza –LP- plutons) are represented toghether. Other abbreviations: NM-VILL: Navas del Marqués and Villacastín plutons.

or by mixing with mafic magmas (*e.g.* Ishihara, 1977; Sant'Ovaia *et al.*, 2013). In marginal parts of epizonal plutonic complexes, the contact with near-surface meteoric ground waters or the proximity to oxygen-rich atmosphere can lead to oxidized Fe^{2+} to Fe^{3+} in the magma (*e.g.* Ishihara, 1977; Best, 2003). Nevertheless, the epizonal emplacement level of most of the leucogranite units of both SCS granite types combined with the graphite-bearing nature of the metamorphic wall-rocks suggest that the trend to more oxidized granitic melts of some of the SCS leucogranites is a primary feature. Moreover, although the local presence of mafic microgranular enclaves in both granite types evidences magma mingling processes in the most primitive monzogranites, these are unlike mechanisms to explain the slight oxidation trend in highly fractionated granites, in which mafic interaction is rarely observed. Thus, the oxidation state of these magmas can be mostly derived from its source, or from crystal fractionation processes, rather than from interaction with external agents, as stated in other works (*e.g.* Carmichael, 1991; Best, 2003). It is remarkable the presence of graphite in some S-type granites of the CIZ (Pérez-Soba *et al.*, 2017), indicating the involvement of graphite-bearing crustal protoliths and an original reduced state of parental granite melts.

The absence of potential external sources of oxidation in the studied SCS granitoids does not mean that their oxidation state is only controlled by the initial redox state of granite sources because magmatic differentiation can play a significant role on the oxidation state of the magma (*e.g.* Pichavant *et al.*, 1996; Kelley and Cottrell, 2012). This is shown by our data because the major changes in fO_2 values (Fig. 6) and the sharp change in magnetic susceptibility values, recorded by the crystallization of magnetite, occur in the highly fractionated I-type leucogranites (Fig. 4). Thus, the redox state of very felsic granitic magmas might be controlled by magmatic processes other than those inherited from the source region.

From a geochemical point of view, water and other volatile or fluxing elements are important in regulating oxygen fugacity in igneous processes (Osborn, 1959; Czamanske and Wones, 1973). Major and trace element contents and variation trends shown by the two granite types in the SCS are very similar, as stated in many previous works, including isotope signatures (Villaseca *et al.*, 1998; Bea *et al.*, 1999; Villaseca and Herreros, 2000; Villaseca *et al.*, 2012). Highly fractionated SCS I-type leucogranites show similar or lesser P, F, Li and B contents than their correlative S-types, and the water content (undersaturated conditions) might be similar in these extremely felsic granite melts. In fact, most of the pegmatite fields associated with Variscan granites in the CIZ are those related to some S-type plutons (*e.g.* Roda-Robles *et al.*, 2016), suggesting also slightly different water undersaturation conditions between granite types. Other potential sources of oxidation in epizonal plutons are related to devolatilization or magma degassing (H, S, Cl) (*e.g.* Kelley and Cottrell, 2012), but again these processes should affect equally both granite types due to their similar volatile contents and their emplacement at equivalent mid-to-shallow crustal levels.

The role of Fe-bearing mineral fractionation in highly felsic peraluminous granites

The existence of I-type granites showing a divergent evolution that leads to highly fractionated leucogranite units which belong either to the magnetite or to the ilmenite series (Fig. 4) poses the question that oxidation conditions in felsic magmas might be primarily controlled by mineral fractionation.

The co-crystallization of different Fe-rich mafic minerals leads to a higher competition for iron in the mineral assemblage of a highly fractionated S-type granite melt compared to the simpler mafic mineralogy in felsic I-type granites of less peraluminous composition (Fig. 7). Thus, in I-type leucogranites, biotite (and in lesser amount, the accessory oxide mineralogy) is the main host of Fe, whereas in S-type leucogranites biotite can coexist with other ferromagnesian silicates as cordierite, garnet or tourmaline, but iron is also hosted in associated muscovite (up to 3.3 FeO wt%), andalusite (up to 0.63 wt%) or apatite (up to 4.2 wt%) (Villaseca

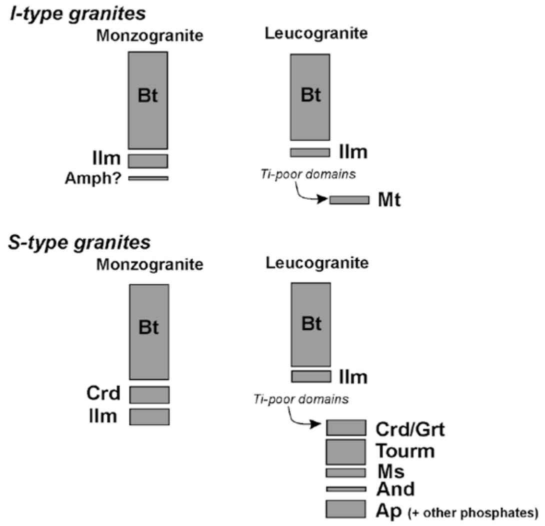

FIGURE 7. Sketch illustrating the evolution of Fe-bearing mineral paragenesis with fractionation degree (monzogranite to leucogranite) in the studied Variscan I- and S-type granites. Relative contributions of the constituent mineral phases to the iron budget is approximated by the height of the bar. Mineral abbreviations are after Kretz (1983). See text for further explanation.

et al., 2008; Chicharro, 2015; Pérez-Soba *et al.*, 2017) (Fig. 7). In residual TiO_2-poor melt domains of highly fractionated I-type leucogranites, only magnetite and Mg-Ti-poor biotite crystallize as the main Fe-rich minerals. The close spatial association of magnetite with the Fe-rich green biotite of the La Pedriza granites attests their co-crystallization (Fig. 8). In equivalent Ti-poor pockets of S-type leucogranite melts, Fe can partition between Al-rich silicates (biotite, garnet, cordierite, muscovite, tourmaline, andalusite) and phosphates (apatite, childrenite-eosphorite), thus reducing the possibility of magnetite crystallization.

In S-type leucogranites, the biotite composition could not reflect the oxidation state of the granite and the redox conditions are difficult to establish (Pichavant *et al.*, 1996). In other words, S-type leucogranites might also have reducing/oxidising trends comparable to those of I-type granites, but this would not be reflected in variable biotite chemistry. For instance, crystallization of magmatic cassiterite has been described in some evolved units of S-type plutons of the CIZ (Everdosa, Gomes and Neiva, 2002; Jálama: Llorens, 2011) indicating more oxidizing redox conditions than those of the Ni-NiO buffer (Linnen *et al.*, 1995). Similar crystallization conditions have been also deduced for muscovite-tourmaline leucogranites of the Himalaya, suggesting that oxidizing trends could be probably common in felsic peraluminous magmas free of magnetite and that Fe^{3+} incorporation can also occur in muscovite and tourmaline (Pichavant *et al.*, 1996), as well as in phosphates (Pérez-Soba *et al.*, 2013). Moreover, magnetite-bearing S-type leucogranites have been described elsewhere (Lachlan Fold Belt: Whalen and Chappell, 1988; Japan island arc: Ishihara, 1990; Himalaya: Guo and Wilson, 2012).

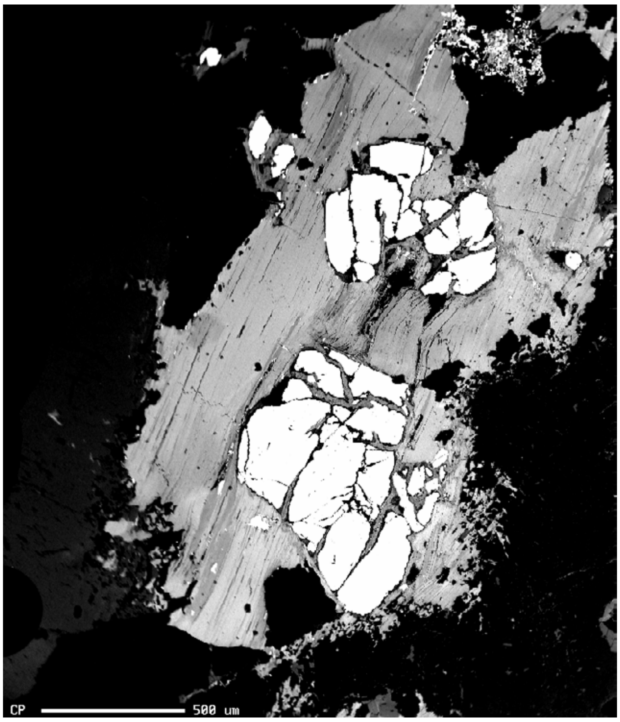

FIGURE 8. Backscattered (BSE) image of green biotite and associated magnetite (bright BSE luminescense) in the La Pedriza G3 unit.

Therefore, the lack of magnetite in the studied highly fractionated S-type granites might not be due to lesser oxidation conditions during late magmatic stages than those in I-type leucogranites. It rather could be a consequence of the different mafic mineral assemblage that crystallized in granite batches of each type. Thus, the whole-rock Fe_2O_3/FeO ratio is a better approach to the oxidation state of felsic magmas than biotite chemistry (Pichavant *et al.*, 1996).

Problems with granite classifications based on MS values

The magnetite- and ilmenite-series classification of granitic rocks from Japan (Ishihara, 1977; 1990) is a descriptive division based on the accessory Fe-rich oxide minerals and on the magnetic susceptibility values. Comparison studies with the alphabetic granite classification concluded that the magnetite series can be correlated with I- type granites and that ilmenite series is composed of both I- and S-type granites (*e.g.* Murata and Itaya, 1987; Whalen and Chappell, 1988). As the occurrence of magnetite or ilmenite is primarily controlled by the oxidation state of the source material and the degree of crystal fractionation of the granite melt, as discussed above, the correlation between granite types and iron oxides occurrence does not necessary match.

The magnetite-series coincides very well with I-type granites from the coastal batholiths in continental margins and island-arc subduction settings (*e.g.* Ishihara *et al.*, 2000). These are the cordilleran I-type granites of the Pitcher's classification related to plate edges (Pitcher, 1993), different in chemical and petrographical features to other I-type granitoids (amphibole-bearing metaluminous or slightly peraluminous granites) in collisional scenarios (*e.g.* Caledonian, Tasmanian, Variscan). For instance, Whalen and Chappel (1988) realized that most I-type granites from the Lachland fold belt showed ilmenite-series characteristic and some S-type granites could be also ascribed to magnetite-series. They concluded that the redox condition may be more important than the nature of the granite protoliths on a classification based in MS values.

In the CIZ of western Iberia only one granite pluton can be considered strictly belonging to the magnetite series: the

Lavadores granite from NW Portugal (Martins *et al.*, 2011; Sant'Ovaia *et al.*, 2013) (Fig. 4). Most other CIZ I-type granites are ilmenite-bearing series except some highly fractionated leucogranitic units showing accessory magnetite (Traba, El Pindo, Caldas de Rey, Gerês and La Pedriza). Low magnetic susceptibility values have also been found in many other Variscan I-type granites of central western Europe (*e.g.* Pyrenees: Gleizes *et al.*, 1998; Carpathians: Gregorová *et al.*, 2003) due to the absence -or insignificant presence- of ferromagnetic minerals (magnetite) in those granites. The apparent contradiction between magnetic values and the geochemical I-type granite assignation was detected in previous works indicating different tectonic processes and granite sources in cordilleran and collisional scenarios (*e.g.* Gregorová *et al.*, 2003).

Oxidation state of parental granite magmas is primarily controlled by the source region, and this depends on the geodynamic scenario. In a subduction setting, devolatilization of the oceanic lithosphere is likely the main oxidizing agent in mantle-to-lower crustal-derived magmas. By contrast, continental biogenic graphite-bearing material is the dominant reducing medium for crustally derived collisional magmas. Most of the studied Variscan I-type granites have a lower crustal meta-igneous origin of graphite-bearing sources (*e.g.* Villaseca *et al.*, 2012), very different in oxidation conditions to those prevalent in magmas derived from subducted oceanic crust below an active continental margin. Thus, these Variscan I-type granite melts mostly belong to ilmenite-bearing series.

CONCLUSIONS

This study focuses on the magnetic susceptibility (MS) values of Variscan granites from central Spain and the mineral chemistry of their Fe-rich phases, which have led to the following remarks:

i) A new empirical formula for Fe_2O_3 estimation in biotite has been achieved, giving more accurate results than the calculation of Bruiyn *et al.* (1983).

ii) Analysed S- and I-type granites show similar MS values except for highly fractionated leucogranites that draw a divergent trend: high MS evolution if late magnetite crystallizes, or low MS evolution if it does not. In the Central Iberian Zone only some magnetite-bearing I-type leucogranites appear, showing the trend towards high MS values.

iii) Redox conditions seem to be very similar for both granite types but magnetite is favoured in I-type leucogranite melts by magmatic crystallization of a simpler mafic (Fe-rich) mineral paragenesis.

iv) In highly felsic granites neither the biotite chemistry nor the presence/absence of magnetite seem to be good indicators of the magma redox state.

v) The assignation of both granite types to the ilmenite-series, as in other Variscan regions, suggests a dominant graphite-bearing (reducing) source for these crustal derived collisional magmas, in contrast to cordilleran granites of subduction settings.

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ELECTRONIC APPENDIX I

Supplementary Figure I. Estimated FeO and Fe_2O_3 contents in biotite according to either Bruiyn *et al.* (1983) formula or to the empirical equation proposed in this study (see formulas in the text), and then compared to their analyses via Mössbauer spectroscopy (data from: Guidotti and Dyar, 1991; Shabani *et al.*, 2003; Bónová *et al.*, 2010). Note the better fit of Fe_2O_3 (and FeO) estimation in biotite using the equation proposed in this study. See text for further explanation.