Probing crustal and mantle lithosphere origin through Ordovician volcanic rocks along the Iberian passive margin of Gondwana

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A B S T R A C T

Northwestern Iberia preserves one of the most complete Paleozoic sequences that document the origin and development of a passive margin along the southern (Gondwanan) flank of the Rheic Ocean. In addition to a well preserved sedimentary record, there is widespread Ordovician volcanic activity that can be used to probe the nature of the lower crust and mantle lithosphere that sourced the volcanic rocks during the Rheic ocean opening. The Ordovician rift-related volcanic sequences provide first-order constraints on the early evolution of the Rheic Ocean. In addition to published and new lithogeochemical data, we provide Sm/Nd isotopic data which together constrain the mantle or crustal source and allow an assessment on the role of the basement in Rheic Ocean magmatism. The data imply that the mafic rocks are derived from a variety of sources, including juvenile mantle that was contaminated by subduction coeval with Early Ordovician magmatism, suggesting the importance of arc activity in northwest Iberia during the opening of the Rheic Ocean. Other basalts were derived from a subcontinental lithospheric mantle that was enriched at about 1.0 Ga. Basalts derived from a mantle enriched at ca. 1.0 Ga occur along other parts of the Gondwanan margin (Avalonia, Oaxaquia) and so the Iberian basalts may be a local representation of a regionally signficant enriched mantle. The Sm–Nd isotopic characteristics permit a genetic connection between this mantle source and the basement rocks recently identified in northwest Iberia. Felsic magmas are predominantly intra- crustal magmas derived from melting a Mesoproterozoic crust, lending support to other lines of data that the Gondwanan margin of northwest Iberia was predominantly underlain by a South American (Rio Negro) source.

Keywords: Rheic Ocean Northwest Iberia Ordovician, Crust Mantle, Sm–Nd isotopes

1. Introduction

The Late Cambrian to Early Ordovician evolution of northern Gondwanan margin preserves passive margin sedimentary, intrusive and volcanic sequences that record the origin of the Rheic Ocean and the evolution of its southern flank (e.g. McKerrow and Scotese, 1990; Cocks and Torsvik, 2002). These sequences have been dispersed by the breakup of Pangea and are recorded from Oaxaquia (Mexico) in the west to the Bohemian Massif in the east (Stampfli and Borel, 2002; Keppie et al., 2003; Murphy et al., 2006; Fig. 1). There is general agreement that the origin of the Rheic Ocean was the result of the northward drift of some peri-Gondwanan terranes, such as Avalonia, Carolinia and Ganderia from the Gondwanan margin (McKerrow and Scotese, 1990; Cocks and Fortey, 1990; Cocks and Torsvik, 2002; Stampfli and Borel, 2002; Murphy et al., 2002). However, various models have been proposed in recent years to explain this rifting event (for example van Staal et al., 1998; Crowley et al., 2000; Matte, 2001; Stampfli et al., 2002; von Raumer et al., 2002; Murphy et al., 2006). Northwestern Iberia preserves Late Cambrian–Early Ordovician sedimentary and igneous rocks that provide one of the most complete records of passive margin development along the southern flank of the Rheic Ocean and the effects of its subsequent closure during the Carboniferous Variscan orogeny (for a complete set of references see Gibbons and Moreno, 2002 and Vera, 2004).

A wealth of lithostratigraphic, paleontological and paleomagnetic data have led to a consensus that Iberia was located adjacent to the West African craton during the Early Paleozoic (Fig. 1). Determination of the age and composition of the basement to these sequences is important for understanding the geodynamic evolution and to make palinspastic reconstructions of the northern Gondwanan margin. Until recently, the basement to the passive margin sequence was thought to

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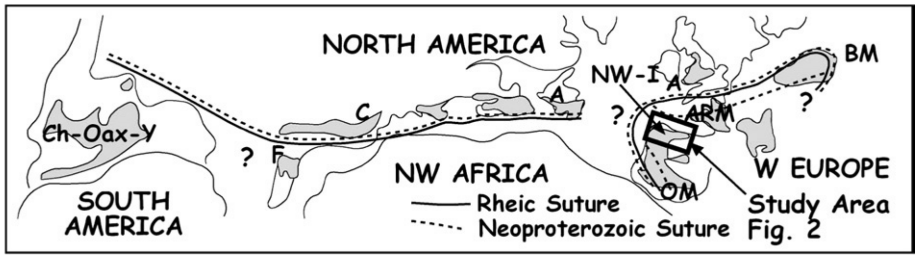

Fig. 1. Localities where the sequences documenting the evolution of northern flank of the Gondwanan margin (southern flank of the Rheic Ocean) are preserved shown in a Pangean reconstruction. Ch-Oax-Y, Chortis-Oaxaquia-Yucatan; F, Florida; C, Carolinia; A, Avalonia; O-M Ossa Morena; NW-I, Northwest Iberia; Arm, Armorica; BM, Bohemian massif.

be part of a Paleoproterozoic (West African) ca 2.0 Ga craton that characterizes the West European Variscan Belt (Guerrot et al., 1989, Samson and D'Lemos, 1998). However, other basement sources in NW Iberia have been identified consisting mainly of Mesoproterozoic (ca. 1.1–1.4 Ga) in addition to some Archaean sources (detrital zircons and white micas, Fernández-Suárez et al., 2000, 2002a,b; Gutiérrez-Alonso et al., 2003, 2005). Also, a recently dated outcrop of presumably basement rocks has yielded a Mesoproterozoic age (Purrido amphi- bolite, 1159 ±39 Ma, U–Pb, zircon, Sánchez-Martínez et al., 2006). However, the Purrido amphibolite is allochthonous relative to the Gondwanan margin. An additional challenge is that the Neoproter- ozoic and Late Paleozoic tectonic events in this region may have involved thrusting of cover sequences relative to their basement. As a result, the relationship between this newly identified basement and the hidden basement that yielded the Ordovician volcanic rocks is unclear. In the Late Neoproterozoic, this region underwent a protracted (ca. 750–550 Ma) low grade tectonothermal evolution during the Cordilleran-type Cadomian orogeny along the northern Gondwanan margin (Gutiérrez-Alonso and Fernández-Suárez, 1996; Fernández- Suárez et al., 1998; Gutiérrez-Alonso et al., 2004; Cuesta et al., 2004; Díaz García, 2006) and Late Cambrian–Early Ordovician extreme stretching (Pérez-Estaún et al., 1990; Martínez-Catalán et al., 1992; Díaz García, 2002; Valverde-Vaquero et al., 2005; Díez Montes, 2006) until the onset of the Rheic ocean lithosphere production. In the Late

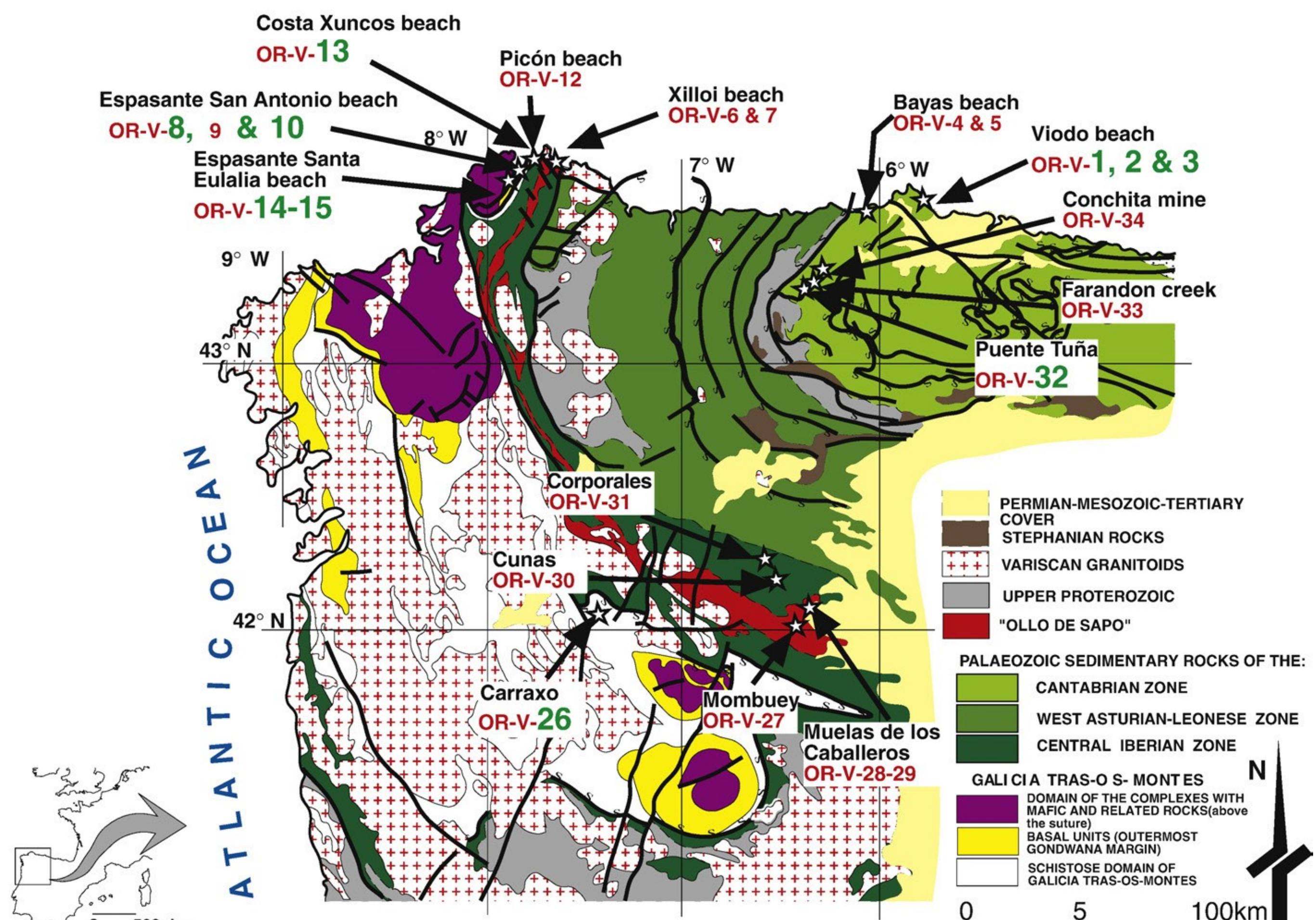

Fig. 2. Geologic map of northwest Iberia (after Farias et al., 1987; Martínez-Catalán et al., 2007) showing the location of samples reported in this study (large numbers) which have been analyzed for REE and Sm–Nd isotopes. More precise locations of samples are given in Table DR-3.

Paleozoic, collision between Laurussia and Gondwana (Variscan orogeny) is manifest in NW Iberia by significant shortening (including thrusting) and ophiolite obduction, which caused the exposure of part of the Rheic Ocean passive margin basement in the so called Basal Units of the Allochthonous Complexes (Martínez-Catalán et al., 1996) (Fig. 2).

The relationship between the inferred and exposed basement and the source or sources of the Ordovician rift-related volcanic sequences would provide first-order constraints on the early evolution of the Rheic Ocean and the nature of the basement and the mantle lithosphere. In addition to a well preserved sedimentary record, there is widespread Ordovician intrusive and volcanic activity, which can be used to probe the nature of the lower crust and mantle lithosphere that provide the source for the volcanic rocks during the Rheic Ocean opening (Murphy et al., 2006).

A focused study on the geochemistry of various igneous rocks exposed in NW Iberia can provide insights into the processes that occurred along this portion of the northern Gondwanan margin. Over the past 20 years, a wealth of geochemical data on the igneous rocks in this region has been published (see Table DR-1) that predominantly focuses on individual tectonostratigraphic zones in the region, and a synthesis of those data is provided here. We also report new geochemical and Sm–Nd isotopic data from representative samples of these igneous rocks, which, together with previously published data, provide constraints on the nature and age of the mantle lithosphere and lower crust at the time of the Rheic Ocean development in northwest Iberia. These data facilitate a comparison between these sources for the various tectonostratigraphic zones in northwest Iberia, an assessment of the degree to which this chemistry may be derived from exposed basement, and an evaluation of their significance in interpreting the evolution of the Rheic Ocean passive margin along the northern margin of Gondwana.

2. Geological setting

Although heterogeneously deformed by Late Paleozoic Variscan orogenesis, one of the most complete sections of the northern Gondwanan platform is exposed in northwestern Iberia (Fig. 2) where Paleozoic rocks lie within an intensely curved Variscan orogenic belt (Weil et al., 2001). In addition to preserving record of passive margin development, northwestern Iberia is characterized by several episodes of voluminous volcanic and intrusive igneous activity.

If the Iberian–Armorican Arc is restored to a pre-Variscan geometry (Weil et al., 2001), the Iberian continental platform of Gondwana is shown to be extremely extensive as indicated by its stratigraphic record, classically represented by a thick, mostly siliciclastic sequence that includes the Late Cambrian–Early Ordovi- cian Armorican quartzite, related quartzose clastic rocks and is covered, sometimes as an unconformity by widespread Silurian black shales (Gutiérrez-Marco et al., 1998). These relationships, together with sedimentological studies are consistent with paleogeo- graphic reconstructions which place NW Iberia adjacent to West Africa along the southern flank of the Rheic Ocean during all the Paleozoic (e.g. Martínez-Catalán et al., 2007; Robardet, 2002, 2003).

Paleozoic rocks in the Iberian Massif are divided into zones based on their Lower Paleozoic sedimentary differences, which are inter- preted to reflect their relative proximity to the Gondwanan margin (Fig. 2). The Cantabrian Zone preserves a coastal environment, whereas the West Asturian Leonese, Central Iberian, Galicia Tras-os- Montes (Schistose Domain) and/or Ossa Morena zones preserve the more outboard tectonostratigraphy (Julivert et al., 1972; Quesada, 1990; Ribeiro et al., 1990; Pérez-Estaún et al., 1990; Quesada et al., 1991; Martínez-Catalán et al., 1997, 1999; Marcos and Farias, 1999; Gutiérrez-Marco et al., 1999; Aramburu et al., 2002; Robardet, 2002, 2003; Robardet and Gutiérrez-Marco, 2004). Boundaries between these zones are major Variscan thrusts and reverse faults that are in some cases reactivated by extension in the aftermath of the Variscan orogeny (Martínez-Catalan et al., 1997, 2003).

Lower Ordovician (Tremadoc-Arenigian) volcanism is widespread and is represented in all the paleotectonic zones (Valverde-Vaquero et al., 2005; Díez Montes 2006; Gutiérrez-Alonso et al., 2007). Coeval with this volcanism, ca. 4500 m of strata accumulated in sub-basins or troughs parallel to the northern Gondwanan margin and are interpreted to reflect a marked increase in subsidence related to tectonic extension and the rift–drift transition stage of Rheic Ocean development (Pérez-Estaún et al., 1990; Martínez-Catalán et al., 1992; Aramburu et al., 2002; Marcos et al., 2004). This extensional event is coeval with the genesis of the widespread Lower Ordovician intrusive granitoid and volcanic rocks which are interpreted as intra-crustal melts generated in response to steep geothermal gradients associated with the rifting event (Ribeiro and Floor, 1987; Gallastegui et al., 1987; Pin et al., 1992; Valverde-Vaquero et al., 2005; Díez Montes, 2006). Although volcanic activity continues until the upper Ordovician, it is relatively scarce and is only locally represented (Heinz et al., 1985, Corretgé and Suárez, 1990, Gallastegui et al., 1992).

The Cantabrian Zone is characterized by voluminous and wide- spread volcanism, and includes several Lower Paleozoic volcanic events that are mostly Lower Ordovician in age although some younger volcanic rocks also occur (Fig. 2; (Loeschke and Zeidler, 1982; Heinz et al., 1985; Gallastegui et al., 1992; Barrero and Corretgé, 2002). Volcanic rocks in the West Asturian Leonese zone (WALZ) are widely distributed but, compared to the Cantabrian Zone are volumetrically minor and their emplacement is thought to have been accompanied by a greater basin subsidence. The northern portion of the Central Iberian Zone (CIZ) preserves the most volumetrically significant Early Ordovician volcanic event in NW Iberia, including the "Ollo de Sapo" belt where voluminous felsic volcanics crop out along a continuous NW- to N-trending belt (Fig. 2). Detailed studies on the age (ca. 495– 480 Ma) origin and geochemistry of these volcanic rocks can be found in Valverde-Vaquero and Dunning (2000), Castro et al. (1999, 2003), Díez Montes (2006) and Montero et al. (2007). Felsic intrusive bodies in the northern CIZ have U–Pb (zircon) ages ranging from the Late Cambrian–Early Ordovician (Miranda de Douro body, 483 ± 3 Ma according to Bea et al., 2006 or 496 ± 3 after Zeck et al., 2007) to 465 ± 10 Ma (Covelo and San Sebastián bodies; Lancelot et al., 1985). In addition to the "Ollo de Sapo belt", in the southern CIZ, mafic sills with tholeiitic chemistry yield a Sm/Nd isochron age of 436 ± 17 Ma (López- Moro et al., 2007).

The Schistose Galicia Tras-os-Montes Domain (SGTMD) (Farias et al., 1987; Martínez-Catalán et al., 1996; Marcos et al., 2002) rests tectonically above the CIZ and consists of a thick siliciclastic sequence with interbedded volcanic rocks. Some of the volcanic rocks yield Lower Ordovician (475 ± 2 Ma, Valverde-Vaquero et al., 2005) ages and have been interpreted as the most outboard parts of the passive margin sedimentary wedge of Gondwana.

On top of the most external parts of the Gondwana sedimentary wedge in the Rheic passive margin, the SGTMD, allochthonous complexes consist of (from bottom to top) the Gondwana basement (known as Basal Units, Fig. 2) structurally overlain by two ophiolitic units of Early Ordovician and Devonian age that are interpreted to be the remnants of the Rheic Ocean or subsidiary oceans closed during the Variscan Orogeny (Martínez-Catalán et al., 1997; Arenas et al., 2007a,b). On top of the ophiolites, the upper units are interpreted to be part of the rocks that constitute the northern (Laurussian) margin of the Rheic Ocean (Martínez-Catalán et al., 1997; Arenas et al., 2007a,b).

Underlying the ophiolites, the Basal Units have a continental affinity and are considered to represent the most external part of the Gondwanan margin (Martínez-Catalán et al., 1996). This margin was subducted below the ophiolitic units during the earliest stages of the Variscan Orogeny and was affected by high-pressure and low- to intermediate temperature metamorphism (Arenas et al., 1995; Rodríguez et al., 2003; Rodríguez Aller, 2005). Extensive geochemical data on these rocks can be found in (Marquínez, 1984; Arenas, 1988; Díaz García, 1990; Pin et al., 1992; Rodríguez Aller, 2005). Despite their complex tectonothermal history, the igneous protoliths have been found to be Lower Ordovician in age (ca. 480 Ma; Santos Zalduegui et al., 1995 and references therein).

Finally, ophiolites within the allochthonous complexes are pri- marily either Lower Ordovician or Devonian in age (e.g. Arenas et al., 2007a,b). The Lower Ordovician ophiolites occur in several structural slices and may represent the vestiges of the first oceanic crust to be formed in the Rheic Ocean.

3. Geochemistry

We combine results from our own samples, with an analysis of geochemical data from the literature to provide an overview of the geochemical and isotopic signatures of the Early Ordovician igneous rocks. The locations of our samples are tabulated (Table DR-3), and their position within the tectonostratigraphic framework of northwest Iberia is shown on a summary map (Fig. 2). In order to facilitate the comparison between rock types, the location of the samples is restored on a schematic cross-section showing their approximate relative positions along the ancient Gondwanan margin (Fig. 3).

4. Sampling and analytical methods

In order to deduce the effects of mantle and crustal sources on Ordovician volcanic rocks along the NW Iberian margin of Gondwana, twenty-two samples from various tectonic zones were analyzed for major and trace elements. In the Cantabrian Zone, the oldest volcanic units were sampled (late Cambrian–Early Ordovician Puente Tuña and Farandón volcanics, samples 32 and 33 respectively), as well as the overlying K-bentonites (sample 34) which are of volcanic origin, and yield a Lower Ordovician age (477.5 ± 1 Ma, U–Pb, zircon; Gutiérrez- Alonso et al., 2007). In addition we sampled volcanic rocks that crop out around the Peñas Cape (Samples 1, 2 and 3, Fig. 2; Suárez et al., 1993). Although there are no precise geochronogical or fossil age constraints, these volcanic rocks are widely interpreted to be Upper Arenig in age (e.g. Gutiérrez-Marco et al., 1999), although they have also been interpreted to be lowermost Upper Ordovician (Dobrotvian, Truyols et al., 1996).

In the northern part of the WALZ, we sampled Middle Ordovician subvolcanic and volcanic rocks within the Luarca Formation (Samples 4 and 5; González Menéndez and Suárez, 2004; Villa et al., 2004) and samples 30 and 31 are representative of the abundant volcanic rocks that crop out in the southern WALZ. There are no published detailed petrologic or geochemical studies available from these rocks. In the CIZ, we present data from several samples taken in the “Ollo de Sapo” region (Samples 6, 7, 27, 28 and 29). In the SGTMD, we selected representative samples of ca. 475 Ma (Valverde-Vaquero et al., 2005) volcanic rocks to represent magmatism located at the most outboard part of the para-autochthonous Gondwanan passive margin (Fig. 3; Samples 11, 12, 13 and 26).

From the allochthonous complexes, we selected samples from the Basal Units (samples 8 and 10) which have 480 Ma protolith ages and represent the most external part of the Gondwanan margin (Fig. 3; Martínez-Catalán et al., 1996).

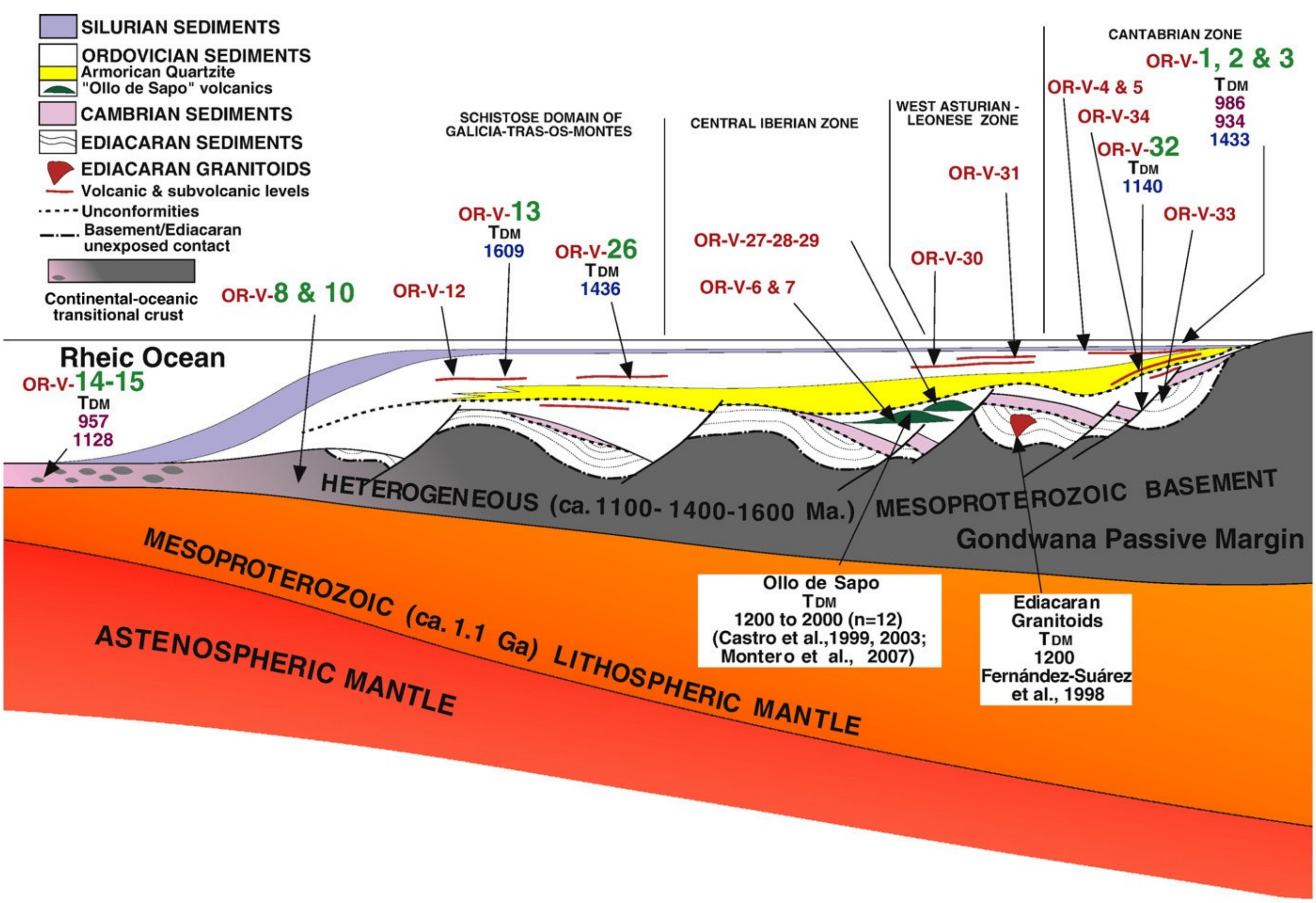

Fig. 3. Location of the analyzed samples restored relative to the northern Gondwanan margin on a schematic cross-section and a summary of the results of our Sm/Nd isotopic data. T_{DM} for the Ediacaran Granitoids from Fernández-Suárez et al. (1998) and for the Ollo de Sapo belt from Castro et al. (1999, 2003), and Montero et al. (2007).

Finally, we sampled the Lower Ordovician ophiolites (Samples 14 and 15) from the Moeche unit in the Ortegal Complex. These rocks have an oceanic signature (e.g. Arenas et al., 2007a,b) and correlate with the better known Vila de Cruces ophiolite in the Ordenes Complex, dated at 497 ± 4 Ma, and both are thought to be the remnant of the earliest Rheic Ocean (Arenas et al., 2007a,b).

Details of analytical methods are given in Supplementary File DR-2. Major and trace element (Rb, Sr, Ba, Ga, Zr, Y, Nb, Co, Cu, Pb, Zn, V, Cr and Ni) geochemistry was determined by X-ray fluorescence spectro- metry in the Nova Scotia Regional Geochemical Centre at Saint Mary's University, Halifax. Rare earth element and Sm–Nd isotopic analyses were determined by ICP-MS at Memorial University, Newfoundland.

Detailed of analytical methods along with all analyses are in given in Supplementary File DR-2 and all analyses are given in Supplementary File DR-3. Analytical procedures, precision and accuracy are described by Dostal et al. (1986) for the X-ray data, by Jenner et al. (1990) for the REE data and by Kerr et al. (1995) for the Sm–Nd isotopic data.

Three samples, ORV 4 (mafic volcaniclastic), 9 (serpentinite) and 34 (K-bentonite) display anomalous geochemical characteristics and are not plotted on geochemical diagrams. ORV 4 has 26.9% SiO_2 very high iron oxide and alumina (38.8 and 19.1 wt.%, respectively) and is clearly highly altered. The probable cumulate nature of the protolith to the serpentinite is indicated by its very high MgO (36.5 wt.%) and Cr (N 2000 ppm) and low Zr (b 5 ppm). Extensive alteration of the K-

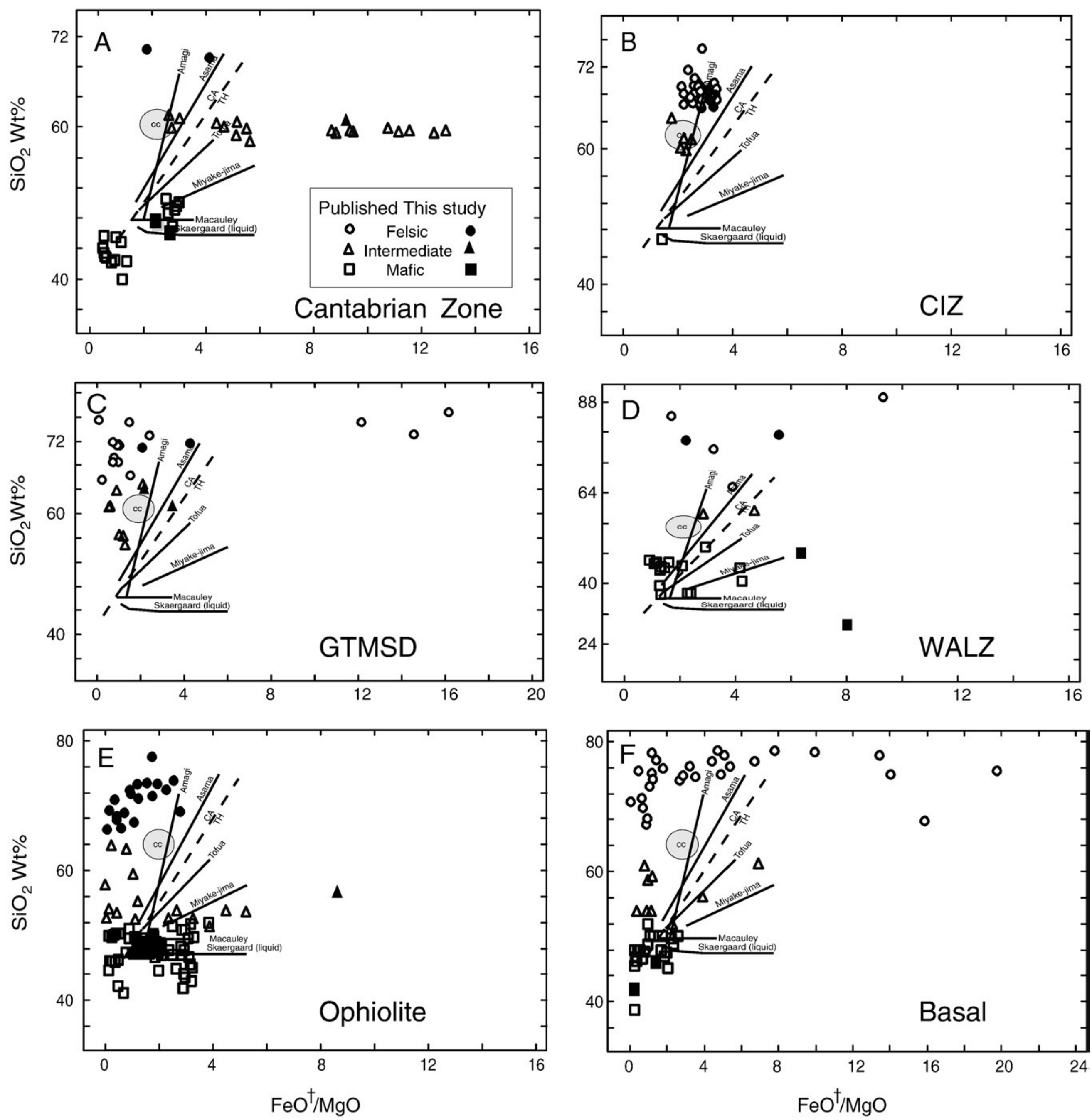

Fig. 4. FeO^t/MgO vs SiO_2 (after Miyashiro, 1974) for (A) Cantabrian Zone, (B) Central Iberian Zone (CIZ), (C) Galicia Tras os-Montes (Schistose Domain), (SGTMD), (D) West Asturian Leonese Zone (WALZ), (E) Ophiolitic units, (F) Basal Units. Sk = Skaergaard trend, CC = continental crust (Tatsumi, 2005). Mafic rocks, squares; intermediate rocks, triangles; felsic rocks, circles. Open symbols = published data; filled symbols, our data.

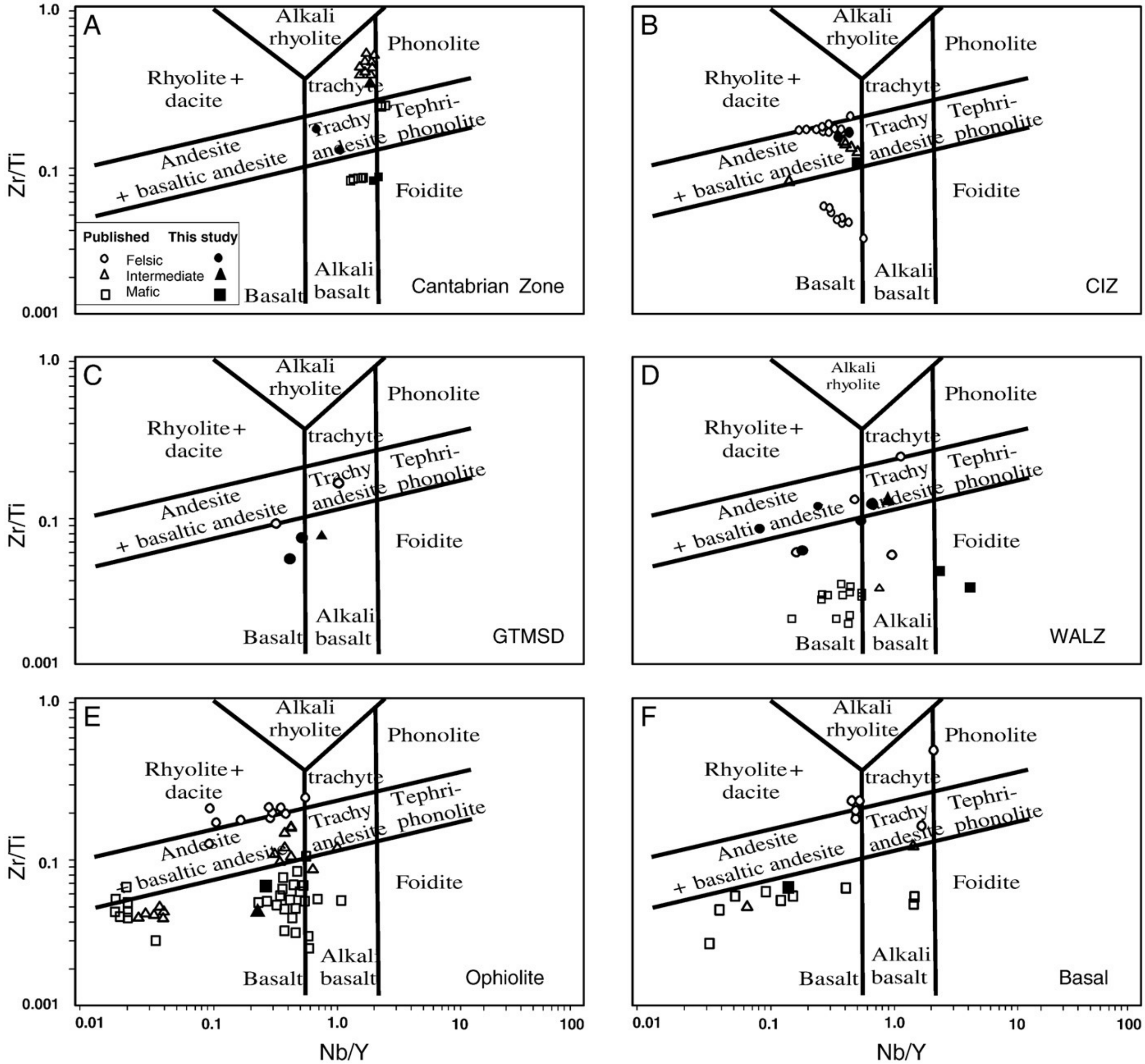

Fig. 5. Zr/Ti vs Nb/Y discrimination diagram (after Winchester and Floyd, 1977; Pearce, 1996) for mafic rocks (A) Cantabrian Zone, (B) Central Iberian Zone (CIZ), (C) Galicia Tras os- Montes (Schistose Domain), (SGTMD), (D) West Asturian Leonese Zone (WALZ), (E) Ophiolitic units, (F) Basal Units. Open symbols=published data; filled symbols, our data.

bentonite is indicated by its very high Al_2O_3 (37.1 wt.%). The remaining 19 samples were selected for REE analysis and 11 of those were selected for Sm–Nd isotopic analysis. The entire lithogeochemical and isotopic dataset and details on the analytical methods are available on-line (Supplementary File DR-2).

A wealth of geochemical data on the igneous rocks of this region (Table DR-1) has been published over the past twenty years. However, many of these data sets do not include a full complement of trace element analyses required to probe the nature of their mantle or crustal sources. In addition, they have been produced by different analytical methods using different standards and analytical proce- dures that have evolved over this time period. Nevertheless, the data are consistent enough to provide a broad overview and some first- order constraints and a summary of these data are shown in Figs. 4 to 7. For comparative purpose, we also show our data on these plots and we categorize and organize them and their description from the described paleogeographic zones.

5. Results

The complex tectonic evolution of this region has resulted in secondary processes, as evidenced by the high loss on ignition (LOI) in several samples, which have affected the primary concentrations of many major and several trace elements. This alteration has obscured many of the primary igneous trends. As a result, we describe the major element abundances only in very general terms, and we focus on the abundances of trace elements such as high field strength (HFS) and rare earth (REE) elements, which are both considered to be “relatively” immobile during hydrous alteration (e.g. Winchester and Floyd, 1977; Pearce, 1996).

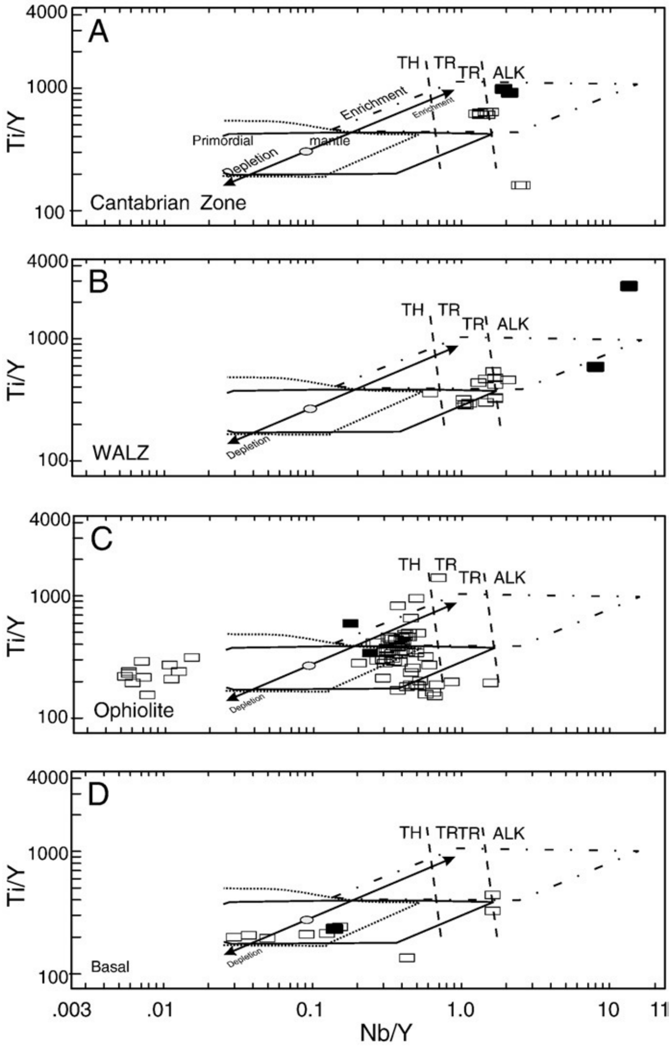

Fig. 6. Ti/Y vs Nb/Y discrimination diagram (after Pearce, 1982, 1996) for mafic rocks (A) Cantabrian zone, (B) Ophiolitic units, (C) West Asturian Leonese Zone (WALZ), (D) Basal Unit. Open symbols = published data; filled symbols, our data. CIZ and WALZ are not included in this plot because of the lack of mafic rocks in these zones.

The Cantabrian Zone volcanic rocks are bimodal, with a gap in SiO_2 from about 52 to 60 wt.%. Both mafic and intermediate rocks have a wide range in FeO^t/MgO which may, in part, be due to secondary alteration. Felsic rocks have FeO^t and FeO^t/MgO that straddle the calc- alkalic tholeiitic boundary (Fig. 4A). The Zr/Ti vs. Nb/Y plot (Fig. 5) is a proxy for the total alkalies vs. silica classification diagram, where Nb/Y measures the degree of alkalinity and Zr/Ti is an index of fractionation (Winchester and Floyd, 1977; Pearce, 1996). Cantabrian zone mafic volcanic rocks are characterized by high Nb/Y (Fig. 5A), varying from alkalic basalt-foidite to tephri-phonolite in composition. The alkalic affinity of the mafic rocks is also indicated on the Ti/Y vs Nb/Y plot (Fig. 6A) whereas the high Zr/Y, Ti and Zr are typical of within plate volcanic rocks (Fig. 7A).

The CIZ and the Galicia Schistose Zone are dominated by

values similar to those of the average continental crust but on average are richer in SiO_2 (Fig. 4B, C). The majority of the samples plot in the calk-alkalic field of Miyashiro (1974).

Basalts from the WALZ show a wide range in FeO^t/MgO (Fig. 4D) and similar ranges in Nb/Y and Zr/Ti to the basalts of the Cantabrian Zone (Fig. 5B). Their high Nb/Y is typical of transitional to alkalic basalts (Figs. 5B, 6B) and the high Zr/Y is typical of within plate basalts (Fig. 7B). Mafic rocks from the ophiolite bodies also have a wide range in FeO^t/MgO (Fig. 4E) and appear to be composed of two different suites. Although they contain similar Zr/Ti, one suite has very low Nb/Y (b 0.02) and a relatively narrow range in Ti/Y (c. 150–350) and is subalkalic (Figs. 5C, 6C). The other suite has much higher Nb/Y (0.3 to 2.0) and a wider range in Ti/Y (c. 150–1000) and their compositions straddle the subalkalic–transitional–alkalic boundaries. These differences are highlighted on the Zr/Y vs Zr diagram (after Pearce and Norry, 1979) in which the subalkalic rocks plot in the island arc basalt field, whereas subalkalic–alkalic rocks plot as within plate basalts (Fig. 7B). The subalkalic rocks have characteristics similar to the coeval Vila de Cruces ophiolite. Recent data from this ophiolite indicate that its geochemical signature is typical of island arc tholeiite and the ophiolite is interpreted to have been generated in a back arc basin (Arenas et al., 2007a).

6. Mafic rocks

Mafic rocks analyzed in this study facilitate a comparison between the Cantabrian Zone (ORV 1, 2), the Central Iberian Zone (ORV 7) of the inner Gondwanan margin and mafic rocks of the Basal Units (the probable Gondwanan basement; ORV 8, 10) and the ophiolites from the Galicia Tras-os-Montes (ORV 14, 15) of the outer margin (Fig. 3). ORV 1, 2 are Early Ordovician basalts characterized by high FeO^t, TiO_2, and FeO^t/MgO. On Zr–Ti–Y discrimination diagrams, they plot in the within plate field, and according to the high Nb/Y, they are clearly alkalic (Figs. 4 to 7). Thus their chemistry is broadly similar to previously published data from the Cantabrian Zone. On Ta/Yb vs Ce/Yb and Th/Yb diagrams, they plot just above the enriched mantle array suggesting only minor crustal contamination (Fig. 8A,B). This same characteristic is also evident on the Th–Hf–Ta diagram (Fig. 8C) and is consistent with their high Nb/Y (1.25 and 1.3, respectively). They display strong LREE enrichment, with high $La/Yb_n \sim 20–30$, which, together with the high Nb/Y, suggests derivation from a garnet lherzolite mantle (Fig. 9A). Trace element abundances are more enriched than typical EMORB, and spidergram plots show that they most closely resemble basalts derived from an OIB-type mantle source (Fig. 9B). The basalts display no Nb–Ta anomaly (Fig. 10), consistent with other evidence for lack of contamination either by crustal or subduction components. These characteristics are broadly similar to coeval rocks in the Ossa Morena Zone described by Sánchez-García et al. (2003). ORV 1 and 2 have very similar Sm–Nd isotopic characteristics with ε_{Nd} (t = 500) values of + 1.0 and + 1.1, respectively and T_{DM} values of ca. 0.93 to 0.99 Ga (Fig. 11A, Table 1). The lack of trace element evidence for crustal contamination suggests that these values reflect derivation from a mantle source that was enriched in LREE and Nd relative to Sm at about 1.0 Ga. Similar trace element and Sm–Nd isotopic characteristics have been identified in other regions that were located along the northern margin of Gondwana at that time (e.g. Acatlan Complex of Oaxaquia, Mexico and the Antigonish Highlands of Nova Scotia; Murphy and Dostal, 2007, 2008).

Sample ORV 7 is a rare example of a mafic volcanic rock within CIZ (Ollo de Sapo zone). This sample has significantly lower TiO_2, Zr, P_2O_5, Nb/Y and higher Zr/P_2O_5 than the Cantabrian Zone mafic rocks, features consistent with subalkalic tholeiitic rocks. However, on Ti–Y–Zr diagrams (Figs. 6, 7), the sample plots in the arc field and the influence of a subduction or crustal component is also indicated on Th–Hf–Ta and Ta/Yb vs Ce/Yb and Th/Yb plots. ORV 7 has LREE enrichment, a intermediate to felsic rocks. Many of the samples have FeO^t/MgO On spidergrams (Fig. 9A, B), ORV 7 has a pronounced Nb–Ta anomaly, typical of subduction or crustal influence.

The difference in the geochemical and isotopic signatures of mafic rocks (Gondwanan basement and ophiolite) that were located along the outer margin of Gondwana apparent from the analysis of the previously published data (Figs. 5 to 7) is clearly visible in our data.

pronounced Eu anomaly and moderate LREE enrichment ($La/Yb_n \sim$ 10).

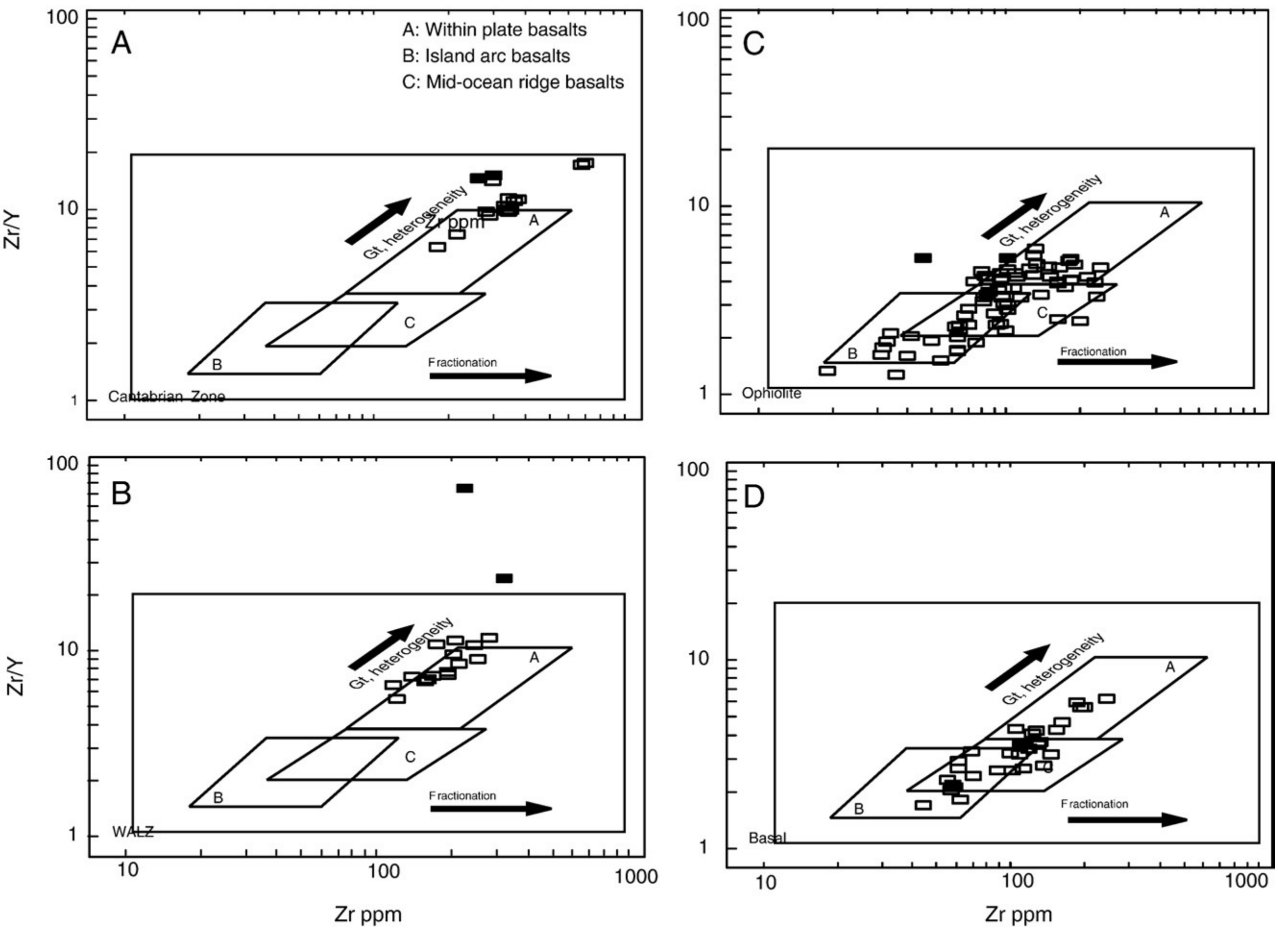

Fig. 7. Zr/Y vs Zr discrimination diagram (after Pearce and Norry, 1979) for mafic rocks (A) Cantabrian zone, (B) Ophiolitic units, (C) West Asturian Leonese Zone (WALZ), (D) basal unit. Open symbols = published data; filled symbols, our data. CIZ and WALZ are not included in this plot because of the lack of mafic rocks in these zones.

Gondwanan basement (ORV 8 and 10) and ophiolitic (ORV 14 and 15) mafic rocks plot in two distinct fields both of which are different from mafic rocks from the inner margin. Sample ORV 10 has low TiO_2, Zr, and P_2O_5, elevated Zr/P_2O_5, and low Nb/Y, features consistent with relatively undifferentiated subalkalic tholeiitic rocks. On Ti–Y–Zr plots, ORV-10 plots in the field of overlap between MORB and WPB (Figs. 6, 7). ORV 8 is intermediate in composition with SiO2 of 64.1 wt.%. Trace element plots such as Ta/Yb vs Ce/Yb and Th/Yb and Th–Hf–Ta show that these rocks are probably generated by partial melting of a depleted mantle with only minor influence of either subduction or crustal components (Fig. 8A–C). ORV 8 and 10 have flat NMORB-like profiles with slight LREE depletion (Fig. 10A,B) and ORV-8 has a pronounced Eu anomaly. The negative Nb anomaly exhibited by ORV-8 relative to NMORB (Fig. 10B) identifies contamination by a subduction zone component that is not apparent on the other plots. Both samples have a Sm/Nd ratio similar to CHUR, are characterized by high $^{147}Sm/^{144}Nd$ (0.196 and 0.205, respectively) and by ε_{Nd} values are similar to those of depleted mantle suggesting that both samples were derived from a juvenile mantle source. Although the high $^{147}Sm/^{144}Nd$ precludes a meaningful calculation of T_{DM}, the similarity of the ε_{Nd} values to that of depleted mantle suggests that the T_{DM} age is similar to its crystallization age. The isotopic data also indicate that the contamination by subduction exhibited by ORV-8 probably occurred at about the same time as magma generation, consistent with published geochemical data that many of the ophiolites were formed in a supra-subduction zone environment (e.g. Arenas et al., 2007a, and references therein).

Samples ORV 14 and 15 are from the lower ophiolite unit (Moeche Unit, equivalent to the better known Vila de Cruces Unit) which is interpreted to be a vestige of Ordovician oceanic crust from the Rheic Ocean (Arenas et al., 2007a,b). Trace element diagrams (Fig. 8A–C) indicate that these rocks contain high Ta/Yb and Ta/Hf that are typical of an enriched mantle. However, the rocks also do not plot along the mantle array indicating that they have been contaminated by either a subduction or crustal component. ORV 14 shows moderate LREE enrichment ($La/Yb_n \sim 6.5$) whereas ORV 15 has lower ΣREE, more subdued LREE enrichment ($La/Yb_n \sim 2.5$) and flat HREE $Gd/Lu_n \sim 0.8$–1.2 (Fig. 10A). Trace element abundances most closely resemble basalts derived from an enriched mantle source although Th enrichment and Nb depletion are consistent with other plots suggesting contamina- tion. (Fig. 10C). Their Sm–Nd characteristics are similar to one another, although these characteristics are very different from ORV 8 and 10.

They have much lower ε_{Nd} ($t = 500$) values of + 2.2 and + 2.6, much lower $^{147}Sm/^{144}Nd$ (0.141 and 0.157, respectively) and T_{DM} values of ca.0.96 to 1.1 Ga. Given the evidence for contamination, the geological meaning of these T_{DM} ages is uncertain. Although the data plot close to calculated assimilation–fractional crystallization curves between depleted mantle and typical upper crust (Fig. 11B and C), their apparent similarity with crustal values would imply a high percentage of assimilation that is not evident in other geochemical features. Alternatively, these values could reflect a combination of influences including derivation from an enriched subcontinental lithospheric mantle (similar to the source of ORV 1 and 2) and contamination either by Mesoproterozoic crust or by a crust enriched in LIL by fluids derived from a subduction zone.

Taken together, these data indicate mafic complexes located along the Gondwanan margin in Ordovician times are isotopically

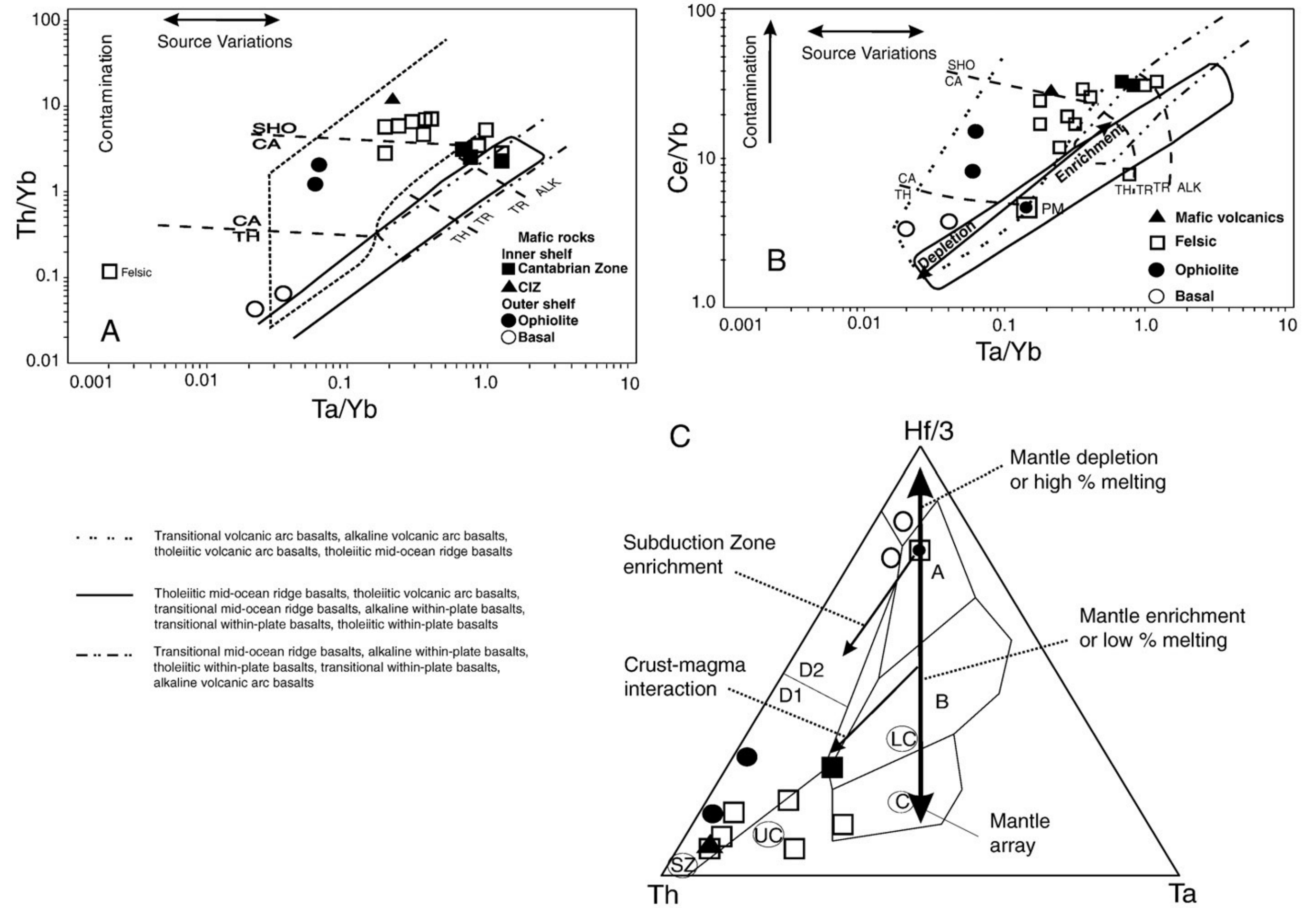

Fig. 8. Discrimination plots to identify subduction or crustal components: (A) Th/Yb and (B) Ce/Yb vs Ta/Yb (after Pearce, 1982), (C) Hf-Ta-Th (after Wood et al., 1979). In Fig. 8C: A = NMORB; B = EMORB; C = alkaline within plate basalt; D1 = Island arc tholeiite; D2 = calc-alkaline basalt. PM = primoidial mantle; MM = NMORB mantle source; UC = Upper crust; LC = Lower Crust; SZ = Subduction Component.

heterogeneous. Gondwanan basement complexes have compositions typical of juvenile depleted mantle at 480 Ma that was affected by coeval subduction. Ophiolite samples, on the other hand, have compositions typical of derivation from an enriched mantle.

7. Felsic rocks

A geochemical comparison between the felsic rocks of various tectonostratigraphic zones offers the opportunity to characterize the sources of crustally-derived melts along this portion of the Gondwa- nan margin. Most felsic rocks from the Cantabrian Zone (3, 30, 32), the SGTMD (12, 13, 26) and CIZ (27, 28, 29, 31) display very similar major element chemistry and are characterized by FeO and FeO/MgO that plot either in the calc-alkalic field or straddle the calc-alkalic- tholeiitic boundary line (Fig. 3). There is no obvious geochemical or isotopic distinction between the felsic rocks of these various tectonostratigraphic zones, and for simplicity of presentation, they are grouped together on geochemical and isotopic plots. They have a wide range in Nb/Y and Zr/Ti ratios, and straddle intermediate to felsic compositions and the alkalic-subalkalic boundary (Figs. 4–6). Other than ORV 30 and 33, which have elevated Nb, Y, Ta and Yb values that are typical of within plate granites, most samples plot in the Volcanic Arc Granite field (Fig. 12A,B), suggesting either an origin in an ensialic arc, or recycling of older crust that was itself formed in an arc environment.

With the exception of ORV 33, the felsic samples display moderate LREE enrichment (Fig. 13A), a moderate to pronounced Eu anomaly (Eu∗ ∼0.1 to 0.6) and flat HREE profiles (Gd/Yb_nYb_n ∼1.5). On an NMORB-normalized plot, all rocks display a pronounced negative Nb anomaly (Fig. 13B). Such REE and spidergram profiles are typical of crustal melts that have undergone plagioclase fractionation. The overall compositional similarity to upper continental crustal (UCC) rocks is shown on the UCC normalized plot (Fig. 13C). Sample ORV 33, a trachyte, has very high ΣREE, La/Yb_n of 12.5, and Gd/ $Yb_n = 3.5$ and high Nb and Ta (Figs. 12, 13) and REE profiles typical of felsic rocks generated by fractional crystallization from a more mafic magma.

Geochemical analyses of CIZ (Montero et al., 2007) shows very similar characteristics to the dominant features described above. These rocks have Nb–Ta–Yb and REE abundances that are indis- tinguishable from those shown in Figs. 12 and 13.

Sm–Nd analyses of the felsic rocks display more negative ε_{Nd} ($t = 500$) values than the mafic rocks (−1.1 to −5.6). Plots of ε_{Nd} versus normalized Nb/La and $^{147}Sm/^{144}Nd$ (Fig. 11B,C) show that the felsic rocks have isotopic and trace element characteristics that are distinct from the mafic rocks and support other geochemical evidence that they are not derived from the mafic rocks by fractionation or assi- milation fractionation mechanisms. Although one sample (ORV 32) has similar T_{DM} (1.1 Ga) to spatially-related mafic rocks (ORV 1 and 2) in the Cantabrian Zone (Figs. 2 and 3), it has significantly lower ε_{Nd}.

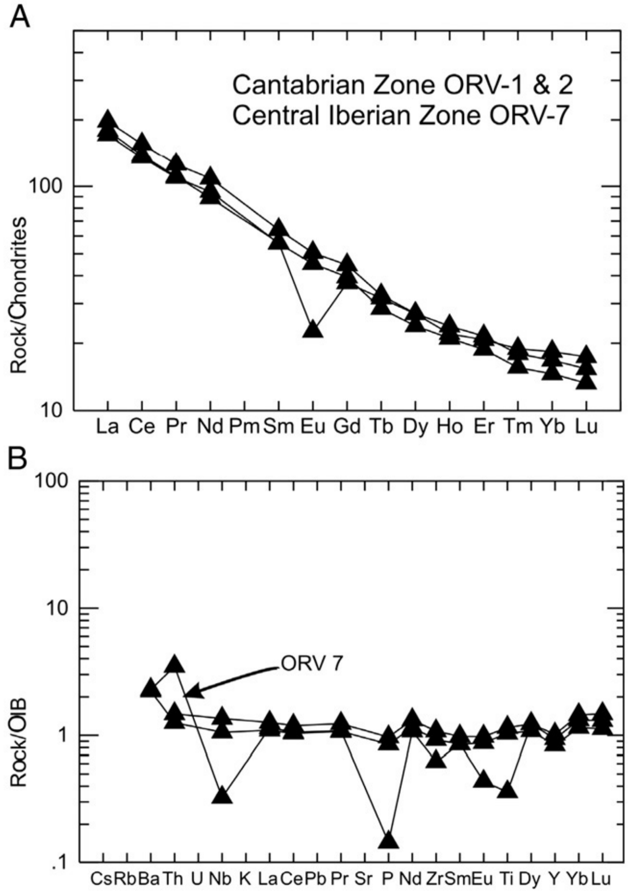

Fig. 9. REE and trace element values of Cantabrian Zone mafic rocks normalized to (A) chondrite, (B) Ocean Island Basalts. Normalizing values from Sun and McDonough (1989).

Although a lithospheric mantle component cannot be ruled out for this sample, these characteristics together with their overall geo- chemical similarity with the composition of the upper continental crust (Fig. 13C) indicate that the sample is dominated by a component derived from a source rock with lower Sm/Nd values that are more typical of crustal rocks. The low ε_{Nd} and the high T_{DM} of the other felsic samples ranges from 1.43 to 1.61 Ga suggesting that these rocks are crustal melts primarily derived from a Mesoproterozoic crustal basement. Therefore, the apparent arc affinity evident in Fig. 12 could have been inherited from an older continental crust that was itself formed in an arc environment. In comparison to typical Avalonian crust, the ε_{Nd} values are lower and the T_{DM} ages are older.

Comparable Sm–Nd isotopic results have been obtained from the CIZ by Castro et al. (1999, 2003) and Montero et al. (2007). These samples have ε_{Nd} ($t = 500$) ranging from −2.4 to −5.0, and eleven of twelve samples have T_{DM} ranging from 1.2 to 1.8 Ga, and the remaining sample has a T_{DM} of 2.2 Ga.

8. Summary and discussion

Geochemical and isotopic analyses indicate that Ordovician mafic rocks in NW Iberia are derived from variable mantle sources in- cluding ophiolites with mafic volcanics derived from a subcontinental lithospheric mantle and a juvenile mantle basement that was contaminated by a subduction component at the time of magma generation. This mixed signature is consistent with a transitional oceanic-continental crustal setting proximal to the northern Gondwanan margin.

Some of the analyzed samples are typical of rift-related basalts derived from garnet lherzolite mantle, with little or no chemical modification due to subduction or crustal contamination. These features are compatible with their proposed genetic relationship to the opening of the Rheic Ocean (Martínez-Catalán et al., 1997; van Staal et al., 1998; Murphy et al., 2006; Arenas et al., 2007a,b). The calculated T_{DM} ages, however, are significantly older than that of the Late Cambrian–Early Ordovician opening of the Rheic (or Iapetus) Oceans. These ages are interpreted to reflect derivation from a subcontinental lithospheric mantle that was heterogeneously meta- somatized, probably at ca. 1.0 to 1.1 Ga. Such features have also been interpreted in the mantle lithosphere beneath Avalonia, the terrane

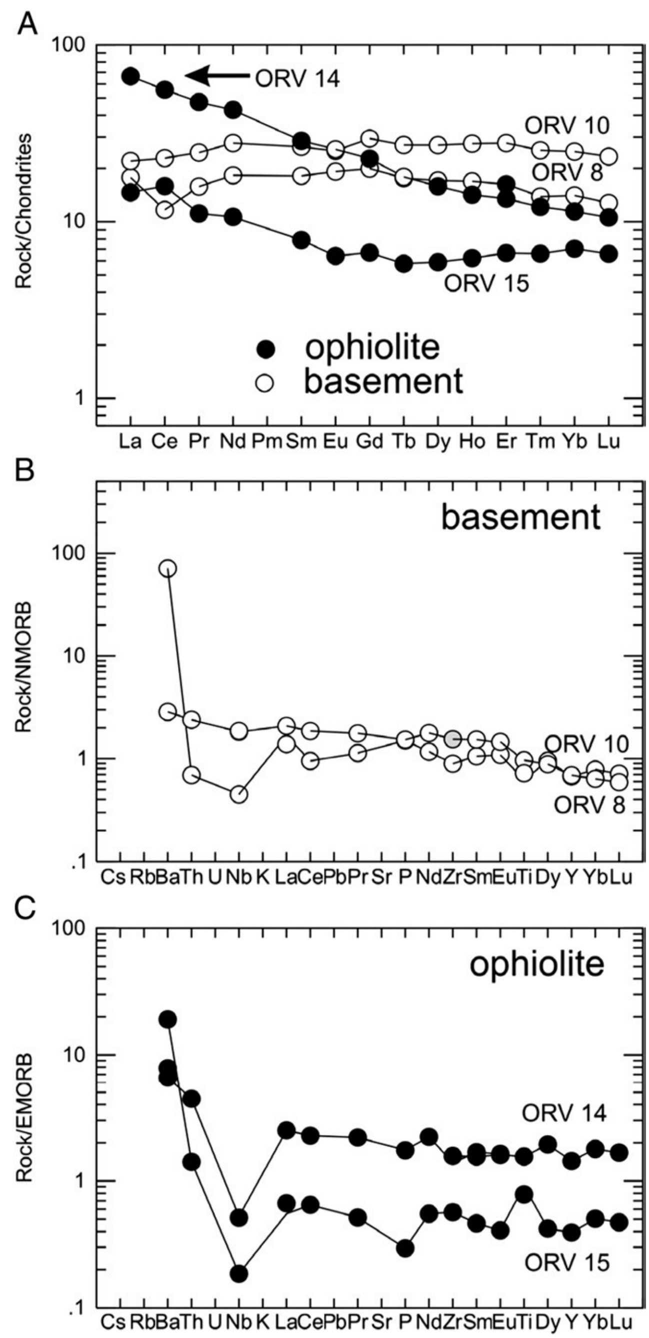

Fig. 10. REE and trace element values of ophiolitic rocks normalized to (A) chondrite. ORV 8 and 10 are shown normalized to NMORB (B), whereas ORV 14 and 15 are show normalized to EMORB (C). Normalizing values from Sun and McDonough (1989).

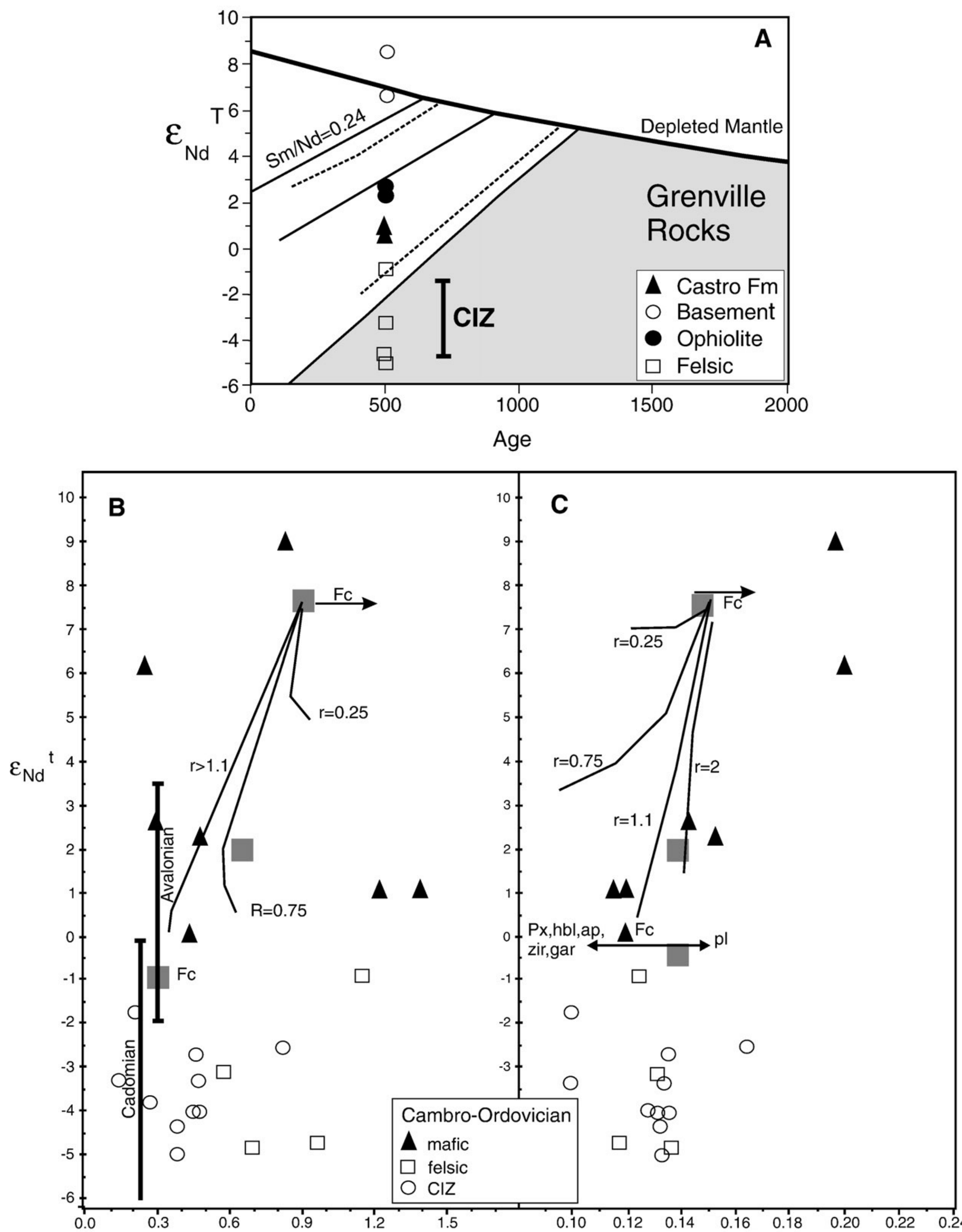

Fig. 11. Sm–Nd isotopic data for representative Ordovician volcanic rocks of northwest Iberia (A) ε_{Nd} versus time plot. Depleted-mantle model ages are calculated using a modern depleted-mantle composition of $^{143}Nd/^{144}Nd = 0.513114$ and a $^{147}Sm/^{144}Nd = 0.213$ (see DePaolo, 1988). The field for Mesoproterozoic source rocks is compiled from the data of Patchett and Ruiz (1989), Dickin et al. (1990), Daly and McLelland (1991), Dickin (2000). The field for Avalonian felsic rocks is from Murphy et al. (2000). (B) ε_{Nd} versus Nb/La_{cn} (chondrite-normalized) and (C) $^{147}Sm/^{144}Nd$ basalts. For means of comparison ε_{Nd} data for all suites are shown at $t = 500$ Ma. Arrows indicate trends for pure fractional crystallization: long arrows for hornblende, clinopyroxene, apatite, and olivine; short arrow for K-feldspar. Curves indicate assimilation–fractional crystallization (AFC; DePaolo, 1988) trends for

crust (C) assimilated by basalt magma (B). Values of r (mass assimilated/mass crystallized) indicated adjacent to curves. For curves with r N 1, curves extend to values of F (mass magma/mass magma initial) ~4, whereas for curves where r b 1, curves end at $F \sim 0.1$. Data for CIZ from Montero et al. (2007).

Table 1
Sm–Nd Isotopic data for Ordovician igneous rocks formed along the Iberian passive margin of Gondwana

	Nd (ppm)	Sm (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	2σ	ε(0)	ε(500)	T(DM)	
Cantabrian Zone									
ORV 1	39.65	7.87	0.1200	0.512440	5	−3.9	1.0	986	Mafic
ORV 2	46.40	9.04	0.1177	0.51	4	−3.9	1.1	934	Mafic
Felsic									
ORV 3	18.43	3.57	0.1170	0.51	7	−10.3	−5.2	1433	Rhyolite
ORV 13	21.22	4.67	0.1329	0.51	5	−9.2	−5.1	1609	Rhyolite
ORV 26	29.82	6.41	0.1300	0.51	4	−7.9	−3.7	1436	Rhyolite
ORV 32	56.12	11.35	0.1223	0.51	5	−5.9	−1.1	1140	Rhyolite
Gondwanan basement									
ORV 8	8.29	2.82	0.21	0.51	4	6.9	6.4	—	Amphibolite
ORV 10	11.96	3.88	0.2	0.51	4	8.7	8.7	—	Mafic
Ophiolite									
ORV 14	18.8	4.4	0.14	0.51	5	−0.9	2.6	957	Ophiolite
ORV 15	5.210	1.350	0.16	0.51	5	−0.3	2.2	1128	Ophiolite

Analyses performed at the Atlantic Universities Regional Isotopic Facility, Memorial University of Newfoundland. Errors on $^{143}Nd/^{144}Nd$ are generally less than 0.002%, and on $^{147}Sm/^{144}Nd$, less than 0.1. The ε_{Nd} values are calculated using a $^{147}Sm/^{144}Nd = 0.1967$ and $^{143}Nd/^{144}Nd = 0.512638$ values for the present day chondrite uniform reservoir (CHUR) and for $t = 500$ Ma. ^{147}Sm decay constant is $6.54\ 10^{-12}\ y^{-1}$ (Steiger and Jäger, 1977), T_{DM} were calculated with respect to the De Paolo mantle model (DePaolo, 1981, 1988). The T_{DM} age for ORV 8 and ORV 10 was not calculated because of the high $^{147}Sm/^{144}Nd$, but they are clearly juvenile. For data on the CIZ, see Castro et al. (1999, 2003) and Montero et al. (2007).

which probably migrated away from the Gondwanan margin when the Rheic Ocean formed and beneath Oaxaquia which remained along the Gondwanan margin (Murphy et al., 2006; Murphy and Dostal, 2007). The data are also compatible with a mantle source similar to that which yielded the Mesoproterozoic (1.159 ± 39 Ma, Purrido Unit) metagabbro exposed in NW Iberia (Sánchez-Martínez et al., 2006). If

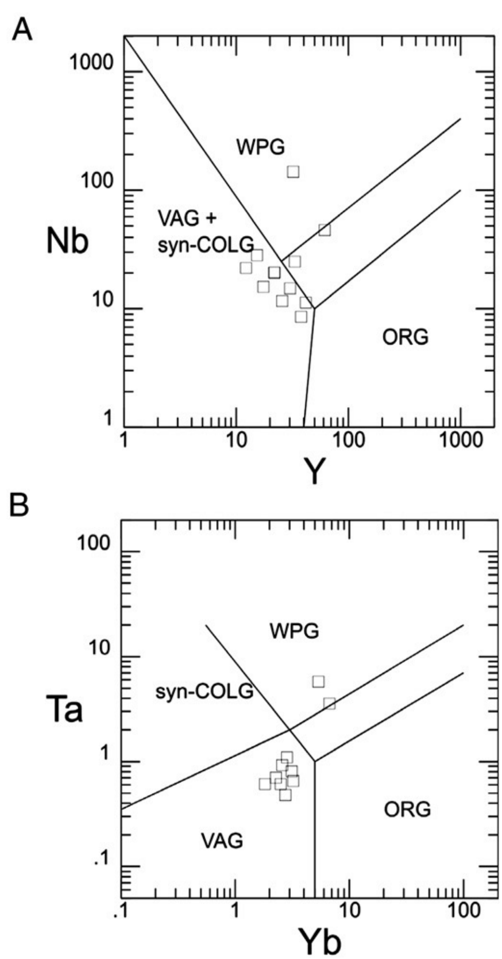

Fig. 12. (A) Nb–Y and (B) Ta–Tb relationships for the felsic rocks (after Pearce et al., 1984).

so, the younger (e.g. 0.95 Ga) T_{DM} ages of some of the mafic samples can be attributed to a minor juvenile component.

Some of the felsic rocks are alkalic, and are probably related to the within plate basalts by fractionation. The remaining felsic rocks, with flat HREE, negative ε_{Nd} isotopic values and T_{DM} ages between 1.1 and 1.6 Ga are probably crustal melts, suggesting derivation from Mesoproterozoic crust. These T_{DM} ages are older than those of Avalonian lower crust (e.g. Murphy et al., 2000). Sánchez-Martínez et al. (2006) identified a 1.6 Ga inherited component in Purrido amphibolite, and it is possible that these model ages reflect that Mesoproterozoic component. Mesoproterozoic basement is also atypical of the West African Craton and is more typical of a South American affinity. The presence of a Mesoproterozoic lower crustal basement in NW Iberia is compatible with the interpretation of Gutiérrez-Alonso et al. (2005) for detrital mica data from Early Paleozoic platformal rocks in the NW Iberia which indicate proximity to Mesoproterozoic South American (Rio Negro) basement. These authors attribute the presence of Mesoproterozoic basement in this region to strike-slip transport along the northern Gondwanan margin of a sliver of South American crust into the West African realm during the Ediacarin-Early Cambrian (Fernández-Suárez et al., 2000, 2002a,b; Gutiérrez-Alonso et al., 2003, 2005).

Taken together, these data suggest that the lower crust in NW Iberia included a significant Mesoproterozoic (ca. 1.4–1.6 Ga) component which overlay a ca. 1.0–1.1 Ga subcontinental mantle lithosphere in Early Ordovician times. This geometry had a significant influence on the geochemistry of the basalts that erupted during the opening of the Rheic Ocean. The data also indicate the juxtaposition of older crust above younger mantle lithosphere by Late Cambrian–Early Ordovician times. The origin of this relationship requires further study. It may reflect an allochthonous relationship between the Rio Negro crust and the underlying mantle that was generated before, during or final delivery of the Rio Negro crust into the West African realm. Alternatively, it may reflect a delamination event between crust and mantle in the Neoproterozoic, i.e. prior to transportation from the South American to the West African realm.

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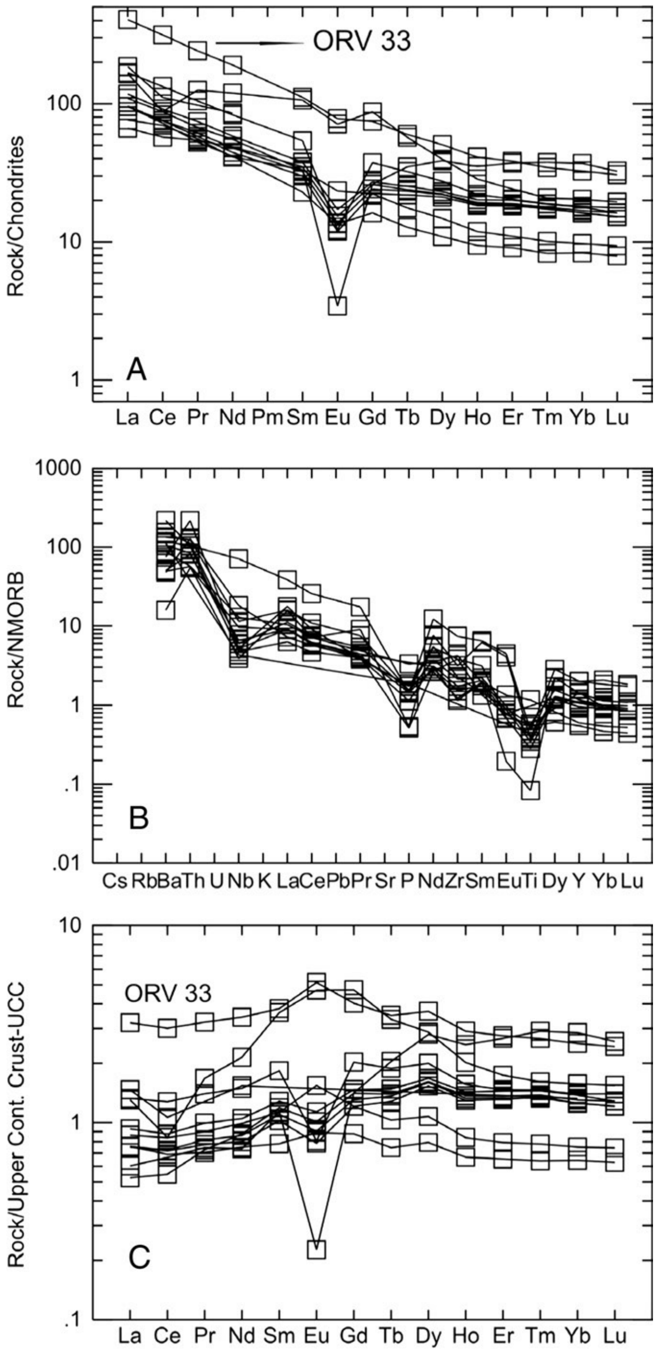

Fig. 13. REE and trace element abundances for the felsic rocks normalized to (A) chondrite (values after Sun and McDonough, 1989), (B) NMORB (values after Sun and McDonough, 1989) and (C) Upper Continental Crust (values after Taylor and McLennan, 1985).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tecto.2008.03.013.

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