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Hybrid zones from the Seville Sierra Norte Batholith: the missing Late Famennian plutonic basement of the Iberian Pyrite Belt

Carmen Rodríguez[1]*, Lola Yesares[2] and Manuel Francisco Pereira[3]

[1] Instituto Andaluz de Ciencias de la Tierra (IACT), Consejo Superior de Investigaciones Científicas (CSIC), Avenida de las Palmeras 4, 18100 Armilla, Granada, Spain
[2] Departamento de Mineralogía y Petrología, Universidad Complutense de Madrid, c/ José Antonio Novais, 2, 28040 Madrid, Spain
[3] Departamento de Geociências, Centro de Pesquisa da Terra e do Espaço (CREATE), Instituto de Ciências da Terra (ICT), Universidade de Évora, Rua Romão Ramalho 59, 7002-554 Évora, Portugal
CR, 0000-0003-4785-6714; LY, 0000-0002-7717-9438; MFP, 0000-0001-9032-2318
* Correspondence: carmen.ralmodovar@csic.es

Abstract: Subvolcanic rocks from hybrid zones provide insights into the parental magmas present in calc-alkaline arc systems. Determining the composition and formation conditions of the parental magma is essential for linking plutonic and volcanic rocks to a common source.

Here, we investigate the genetic relationships between plutonic rocks from the bimodal Seville Sierra Norte Batholith (SSNB) and coeval bimodal volcanic rocks from the Iberian Pyrite Belt, one of the largest massive sulfide provinces on Earth, hosted by the Volcanic–Sedimentary Complex in the South Portuguese Zone (Iberian Variscan Belt). Metadata analysis of geochemical signatures from the SSNB and the Volcanic–Sedimentary Complex indicates a common arc-like magma source. The Gerena hybrid zone, located in the southern section of the SSNB, provides evidence of a genetic link between mafic and felsic end members of this magmatism. Experiments on the hybrid zone, performed at 300 MPa and 1000°C, and subsequently quenched, produced a liquid composition consistent with the Andean cotectic. Furthermore, the crystallization ages of the granodiorites (356 ± 1 Ma) and quartz-diorites from the Gerena hybrid zone (368 ± 3 Ma) overlap the age range of volcanic felsic rocks from the Iberian Pyrite Belt. We propose that: (i) the quartz-diorite of the Gerena hybrid zone corresponds to the missing Late Famennian plutonic roots of the Iberian Pyrite Belt; and (ii) the Late Famennian–Tournaisian arc-like magmatism in the South Portuguese Zone was related to the termination of subduction of the Rheic oceanic lithosphere. Our findings can help in understanding the links between magmatic systems and metallogenic provinces.

Supplementary material: Supplementary material includes cathodoluminescence images of zircon crystals; geochemical, isotopic and geochronological data of the samples from this study and from bibliography, thermobarometry results from amphibole microanalysis and microprobe analyses of phases from experimental runs, and is available at https://doi.org/10.6084/m9.figshare.c.7953831

Thematic collection: This article is part of the Diversity and origins of enclaves in granitoids and their petrogenetic significance collection available at: https://www.lyellcollection.org/topic/collections/enclaves-in-granitoids

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The Iberian Pyrite Belt (IPB), located in the South Portuguese Zone of the Iberian Variscan Belt, is one of the Earth's most productive volcanogenic massive sulfide (VMS) metallogenic provinces (Leistel *et al.* 1997) and was a renowned area of metal production during the Chalcolithic period (Nocete *et al.* 2005). With a surface exposure of *c.* 8000 km^2 from Grândola (Portugal) to Seville (Spain), this metallogenic province hosts about 2000 Mt of massive sulfide ore, with more than 90 known polymetallic deposits, including Cu, Pb, Zn, Au and Ag, mainly hosted by black shales, felsic volcanic and volcaniclastic rocks of the Volcanic–Sedimentary Complex (VSC) (Sáez *et al.* 1996, 2024; Leistel *et al.* 1997; Casquet *et al.* 1998; Oliveira *et al.* 2019; Yesares *et al.* 2023).

Volcanic units are bimodal and comprise dacites, rhyolites and basalts (Mitjavila *et al.* 1997; Donaire *et al.* 2020). Intermediate compositions, including basaltic andesites and andesites, as well as more evolved compositions such as dacites and rhyolites, have been attributed to varying degrees of crustal partial melting, which may involve mixing with mantle magmas (Mitjavila *et al.* 1997; Donaire *et al.* 2020). VSC mafic rocks have been classified as either continental tholeiites or arc-related basalts (Mitjavila *et al.* 1997; Thiéblemont *et al.* 1997).

The genetic relationship between ore deposits and Mississippian volcanic sequences from the IPB has been studied extensively (Leistel *et al.* 1997; Thiéblemont *et al.* 1997; Sáez *et al.* 2024). Most genetic models of ore deposits at the IPB include hydrothermal fluids derived from connate or basin waters, where the underlying PQ Group, and to lesser extent the VSC, act as the primary source of metals (Sáez *et al.* 1999; Tornos 2006; Tornos and Heinrich 2008). These mineralizing fluids were discharged near the seafloor, where massive sulfides formed (Sáez *et al.* 2024). In this scenario, Mississippian bimodal volcanism has been proposed as the primary driver of hydrothermal fluid circulation in the area (Leistel *et al.* 1997; Thiéblemont *et al.* 1997; Sáez *et al.* 2024). Although the relationship between ore deposits and Mississippian volcanic sequences has been studied extensively (Leistel *et al.* 1997; Thiéblemont *et al.* 1997; Donaire *et al.* 2020; Sáez *et al.* 2024), the magmatic source and its plutonic counterpart remain poorly constrained.

Plutonic systems record the thermal history of magmatic reservoirs, which solidify slowly at depth from the liquidus to the solidus. However, subvolcanic rocks from hybrid zones offer a snapshot of the magmatic cooling history (Rodríguez *et al.* 2025), which can be even more interesting than the plutonic record.

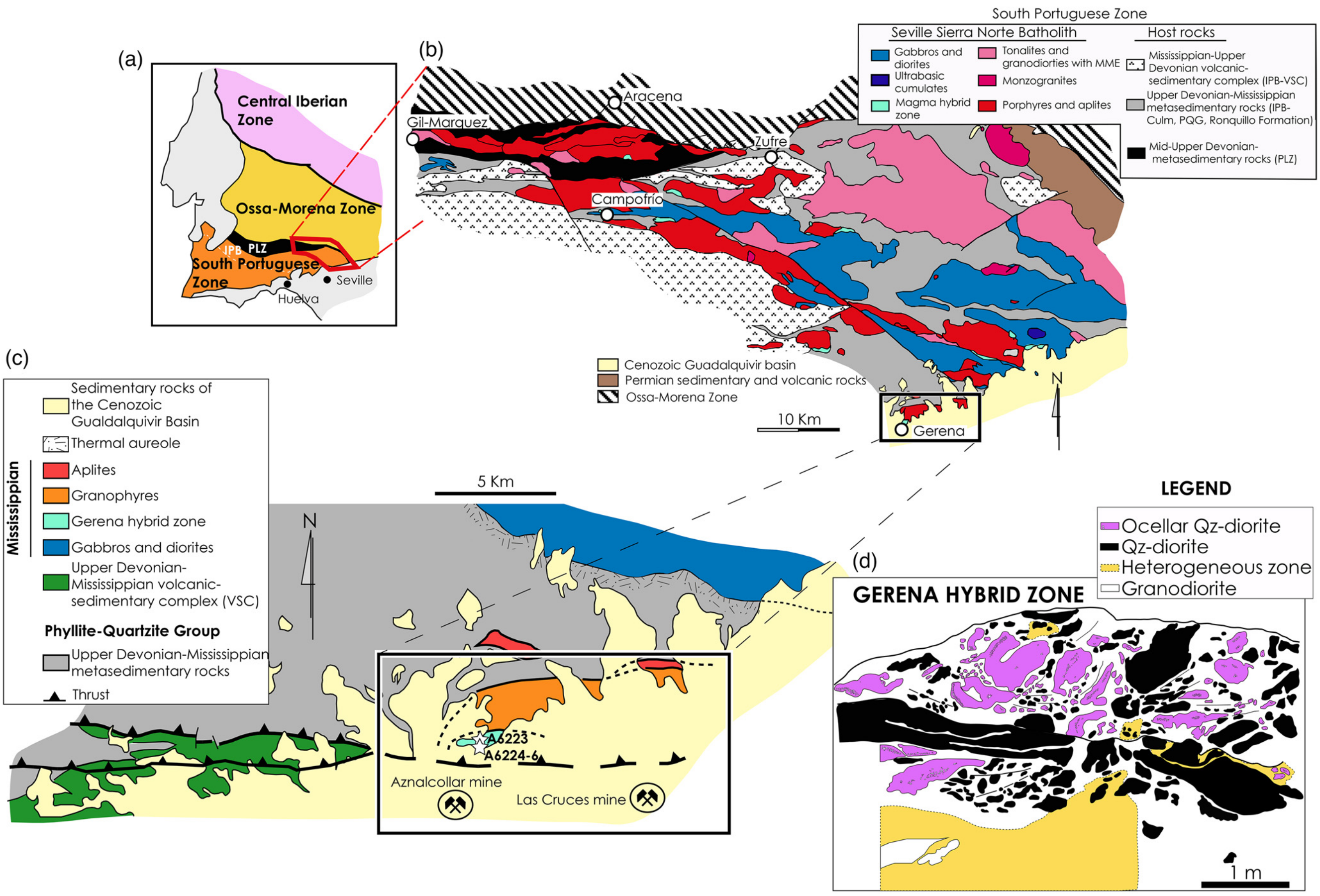

Fig. 1. (**a**) General map of geological domains in the western Iberian Massif including the South Portuguese Zone, Iberian Pyrite Belt (IPB) and Pulo do Lobo Zone (PLZ). (**b**) Geological map of the Seville Sierra Norte Batholith (SSNB) showing the study area. (**c**) Geological map showing the location of Gerena hybrid zone (marked by a white star). (**d**) Detailed map at the outcrop scale of the Gerena hybrid zone. Source: (a–c) maps modified from Instituto Geológico y Minero de España, GEODE (accessed in 2025, available for public access at http://info.igme.es/cartografiadigital/geologica/geode zona.aspx?Id=Z1500); (d) Chacón (2006).

The Seville Sierra Norte Batholith (SSNB), emplaced during the Devonian–Lower Carboniferous in the northeastern domains of the South Portuguese and Pulo do Lobo zones (PLZ on Fig. 1a, b), also has a bimodal nature (De la Rosa 1992). It may be the plutonic counterpart of the VSC, given their proximity, common bimodal character and age similarities. A connection between the magmatic rocks of the IPB and the SSNB has previously been proposed by Diez-Montes and Bellido (2008) and Albardeiro *et al.* (2023).

One of the peculiarities of the SSNB is the presence of hybrid zones (Fig. 1d): areas where mafic and leucocratic magmas are in mutual contact, exhibiting magma–magma interactions (De la Rosa and Castro 2004).

Using geochemistry, petrography, experimental petrology and geochronology, we investigate the potential linkage between the SSNB and the volcanic rocks that host massive sulfide deposits in the IPB. Our results enable us to provide a geodynamic model that explains the origin of arc-type hybrid zones in collisional settings, such as the Mississippian Gerena hybrid zone.

Geological framework

The Variscan belt in the SW Iberian Massif includes the South Portuguese Zone, the Pulo do Lobo Zone and the southern boundary of the Ossa-Morena Zone, defined by the Beja-Acebuches Ophiolitic Complex (Quesada *et al.* 1994) (Fig. 1). The boundary between these three Late Paleozoic tectonic units is interpreted as a reworked suture zone formed by the collision between Laurussia (Pulo do Lobo and South Portuguese zones) and Gondwana (Ossa-Morena Zone: Pereira *et al.* 2017 and references therein), formed after the closure of the Rheic Ocean during Devonian times (Pérez-Cáceres *et al.* 2015 and references therein).

The IPB is the northernmost domain of the South Portuguese Zone (Fig. 1). It is a Middle–Upper Devonian–Mississippian stratigraphic succession that consists of four main lithostratigraphic units (Pereira *et al.* 2021 and references therein): (i) the Middle–Upper Devonian Ronquillo Formation (PLZ: Fig. 1a); (ii) the Upper Devonian–Mississippian Phyllite–Quartzite Formation (Fig. 1c); (iii) the Upper Devonian–Mississippian VSC (Fig. 1b, c); and (iv) the Mississippian Culm Group or Baixo Alentejo Flysch Group (Schermerhorn 1971; Oliveira *et al.* 2019). Massive sulfide deposits in the IPB were deposited between the Late Famennian and Early Visean (*c.* 374–345 Ma) (Nesbitt *et al.* 1999; Barrie *et al.* 2002; González *et al.* 2002; Rosa *et al.* 2009; Albardeiro *et al.* 2023; Cravinho *et al.* 2024). Subsequent deformation of the IPB during the Pennsylvanian caused shearing of the ore bodies (Schermerhorn 1971; Silva *et al.* 1990).

The SSNB was emplaced in the northeastern domain of the SPZ and crystallized over *c.* 10 Myr, from *c.* 355 to 345 Ma (De la Rosa 1992; Gladney *et al.* 2014) (Fig. 1). It is intrusive in the Middle–Upper Devonian–Mississippian IPB and the Pulo do Lobo Zone's Devonian–Mississippian metasedimentary and meta-igneous rocks (Castro *et al.* 1995; De la Rosa *et al.* 2002; Gladney *et al.* 2014). It is a bimodal batholith composed of mafic rocks, including gabbros and diorites, as well as subordinate ultramafic cumulates, tonalites and granodiorites. Hybrid zones (Fig. 2a) are dispersed throughout the entire SSNB, including the Gerena (De la Rosa and Castro 1989; Castro *et al.* 1990), Gil Marquez (Castro *et al.* 1995) and Campofrio

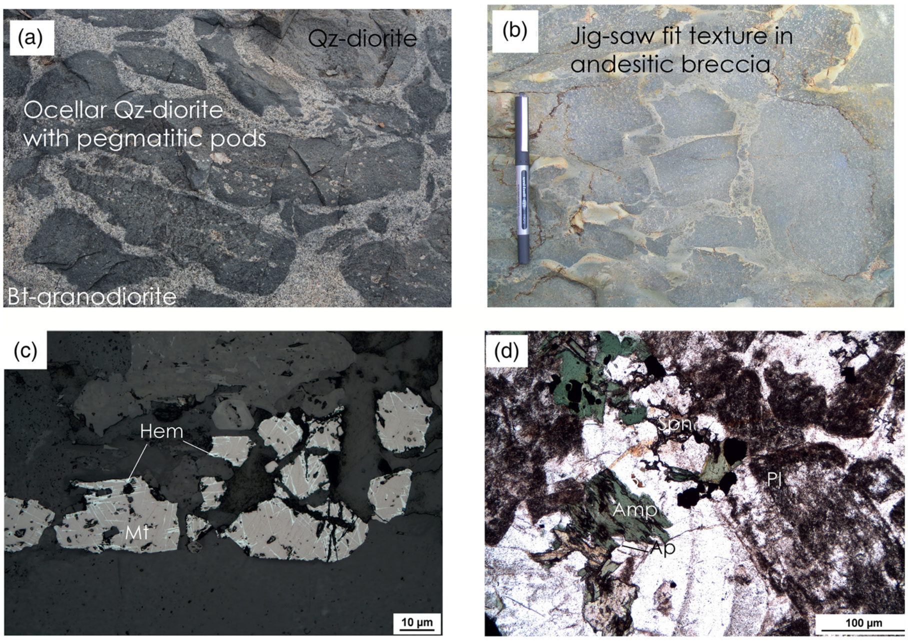

Fig. 2. (**a**) Field photographs of rock textures from the Gerena hybrid zone and (**b**) jigsaw textures in andesitic rocks from the Iberian Pyrite Belt (IPB). (**c**) and (**d**) Microphotographs of main granodiorite textures showing opaque relations with silicate phases from the Gerena hybrid zone. Source: (a) and (b) from Valenzuela *et al*. (2011); and (c) and (d) mineral abbreviations after Whitney and Evans (2010).

plutons (Stein *et al.* 1996). This Andean-type composite batholith has been interpreted as collisional (Gladney *et al.* 2014) and formed coevally with the IPB volcanic rocks (Dunning *et al.* 2002).

The Gerena hybrid zone

Different magmas interact at hybrid zones where rocks with contrasting textures and colours come into contact. Fine-grained textures found in hybrid zones are the result of quenching processes. These quenched portions of hybrid zones are crucial for identifying the parental magma responsible for the calc-alkaline series (Rodríguez *et al.* 2025). The Gerena hybrid zone has an intermediate (quartz-dioritic) composition and is part of the voluminous intrusive SSNB. According to the classification proposed by Rodríguez *et al.* (2025), the Gerena hybrid zone corresponds to the monocompositional type, as the mafic and felsic members do not differ significantly in composition. It preserves mafic–felsic magma interactions and quenching textures formed at shallow depths, where isolated dark bodies of variable size, ranging from a few centimetres to several metres, of fine-grained quartz-diorites are enclosed in a matrix of medium-grained Bt-granodiorite (Figs 1c and 2a). A heterogeneous zone resulting from the quartz-diorite and granodiorite hybridization is also recognized (Fig. 1d). Hybrid zones have been interpreted as quenched magma portions where the rapid magma ascent to shallow levels also allows parental magma to be split by gas-driven filter pressing (Rodríguez *et al.* 2025). These portions of quenched magma preserve the parental intermediate composition by *in situ* crystallization and compositional magma splitting at shallow depths (Rodríguez *et al.* 2025).

Compositional magma splitting is defined as a critical phenomenon in which an initially homogeneous magma separates into two distinct magma systems with sharp boundaries (Rodríguez and Castro 2017). This intermediate composition aligns with the silica gap typically observed in calc-alkaline systems (Bacon and Druitt 1988; Brophy 1991). This gap is also linked to the missing parental magmas that give rise to batholiths and volcanic products. In the volcanic intermediate rocks, andesites (equivalent in composition to quartz-diorites) from the Odiel River section within the IPB (Valenzuela *et al.* 2011) exhibit a jigsaw texture (Fig. 2b), also produced by *in situ* quench fragmentation of hot bimodal magmas (Colombier *et al.* 2019). To establish whether there is a genetic relationship between the hybrid zones present in the coeval plutonic and volcanic rocks, and the processes involved, we focus on intermediate rocks in hybrid zones in this study.

Methods

A metadata analysis of geochemical signatures of plutonic rocks was carried out, categorizing them into mafic, felsic and hybrid zones, with the latter defined as areas displaying mixing and mingling textures. For volcanic rocks, the analysis excluded samples with a high degree of alteration (LOI >5 wt%) and were differentiated between mafic and felsic compositions. The Supplementary material presents the data compilation for the major and trace elements, as well as the isotope geochemistry, for the SSNB and IPB magmatic rocks. The Guadalupe Igneous Complex was used for comparison in the geochemical diagrams due to its similarity with the SSNB, given the bimodal nature of the magmatic system, its connection with the volcanics and the presence of hybrid zones (Putirka *et al.* 2014).

The sampling site used for this study (Fig. 1) encompasses a range of facies from the Gerena hybrid zone and the host granodiorite. Four samples of each rock type (Fig. 1d) were collected: (i) a massive quartz-diorite with ocelli; (ii) the host granodiorite; (iii) a quartz-dioritic enclave with ocelli and pegmatitic pods; and (iv) an ocelli-free quartz-dioritic enclave.

Whole-rock geochemistry

Samples were crushed and milled into a fine powder for whole-rock geochemical and Sr–Nd isotope analyses. Analytical work was performed using X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) at the Centro de Instrumentación Científica (CIC, University of Granada), following the standard procedures described by Baedecker (1987). Precision for major elements is better than 1% and better than ±5% for 100 ppm Zr. Analyses of trace elements, except Zr, which XRF analysed, were performed according to the method described by Bea (1996). The precision was *c.* 2 and 5% error on concentrations of 50 and 5 ppm, respectively.

Whole-rock geochemistry results are plotted in Figures 3 and 4, and are listed in Supplementary Tables S1 and S2, respectively. See the Supplementary material for all the technical details.

Because a significant dataset of isotopic geochemistry already exists, only one sample (A6223) of quartz-diorite from the Gerena hybrid zone was selected for the Sr and Nd isotope analyses to complement the existing data from the SSNB.

Samples for the Sr and Nd isotope analyses were digested in a clean room using ultraclean reagents, and then analysed by thermal ionization mass spectrometry (TIMS) in a Finnigan Mat 262 spectrometer after chromatographic separation with ion-exchange resins. Normalization values were $^{86}Sr/^{88}Sr = 0.1194$ and $^{146}Nd/^{144}Nd = 0.7219$. Isotopic ratios of $^{87}Rb/^{86}Sr$ and $^{147}Sm/^{144}Nd$ were directly determined by ICP-MS (Montero and Bea 1998) with a precision, estimated by analysing 10 replicates of the standard Whin Sill dolerite (WS-E), of better than 1.2 and 0.9% (2σ), respectively.

Thermobarometry

Amphibole thermobarometry was calculated according to Ridolfi (2021) (see Supplementary Table S3) using microanalytical data of Mg-hornblende from the quartz-diorite with ocelli and pegmatitic pods in the Gerena hybrid zone (Chacón 2006).

U–Pb zircon analyses

Zircon grains were separated from two selected samples: one from the granodiorite (sample A6224), which hosts the Gerena hybrid zone from the SSNB; and the other from a quartz-dioritic enclave with ocelli and pegmatitic pods within the hybrid zone (sample A6226). These selected samples were crushed, sieved and gravity separated via water-based techniques to obtain heavy mineral concentrates. Zircon grains were hand-picked under a binocular microscope, cast together with zircon standards (TEMORA zircon, SL13 zircon and GAL zircon) on a 3.5 cm-diameter epoxy mount and polished. Zircon grains were documented using cathodoluminescence (CL: Fig. 4a, b) imaging to select the targets that were later analysed for U–Pb–Th isotopes using the sensitive high-resolution ion microprobe (SHRIMP) at IBERSIMS (University of Granada, Spain: www.ugr.es/~fbea; see the Supplementary material for technical details).

Experimental strategy and techniques

Experiments were conducted in Boyd and England piston-cylinder apparatus at the experimental laboratory of the Instituto Andaluz de Ciencias de la Tierra (Granada, Spain) using Au_{70}–Pd_{30} capsules (3 mm diameter) and 0.5 inch talc-Pyrex assemblies. Capsules were sealed by arc welding and then filled with ultrafine crushed powder of the quartz-diorite with ocelli and pegmatitic pods sampled from the Gerena hybrid zone (the starting material selection and experimental strategy are described below). The upper part of the capsule was sealed by pressure folding. The filled and sealed capsule was introduced into MgO pressure containers. Temperatures were measured and controlled using Pt_{100}–$Pt_{87}Rh_{13}$ thermocouples, which were wired to Eurotherm 808 controllers. Oil pressures were measured with electronic Druck PTX 1400 pressure transmitters connected to Omron E5CK controllers. The pressure was corrected manually and maintained within a narrow range of ±5 bar oil pressure, equivalent to ±250 bar on the sample. The upper part of the experimental capsule was separated from the thermocouple using a thin MgO disc. After applying run conditions, fast quenching at a rate of 100°C s^{-1} was forced by turning the power off (‘hot piston-out’ approach). Capsules were embedded in epoxy, cut in half, and examined by studying polished sections with electron microscopy imaging, energy-dispersive spectrometry (EDS) and electron probe microanalyses (EPMA).

Following the procedure proposed by Rodríguez *et al.* (2025), the starting material from the monocompositional Gerena hybrid zone was composed of magma with a composition close to the silica gap between mafic and silicic members of this magmatic system. Quartz-diorite with ocelli and pegmatitic pods (sample A6226) was used as a representative of these quenched magma portions, preserving the parental composition.

To investigate the pre-emplacement conditions of the magma, the ultrafine powdered sample (A6226) was melted at 1100°C and 300 MPa for 2 h, and then a cooling ramp of 0.1°C h^{-1} was imposed to reach 1000°C. The total duration of the experiment was 43 h.

Results

Petrological and geochemical signature of shallow arc magmas

The Gerena hybrid zone offers a unique snapshot of cooling dynamics within magmatic systems where mafic and felsic magmas interact. The mafic rocks occur as disrupted globules with lobate contacts and chilled margins, supporting the theory that this is caused by instantaneous fragmentation within a partially crystallized magma, as observed in the Gerena plutonic outcrops.

Amphibole, plagioclase and biotite are the main phases of mafic rocks, whereas biotite, plagioclase, K-feldspar and quartz are more abundant in granodiorites. Plagioclases are normally zoned with anorthitic skeletal cores and albitic rims. Amphibole (Mg-hornblende) is the main mafic phase of the quartz-diorites with ocelli and pegmatitic pods (see Supplementary Table S3), with biotite being scarce but concentrated at the chilled margins. Magnetite and hematite are intergrown in the host granodiorites (Fig. 2c). Oxides and minor sulfides are concentrated around amphiboles in the quartz-diorites with ocelli and pegmatitic pods (Fig. 2c, d).

The major and trace elements from the SSNB follow a calc-alkaline differentiation trend (Fig. 3a, b). The metadata analysis of the geochemistry of the SSNB reveals a bimodal character, similar to that of the IPB volcanism, and indicates the formation of cumulates (scattered analyses with low silica content) and compositionally evolved rocks (following a cotectic pattern). The bimodal nature of the SSNB is evident from a gap in silica content at *c.* 55–60 wt% (Gómez-Frutos *et al.* 2024), a characteristic typically found in arc (calc-alkaline) magmatism (Brophy 1991; Rodríguez *et al.* 2021*a*)

Non-altered volcanic rocks within the IPB are scarce. For this reason, trace element discrimination diagrams were used for geochemical comparisons (Fig. 3c–f). Geochemical trends observed in the IPB volcanic rocks and plutonic rocks from the SSNB are remarkably similar, and follow a shared pattern (Fig. 3).

Rocks from the hybrid zones plot between mafic and felsic end members, coinciding with a silica gap at *c.* 60 wt% of SiO_2 in a bimodal series (Fig. 3a), such as the SSNB and the Guadalupe Igneous Complex (Sierra Nevada Batholith, California: Putirka *et al.* 2014).

In addition, the isotopic signature of the Gerena hybrid zone preserves the parental composition of the mafic and felsic rocks from the SSNB (Fig. 4a). Altered volcanic rocks often exhibit a scattered Sr-isotopic signature due to contamination during their ascent, subsequent alteration at the level of emplacement, weathering or, more likely in this case, the influence of seawater input (Fig. 4a). There is no doubt that the isotopic signature for the SSNB differs from typical signatures of the Iberian syn- to post-collisional granites from the Variscan cycle (Fig. 4a). However, the Guadalupe Igneous Complex from the Sierra Nevada Batholith (California, USA), a reference for arc-like magmatism (Putirka *et al.* 2014; Ratschbacher *et al.* 2024), has a signature close to the South Portuguese Zone magmatism, including both the IPB and the SSNB (Fig. 4a).

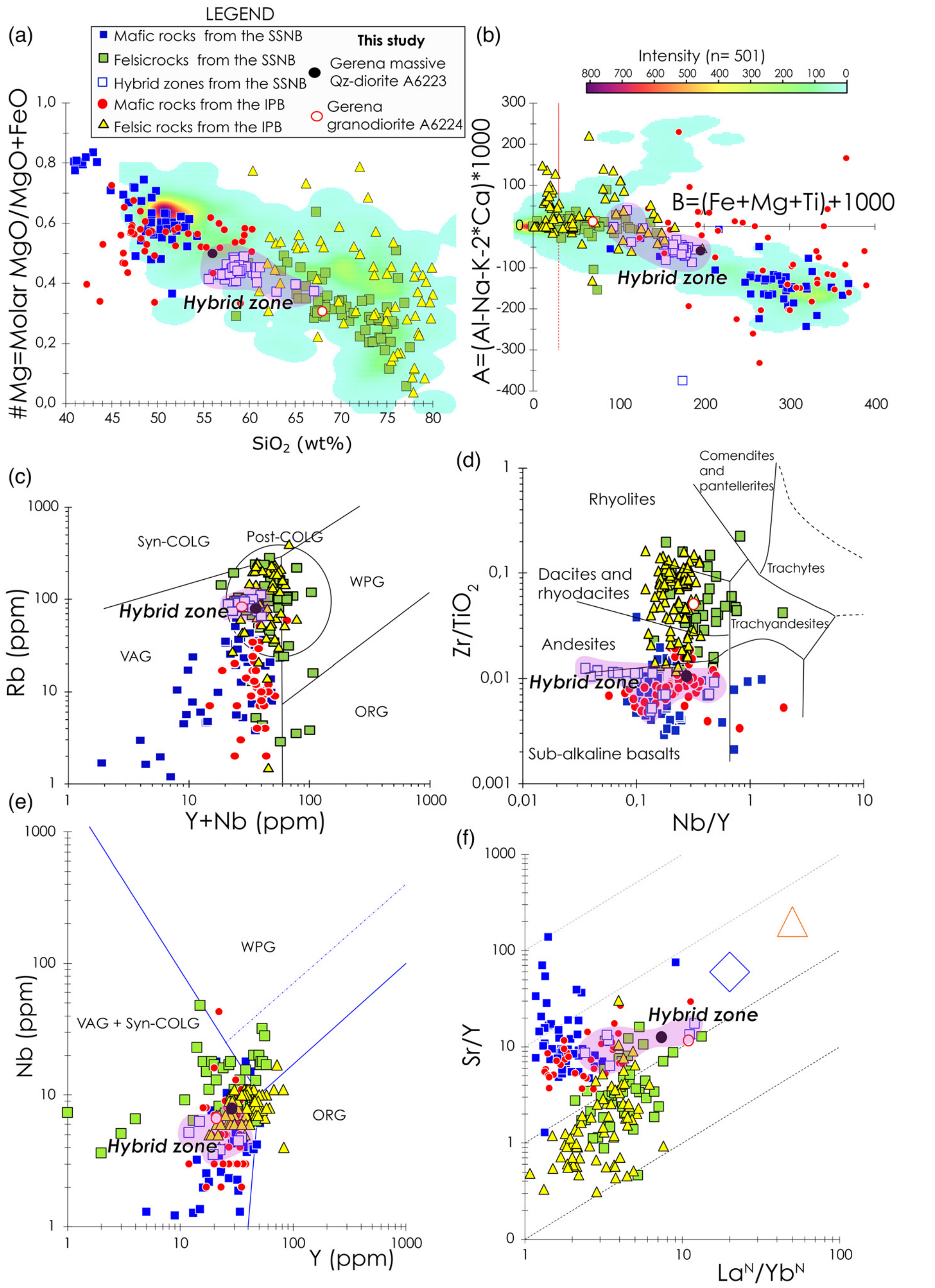

Fig. 3. (**a**) SiO_2 v. #Mg and (**b**) B–A diagrams (de la Roche 1978) showing the bimodal trend of the Seville Sierra Norte Batholith (SSNB) and the hybrid zone between both end members. The geochemistry of the Guadalupe Igneous Complex (Putirka *et al*. 2014) is illustrated in the Kernel diagrams in (a) and (b) as an example of batholiths with a strong compositional bimodality. In these diagrams, volcanic rocks from the Iberian Pyrite Belt (IPB) are dispersed due to the degree of alteration. (**c**)–(**f**) Main trace element diagrams showing the geochemical patterns of the SSNB and volcanic rocks from the Iberian Pyrite Belt (IPB). The purple area defines the projection of subvolcanic rocks from the Gerena hybrid zone. The blue diamond and the red triangle in (f) corresponds to high-silica and low-silica adakites, respectively. ORG, ocean ridge granites; Post-COLG, post-collisional granites; Syn-COLG, syncollisional granites; VAG, volcanic arc granites; WPG, within-plate granites.

Geochronological evidence for Late Fammenian–Tournaisian arc-like plutonism in the South Portuguese Zone

New SHRIMP U–Th–Pb results from the granodiorite hosting the Gerena hybrid zone (sample A6224) and from the quartz-diorite with ocelli and pegmatitic pods (sample A6226) are plotted in Figure 4 and listed in Supplementary Table S4. Cathodoluminescence images of zircon grains are presented in Supplementary Figure S1. A study of the internal morphology of the zircon grains was useful for selecting targets for isotopic analysis, thereby avoiding fractures and inclusions.

A total of 44 U–Th–Pb SHRIMP analyses from the granodiorite (sample A6224) yield U contents ranging from 205 to 1598 ppm and Th/U ratios of 0.15–1.49, suggesting felsic–intermediate metaluminous to mafic sources. A concordia age of 356 ± 1 Ma (N = 41; MSWD = 0.14: Fig. 4b) was calculated for the crystallization of the granodiorite (Tournaisian). However, the low MSWD value of 0.14 suggests that the uncertainty of this age may be overestimated. The probability density plot, showing two major age peaks at 354 and 365 Ma, indicates that we are dealing with a composite population. The younger age peak, almost coincident with the concordia age, may represent the crystallization age of the granodiorite, while the oldest corresponds to a previous magmatic event (inherited grains). The separation of these two subgroups is not straightforward because a continuum of overlapping error intervals for each analysis defines the age distribution.

A total of 10 U–Th–Pb SHRIMP analyses from the quartz-diorite with ocelli and pegmatitic pods (sample A6226) yield U contents ranging from 750 to 3402 ppm and Th/U ratios of 0.55–1.1, indicating felsic–intermediate metaluminous to mafic sources. A concordia age of 368 ± 3 Ma (N = 4; MSWD = 0.38: Fig. 4c) was calculated. This Late Famennian age, which is the best estimate for the crystallization age of the quartz-diorite, matches the oldest age peak defined by the inherited zircon grains of the granodiorite (sample A6224).

Shallow emplacement of hybrid zones

Pressure estimates from amphibole thermobarometry are below 100 MPa and temperatures are estimated to be close to 750°C (see

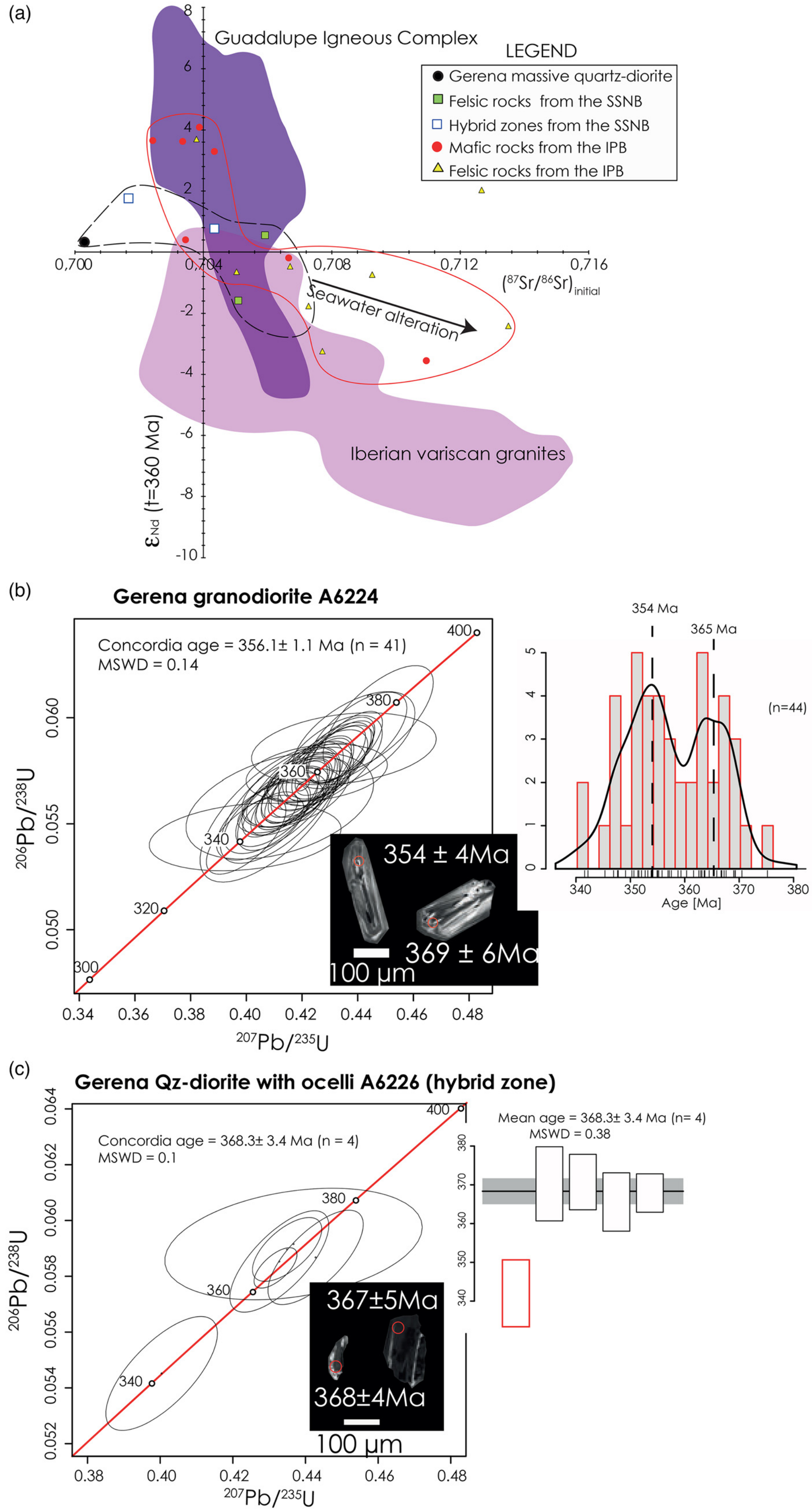

Fig. 4. (**a**) Initial ratios of $^{87}Sr/^{86}Sr$ isotopes v. ε_{Nd} for the Seville Sierra Norte Batholith (SSNB) plutonic rocks and the Iberian Pyrite Belt (IPB) volcanic rocks. The initial isotopic ratios are calculated at 360 Ma. Iberian Variscan granites (see the Supplementary material for the references) and the Guadalupe Igneous Complex (Ratschbacher *et al.* 2024) are shown for comparison. The black dashed line delimits samples from the SSNB (Gómez-Frutos *et al.* 2024). The red line comprises volcanic rocks from the IPB. (**b**) Concordia diagram and probability density plot for the Gerena hybrid zone granodiorite. (**c**) Concordia and weighted mean diagrams for the Gerena hybrid zone quartz-diorite with ocelli, both including selected cathodoluminescence (CL) images.

Supplementary Table S3). Given the greater uncertainties associated with low-pressure thermobarometric calculations (<73 MPa: Ridolfi 2021), the pressure values are interpreted only as indicative of a subvolcanic pressure of emplacement. The water content of the melt in equilibrium with amphibole exceeds 5 wt% (see Supplementary Table S3).

Thermobarometry results report the highest temperature values corresponding to ocelli from the quartz-diorite of the Gerena hybrid zone and the lowest values corresponding to the host quartz-diorite (Fig. 5). Still, both are close to the solidus (below 800°C) for the hybrid zone system and were subjected to pressures below 100 MPa (see Supplementary Table S3).

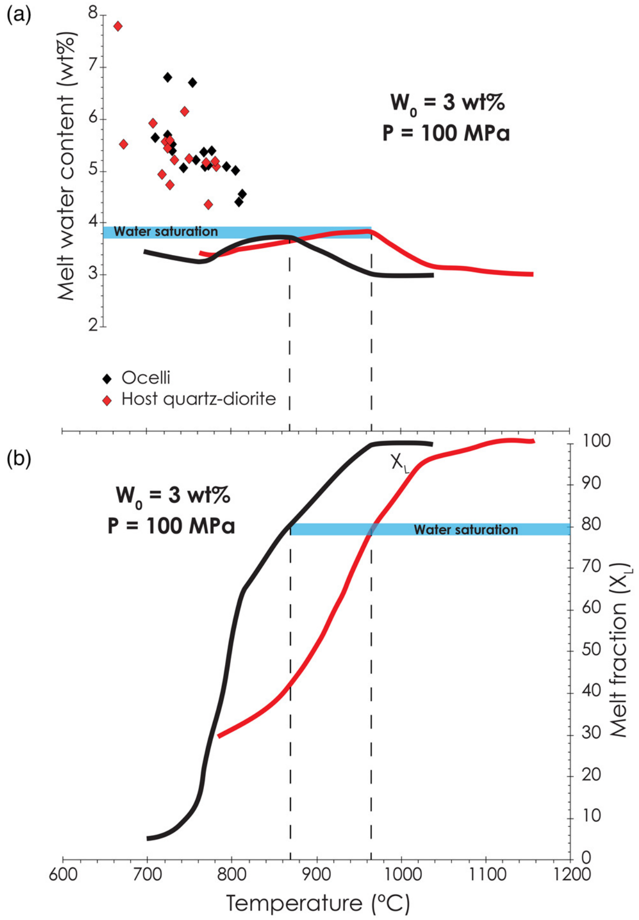

Fig. 5. Thermobarometry results from amphibole geochemistry and phase-equilibria modelling by rhyolite-MELTS code for quartz-diorite with ocelli and pegmatitic pods. W_0 is the initial water content used in the phase-equilibria modelling. Source: from Gualda *et al.* (2012).

High-temperature experiments of the Gerena hybrid zone

The experimental strategy is focused on determining the near-liquidus conditions of this magmatic system and the geochemical signature of liquids from hybrid zones.

The results from the quenching experiment using the quartz-diorite with ocelli and pegmatitic pods (sample A6226) from the Gerena hybrid zone indicated that the existence of relicts of primary minerals, such as plagioclase (Fig. 6a), supports a liquidus greater than 1100°C.

The mineral assemblage from the run at 1000°C is orthopyroxene, clinopyroxene, plagioclase, ulvöspinel apatite and ilmenite (see Supplementary Table S5), with a crystal fraction of around 0.4 (Fig. 6a). The liquid fraction (0.61) has been estimated by mass balance (Herrmann and Berry 2002) and image analysis. The geochemical signature of experimental liquids matches the main cotectic array defined for calc-alkaline systems (MCA: Castro 2020) (Fig. 6b, c).

Discussion

A genetic link between arc plutonic and volcanic counterparts of the Iberian Pyrite Belt

The relationship between the SSNB and the volcanic rocks of the IPB provides a temporal model for establishing links between the formation of bimodal magmatic systems and related volcanogenic ore-forming processes. Geochemical, petrological and temporal relations between the SSNB and volcanic rocks from the IPB support a common magmatic source for both systems. The major and trace element signatures overlap between volcanic and plutonic equivalents, and pristine compositions recorded in magmas from the Gerena hybrid zone also support a petrological link between the plutonic and volcanic counterparts.

The magmatic systems of the IPB are believed to have formed in a collisional setting, characterized by decompression melting of the asthenosphere following an oblique impact between Gondwana and Laurussia (Mitjavila *et al.* 1997). The collision between the Gondwana (Ossa-Morena Zone) and Laurussia (South Portuguese and Pulo do Lobo zones) megacontinents triggered regional strike-slip tectonics, facilitating the ascent of basaltic magmas to the crust (Mitjavila *et al.* 1997). The influx of mantle melts into the crust provided heat for large-scale melting. Andesites formed through mixing of mafic melts and melted crustal material. The basalts of the IPB, which also exhibit arc-type characteristics, have also been interpreted as the products of subduction (Thiéblemont *et al.* 1997). The composition of volcanics, which follows the SSNB composition trend and has an intermediate andesitic signature in hybrid zones (Fig. 4), is similar to the geochemical distribution that is typically associated with the inception of arc magmatism (Putirka *et al.* 2014). The petrological and geochemical characteristics of the plutonic and volcanic counterparts from the South Portuguese Zone closely resemble those of Andean-type calc-alkaline magmatism (Castro 2020). This compositional similarity suggests that the SSNB probably represents the plutonic roots of an arc magmatic system genetically and temporarily linked to the IPB volcanic rocks, which subsequently initiated the hydrothermal system responsible for ore deposition.

Water saturation for the quartz-diorite with ocelli and pegmatitic pods at 100 MPa is reached when the melt contains more than 3.9 wt % H_2O (Ghiorso and Gualda 2015), corresponding to a melt fraction above 0.75 and temperatures around 960°C (Fig. 5). By adding a CO_2 content of 0.05, the water saturation of this magma decreases to 2.1 wt%. Water saturation in the granodiorite from the Gerena hybrid zone is also reached at *c.* 4 wt% H_2O. The melt fraction at this point is close to 0.8 and temperatures around 870°C (Fig. 5). The melt water content when the amphibole crystallizes in the quartz-diorite with ocelli and pegmatitic pods exceeds the water saturation for both systems forming the hybrid zones (Fig. 5).

Most dark bodies represent mafic magma globules, which preserve a marked chilled margin and lobate contacts against the host granodiorite (Fig. 2). The mafic rocks can show ocelli with varying sizes and distributions; however, they are usually concentrated next to the chilled margin (Fig. 2a). These dark bodies are interpreted as fragments of the rigid outer carapace produced by magma-in-magma injection processes. This fragmentation can result from the *in situ* crystallization of ultrahigh-temperature hydrous parental magmas that reach subvolcanic depths (Rodríguez *et al.* 2025) with water contents close to 3.9 wt% (water saturation content) and a high melt fraction of around 0.75 (Fig. 5). Experimental results using the quartz-diorite with ocelli and pegmatitic pods without added water show ultrahigh temperatures (>1000°C) for near-liquidus conditions. Even considering that these magmas originally had higher water contents when they were emplaced, the high crystallinity (0.4) observed in this system without added water at 1000°C supports the idea that ultra-hot parental magmas reached the crust. The addition of water (W_0 = 3 wt %) descends the liquidus to 1160°C (Fig. 5b). The composition of these liquids at 0.6 of melt fraction aligns with that of the granodiorite (the felsic end member) hosting the hybrid zone and follows the main cotectic array (Fig. 6).

The mafic and felsic end members observed in the Gerena hybrid zone are likely to have been derived from the splitting of a common parental magma. Magma splitting occurs through gas-driven filter

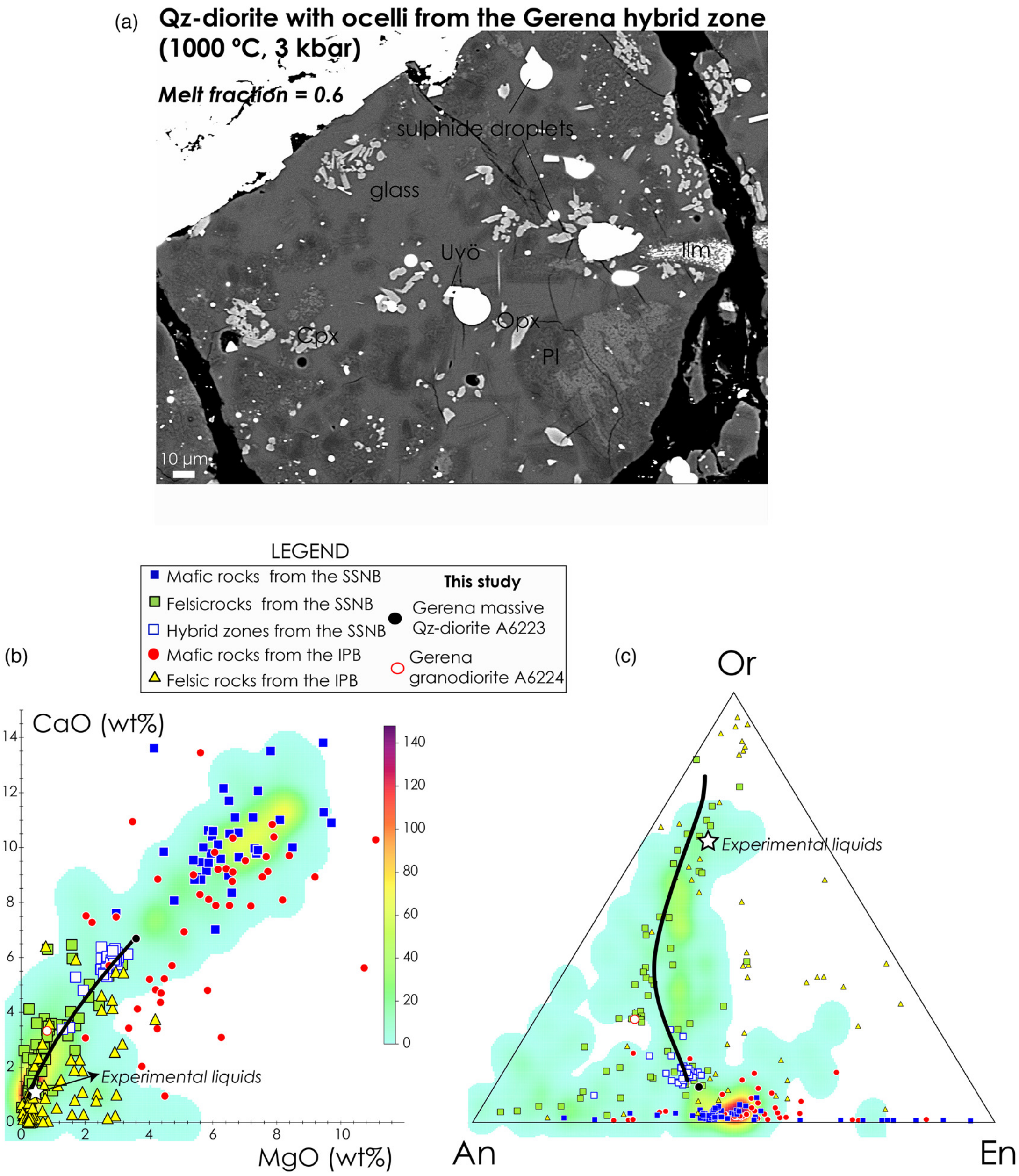

Fig. 6. (**a**) BSE images of the experimental capsule showing the phase-equilibria association. (**b**) and (**c**) CaO v. MgO and An–Or–En diagrams for the experimental glasses in comparison with the magmatic rocks from the South Portuguese Zone. The geochemistry of the Guadalupe Igneous Complex is also illustrated in the kernel diagrams for comparison. Source: Putirka *et al.* (2014).

pressing within the solidification and water-saturation fronts at shallow depths (Rodríguez *et al.* 2025). Ultra-hot magmas arriving at shallow levels of the crust will reach the volatile saturation upon emplacement. The pressure increment caused by the bubble exsolution can produce magma splitting, resulting in two subsystems with sharp boundaries (Rodríguez and Castro 2017).

Numerous VMS deposits from the Archean to modern seafloors are spatially associated with composite shallow magma chambers (Galley 2003; Jeanvoine *et al.* 2024 and references therein). Most VMS mining districts are clusters of ore deposits formed within rifts or calderas, attributed to a common heat source that triggered large-scale subseafloor systems of fluid convection. The characteristics of the sedimentary and volcanic rocks of the IPB suggest that they were deposited on the seafloor in association with numerous volcanic centres (Oliveira 1990). Although it is recognized that there are Mississippian plutonic rocks in the South Portuguese Zone that are contemporaneous with the VSC, a representative model linking the Late Famennian volcanic and plutonic rocks has yet to be proposed.

The Late Famennian quartz-diorite enclave (*c.* 368 Ma) of the Gerena hybrid zone probably represents a shallow-crustal magma reservoir connected to volcanic centres (*c.* 358 Ma: Cercal, Neves Corvo, Aljustrel, Serra Branca, Zufre and Las Cruces) (Barrie *et al.* 2002; Rosa *et al.* 2009; Oliveira *et al.* 2013; Paslawski *et al.* 2021). These plutonic rocks can be considered as the missing Late Famennian plutonic basement of the IPB.

The hybrid zones studied here shed light on the volatile exsolution processes by *in situ* magma differentiation. Further discussions will highlight the complexity of the geological processes involved and underscore the need for additional research to clarify the mechanisms responsible for the magmatic and tectonic evolution of the region, as well as to identify the triggers for metal concentration.

Geodynamic reconstruction

A temporal and spatial link between volcanic and plutonic rocks from the South Portuguese Zone has been discussed recently, based

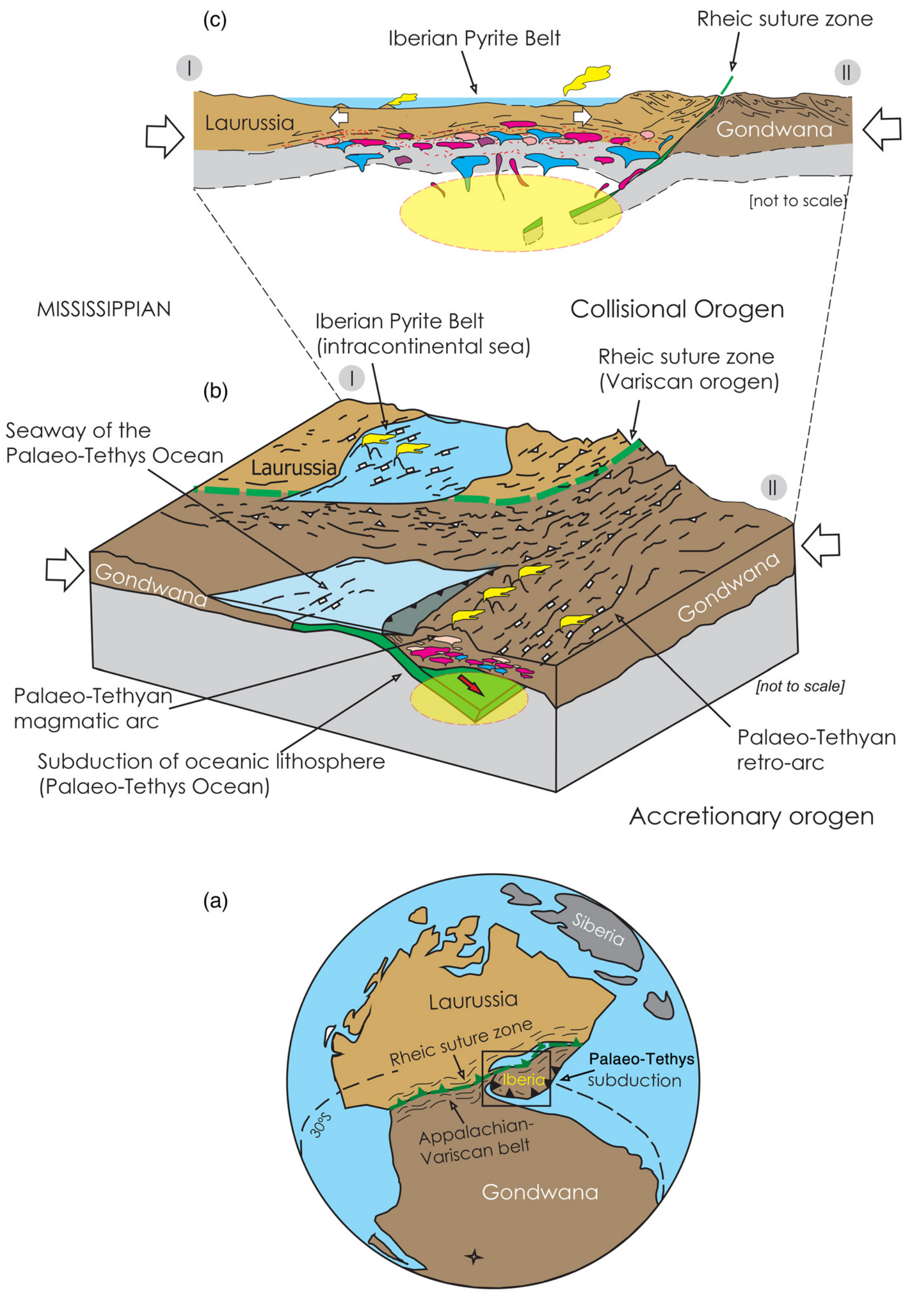

Fig. 7. (**a**) Palaeogeographical reconstruction of Pangaea for the Mississippian showing the Rheic suture zone, the Appalachian–Variscan orogenic belt and the subduction of the Palaeo-Tethys oceanic lithosphere. Note the Laurussian intracontinental sea and the Palaeo-Tethys seaway, both surrounding Iberia. (**b**) 3D sketch of the inferred tectonic model for SW Iberia, during the Mississippian, showing the arc-type magmatism that took place, on both sides of the Rheic suture zone, during the Laurussia–Gondwana oblique collision and the ongoing subduction of the Palaeo-Tethys oceanic lithosphere under the Gondwana side. (**c**) 2D sketch showing the alleged demise of the subduction of the Rheic oceanic lithosphere, and slab break-up under the Laurussian side of the collisional orogen where the Iberian Pyrite Belt was probably formed. Source: modified from Rodríguez *et al.* (2021*b*) and Pereira *et al.* (2022).

on a compilation of zircon U–Pb ages (*c.* 354–337 Ma: Albardeiro *et al.* 2023 and references therein), with a focus on Mississippian ages that are dominant. U–Pb zircon geochronology of Mississippian volcanic rocks from the IPB has highlighted that they carried source-inherited zircon grains (pre-Devonian), but also zircon that crystallized from previous Middle–Late Devonian magmas (Oliveira *et al.* 2013; Cravinho *et al.* 2024). The younger magmas probably promoted remelting of older igneous rocks, implying a sustained heat flow for tens of millions of years, which was favourable to the development of VMS deposits (Rosa *et al.* 2009). The ultrahigh-temperature events (>1100°C), typically found at hybrid zones (Rodríguez *et al.* 2025), can produce coupled dissolution–precipitation (CDP) in zircon grains (Asimus *et al.* 2024). However, no evidence of replacement by CDP was found in the studied zircon grains, discarding the hypothesis of age overlap between the quartz-diorite of the hybrid zone and the granodiorite. The estimated crystallization age calculated for the granodiorite of the Gerena hybrid zone (356 ± 1 Ma) is older than previously reported for the plutonic rocks of the SSNB, coinciding with the crystallization age of the hanging-wall dacite of the Las Cruces ore deposit (354 ± 1 Ma: Barrie *et al.* 2002). This magmatism falls between Axis VII and Axis VIII of the volcanic alignments defined by Albardeiro *et al.* (2023) for the South Portuguese Zone, with an average age similar to that of the gabbro-dioritic rocks of the Beja Igneous Complex (Ossa-Morena Zone). The *c.* 350 Ma Beja Igneous Complex was possibly emplaced in the Gondwanan crust with concomitant low pressure–high temperature metamorphism resulting from slab break-off following the Laurussia–Gondwana collision (Pin *et al.* 2008). The tectonic models proposed to explain the origin of the Mississippian arc magmatism of the South Portuguese Zone are still under discussion. The attempt to relate it, in palaeogeographical terms, to the arc magmatism of the IPB and the Beja Igneous Complex must consider that they were separated by *c.* 100 km (Pérez-Cáceres *et al.* 2017) (Fig. 7).

The generation and crystallization of magmas in the South Portuguese Zone during the early Mississippian may be spatially associated with the subduction of the Rheic oceanic lithosphere. However, different models for the timing of the final closure of the oceanic basin and the polarity of the subduction zone or zones have been proposed (Pereira *et al.* 2017). Some tectonic models assumed the birth and demise of the Devonian arc system along the Laurussian active margin during subduction of the Rheic Ocean (Pereira *et al.* 2017, 2021). Other authors suggest that the IPB magmatism is related to north-dipping (present-day coordinates) oblique subduction of the Rheic oceanic lithosphere, and subsequent collision between Laurussia and Gondwana (Silva *et al.* 1990; Braid *et al.* 2018). It was also proposed that this subduction process may have caused the progressive delamination of the lower plate and underplating with mantle melt, leading to extension and partial melting of the Laurussian crust (Paslawski *et al.* 2021). This tectonic model posits that, due to such an oblique collision, the lateral escape of a Laurussian crust – containing the South Portuguese Zone – led to regional extension and related volcanism, spanning from *c.* 370 to 340 Ma in the IPB (Albardeiro *et al.* 2023 and references therein).

Alternatively, it has been suggested that for the tectonic evolution of the Laurussia margin during the Late Devonian–Mississippian, in the sequence of the south-dipping (present-day coordinates) Rheic Ocean subduction and arc magmatism, a process of slab break-up may have created conditions for collisional delamination and partial melting of continental crust and lithospheric mantle (Fig. 7) (Pereira *et al.* 2017; Rodríguez *et al.* 2021*b*). This tectonic model assumes that a Mississippian magmatic arc developed in the Gondwanan crust due to the subduction of the Palaeo-Tethys oceanic lithosphere, which would be coeval with the IPB. The typical compositional signature of arc magmatism observed in both the IPB and the SSNB supports the proposed tectonic setting in which the subduction of the Rheic oceanic lithosphere and slab break-off are responsible for the generation of the South Portuguese Zone magmatism during the Pangaea assemblage (Fig. 7).

Conclusions

The SSNB shares a geochemical signature with volcanic rocks from the IPB, consistent with calc-alkaline arc magmatism. The crystallization age of magmas from the Gerena hybrid zone (*c.* 354 and 368 Ma) coincides with those of volcanic rocks and ore deposits from the IPB. Notably, the quartz-dioritic enclave of the Gerena hybrid zone is likely to represent the missing Late Famennian plutonic roots of the IPB.

The Gerena hybrid zone overlaps the compositional gap between mafic and felsic end members observed in both plutonic and volcanic counterparts from the South Portuguese Zone. This compositional gap is attributed to parental magmas that ascend to the upper crust, where they are capable of splitting through *in situ* crystallization. The delamination of the Rheic oceanic lithosphere from the continental lithosphere –associated with the subduction demise, slab break-off, and the continental collision between Gondwana and Laurussia– may have been the processes that boosted the production of magmas with arc-like signature during the Late Famennian–Tournaisian in this region of the Iberian Variscan belt.

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