Was there a super-eruption on the Gondwanan coast

477 My ago?

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ABSTRACT

Precise zircon and monazite ID-TIMS U-Pb dating of three Lower Ordovician altered ash-fall tuff beds (K-Bentonites) in the Cantabrian Zone of NW Iberia yielded coeval ages together with an equivalent previously studied sample (477.5±1 (Gutiérrez-Alonso et al., 2007)), of 477±1.3 Ma, 477.2±1.1 Ma and 477.3±1 Ma, with a pooled concordia age (all analyses in the four samples) of 477.2±0.74 Ma. A conservative estimation of the volume and mass of the studied K-bentonite beds (using exclusively the CZ data) yields a volume for the preserved deposits of ca. 37.5 km³ (Volcanic Explosivity Index - VEI = 6, Colossal). When considering other putative equivalent beds in Iberia and neighboring realms (i.e. Armorica, Sardinia) the volume of ejecta associated to this

event would make it reach the Supervolcanic-Apocalyptic status (VEI=8, >1000 km³). At variance with most known cases of this kind of gigantic eruption events, geological observations indicate that the studied magmatic event was related to continental margin extension and thinning and not to plate convergence. We speculate that a geochronologically equivalent large caldera event recognized in the geological record of NW Iberia could be *ground zero* of this super-eruption.

INTRODUCTION

Volcanic supereruptions (Rampino and Self, 1992) are considered to be those that eject magma in excess of 10¹⁵ kg, equivalent to a volume of more than 450 km³ (Self, 2006; Sparks et al., 2005) in a relatively short period of time (Mason et al., 2004; Miller and Wark, 2008) with a Volcanic Explosivity Index (VEI) (Newhall and Self, 1982) usually above 8. These singular volcanic events appear to happen triggered by melt buoyancy (Malfait et al., 2014) with a worldwide frequency ranging from 1.4 to 22 events/Ma (Mason et al., 2004), which should make them abundant in the geological record.

Nevertheless, few such eruptions are recognised in the geological record because: i) the chances of preservation are scarce as the deposits they generate are easily eroded and ii) even if the deposits are preserved, they are difficult to recognize and reconstruct once they have been altered, deformed, metamorphosed and dismembered by subsequent geological events. For example, the last 45 My of Earth history preserve deposits caused by at least 45 supereruptions (Mason et al., 2004) while in the Ordovician period, which covers the same time span (*ca.* 42 My), only two supereruptions, preserved as heavily altered volcanic ash-fall (tephra) deposits (K-bentonites), have been identified so far (Huff, 2008; Huff et al., 1992; Huff et al., 2010; Huff et al., 1996; Sell et al., 2013; Sell et al., 2015, in press) in the early Late Ordovician. The events represented by these

deposits took place in Laurentia and Baltica, on the northern coast of the Rheic Ocean (Murphy et al., 2006) in a subduction related environment.

In this paper we will focus on the Lower Ordovician ash-fall deposits found in northern Iberia and related realms (Fig. 1) and provide geological and geochronological data and arguments that support the idea that these deposits were the product of one such super-eruption that took place in the rifted and extended northern margin of west Gondwana during Floian times. At variance with other subduction-related Ordovician super-eruptions this event took place at a passive margin while it was being thinned and extended during the early stages of the Rheic Ocean opening (see Murphy et al., 2006, 2008) (Fig. 2).

Geological setting

A well-known feature of the Lower Paleozoic succession in western Europe is the abundance of long-lived magmatism which is represented mainly by the so called “Ollo de Sapo” plutonic and volcanic event ranging in age between ca. 490 and 465 Ma (Montero et al., 2009b; Talavera et al., 2013), with a maximum at ca. 477 Ma, (Fig. 3).

Within the core of the Cantabrian Arc, in the Cantabrian Zone (CZ), this event is represented by alkaline basalts and volcanoclastic rocks located mostly within Upper Cambrian and Lower Ordovician strata (Barrero and Corretgé, 2002; Gallastegui et al., 1992; Gallastegui et al., 2004; Heinz et al., 1985; Loeschke and Zeidler, 1982; Suárez et al., 1993) together with an extensive K-bentonite (known either as the Pedroso or Valverdín bed) interstratified within the Lower Ordovician succession (Figs. 1 and 4), (García-Ramos et al., 1984) which is the main object of this study. Ash-tuff beds stratigraphically correlatable with the Pedroso-Valverdín bed crop out in the Iberian Ranges (IR) (Tranquera bed, Fig. 1, (Alvaro et al., 2008)).

The Lower Ordovician shallow-water siliciclastic succession hosting the studied ash beds is widely exposed in Western Europe, especially in northern Iberia (e.g. (Alvaro et al., 2008; Aramburu, 1989; Aramburu and García-Ramos, 1993) and its provenance established through detrital zircon studies (Fernandez-Suarez et al., 2002; Shaw et al., 2014). This succession is partly correlatable with the widespread Armorican quartzite, which is largely exposed in Western Iberia providing a useful mapping marker to unravel the structure of the Variscan belt in this region. In the Cantabrian Zone, the transitional Cambro-Ordovician sequence is represented by the Barrios Formation, a dominantly sandstone unit. This unit was first studied by Barrois (1882) and Comte (1937) formally defined as Formation by Van den Bosch (1969), and sedimentologically studied by Gietelink (1973), Aramburu (1989) and Aramburu and García-Ramos (1993). The latter authors divided the formation into three members of which the lowermost one (La Matosa Mb.) is mainly of Furongian age, the middle member (Ligüeria Mb.) is Tremadocian and the uppermost member (Tanes Mb.) is the alleged equivalent to the Armorican Quartzite of SW Europe, and from which the studied samples have been collected (Fig. 4). According to Aramburu (1989) and Aramburu and García-Ramos (1993), a single altered ash-fall tuff bed (described as a “kaolinite tonstein”) was either recorded in the Tanes Member of the western Cantabrian Zone (their “Pedroso bed”) or in a much lower position within the La Matosa Member (the so-called “Valverdín bed”), restricted in this case to the southern Cantabrian Zone. Our geochronological study on representative outcrops of the Pedroso and Valverdín beds indicate that both horizons are equivalent, and therefore the stratigraphy of the La Matosa Member (typical of the eastern Cantabrian Zone and absent to the west) must be reconsidered.

Figure 4 shows representative columns of the Barrios Formation in the northern (left) and southern (right) parts of the Cantabrian Zone. The first illustrates the stratigraphic position of the Pedroso bed, mined for kaolinite in the western Cantabrian Zone where it defines the “Sierra del Pedroso subtype” of the “Asturias” type of kaolinite sedimentary ore (Galán Huertos, 1974; Galán Huertos and Espinosa de los Monteros, 1974). The second column represents a general stratigraphic scheme for the Barrios Formation at the homonymous section of Los Barrios de Luna (León province), showing the occurrence of the Valverdín bed (Aramburu, 1989, column 13; Aramburu and García-Ramos, 1993, column 4). Although the main sandstone bodies in this section were originally were adscribed to the Barrios Formation, the upper quartzite of the Luna dam changed from being considered as the Tanes Member to being separated as a different unit of Hirnantian-earliest Silurian age (Gutiérrez-Marco et al., 2010), recently renamed as La Serrona Formation (Toyos and Aramburu, 2014).

With regard to the strata preceding the *Skolithos* sandstone and belonging to the La Matosa Member, a great part of its thickness was recently assigned to the Cambrian (IMC6 and A3 acritarch biochronozones of Palacios, 2015). Thus, the beds tentatively correlated with the Tanes Member by Toyos and Aramburu (2014, fig. 9) are virtually restricted in this section to the <7 m of strata immediately below the *Skolithos* sandstone underlying the K-bentonite, to the top of the Barrios Formation. As an alternative hypothesis, these authors suggested the possibility that the Valverdín and El Pedroso beds may be equivalent, which is confirmed by the new zircon ages presented in this work. However, this implies the putative existence of diverse sedimentary gaps below the K-bentonite bed during the Tremadocian that are difficult to identify and correlate. In addition, another argument for the correlation of the K-bentonite outcrops may be the widespread association of the K-bentonite bed with strata showing densely

packed vertical burrows (*Skolithos* “piperock”). This was firstly noticed by Gómez de Llarena (1955), although they were previously known by mine workers. Aramburu and Garcia Ramos (1993) reported other *Skolithos* beds in the Barrios Formation, interpreting them as related to the initial stages of marine transgressions over fluvial facies of a braid plain delta that dominates the sedimentation of the entire formation. The massive colonization of the shallow shelf by *Skolithos* could be considered a bio-event in which the trace-makers acted as opportunistic species, being the main filter-feeding burrower organism that first colonized the incipient marine shelf. Taking into account the extremely shallow slope of the platform and the reduced water sheet involved in these slightly diachronic events, their temporal duration should have been relatively short, perhaps of some tens to no more than one hundred thousand years. The K-bentonite shows very sharp upper and lower contacts, and, to our knowledge, was never affected by sin- or post-depositional burrowing. In contrast, the layer immediately above the K-bentonite commonly shows numerous vertical trace fossils. The lack of endobenthonic fauna at the time of deposition may have been the result of water poisoning by volcanism or of an almost instantaneous induration of the sediments surface. The rapid, if not instantaneous, recovery of endobenthonic life after the ash-fall implies a very short duration of the volcanic event, perhaps even in the range of days or weeks, with only some ripple reworking of the surface and the preservation of a single to few positive graded sequences. The massive ash-fall apparently did not affect the population structure and the development of the benthic communities, which attained a rapid recovery and re-colonization of the shallow marine environment in a way similar to that observed in other Ordovician and modern ash-falls (Huff et al., 1992; Kuhnt et al., 2005).

In the key reference section of the El Fabar highway tunnel (Fig. 4), Gutiérrez-Marco and Bernárdez (2003) identified three of such *Skolithos* horizons within the Tanes Member of the Barrios Formation. In this section a relatively good biostratigraphic control favoured paleontological dating of the Tanes member as ranging from the Tremadocian to at least the late Floian, perhaps reaching the earliest Dapingian. A time span for the deposition of the Barrios Formation of 10 My may be a conservative estimate. Of the three identified *Skolithos* “pipe-rock” only one is associated with the K-bentonite; the lower *Skolithos* “pipe-rock” has been confidently identified only along the eastern thrust units (Laviana-Rioseco); whereas the upper one has been identified also in the western ones (Somiedo nappe section), and the middle one, to which the k-bentonite horizon is associated seems to be present in all the tectonic units of the Cantabrian zone. The sedimentary setting of the Tanes member, with a siliciclastic dominantly fluvial sedimentation involving erosional surfaces and cryptic gaps, makes it very difficult if not impossible to ascertain their sequence stratigraphic interpretation and to explain the non-preservation of the lower and upper *Skolithos* “pipe-rock” in many sections. The record of a maximum of three short-lived *Skolithos* events in a time span of ca. 10 Ma, results in a highly improbable preservation ratio. The same argument can be used for the association of a particular widespread *Skolithos* horizon with the k-bentonite bed towards the middle part of the Tanes Member, which indirectly supports the notion of a single ash-fall event and enables its use in stratigraphic correlation.

Within the geological framework described, the Pedroso-Valverdín K-bentonite bed (Figs.1 and 4) extends over the whole Cantabrian Zone (Fig. 5), more than 1800 km² with a thickness between 45 and 80 cm (Aramburu, 1989). The origin of the Lower Ordovician magmatism in the studied sector of the Gondwanan margin (Figs. 1 and 2)

is interpreted to be related to extension, linked to the undocking of Avalonia (Murphy et al., 2006).

Three new studied samples plus a sample from Mina Conchita (Fig. 5) (Gutiérrez Alonso et al., 2007), were collected in the Cantabrian Zone. The first sample, named as “GRADO”, comes from the Peñaflor mine placed east of Grado (Asturias), close to the southern termination of the Sierra del Pedroso (N43°24'10.54" W006°02'27.05"). The second sample (“TUN-194“, Fig. 5) was collected during the construction of the “Túnel Ordovícico del Fabar” in the Cantabrian A-8 highway, southwest of Ribadesella (Asturias, ca. N043°27'49.70" W005°08'41.11"). The third sample (designated as “LBL”) corresponds to the alleged Valverdín bed cropping out at the road section from Los Barrios de Luna to Mallo de Luna, near the dam of the Barrios de Luna water reservoir (León province: N42°50'57.22" W005°51'57.74"). In addition to these samples, the already-published one from Mina Conchita (“AST-1” Fig. 5; Gutiérrez Alonso et al., 2007) was collected from the core of the Viyazón-Reigada syncline within the Somiedo Unit, in the eastern bank of the Narcea river immediately downstream of the La Barca reservoir (Asturias, N43°19'25.7" W006°18'0.07")

It is important to note that all the studied K-bentonite samples contained mainly zircon, monazite and pyrite as heavy minerals, which are indicative of limited reworking in the sedimentary environment, in contrast to other K-bentonites with the heavy mineral association zircon-tourmaline-rutile, which is a common feature of highly reworked K-bentonites in which the proportion of *remanié* zircons is usually high.

Geochronology

U-Pb ID-TIMS analytical method

Zircon separation was carried out at the Complutense University of Madrid and the University of Oslo. The K-bentonite samples were crushed with a jaw crusher and pulverized with a disc mill. Minerals were separated by heavy fraction enrichment on a Wilfley table, magnetic separation in a Frantz isodynamic separator, and density separation using di-iodomethane (CH_2I_2). Finally, zircon and monazite were handpicked from the non-magnetic heavy fraction in an alcohol medium under a binocular microscope. Zircons were mostly idiomorphic, long prismatic crystals having an aspect ratio of 3:1 to 4:1, with frequent melt inclusions that in many cases ran along most of the crystal and were thus helpful in the selection of grains devoid of inherited cores.

U-Pb analytical work was conducted at the Department of Geosciences, University of Oslo. Zircon and some of the monazite grains selected for analysis were strongly air-abraded following the method of (Krogh, 1982). Abraded grains were washed in 4N HNO_3 on a hotplate and rinsed repeatedly with H_2O and acetone (with ultrasonication after each rinsing step). After washing and drying, the grains were individually weighed in a precision balance (Table 1). A mixed ^{202}Pb - ^{205}Pb - ^{235}U spike was added to the sample after weighing and transfer to the dissolution vessel. Zircon was dissolved in HF (+ HNO_3) in Teflon mini-bombs at $\sim 185^\circ\text{C}$ for 5 days, and monazite in Savillex vials in 6N HCl on a hot plate. Chemical separation of U and Pb in anion exchange resin in a HCl medium was performed only on zircon grains weighing more than a few micrograms. All monazite solutions were instead purified with a single stage HCl-HBr procedure. The samples were subsequently loaded on outgassed Rhenium filaments with H_3PO_4 and silica gel. Isotopic ratios were measured on a Finnigan-MAT 262 mass spectrometer by static multicollection on Faraday cups and/or peak jumping on a secondary electron multiplier (ion counting mode). Total procedural blanks were less than 2-5 pg Pb and 0.1-0.3 pg U. The (Stacey and Kramers, 1975) model was used to

subtract initial common Pb in excess of the laboratory blank, and decay constants are those of (Jaffey et al., 1971). Concordia plots were created using Isoplot 3.7 (Ludwig, 2009).

Results

For sample AST-1 (Gutierrez-Alonso et al., 2007) we use the published age of 477.5 ± 1 Ma (Concordia age of 6 concordant and overlapping analyses on single abraded grains, Fig. 6) and the details are described in the aforementioned publication.

For the 3 new samples selected for this study (LBL, GRADO and TUN-194) the best U-Pb age estimate has been calculated as described below:

Sample LBL: 11 zircon and 3 monazite fractions were analysed (see details in Table 1). Of the 11 zircon analyses, 5 are discordant and are no longer considered in age calculations. The six concordant analyses (bold type in Table 1) yield a Concordia age of 477 ± 1.3 Ma (Fig. 6). This age is within error of the weighted average of the $^{207}\text{Pb}/^{235}\text{U}$ age (chosen because of reverse discordance, see (Scharer, 1984) of the 3 monazite analyses (478 ± 2.7 Ma) from the same sample.

Sample GRADO: Nine zircon and one monazite fractions were analysed. Of the 9 zircon fractions 3 are >5% discordant and were not considered for age calculation. With the remaining analyses (discordance between -0.2% and 3.8%, Table 1, DR1) we calculated an upper intercept age anchored at 0 ± 10 Ma (Fig. 6) of 477.2 ± 2.3 Ma, and a concordia age with the two top analyses (Fig. 6) of 477.2 ± 1.1 Ma. This age is within error of the $^{207}\text{Pb}/^{235}\text{U}$ age of the reversely discordant monazite analysis (478 ± 1 Ma).

Sample TUN-194: 10 zircon and one monazite analyses were performed on fractions separated from this sample. Of the 10 zircon analyses, 3 were discordant and are not considered in the age calculation (Table 1). The remaining 7 concordant zircon analyses

yield a concordia age of **477.3±1 Ma** (Fig. 6), within error of the $^{207}\text{Pb}/^{235}\text{U}$ age of the reversely discordant monazite analysis (479±1 Ma).

Within the precision of the U-Pb analyses in this study, it can be considered that the four samples are equivalent and belong to the same volcanic event. The best age estimation for the volcanic event can be obtained by the pooled 21 concordant analyses from the four samples (Fig. 7), yielding a concordia age of **477.2±0.74 Ma**, which coincides with the Tremadocian-Floian boundary (477.7±1.4 Ma, (Gradstein et al., 2012)). This concordia age is consistent with the age calculated using the TuffZirc algorithm of Isoplot 3.7 (Ludwig, 2009) which yields an age of 477.5 +0.75/-1.1 Ma using the $^{206}\text{Pb}/^{238}\text{U}$ ages of the same set of 21 concordant analyses (Fig. 7).

All the monazite analyses show reverse discordance and their average $^{207}\text{Pb}/^{235}\text{U}$ age is 1 to 2 Myr older than the concordia age of the zircons in the same samples (Table 1). Although it is beyond the scope of this paper to discuss this issue, since the closure temperature of monazite for the U-Pb system and its Pb retentivity can be higher than those of zircon (e.g. (Cherniak and Watson, 2003; Cherniak et al., 2004) the monazite ages could represent an older pre-eruptive stage and the zircon be closer to the eruption stage. In any case, this observation does not challenge the inference that all the studied samples are equivalent at the level of precision achieved in this study.

Volume and mass calculation

Given the aerial extension and the thickness of the studied K-bentonite, and given the geochronological evidence reported above for its assignment to a single event, we can attempt to restore its initial mass and volume in order to evaluate the magnitude of the volcanic event. For this purpose, we have reconstructed the Variscan deformation by first unfolding the Cantabrian Arc (e.g. Weil et al., 2013) (Fig. 1) and secondly by

restoring the shortening caused by the Variscan thrusting and folding (e.g. Martínez Catalán et al., 2007). Upon a conservative restoration considering the minimum shortening during the late Devonian-Carboniferous Variscan orogeny of the different units involved (ranging from 100% in the foreland to more than 200% in the hinterland), the areal extent of the K-bentonite bed, based on the locations of the known outcrops in the Cantabrian Zone can be surmised to have exceeded 15000 km², and 100000 km² when considering the stratigraphically equivalent beds in the Iberian Ranges, the West Asturian-Leonese Zone and the Central Iberian Zone (CIZ, Fig. 1). The thickness of the studied bed shows a consistent thinning trend from the westernmost outcrops in the CZ, where the thickness reaches up to 80 cm. In the surrounding regions, thickness estimations should be taken cautiously as the tuff beds have suffered internal strain and their present-day thickness (ranging from a few centimeters to several meters) should be considered a minimum.

A conservative estimation of the volume and mass of the studied K-bentonite (using exclusively the CZ data, Fig. 1A) done with the Weibull fit method (Bonadonna and Costa, 2012) yields a volume for the preserved deposits of ca. 37.5 km³ (Volcanic Explosivity Index - VEI = 6, Colossal) which would correspond to a mass of 8.3·10¹³ kg using a measured average density value of the studied samples of 2200 kg/m³.

When considering other occurrences in northern Iberia which are likely correlated with the dated K-bentonites, these values increase to ca. 400 km³ (VEI = 7, Mega-colossal) which would correspond to a mass of 9·10¹⁴ kg. These occurrences correspond mostly to the large magmatic event regionally known as "Ollo de Sapo" (i.e. Talavera et al., 2013 and references therein) whose main age (including many volcanic rocks and their plutonic correlatives) peaks at ca. 477 Ma (Fig. 3) and also with the intrusion of peralkaline rocks in SW Iberia (Díez Fernandez et al., 2015). Moreover, the studied K-

bentonites are coeval with the intrusion of peralkaline ring complexes attributed to a large caldera event in NW Iberia (Fig. 1), (Diez Fernandez et al., 2012; Diez Fernandez and Martinez Catalan, 2009; Montero et al., 2009a). Whether or not this caldera was the main source of the dated ash-fall beds (and their correlatives) cannot be ascertained with available geological data. Given the magmatic activity peak at ca. 477 Ma according to the available data for western Europe (Fig. 3), the extent and volume of ash-fall material that could be correlated with the putative supervolcano should be further investigated and could even represent a larger event than the one postulated in this paper.

Discussion

The data presented herein document the first described occurrence of a putatively gigantic volcanic ash-fall/event in the Lower Ordovician. For the lower Paleozoic, such an event has so far only been recognized in the Upper Ordovician (ca. 454 Ma), (Fig. 1B) (Huff, 2008; Huff et al., 1998; Sell et al., 2013).

The apparent equivalent nature (same U-Pb zircon age within a ca. 1Ma uncertainty) of the dated samples occurring in the same stratigraphic position is a strong argument for the existence of a large eruptive event in Gondwana ca. 477 Ma ago. The CZ is the domain where the K-bentonite layer is better represented but, given its thickness, its areal extension should have been much larger; probably covering most of Iberia and adjacent realms. Preservation of ash-fall beds (ultimately occurring as K-bentonite layers) requires a lack of intense sedimentary reworking and the existence of large basins. In Iberia, the Lower Ordovician stratigraphic record is restricted to relatively small domains due to basin fragmentation and the presence of large emerged areas, especially in the southern part of the CIZ (Sá et al., 2013). Because in northern Iberia there is an almost continuous sedimentary record for the Lower Ordovician, the best

preservation occurs there and therefore the studied K-bentonite is ubiquitously recognized in areas lacking metamorphism and internal strain.

The large amount of igneous rocks (intrusive and extrusive) coeval with the studied K-bentonite layer found in Iberia and neighboring areas (see Fig. 3, where the peak age of ca. 85 rocks dated by the U-Pb method is 477 Ma) is consistent with the notion that the K-bentonite could have been much more extensive than recorded in the CZ. Because of the aforementioned fragmented stratigraphic record, it is not possible to assess the true size of the volcanic episode recorded in NW Iberia. Nevertheless, when considering other putative equivalent areas in Iberia and nearby realms (i.e. Armorica, Sardinia, etc. (Bonjour and Odin, 1989), the volume of ejecta associated to this event would make it reach the Supervolcanic-Apocalyptic status (VEI=8, >1000 km³).

Finally, this work shows that although most large volcanic events (past and recent) are associated with processes at destructive plate margins, they can also reach comparable magnitude in a rifting (continental margin thinning and extension and subsequent onset of oceanization) environment (Fig. 2).

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References

Alexandre, P., 2007; U–Pb zircon SIMS ages from the French Massif Central and implication for the pre-Variscan tectonic evolution in Western Europe. *Comptes Rendus Geoscience*, 339, 613–621.

Alonso, J.L., Marcos, A., Suarez, A., 2009. Paleogeographic inversion resulting from large out of sequence breaching thrusts: the Leon Fault (Cantabrian Zone, NW Iberia). A new picture of the external Variscan Thrust Belt in the Ibero-Armorican Arc. *Geologica Acta* 7, 451–473.

Alvaro, J.J., Ezzouhairi, H., Ribeiro, M.L., Ramos, J.F., Sola, A.R., 2008. Early Ordovician volcanism in the Iberian Chains (NE Spain) and its influence on the preservation of shell concentrations. *Bulletin De La Societe Geologique De France* 179, 569–581.

Andonaegui, P., Castiñeiras, P., González Cuadra, P., Arenas, R., Sánchez Martínez, S., Abati, J., Díaz García, F., Martínez Catalán, J.R. 2012, The Corredoiras orthogneiss (NW Iberian Massif): Geochemistry and geochronology of the Paleozoic magmatic suite developed in a peri-Gondwanan arc. *Lithos* 128–131, 84–99

Antunes, I. M. H. R., Neiva, A. M. R., Silva, M. M. V. G., and Corfu, F., 2009, The genesis of I- and S-type granitoid rocks of the Early Ordovician Oledo pluton, Central Iberian Zone (central Portugal): *Lithos*, v. 111, no. 3–4, p. 168–185.

- 373 Aramburu, C., 1989. El Cambro-Ordovícico de la Zona Cantábrica (NO de España).
374 Oviedo University, Oviedo (Spain), p. 530.
- 375 Aramburu, C., García-Ramos, J.C., 1993. La sedimentación Cambro-Ordovícica en la
376 Zona Cantábrica (NO de España). Trabajos de Geología, Universidad de Oviedo
377 19, 45-73.
- 378 Ballevre, M., Fourcade, S., Capdevila, R., Peucat, J. J., Cocherie, A., and Fanning, C.
379 M., 2012, Geochronology and geochemistry of Ordovician felsic volcanism in
380 the Southern Armorican Massif (Variscan belt, France): Implications for the
381 breakup of Gondwana: Gondwana Research, v. 21, no. 4, p. 1019-1036.
- 382 Barrero, O., Corretgé, L.G., 2002. La diferenciación petrográfica y geoquímica de las
383 rocas ígneas del Arroyo Farandón, Geogaceta, pp. 135-138.
- 384 Barrois, C., 1882. Recherches sur les terrains anciens des Asturies et de la Galicie.
385 Mémoires de la Société Géologique du Nord, Lille 2, 1-630.
- 386 Bea, F., Montero, P., Talavera, C., Zinger, T., 2006. A revised Ordovician age for the
387 Miranda do Douro orthogneiss, Portugal. Zircon U-Pb ion-microprobe and LA-
388 ICPMS dating. Geologica Acta, 4, 395-401.
- 389 Bonadonna, C., Costa, A., 2012. Estimating the volume of tephra deposits: A new
390 simple strategy. Geology 40, 415-418.
- 391 Bonjour, J.L., Odin, G.S., 1989. Recherche sur les volcanoclastites des Séries Rouges
392 Initiales en presqu'île de Crozon: premier âge radiométrique de l'Arénig.
393 Géologie de la France 4, 3-8.
- 394 Casas, J.M., Castiñeiras, P., Navidad, M., Liesa, M., Carreras, J., 2010. New insights
395 into the Late Ordovician magmatism in the Eastern Pyrenees: U-Pb SHRIMP
396 zircon data from the Canigó massif. Gondwana Research, 17, 317-324.

397 Castiñeiras, P., Navidad, M., Liesa, M., Carreras, J., and Casas, J. M., 2008, U-Pb
398 zircon ages (SHRIMP) for Cadomian and Early Ordovician magmatism in the
399 Eastern Pyrenees: New insights into the pre-Variscan evolution of the northern
400 Gondwana margin: *Tectonophysics*, v. 461, no. 1-4, p. 228-239.

401 Cherniak, D.J., Watson, E.B., 2003. Diffusion in zircon, in: Hanchar, J.M., Hoskin,
402 P.W.O. (Eds.), *Zircon*, pp. 113-143.

403 Cherniak, D.J., Watson, E.B., Grove, M., Harrison, T.M., 2004. Pb diffusion in
404 monazite: A combined RBS/SIMS study. *Geochimica et Cosmochimica Acta*,
405 68, 829–840.

406 Cocherie, A., Baudin, T., Autran, A., Guerrot, C., Fanning, C.M., Laumonier, B., 2005.
407 U-Pb zircon (ID-TIMS and SHRIMP) evidence for the early ordovician
408 intrusion of metagranites in the late Proterozoic Canaveilles Group of the
409 Pyrenees and the Montagne Noire (France). *Bulletin De La Societe Geologique*
410 *De France* 176, 269-282.

411 Compte, P., 1937. La série cambrienne et silurienne du León (Espagne). *Comptes*
412 *Rendus de l'Academie de Sciences de Paris* 204.

413 Cruciani, G., Franceschelli, M., Musumeci, G., Spano, M.E., Tiepolo, M., 2013. U–Pb
414 zircon dating and nature of metavolcanics and metarkoses from the Monte
415 Grighini Unit: new insights on Late Ordovician magmatism in the Variscan belt
416 in Sardinia, Italy, *International Journal of Earth Sciences*, 102, 2077-2096.

417 Dallmeyer, R.D., Tucker, R.D., 1993. U-Pb zircon age for the Lagoa augen gneiss,
418 Morais complex, Portugal: tectonic implications. *Journal of the Geological*
419 *Society*, 150, 405-410.

420 Deloule, E., Alexandrov, P., Cheilletz, A., Laumonier, B., and Barbey, P., 2002, In-situ
421 U-Pb zircon ages for Early Ordovician magmatism in the eastern Pyrenees,
422 France: the Canigou orthogneisses: *International Journal of Earth Sciences*, v.
423 91, no. 3, p. 398-405.

424 Denéle, Y., Barbey, P., Deloule, E., Pelleter, E., Olivier, Ph., Gleizes, G., 2009. Middle
425 Ordovician U–Pb age of the Aston and Hospitalet orthogneissic laccoliths: their
426 role in the Variscan evolution of the Pyrenees. *Bulletin de la Société Géologique*
427 *de France*, 180, 209–216.

428 Dias da Silva, I., Díez Fernández, R., Díez-Montes, A., González Clavijo, E., Foster,
429 D.A., in press, Magmatic evolution in the N-Gondwana margin related to the
430 opening of the Rheic Ocean—evidence from the Upper Parautochthon of the
431 Galicia-Trás-os-Montes Zone and from the Central Iberian Zone (NW Iberian
432 Massif). *International Journal of Earth Sciences*.

433 Díez Fernández, R., Castineiras, P., and Gomez Barreiro, J., 2012, Age constraints on
434 Lower Paleozoic convection system: Magmatic events in the NW Iberian
435 Gondwana margin: *Gondwana Research*, v. 21, no. 4, p. 1066-1079.

436 Díez Fernández, R., Pereira, M., Foster, D.A., 2015. Peralkaline and alkaline
437 magmatism of the Ossa-Morena zone (SW Iberia): Age, source, and
438 implications for the Paleozoic evolution of Gondwanan lithosphere. *Lithosphere*
439 7, 73-90.

440 Díez Fernández, R., Martínez Catalan, J.R., 2009. 3D Analysis of an Ordovician
441 igneous ensemble: A complex magmatic structure hidden in a polydeformed
442 allochthonous Variscan unit. *Journal of Structural Geology*. 31, 222-236.

- 443 Díez Montes, A., Martínez Catalan, J. R., Bellido Mulas, F., 2010, Role of the Ollo de
444 Sapo massive felsic volcanism of NW Iberia in the Early Ordovician dynamics
445 of northern Gondwana: *Gondwana Research*, v. 17, no. 2-3, p. 363-376.
- 446 El Khor, A., Schmidt, S. Th., Ballèvre, M., Ulianov, A., Brugier, O., 2012. Discovery of
447 an albite gneiss from the Ile de Groix (Armorican Massif, France): geochemistry
448 and LA-ICP-MS U–Pb geochronology of its Ordovician protolith. *International*
449 *Journal of Earth Sciences*, 101, 1169-1190.
- 450 Farias, P., Ordóñez-Casado, B., Marcos, A., Robio-Ordóñez, A., Fanning, C.M., 2014.
451 U–Pb zircon SHRIMP evidence for Cambrian volcanism in the Schistose
452 Domain within the Galicia-Trás-os-Montes Zone (Variscan Orogen, NW Iberian
453 Peninsula), *Geologica Acta*, 12, 209-218.
- 454 Fernandez-Suarez, J., Gutiérrez-Alonso, G., Cox, R., Jenner, G.A., 2002. Assembly of
455 the Armorica microplate: A strike-slip terrane delivery? Evidence from U-Pb
456 ages of detrital zircons. *Journal of Geology* 110, 619-626.
- 457 Galán Huertos, E. 1974. Caolines españoles: geología, mineralogía y génesis. Parte VI:
458 depósitos paleozoicos, neógenos y cuaternarios. *Boletín de la Sociedad Española*
459 *de Cerámica y Vidrio*, 13 (6), 523-546.
- 460 Galán Huertos, E., Espinosa de los Monteros, J. 1974. El caolín en España.
461 Características, identificación y ensayos cerámicos. *Sociedad Española de*
462 *Cerámica y Vidrio*, Madrid, 230 pp.
- 463 Gallastegui, G., Aramburu, C., Barba, P., Fernandez, L.P., Cuesta, A., 1992. Volcanism
464 of the lower Paleozoic in the Cantabrian Zone (Northwestern Spain). In:
465 Rabano, I., Gutiérrez-Marco, J.C. & Saavedra, J. (eds) *El Paleozoico Inferior de*
466 *Ibero-América*. Universidad de Extremadura, Mérida, 435–452.

467 Gallastegui, G., Suárez, O., Cuesta, A., 2004. Magmatismo, in: Vera, J.A. (Ed.),
 468 Geología de España. Sociedad Geológica de España-Instituto Geológico y
 469 Minero, Madrid, pp. 47-49.

470 Garbarino, C., Naitza, S., Rizzo, R., Tocco, S., Barca, S., Farci, A., Forci, A., and Serri,
 471 R., 2005, New evidence of Pre-Hercynian volcanics from Southern Sulcis
 472 (Southwestern Sardinia): Bollettino Della Societa Geologica Italiana, v. 124, no.
 473 1, p. 69-85.

474 García-Ramos, J.C., Aramburu, C., Brime, C., 1984. Kaolin tonstein of volcanic ash
 475 origin in the Lower Ordovician of the Cantabrian Mountains (NW Spain).
 476 Trabajos de Geología, Universidad de Oviedo 14, 27-33.

477 Giacomini, F., Bomparola, R.M., Ghezzi, C., Guldbransen, H., 2006. The geodynamic
 478 evolution of the Southern European Variscides: constraints from the U/Pb
 479 geochronology and geochemistry of the lower Palaeozoic magmatic-sedimentary
 480 sequences of Sardinia (Italy). Contributions to Mineralogy and Petrology, 152,
 481 19-42.

482 Gietelink, G. 1973. Sedimentology of a linear prograding coastline followed by three
 483 high-destructive delta complexes (Cambro-Ordovician, Cantabrian Mountains,
 484 NW Spain). Leidse Geologische Mededelingen, 49, 125-144.

485 Gómez de Llarena, J. 1955. Un yacimiento de caolín sedimentario en la Cuarcita
 486 Armorica de la Sierra del Padroso (La Reigada, Avilés, Asturias). Notas y
 487 Comunicaciones del Instituto Geológico y Minero de España, 37, 73-93.

488 Gradstein, F.M., Ogg, J.G., Schmitz, M.D., Ogg, G.M., 2012. The Geological Time
 489 Scale 2012 Elsevier, Amsterdam, p. 1144.

490 Gutierrez-Alonso, G.F.-S., J., Gutiérrez-Marco, J.C.C., F., Murphy, J.B., Suárez, M.,
491 2007. U-Pb depositional age for the upper Barrios Formation (Armorican
492 Quartzite facies) in the Cantabrian zone of Iberia: Implications for stratigraphic
493 correlation and paleogeography, in: Linnemann, U., Nance, R.D., Kraft, P.,
494 Zulauf, G. (Eds.), The Evolution of the Rheic Ocean: From Avalonian-
495 Cadomian Active Margin to Alleghenian-Variscan Collision. Geological Society
496 of America, Boulder (USA), pp. 287-296.

497 Gutiérrez-Marco, J.C., Bernárdez, E. 2003. Un tesoro geológico en la Autovía del
498 Cantábrico. El Túnel Ordovícico del Fabar, Ribadesella (Asturias). Ministerio de
499 Fomento, Madrid, 398 pp. ISBN 84-607-9268-4.

500 Gutierrez-Marco, J.C., Ghienne, J.F., Bernardez, E., Hacar, M.P., 2010. Did the Late
501 Ordovician African ice sheet reach Europe? *Geology* 38, 279-282.

502 Heinz, W., Loeschke, J., Vavra, G., 1985. Pheratomagmatic volcanism during the
503 Ordovician of the Cantabrian Mountains (NW Spain). *Geologische Rundschau*
504 74, 623-639.

505 Helbing, H., and Tiepolo, M., 2005, Age determination of Ordovician magmatism in
506 NE Sardinia and its bearing on Variscan basement evolution: *Journal of the*
507 *Geological Society*, v. 162, p. 689-700.

508 Huff, W.D., 2008. Ordovician K-bentonites: Issues in interpreting and correlating
509 ancient tephras. *Quaternary International* 178, 276-287.

510 Huff, W.D., Bergstrom, S.M., Kolata, D.R., 1992. Gigantic Ordovician colcanic ash-fall
511 in North America and Europe-Biological, tectonomagmatic and event-
512 stratigraphy significance. *Geology* 20, 875-878.

513 Huff, W.D., Bergstrom, S.M., Kolata, D.R., 2010. Ordovician explosive volcanism, in:
514 Finney, S.C., Berry, W.B.N. (Eds.), The Ordovician Earth System. Geological
515 Society of America, pp. 13-28.

516 Huff, W.D., Bergstrom, S.M., Kolata, D.R., Cingolani, C.A., Astini, R.A., 1998.
517 Ordovician K-bentonites in the Argentine Precordillera: relations to Gondwana
518 margin evolution. *Proto-Andean Margin of Gondwana*, 107-126.

519 Huff, W.D., Kolata, D.R., Bergstrom, S.M., Zhang, Y.S., 1996. Large-magnitude
520 Middle Ordovician volcanic ash falls in North America and Europe:
521 Dimensions, emplacement and post-emplacement characteristics. *Journal of*
522 *Volcanology and Geothermal Research* 73, 285-301.

523 Jaffey, A. H., Flynn, K. F., Glendeni.Le, Bentley, W. C., and Essling, A. M., 1971,
524 Precision measuremen of half lives and specific activities of U-235 and U-238:
525 *Physical Review C*, v. 4, no. 5, p. 1889-&.

526 Krogh, T. E., 1982, Improved accuracy of U-Pb zircon ages by the creation of more
527 concordant systems using an air brasion technique: *Geochimica Et*
528 *Cosmochimica Acta*, v. 46, no. 4, p. 637-649.

529 Kuhnt, W., Hess, S., Holbourn, A., Paulsen, H., Salomon, B., 2005. The impact of the
530 1991 Mt. Pinatubo eruption on deep-sea foraminiferal communities: A model for
531 the Cretaceous-Tertiary (K/T) boundary? *Palaeogeography Palaeoclimatology*
532 *Palaeoecology* 224, 83-107.

533 Liesa, M., Carreras, J., Castineiras, P., Casas, J. M., Navidad, M., and Vila, M., 2011,
534 U-Pb zircon age of Ordovician magmatism in the Albera Massif (Eastern
535 Pyrenees): *Geologica Acta*, v. 9, no. 1, p. 93-101.

536 Loeschke, J., Zeidler, N., 1982. Early Paleozoic sills in the Cantabrian Mountains
 537 (Spain) and their geotectonic environment., *Neues Jahrbuch für Geologie und*
 538 *Paläontologie, Monatshefte* pp. 419-439.

539 López-Guijarro, R., Quesada, C., Fernández-Suárez, J., Jeffries, T., Pin, C. (2007): Age
 540 of the rift-drift transition of the Rheic Ocean in the Ossa Morena Zone: K-
 541 bentonite in the Early Ordovician succession at “Venta del Ciervo”. En: The
 542 rootless Variscan suture of NW Iberia (Galicia, Spain). Abstracts and
 543 Programme IGCP-497 Meeting, The Rheic Ocean: Its origin, evolution and
 544 correlatives, (R. Arenas, J.R. Martínez Catalán, J. Abati y J. Sánchez Martínez,
 545 Eds.). Publicaciones del Instituto Geológico y Minero de España, Madrid. 142-
 546 143.

547 López-Sánchez, M., Iriondo, A., Marcos, A., Martínez, F.J., 2014. A U–Pb zircon age
 548 (479±5 Ma) from the uppermost layers of the Ollo de Sapo Formation near
 549 Viveiro (NW Spain): implications for the duration of rifting-related Cambro-
 550 Ordovician volcanism in Iberia. *Geological Magazine*, 152, 341-350.

551 Ludwig, K. R., 2009, Isoplot v. 3.71: a geochronological toolkit for Microsoft Excel,
 552 Volume Special Publication: California (USA), Berkeley Geochronology
 553 Center.

554 Ludwig, K.R., Turi, B., 1989. Paleozoic age of the Capo Spartivento Orthogneiss,
 555 Sardinia, Italy. *Chemical Geology*, 79, 147-153.

556 Malfait, W.J., Seifert, R., Petitgirard, S., Perrillat, J.-P., Mezouar, M., Ota, T.,
 557 Nakamura, E., Lerch, P., Sanchez-Valle, C., 2014. Supervolcano eruptions
 558 driven by melt buoyancy in large silicic magma chambers. *Nature Geoscience* 7,
 559 122-125.

560 Martínez, F.J., Iriondo, A., Dietch, C., Aleinikoff, J.N., Peucat, J.J., Cirès, J. Reche, J.,
 561 Capdevila, R., 2011. U-Pb SHRIMP-RG zircon ages and Nd signature of lower
 562 Paleozoic rifting-related magmatism in the Variscan basement of the Eastern
 563 Pyrenees. *Lithos*, 127, 10-23.

564 Martínez-Catalán, J. R., Arenas, R., Garcia, F. D., Cuadra, P. G., Gomez-Barreiro, J.,
 565 Abati, J., Castineiras, P., Fernandez-Suarez, J., Martinez, S. S., and Andonaegui,
 566 P., 2007, Space and time in the tectonic evolution of the northwestern Iberian
 567 Massif: Implications for the Variscan belt: 4-D Framework of Continental Crust,
 568 v. 200, p. 403-423. Mason, B.G., Pyle, D.M.,

569 Mason, B.G., Pyle, D.M., Oppenheimer, P., 2004. The size and frequency of the largest
 570 explosive eruptions on Earth. *Bulletin of Volcanology*, 66, 735-748. Melleton, J.,
 571 Cocherie, A., Faure, M., and Rossi, P., 2010, Precambrian protoliths and Early
 572 Paleozoic magmatism in the French Massif Central: U-Pb data and the North
 573 Gondwana connection in the west European Variscan belt: *Gondwana Research*,
 574 v. 17, no. 1, p. 13-25.

575 Mezger, J.E., Gerdes, A., in press. Early Variscan (Visean) granites in the core of
 576 central Pyrenean gneiss domes: implications from laser ablation U-Pb and Th-Pb
 577 studies. *Gondwana Research*.

578 Miller, C.F., Wark, D.A., 2008. Supervolcanoes and their explosive supereruptions.
 579 *Elements* 4, 11-15.

580 Montero, P., Bea, F., Corretge, L.G., Floor, P., Whitehouse, M.J., 2009a. U-Pb ion
 581 microprobe dating and Sr and Nd isotope geology of the Galineiro Igneous
 582 Complex A model for the peraluminous/peralkaline duality of the Cambro-
 583 Ordovician magmatism of Iberia. *Lithos* 107, 227-238.

584 Montero, P., Talavera, C., Bea, F., Lodeiro, F.G., Whitehouse, M.J., 2009b. Zircon
585 Geochronology of the Ollo de Sapo Formation and the Age of the Cambro-
586 Ordovician Rifting in Iberia. *Journal of Geology* 117, 174-191.

587 Murphy, J.B., Gutierrez-Alonso, G., Nance, R.D., Fernandez-Suarez, J., Keppie, J.D.,
588 Quesada, C., Strachan, R.A., Dostal, J., 2006. Origin of the Rheic Ocean: Rifting
589 along a Neoproterozoic suture? *Geology* 34, 325-328.

590 Murphy, J.B., Gutierrez-Alonso, G., Fernandez-Suarez, J., Braid, J.A., 2008. Probing
591 crustal and mantle lithosphere origin through Ordovician volcanic rocks along
592 the Iberian passive margin of Gondwana. *Tectonophysics*, 461, 166-180.

593 Navidad, M., Castineiras, P., Casas, J.M., Liesa, M., Suárez, J.F., Barnolas, A.,
594 Carreras, J., Gil-Peña, I., 2010. Geochemical characterization and isotopic age of
595 Caradocian magmatism in the northeastern Iberian Peninsula: insights into the
596 late Ordovician evolution of northern Gondwana margin. *Gondwana Research*
597 17, 325–337.

598 Neiva, A. M. R., Williams, I. S., Ramos, J. M. F., Gomes, M. E. P., Silva, M. M. V. G.,
599 and Antunes, I. M. H. R., 2009, Geochemical and isotopic constraints on the
600 petrogenesis of Early Ordovician granodiorite and Variscan two-mica granites
601 from the Gouveia area, central Portugal: *Lithos*, v. 111, no. 3-4, p. 186-202.

602 Newhall, C.G., Self, S., 1982. The volcanic explosivity index (VEI) - an estimate of
603 explosive magnitude for historical volcanism. *Journal of Geophysical Research-*
604 *Oceans and Atmospheres* 87, 1231-1238.

605 Oggiano, G., Gaggero, L., Funedda, A., Buzzi, L., and Tiepolo, M., 2010, Multiple
606 early Paleozoic volcanic events at the northern Gondwana margin: U-Pb age

607 evidence from the Southern Variscan branch (Sardinia, Italy): Gondwana
608 Research, v. 17, no. 1, p. 44-58.

609 Oppenheimer, C., 2004. The size and frequency of the largest explosive eruptions on
610 Earth. *Bulletin of Volcanology* 66, 735-748.

611 Padovano, M., Dörr, W., Elter, F.M., Gerdes, A., 2014, The East Variscan Shear Zone:
612 Geochronological constraints from the Capo Ferro area (NE Sardinia, Italy).
613 *Lithos*, 196-197, 27-41.

614 Palacios, T. 2015. Acritarch assemblages from the Oville and Barrios formations,
615 northern Spain: A pilot proposal of a middle Cambrian (Series 3) acritarch
616 biozonation in northwestern Gondwana. *Review of Palaeobotany and*
617 *Palaeoecology*, 219, 71-105.

618 Pavanetto., P., Funedda, A., Northrup, C.J., Schmitz, M., Crowley, J., Loi, A., 2012,
619 Structure and U–Pb zircon geochronology in the Variscan foreland of SW
620 Sardinia, Italy. *Geological Journal*, 47, 426-445.

621 Pitra, P., Poujol, M., Van Den Driessche, J., Poilvet, J.-C., Paquette, J.-L., 2012 Early
622 Permian extensional shearing of an Ordovician granite: The Saint-Eutrope
623 “C/S-like” orthogneiss (Montagne Noire, French Massif Central). *Comptes*
624 *Rendus Geoscience*, 334, 377-384.

625 Rampino, M.R., Self, S., 1992. Volcanic winter and accelerated glaciation following the
626 Toba supereruption. *Nature* 359, 50-52.

627 Roger, F., Respaut, J.-P., Brunel, M., Matte, Ph., Paquette, J.-L. Première datation U–Pb
628 des orthogneiss ocellés de la zone axiale de la Montagne noire (Sud du Massif
629 central) : nouveaux témoins du magmatisme ordovicien dans la chaîne Varisque.
630 *Comptes Rendus Geoscience*. 336, 18-28.

631 Rossi, P., Oggiano, G., Cocherie, A., 2009, A restored section of the "southern Variscan
632 realm" across the Corsica-Sardinia microcontinent: *Comptes Rendus*
633 *Geoscience*, v. 341, no. 2-3, p. 224-238.

634 Rubio-Ordóñez, A., Valverde-Vaquero, P., Corretge, L. G., Cuesta-Fernández, A.,
635 Gallastegui, G., Fernández-González, M., Gerdes, A., 2012, An Early
636 Ordovician tonalitic-granodioritic belt along the Schistose-Greywacke Domain
637 of the Central Iberian Zone (Iberian Massif, Variscan Belt): *Geological*
638 *Magazine*, v. 149, no. 5, p. 927-939.

639 Sá, A.A., Gutiérrez-Marco, J.C., Meireles, C.A.P., García-Bellido, C., Rábano, I., 2013.
640 A revised correlation of Lower Ordovician sedimentary rocks in the Central
641 Iberian Zone (Portugal and Spain), in: R.B. Rocha, J.P., C. Kulberg, S. Finney
642 (Ed.), *Strati 2013, at the cutting edge of Stratigraphy*. Springer Geology Series,
643 Lisbon, pp. 441-446.

644 Scharer, U., 1984. The effect of initial Th-230 disequilibrium on young U-Pb ages - the
645 Makalu case, Himalaya. *Earth and Planetary Science Letters* 67, 191-204.

646 Self, S., 2006. The effects and consequences of of very large explosive volcanic
647 eruptions. *Philosophical Transactions of the Royal Society A*364.

648 Sell, B., Ainsaar, L., Leslie, S., 2013. Precise timing of the Late Ordovician (Sandbian)
649 super-eruptions and associated environmental, biological, and climatological
650 events. *Journal of the Geological Society* 170, 711-714.

651 Sell, B.K., Samson, S.D., Mitchell, C.E., McLaughlin, P.I., Goenig, A.E., Leslie, S.A.,
652 2015. Stratigraphic correlations using trace elements in apatite from Late
653 Ordovician (Sandbian-Katian) K-bentonites of eastern North America.
654 *Geological Society of America Bulletin*, 127. doi:10.1130/B31194.1

655 Shaw, J., Gutierrez-Alonso, G., Johnston, S.T., Pastor-Galán, D.P., 2014. Provenance
656 variability along the Early Ordovician north Gondwana margin:
657 Paleogeographic and tectonic implications of U-Pb detrital zircon ages from the
658 Armorican Quartzite of the Iberian Variscan belt. Geological Society of America
659 Bulletin 126, 702-719.

660 Solá, A.R., Pereira, M.F., Williams, I.S., Ribeiro, M.L., Neiva, A.M.R., Montero, P.,
661 Bea, F., Zinger, T., 2008. New insights from U-Pb zircon dating of Early
662 Ordovician magmatism on the northern Gondwana margin: The Urro Formation
663 (SW Iberian Massif, Portugal). Tectonophysics, 461, 114-129.

664 Sparks, R.S.J., Self, S., Grattan, J.P., Oppenheimer, C., Pyle, D.M., Rymer, H., 2005.
665 Supereruptions: global effects and future threats., Report of a Geological Society
666 of London Working group. The Geological Society, London, p. 24.

667 Stacey, J.S., Kramers, J.D., 1975. Approximation of terrestrial lead isotope evolution by
668 a 2-stage model. Earth and Planetary Science Letters 26, 207-221.

669 Suárez, O., Gallastegui, G., Cuesta, A., Corretgé, L.G., Tarrío, L., 1993. Geoquímica de
670 las rocas volcánicas del Cabo Peñas (Zona Cantábrica), V Congreso de
671 Geoquímica de España, Soria (Spain).

672 Talavera, C., Bea, F., Montero, P., and Whitehouse, M., 2008, A revised Ordovician age
673 for the Sisargas orthogneiss, Galicia (Spain). Zircon U-Pb ion-microprobe and
674 LA-ICPMS dating: Geologica Acta, v. 6, no. 4, p. 313-317.

675 Talavera, C., Montero, P., Bea, F., Gonzalez Lodeiro, F., and Whitehouse, M., 2013, U-
676 Pb Zircon geochronology of the Cambro-Ordovician metagranites and
677 metavolcanic rocks of central and NW Iberia: International Journal of Earth
678 Sciences, v. 102, no. 1, p. 1-23.

679 Teixeira, R., Coke, C., Gomes, M. H., Corfu, F., and Dias, R., ID-TIMS U-Pb ages of
680 Tremadocian-Floian ash-fall tuff beds from Marão and Eucísia areas, Northern
681 Portugal, in Proceedings William Smith Meeting 2013: The First Century of
682 Isotope Geochronology, London, 2013.

683 Toyos, J.M., Aramburu, C., 2014. El Ordovícico en el área de Los Barrios de Luna,
684 Cordillera Cantábrica (NW de España). Trabajos de Geología, Universidad de
685 Oviedo 34, 61-96.

686 Trombetta, A., Cirrincione, R., Corfu, F., Mazzoleni, P., Pezzino, A., 2004. Mid-
687 Ordovician U-Pb ages of porphyroids in the Peloritan Mountains (NE Sicily):
688 palaeogeographical implications for the evolution of the Alboran microplate.
689 Journal of the Geological Society, 161, 265-276.

690 Valverde-Vaquero, P., Dunning, G. R., 2000, New U-Pb ages for Early Ordovician
691 magmatism in Central Spain: Journal of the Geological Society, v. 157, p. 15-26.

692 Valverde-Vaquero, P., Marcos, A., Farias, P., and Gallastegui, G., 2005, U-Pb dating of
693 Ordovician felsic volcanism in the schistose domain of the Galicia- Trás-os-
694 Montes zone near Cabo Ortegal (NW Spain): Geológica Acta, v. 3, p. 27-37.

695 van den Bosch, W.J., 1969. Geology of the Luna-Sil region, Cantabrian Mountains
696 (NW Spain). Leidse Geologische Mededelingen, 44, 137-225.

697 Villaseca, C., Castiñeiras, P., Orejana, D., 2015, Early Ordovician metabasites from the
698 Spanish Central System: A remnant of intraplate HP rocks in the Central Iberian
699 Zone. Gondwana Research, 27, 392-409.

700 Weil, A. B., Gutierrez-Alonso, G., Johnston, S. T., and Pastor-Galan, D., 2013a,
701 Kinematic constraints on buckling a lithospheric-scale orocline along the

702 northern margin of Gondwana: A geologic synthesis: Tectonophysics, v. 582, p.
703 25-49.

704 Zeck, H.P., Whitehouse, M.J., Ugidos, J.M., 2007, 496±3Ma zircon ion microprobe age
705 for pre-Hercynian granite, Central Iberian Zone, NE Portugal (earlier claimed
706 618±9Ma). Geological Magazine, 144, 21-31.

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709 **Figure Captions:**

710 Figure 1.- Paleogeographic reconstruction of Western Europe in early Mesozoic times
711 with the sample locations, the known outcrops of ca. 477 Ma intrusive and extrusive
712 rocks and the extension of the recognized ash-fall layer studied as well as the
713 conservatively considered extension of correlative volcanic rocks for a more
714 interpretative volume calculation.

715

716 Figure 2.- Early Paleozoic reconstruction of the Rheic Ocean opening and the origin and
717 putative extension of the super eruptions identified in Ordovician times (Based in
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725 Ma), which reveal a significant maxima at 477 Ma, equivalent in age to the identified
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2006; Casas et al., 2010; Castiñeiras et al., 2008; Cocherie et al., 2007; Cruciani et al., 2013; Dallmeyer and Tucker, 1993; Deloule et al., 2002; Denéle et al., 2009; Días da Silva et al., in press; Díez Montes et al., 2010; Díez-Fernández et al., 2012; El Khor et al., 2012; Farias et al., 2014; Garbarino et al., 2005; Giacomini et al., 2006; Gutiérrez-Alonso et al., 2007; Helbing and Tiepolo, 2005; Liesa et al., 2011; López-Sánchez et al., 2014; López-Guijarro et al., 2007; Ludwig and Turi, 1989; Martínez et al., 2011; Melleton et al., 2010; Mezger and Gerdes. in press; Montero et al., 2007; 2009; Navidad et al., 2010; Navidad and Castiñeiras, 2011; Neiva et al., 2009; Oggiano et al., 2010; Padovano et al., 2014; Pavanetto et al., 2012; Pitra et al., 2012; Roger et al., 2004; Rossi et al., 2009; Rubio-Ordoñez et al., 2012; Solá et al., 2008; Talavera et al., 2008, 2013; Teixeira et al., 2013; Trombetta et al., 2004; Valverde-Vaquero and Dunning 2000; Valverde-Vaquero et al., 2005; Villaseca et al., 2015; Zeck et al., 2007). Upper Ordovician ages have not been included as they can be likely assigned to another magmatic cycle.

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762 dates that are statistically coherent, and it is interpreted as the best statistical estimate of
763 the eruption age.

764

Table 1

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Table 1. U-Pb data																		
Properties	Weight	U	Th/U	Pbc	206/204	207/235	2 sigma	206/238	2 sigma	rho	207/206	2 sigma	206/238	2 sigma	207/235	2 sigma	207/206	2 sigma
(1)	[vg] (2)	[ppm] (2)	(3)	[pg] (4)	(5)	(6)	[abs] (6)	(6)	[abs] (6)		(6)	[abs] (6)	(6)	[abs] (6)	(6)	[abs] (6)	(6)	[abs] (6)
LBL (N42°50'57.22" W005°51'57.74")																		
Z sp [1]	1	2127	0.19	1.3	10612	0.9018	0.0052	0.10247	0.00058	0.98	0.06383	0.00008	628.9	3.4	652.7	2.8	735.9	2.5
Z tip [1]	1	823	0.21	1.2	3653	0.7057	0.0095	0.08648	0.00115	0.95	0.05918	0.00026	534.7	6.8	542.2	5.7	573.7	9.5
Z tip el p [1]	1	652	0.28	1.0	3565	0.6637	0.0034	0.08331	0.00037	0.89	0.05778	0.00013	515.9	2.2	516.9	2.1	521.4	5.1
Z lp tips [8]	2	518	0.15	1.1	4626	0.6049	0.0058	0.07719	0.00074	0.97	0.05684	0.00013	479.3	4.4	480.3	3.7	485.1	5.2
Z lp [4]	11	319	0.17	2.1	7924	0.6015	0.0040	0.07693	0.00057	0.83	0.05671	0.00024	477.8	3.4	478.2	2.5	480.2	9.2
Z lp [9]	13	277	0.18	2.0	8633	0.5991	0.0016	0.07672	0.00019	0.85	0.05664	0.00008	476.5	1.1	476.7	1.0	477.5	3.1
Z lp fr [1]	1	1255	0.11	3.6	1689	0.6011	0.0033	0.07671	0.00035	0.83	0.05684	0.00018	476.4	2.1	478.0	2.1	485.3	6.8
Z lp fr [1]	2	451	0.41	0.9	4592	0.5990	0.0030	0.07669	0.00035	0.86	0.05664	0.00014	476.3	2.1	476.6	1.9	477.7	5.6
Z lp tip[1]	1	1218	0.15	1.2	4890	0.5965	0.0034	0.07652	0.00041	0.93	0.05654	0.00012	475.3	2.4	475.0	2.2	473.5	4.7
Z lp [1]	6	149	0.25	2.6	1672	0.5915	0.0024	0.07556	0.00020	0.59	0.05677	0.00019	469.6	1.2	471.8	1.5	482.8	7.2
Z lp [1]	11	100	0.19	1.7	2988	0.5869	0.0020	0.07488	0.00019	0.69	0.05685	0.00014	465.5	1.1	468.9	1.3	485.7	5.5
MON NA [8]	18	900	33.08	10.6	7433	0.6045	0.0015	0.07760	0.00016	0.94	0.05650	0.00005	481.8	1.0	480.1	0.9	471.9	1.9
MON [1]	3	559	34.31	4.5	1815	0.5981	0.0022	0.07732	0.00022	0.75	0.05611	0.00013	480.1	1.3	476.0	1.4	456.6	5.3
MON [4]	4	261	30.26	3.4	1492	0.6019	0.0025	0.07739	0.00020	0.60	0.05641	0.00018	480.5	1.2	478.4	1.6	468.6	7.2
TUN 194 (N043°27'49.70" W005°08'41.11")																		
Z sp [1]	<1	>410	0.19	0.8	9917	8.9681	0.0358	0.30603	0.00116	0.98	0.21253	0.00019	1721.2	5.7	2334.8	3.6	2925.0	1.4
Z sp [1]	1	827	0.21	1.0	6447	1.5837	0.0051	0.12006	0.00037	0.89	0.09567	0.00014	730.9	2.1	963.8	2.0	1541.3	2.8
Z lp [1]	<1	>670	0.13	1.5	2240	0.6029	0.0033	0.07717	0.00033	0.79	0.05666	0.00019	479.2	2.0	479.1	2.1	478.4	7.4
Z lp [1]	<1	>620	0.09	3.3	923	0.6019	0.0036	0.07711	0.00028	0.60	0.05661	0.00027	478.8	1.7	478.4	2.3	476.4	10.4
Z lp [1]	1	463	0.17	1.1	2068	0.6015	0.0032	0.07694	0.00029	0.72	0.05670	0.00021	477.8	1.8	478.2	2.0	479.9	8.1
Z lp [1]	<1	>680	0.14	1.1	2966	0.5997	0.0031	0.07679	0.00033	0.84	0.05664	0.00016	476.9	2.0	477.0	2.0	477.4	6.2
Z lp [1]	<1	>420	0.08	5.3	408	0.5935	0.0059	0.07666	0.00033	0.51	0.05615	0.00048	476.2	2.0	473.1	3.7	458.2	18.7
Z lp [1]	1	95	0.10	0.7	712	0.5980	0.0070	0.07653	0.00053	0.58	0.05667	0.00054	475.4	3.2	476.0	4.4	478.9	20.9
Z lp [1]	<1	>100	0.13	1.3	379	0.5980	0.0111	0.07646	0.00046	0.37	0.05672	0.00098	474.9	2.8	475.9	7.0	480.9	37.6
Z lp [1]	<1	>530	0.12	1.1	2309	0.5968	0.0034	0.07634	0.00035	0.79	0.05669	0.00020	474.3	2.1	475.2	2.1	479.6	7.6
MON NA [8]	12	1168	27.93	5.8	11692	0.6028	0.0014	0.07736	0.00016	0.95	0.05652	0.00004	480.3	1.0	479.0	0.9	472.8	1.7
GRADO (N43°24'10.54" W006°02'27.05")																		
Z lp [1]	1	521	0.51	1.7	2740	1.9436	0.0070	0.14398	0.00047	0.85	0.09791	0.00018	867.1	2.6	1096.2	2.4	1584.7	3.5
Z lp-flat fr [1]	6	432	0.13	17.0	774	0.6355	0.0028	0.07896	0.00020	0.54	0.05837	0.00022	489.9	1.2	499.5	1.8	543.8	8.2
Z lp-flat fr [9]	1	1005	0.33	1.0	4848	0.5803	0.0052	0.07397	0.00065	0.97	0.05690	0.00013	460.0	3.9	464.7	3.3	487.7	5.0
Z lp [1]	<1	>380	0.48	1.4	1311	0.5977	0.0038	0.07685	0.00026	0.63	0.05641	0.00028	477.3	1.5	475.8	2.4	468.4	11.1
Z lp [1]	8	149	0.32	2.3	2528	0.6003	0.0026	0.07679	0.00024	0.77	0.05670	0.00016	476.9	1.4	477.4	1.6	479.7	6.1
Z lp[1]	<1	>440	0.21	1.9	1111	0.5946	0.0045	0.07630	0.00033	0.62	0.05652	0.00034	474.0	2.0	473.8	2.9	472.8	13.1
Z lp-flat fr [1]	<1	>320	0.12	0.6	2799	0.5913	0.0030	0.07578	0.00032	0.80	0.05660	0.00017	470.9	1.9	471.7	1.9	475.9	6.7
Z lp [18]	6	289	0.17	3.7	2225	0.5798	0.0018	0.07420	0.00018	0.75	0.05667	0.00012	461.4	1.1	464.3	1.2	478.8	4.6
Z lp [1]	3	505	0.15	1.0	6835	0.5833	0.0021	0.07475	0.00025	0.89	0.05660	0.00009	464.7	1.5	466.6	1.3	476.0	3.6
MON NA [8]	14	364	34.35	4.2	5875	0.6015	0.0017	0.07727	0.00020	0.90	0.05646	0.00007	479.8	1.2	478.2	1.1	470.7	2.7
AST-1, Mina Conchita (Gutiérrez Alonso et al., 2007) (N43°19'25.7" W006°18'0.07")																		
Z lp [1]	5	127	0.14	1.9	1623	0.6030	0.0035	0.07703	0.00030	0.69	0.05677	0.00024	478.4	1.8	479.1	2.8	482.6	9.4
Z lp [1]	4	152	0.22	2.9	1004	0.5968	0.0040	0.07650	0.00031	0.63	0.05658	0.00029	475.2	1.9	475.2	3.2	475.4	11.4

Figure1

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Figure 1.- Paleogeographic reconstruction of Western Europe in early Mesozoic times with the sample locations, the known outcrops of ca. 477 Ma intrusive and extrusive rocks and the extension of the recognized ash-fall layer studied as well as the conservatively considered extension of correlative volcanic rocks for a more interpretative volume calculation.

Figure 2.- Early Paleozoic reconstruction of the Rheic Ocean opening and the origin and putative extension of the super eruptions identified in Ordovician times (Based in Murphy et al., 2008) Arrows point to the known areas recording supereruptions in Ordovician times.

Figure3
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Figure4
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Figure6

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Figure7

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Figure 7. A)- Wetherill concordia plot of the pooled concordia age using all the analyzed zircons from the 4 samples used in this study. B)- Age obtained using the TuffZirc algorithm on a group of 21 analyses of the studied rocks. This age is the median obtained by pooling together twenty analyses, considering the largest set of internally concordant dates that are statistically coherent, and it is interpreted as the best statistical estimate of the eruption age.