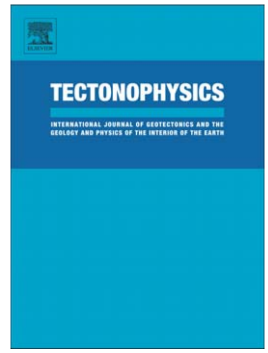
Accepted Manuscript



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PII: S0040-1951(15)00675-7
DOI: doi: 10.1016/j.tecto.2015.12.012
Reference: TECTO 126877

To appear in: *Tectonophysics*

Received date: 2 September 2015
Revised date: 25 November 2015
Accepted date: 17 December 2015

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 (Gutierrez-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 km^3 (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 10^{15} kg, equivalent to a volume of more than 450 km^3 (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 volcaniclastic 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 sedimetologically 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 geocronological 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 km^2 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 (N43º24'10.54" W006º02'27.05"). 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, N43º19’25.7” W006º18’0.07”)

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 ~ 185ºC 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 Renium 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 $^{207}Pb/^{235}U$ 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 $^{207}Pb/^{235}U$ 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 $^{207}Pb/^{235}U$ 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 $^{206}Pb/^{238}U$ ages of the same set of 21 concordant analyses (Fig. 7).

All the monazite analyses show reverse discordance and their average $^{207}Pb/^{235}U$ 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 km^2, and 100000 km^2 when considering the stratigraphycally 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 km^3 (Volcanic Explosivity Index - VEI = 6, Colossal) which would correspond to a mass of $8.3 \cdot 10^{13}$ kg using a measured average density value of the studied samples of 2200 kg/m^3.

When considering other occurrences in northern Iberia which are likely correlated with the dated K-bentonites, these values increase to ca. 400 km^3 (VEI = 7, Mega-colossal) which would correspond to a mass of $9 \cdot 10^{14}$ 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).

Acknowledgements

This work has been supported by the Spanish Ministry of Economy and Competitiveness projects CGL2012-34618/BTE (to JFS), CGL-2012-39471/BTE (to JCGM) and CGL2013-46061-P/BTE (to GGA), all from the Spanish Ministry of Economy and Competitivity. Financial support to E. Bernardez was provided by DIUDA-22258 research fund from the Universidad de Atacama, Chile. Insightful comments by J.M Casas and an anonymous reviewer are warmly thanked. Adolfo Carlos Íñigo and Jacinta García Talegón are thanked for providing the density measurements of the samples used in this work. This paper is devoted to the memory of M. Hacar, geologist, Ordovician fan and friend who was a great field companion and discusser when working (and not working) with him.

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Figure Captions:

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., 2006) Arrows point to the known areas recording supereruptions in Ordovician times.

Figure 3.- Histogram, Probability Density Diagrams (dashed line stands for all data from western Europe (n=98), double line is selected data from NW Iberia and Armorica (n=73)), and Kernel analysis (continuous line) plot of the available U-Pb zircon intrusive and extrusive age data of Furgonian to Darriwilian rocks (between 458 and 497 Ma), which reveal a significant maxima at 477 Ma, equivalent in age to the identified ash-fall layer. Data used from this work and other present in the literature (Alexandre, 2007; Andonaegui et al., 2012; Antunes et al., 2009; Ballevre et al., 2012; Bea et al.,

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.

Figure 4.- Stratigraphic location of the studied k-bentonite ash-fall bed within the Barrios Formation, with reference to representative columns lying north (left) and south (right) of the Cantabrian Zone. The section TUN corresponds to subsurface data obtained during construction of the “Túnel Ordovícico del Fabar” in Ribadesella (Asturias); section LBL is located west of Los Barrios de Luna village (León Province). For a general geological situation of both sections, see Fig. 5.

Figure 5.- Simplified structure/tectonic map of the Cantabrian Zone, highlighting the geometry of major thrusts and the orientation of arc-parallel and arc-perpendicular folds.Tectonic unit divisions are from Alonso et al. (2009). Location of the studied

samples, locations of known occurrences of the K-bentonite layer (García-Ramos et al., 1984; Aramburu, 1989) and the new sections where the ash-fall layer has been identified.

Figure 6.- Wetherill concordia plots of the studied samples and ages obtained.

Figure 7.- A)- Wetherill concordia plot of the pooled concordia age using al the analized 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.

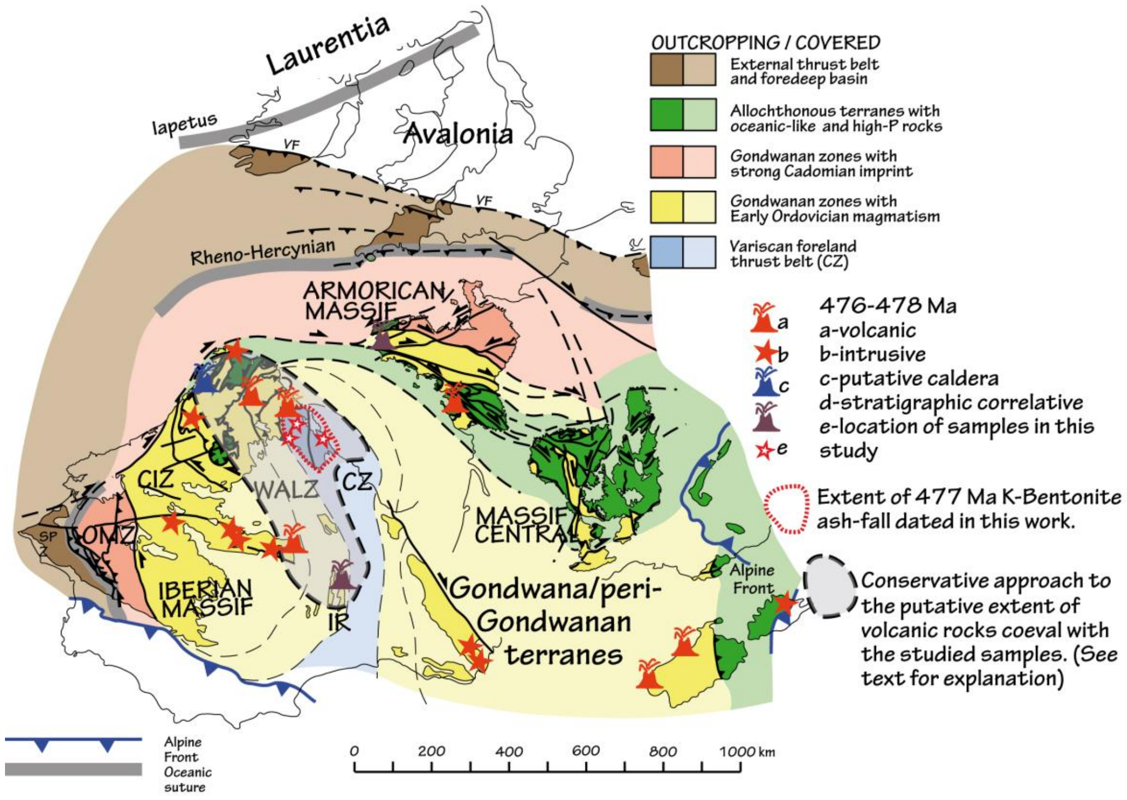


Figure 1.- Paleogeographic reconstruction of Western Europe in early Mesozoic times with the sample locations, the known outcrops of ca. 477 Ma intrusive and extrusive rocks and the extension of the recognized ash-fall layer studied as well as the conservatively considered extension of correlative volcanic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

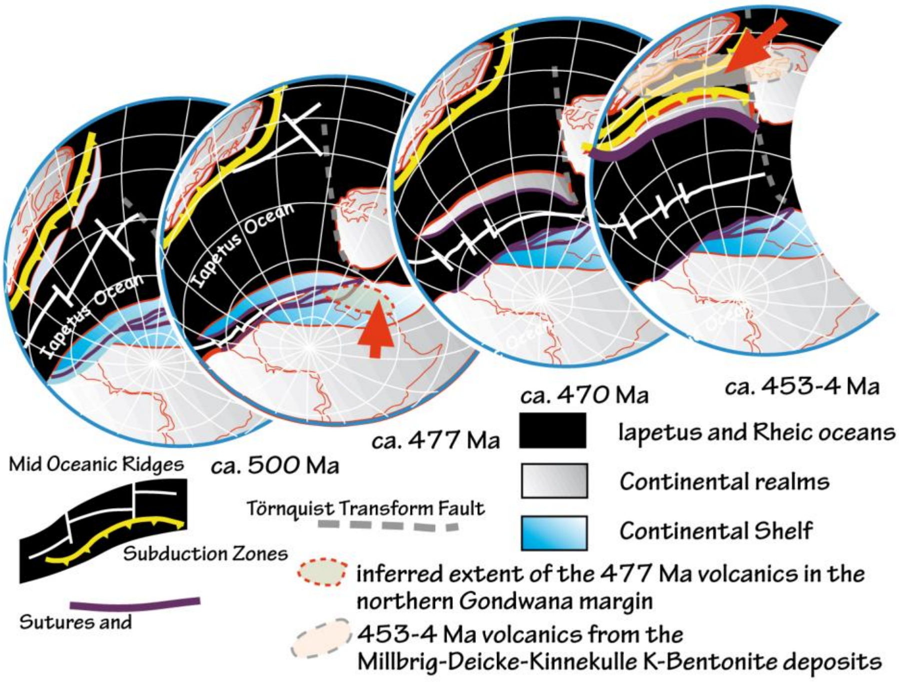
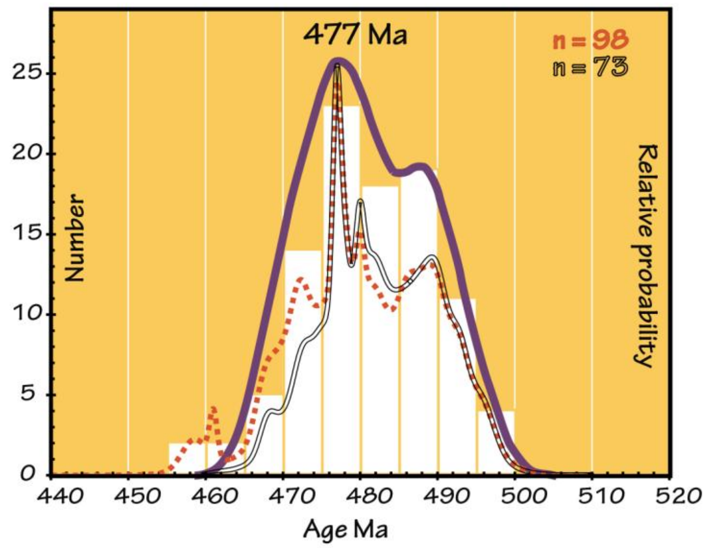


Figure 2.- Early Paleozoic reconstruction of the Rheic Ocean opening and the origin and putative extension of the super eruptions identified in Ordovician times (Based in Murphy et al., 2008) Arrows point to the known areas recording supereruptions in Ordovician times.



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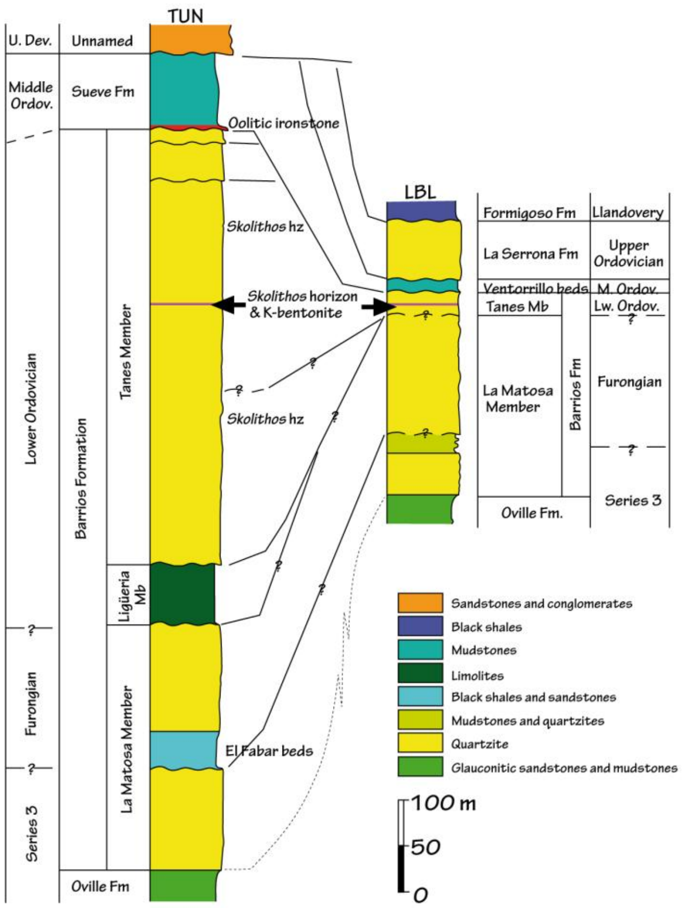

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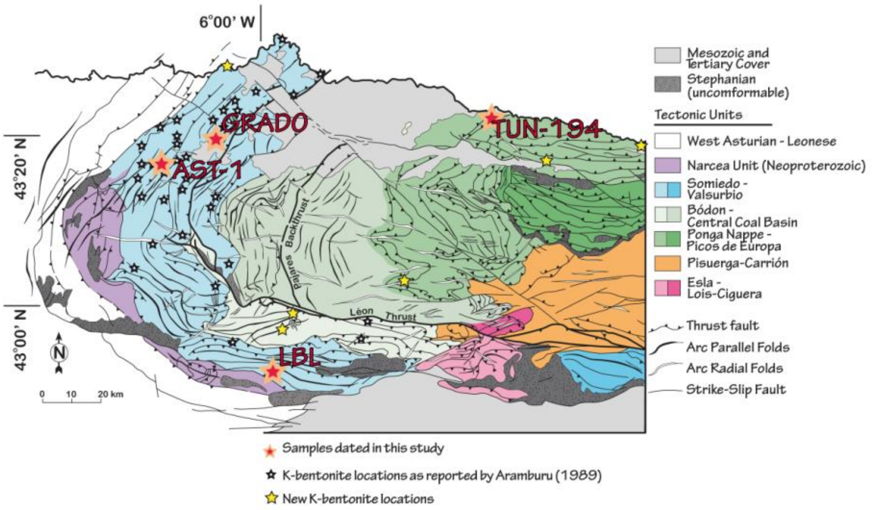

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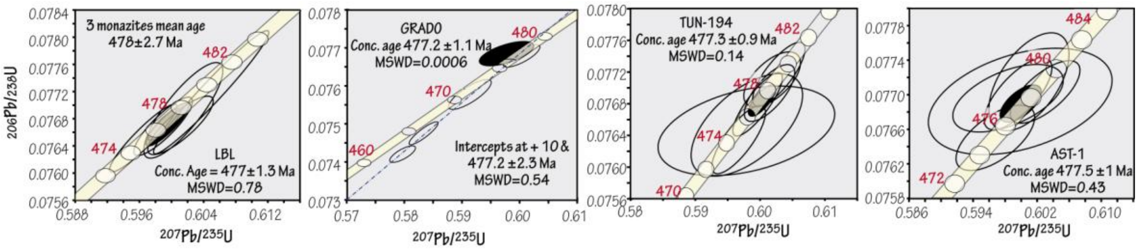

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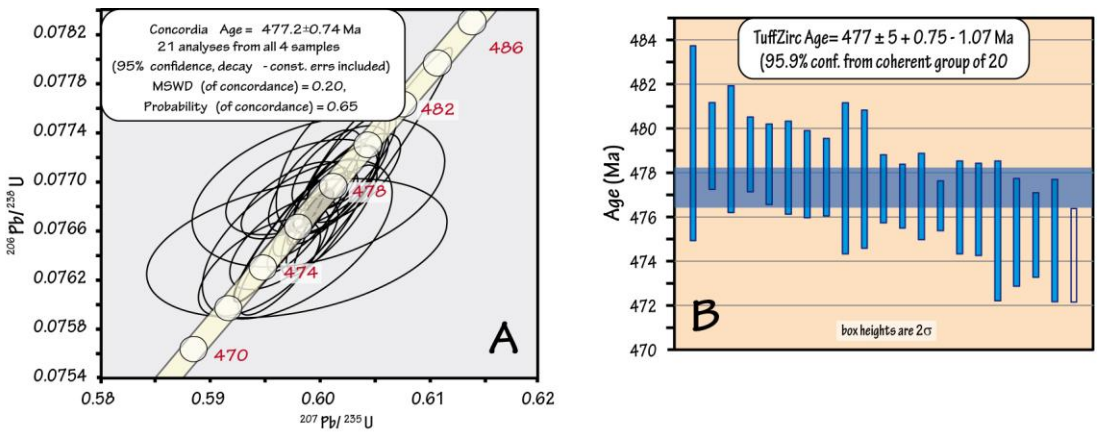

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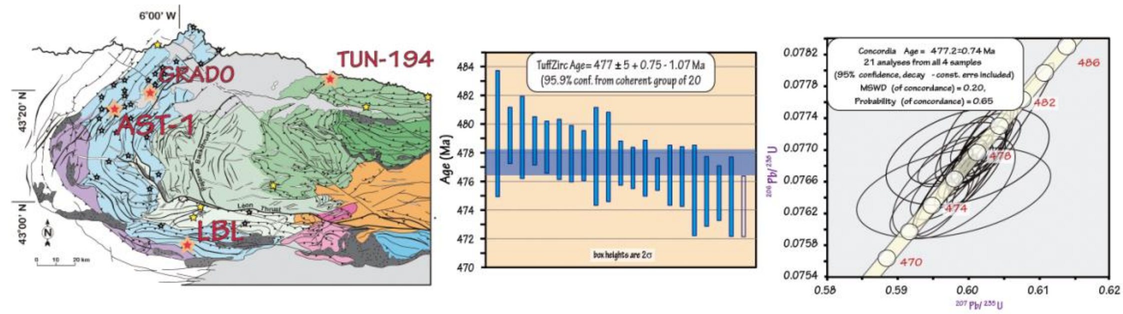

Graphical Abstract

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
	[υg]	[ppm]		[pg]			[abs]		[abs]			[abs]		[abs]		[abs]		[abs]
(1)	(2)	(2)	(3)	(4)	(5)	(6)	(6)	(6)	(6)		(6)	(6)	(6)	(6)	(6)	(6)	(6)	(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.	4.5	1815	0.598	0.00	0.077	0.000	0.7	0.056	0.000	480.1	1.3	476.0	1.4	456.6	5.3

			31			1	22	32	22	5	11	13					
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 (N43º24'10.54'' W006º02'27.05'')																	
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	0.3	1.0	4848	0.580	0.00	0.073	0.000	0.9	0.056	0.000	460.0	3.9	464.7	3.3	487.7	5.0

			3			3	52	97	65	7	90	13						
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) (N43º19'25.7'' W006º18'0.07'')																		
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**
Z lp [1]	**4**	**143**	**0.22**	**7.3**	**397**	**0.5984**	**0.0056**	**0.07696**	**0.00032**	**0.53**	**0.05640**	**0.00045**	**477.9**	**2**	**476.2**	**4.5**	**468.0**	**17.6**
Z lp [1]	**6**	**165**	**0.19**	**2.9**	**1675**	**0.6010**	**0.0040**	**0.07715**	**0.00046**	**0.56**	**0.05650**	**0.00034**	**479.1**	**2.9**	**477.9**	**3.2**	**472.0**	**13.3**
Z lp [1]	**4**	**78**	**0.29**	**5.4**	**298**	**0.5999**	**0.0093**	**0.07692**	**0.00050**	**0.39**	**0.05656**	**0.00081**	**477.7**	**3.1**	**477.2**	**7.4**	**474.6**	**31.3**
Z lp [1]	**5**	**84**	**0.30**	**1.0**	**1951**	**0.5996**	**0.0034**	**0.07701**	**0.00034**	**0.72**	**0.05647**	**0.00022**	**478.2**	**2.1**	**477.0**	**2.7**	**471.0**	**8.7**

1) Z = zircon; MON = monazite; all euhedral clear grains; sp= short prismatic; lp = long prismatic; el = elongated; fr = fragment, broken prism; p = pink; NA = not air abraded, all other grains abraded; [1] number of grains in fractions; **Bold** indicates analyses considered in the age calculation
(2) concentration better than 10%, except for grains of 1-2 ug where uncertainty is up to 50%
(3) Th/U model ratio inferred from 208/206 ratio and age of sample
(4) Pbc= total amount of common Pb (initial + blank)

(5) raw data corrected for fractionation
(6) corrected for fractionation, spike, blank and initial common Pb; error calculated by propagating the main sources of uncertainty; initial common Pb corrected using Stacey & Kramers (1975) model compositions

Highlights (3 to 5 bullet points (maximum 85 characters, including spaces, per bullet point)

Dated ash-fall beds (k-bentonites) from NW Iberia yield a consistent age of 477 Ma.

Coeval k-bentonites are interpreted to be linked to a single volcanic event.

Volume estimations of ejecta range from tens to hundredths of km^3

Volcanic Explosivity Index ranges from Colossal (6) to Mega-colossal (7)

Further work may reveal that the super-eruption was larger than herein estimated.