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An extensive K-bentonite as an indicator of a super-eruption in northern Iberia 477 My ago

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Abstract. Zircon and monazite ID-TIMS U-Pb dating of four Lower Ordovician altered ash-fall tuff beds (K-Bentonites) in NW Iberia provided coetaneous ages of 477.5±1, 477±1.3 Ma, 477.2±1.1 Ma and 477.3±1 Ma, with a pooled concordia age of 477.2±0.74 Ma. A conservative estimation of the volume and mass of the studied K-bentonite beds (using data from the Cantabrian Zone) returns a minimum volume for the preserved deposits of *ca.* 37.5 km^3 (Volcanic Explosivity Index - VEI = 6, Colossal). When considering other putative equivalent beds in other parts of Iberia and neighbouring realms the volume of ejecta associated to this event would make it reach the Supervolcanic-Apocalyptic status (VEI=8, >1000 km^3). Contrary to most cases of this kind of gargantuan eruption events, the studied magmatic event took place in relation to continental margin extension and thinning and not to plate convergence. We speculate that a geochronologically coincident large caldera event observed in the geological record of NW Iberia could be ground zero of this super-eruption.

1. Introduction

Volcanic supereruptions [1] are contemplated to be those that discharge magma in excess of 10^{15} kg, commensurate to a volume of more than 450 km^3 [2,3] in a relatively brief period of time [4,5] with a Volcanic Explosivity Index (VEI) [6] commonly over 8. These singular volcanic episodes appear to happen prompted by melt buoyancy [7] with a worldwide prevalence ranging from 1.4 to 22 events/My [4], which should make them ample in the geological record.

Still, few such eruptions are noticed in the geological record on account of: i) the odds of preservation are scant as the deposits they generate are easily eroded and ii) even if the deposits are perpetuated, they are challenging to recognize and reconstruct once they have been altered, deformed, metamorphosed and dismembered by ensuing geological events. For instance, the last 45 My of Earth history preserve deposits caused by at least 45 supereruptions [4] while in the Ordovician period, covering the same time span (*ca.* 42 My), only two supereruptions, preserved as altered volcanic ash-fall deposits (K-bentonites), have been diagnosed so far [8, 9, 10, 11, 12].

In this paper we target on the Lower Ordovician ash-fall deposits found in northern Iberia and contribute geological and geochronological data, as well as arguments, that support the idea that the deposits were the result of one super-eruption that occured in the rifted and extended northern margin of west Gonwana during Floian times. This event took place at a passive margin while it was being thinned and extended during the initial phases of the Rheic Ocean opening (see [13]).

2. Geological setting

The Lower Paleozoic succession in northwest Iberia is characterized by the profusion of long-lived magmatism, which is expressed mainly by the so called “Ollo de Sapo” plutonic and volcanic episode extending in age between *ca.* 490 and 465 My, with a maximum at *ca.* 477 My, *Figure. 1C* [14, 15].

Within the Cantabrian Zone (CZ), this event is represented by alkaline basalts and volcaniclastic rocks interbedded within Upper Cambrian and Lower Ordovician strata [16, 17, 18] together with an extensive K-bentonite (Pedroso-Valverdín bed) within the Lower Ordovician succession (*Figure. 1A*), [19] which is the main object of this study. Ash-tuff beds correlatable with the Pedroso-Valverdín bed also crop out in other parts of Iberia as the Iberian Ranges (IR) (Tranquera bed, *Figure. 1A* [20] and in the Westasturian-Leonese Zone (WALZ) [21].

The Lower Ordovician shallow-water siliciclastic succession hosting the studied ash beds is widely exposed in Western Europe (e.g. [20, 22, 23]) and its provenance established through detrital zircons [24]. The Pedroso-Valverdín K-bentonite bed (*Figure. 1A*) extends over the whole CZ (*Figure. 1A*) more than 1800 km^2 with a thickness between 45 and 80 cm [22, 23]. It is interpreted as an altered ash-fall tuff ("kaolinite tonstein" [22, 23]). The upper and lower contacts are very sharp and 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 [9, 25].

The origin of the Lower Ordovician magmatism in the studied sector of the Gondwanan margin (*Figure. 1B*) is interpreted to be related to extension, linked to the undocking of Avalonia [13].

The three new studied samples plus a sample from Mina Conchita (*Figure. 1A*) [26], were collected in the Cantabrian Zone. The K-bentonite samples contained mainly zircon, monazite and pyrite as heavy minerals, which is 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 bentonites in which the proportion of *remanié* zircons is usually high.

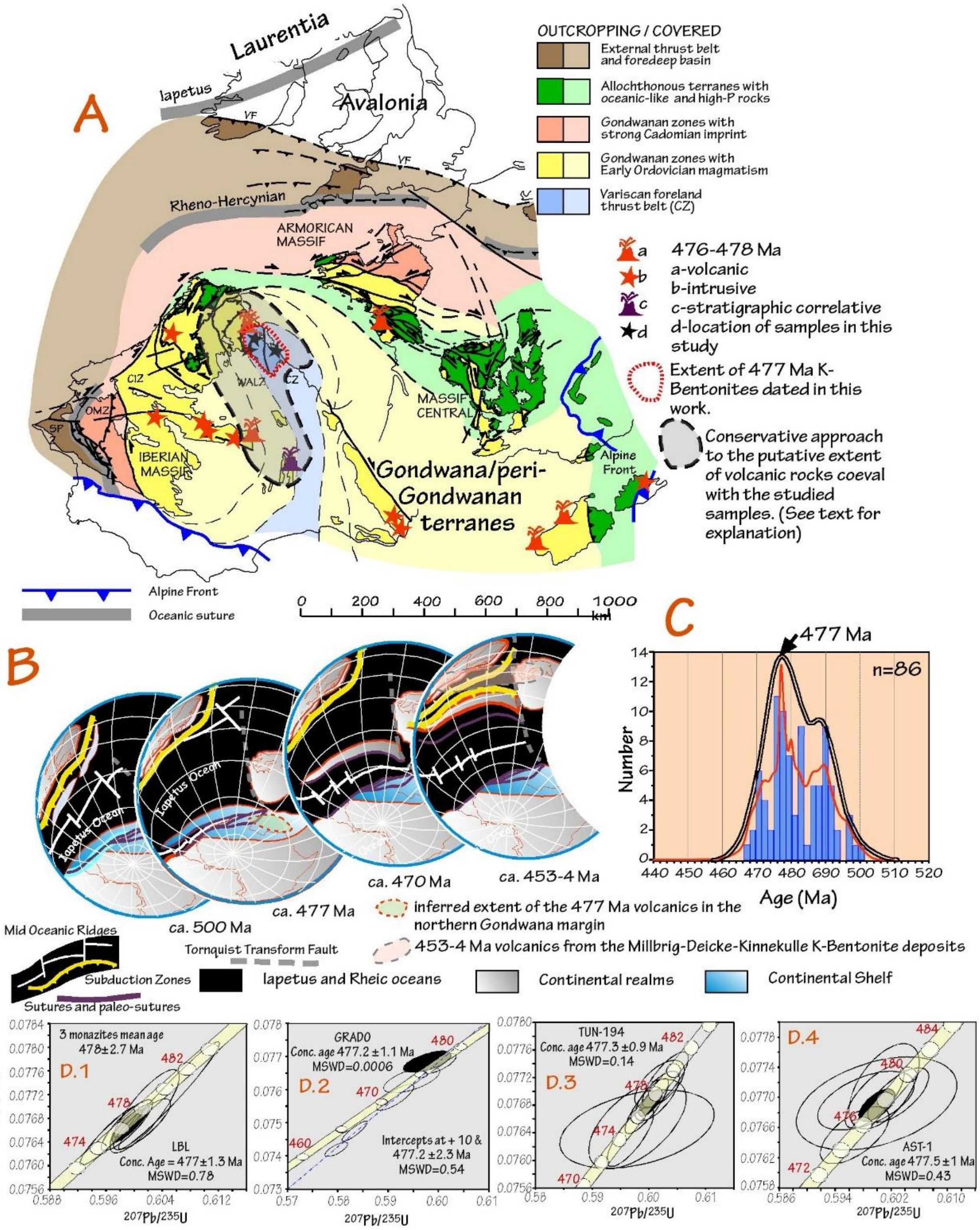

Figure 1. (A) Paleogeographic reconstruction of Western Europe in early Mesozoic times with the sample locations, the known outcrops of *ca.* 477 My intrusive and extrusive rocks and the extension of the recognized ash-tuff layer studied as well as the conservatively considered extension for a more interpretative volume calculation. (B) Early Paleozoic reconstruction of the Rheic Ocean opening and the origin and putative extension of the super eruptions identified in Ordovician times. (C) Histogram, Probability Density Diagram, and Kernel analysis plot of the available intrusive and extrusive age data between 465 and 500 My. In Western Europe, which reveals a significant maximum at 477 My, coeval with the age of the identified ash-tuff layer. (D) Wetherill concordia plots of the studied samples. (Modified from [27]).

3. Geochronology

3.1. U-Pb ID-TIMS analytical method

U-Pb analytical work was conducted at the Department of Geosciences, University of Oslo, Norway. Isotope data and details of each analyzed fraction are given in *Table 1*. The analytical procedure for zircon and monazite analyses is also described in [27]. U-Pb data are shown as Wetherill concordia plots in *Figure. 1D*.

3.2. Results

For sample AST-1 [26] we use the published age of 477.5±1 My (Concordia age of 6 concordant and overlapping analyses on single abraded grains, *Figure. 1D.4*).

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 (*Table 1*) yield a concordia age of 477±1.3 My (*Figure. 1D.1*). This age is within error of the weighted average of the ^{207}Pb/^{235}U age (chosen because of reverse discordance, see [28] of the 3 monazite analyses (478±2.7 My) 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*) we calculated an upper intercept age anchored at 0±10 My (*Figure. 1D.2*) of 477.2±2.3 My, and a concordia age with the two top analyses (*Figure. 1D.2*) of 477.2±1.1 My. This age is within error of the ^{207}Pb/^{235}U age of the reversely discordant monazite analysis (478±1 My).

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 My (*Figure. 1D.3*), within error of the ^{207}Pb/^{235}U age of the reversely discordant monazite analysis (479±1 My).

Within the precision of the U-Pb analyses in this study, it can be stated that the four samples are coeval and possibly belong to the same volcanic event. The best age assesment for the volcanic event can be gathered by the pooled 21 concordant analyses from the four samples described above (*Figure. 1*), yielding a concordia age of 477.2±0.74 My which concurs with the Tremadocian-Floian boundary (477.7±1.4 My, [30]). This concordia age is consistent with the age obtained using the TuffZirc algorithm of Isoplot 3.7 [30] which provides an age of 477.5 +0.75/-1.1 My using the ^{206}Pb/^{238}U ages of the same set of 21 concordant analyses.

All the monazite analyses show reverse discordance and their average ^{207}Pb/^{235}U age is 1 to 2 My older than the concordia age of the zircons in the same samples (*Table 1*). Since the closure temperature of monazite for the U-Pb system and its Pb retentivity can be higher than those of zircon (e.g. [31]), 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 coeval at the level of precision achieved in this study.

4. Volume and mass calculations

Given the aerial extension and the thickness of the studied K-bentonite, and given the geochronological evidence aforementioned for its assignment to a single event, we can attempt to reconstruct its initial mass and volume to grade the magnitude of the volcanic event. For this scope, we have reconstructed the Variscan deformation by unfolding the Cantabrian Arc (*Figure. 1A*) and restoring the shortening caused by the Variscan thrusting and folding (*Figure. 1A*). 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 may have exceeded *ca.* 15000 km^2, and 100000 km^2 when considering the correlatable beds in the proximal IR and WALZ and Central Iberian Zone (CIZ, *Figure. 1A*). The thickness of the studied tonstein shows a steady thinning trend from the westernmost outcrops in the CZ, where the thickness attains up to 80 cm. In the surrounding regions, thickness estimations should be taken cautiously as the tuff beds have suffered internal strain and their thickness (from a few centimeters to several meters) should be treated as a minimum.

A conservative evaluation of the volume and mass of the studied K-bentonite (using exclusively the Cantabrian Zone data, *Figure. 1A*) done with the Weibull fit method [32] provides a volume for the preserved deposits of *ca.* 37.5 km^3 (Volcanic Explosivity Index - VEI = 6, Colossal) which corresponds to a mass of *ca.* $8.3 \cdot 10^{13}$ kg using a measured mean density value of 2200 kg/m^3.

When considering other outcrops in northern Iberia which can be 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 *ca.* $9 \cdot 10^{14}$ kg. These occurrences may be linked to the large magmatic event regionally known as "Ollo de Sapo" (i.e. [15] and references therein) whose main age (including many volcanic rocks and their plutonic correlatives) peaks at *ca.* 477 Mya (*Figure. 1C*). Furthermore, the studied K-bentonites are coeval with the intrusion of a peralkaline ring complex attributed to a large caldera event in NW Iberia (*Figure. 1A*, [33, 34, 35]. 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.

Properties (1)	Weight [υg] (2)	U [ppm] (2)	Th/U (3)	Pbc [pg] (4)	206/204 (5)	207/235 (6)	2 sigma [abs] (6)	206/238 (6)	2 sigma [abs] (6)	rho	207/206 (6)	2 sigma [abs] (6)	206/238 (6)	2 sigma [abs] (6)	207/235 (6)	2 sigma [abs] (6)	207/206 (6)	2 sigma [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 (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	0.33	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) (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

Table 1. U-Pb data from the studied samples.

5. Discussion

The data presented document the first described occurrence of a gigantic volcanic ash-fall/event in the Lower Ordovician. Such an event has only been recognized in the Upper Ordovician (*ca.* 454 My), (*Figure*. 1B) [8, 36, 12].

The apparent coeval nature. same U-Pb zircon age within a *ca.* 1My uncertainty, of the studied samples present in the same stratigraphic position is an argument for a large eruptive episode in Gondwana *ca.* 477 My ago. The CZ is the domain where the K-bentonite layer is better preserved but its areal extension should have been much larger; covering most of Iberia and adjacent realms. Preservation of ash-fall beds (ultimately occurring as K-bentonite layers) requires lack of sedimentary reworking and the existence of large basins. In Iberia, the Lower Ordovician stratigraphic record is interpreted to be restricted to relatively small domains due to basin fragmentation and large emerged areas, especially in the southern part of the CIZ [37]. Given that in northern Iberia there is a continuous sedimentary record for the Lower Ordovician, the best preservation occurs in it and the studied K-bentonite is ubiquitously recognized in areas lacking metamorphism and internal strain.

The large amount of igneous rocks coetaneous with the studied K-bentonite layer found in Iberia and neighboring areas (see *Figure*. 1C) is consistent with the notion that the K-bentonite could have been much more extensive than what is preserved in the Cantabrian Zone. Because of the fragmented stratigraphic record, it is not possible to appraise the real size of the volcanic episode recorded in NW Iberia. Still, when considering other possible equivalent areas in Iberia and neighboring terranes (i.e. Armorica, Sardinia, etc. [38]. the volume of ejecta related to this event would make it grasp the Supervolcanic-Apocalyptic category (VEI=8, >1000 km^3).

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