A new sedimentary benchmark for the Deccan Traps volcanism?

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Eric Font,[1] Anne Nédélec,[2] Brooks B. Ellwood,[3] José Mirão,[4] and Pedro F. Silva[1,5]

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[1] The origin of the Cretaceous-Paleogene boundary (KPB) mass extinction is still the center of acrimonious debates by opposing partisans of the bolide impact theory to those who favored a terrestrial origin linked to the Deccan Traps volcanism. Here we apply an original and high-resolution environmental magnetic study of the reference Bidart section, France. Our results show that the KPB is identified by an abrupt positive shift of the magnetic susceptibility (MS), also observed by others at the KPB elsewhere. In addition, an anomalous interval of very low MS, carried by an unknown Cl-bearing iron oxide similar to specular hematite, is depicted just below the KPB. Grain-size and morphology of the Cl-iron oxide are typically in the range of hematitic dust currently transported by winds from Sahara to Europe. This discovery is confirmed in the referenced Gubbio section (Italy) suggesting a global scale phenomenon. As a conjecture we suggest an origin by heterogeneous reaction between HCl-rich volcanic gas and liquid-solid aerosols within buoyant atmospheric plumes formed above the newly emitted Deccan flood basalts. Based on this hypothesis, our discovery provides a new benchmark for the Deccan volcanism and witnesses the nature and importance of the related atmospheric change.
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1. Introduction

[2] The origin of the KPB mass extinction is a long debated topic and despite the availability of numerous data sets there is still no unique model for this extinction event. The role of the Chicxulub impact on the KPB mass extinction is now well established and its stratigraphic position is well constrained in distal sections by the typical dark clay deposit containing an Iridium anomaly [*Alvarez et al.*, 1980; *Bonté et al.*, 1984]. However, its contribution as the unique trigger of the KPB mass extinction is questionable. Multiple impacts [e.g., *Keller et al.*, 2003] or Deccan Trap volcanism [e.g., *Courtillot et al.*, 1986; *Keller et al.*, 2008, 2009] are proposed as potential alternatives. The multi-impact hypothesis is based on the presence of multiple impact ejecta layers in both Late Maastrichtian and Early Danian sediments in Mexico and Texas [*Keller et al.*, 2003, 2007]. However, it was proposed that these deposits are better explained by impact-related liquefaction and slumping, consistent with a single, very-high-energy Chicxulub impact [*Schulte et al.*, 2010]. The Deccan Traps volcanism in India, for which huge volumes of tholeitic lavas were emplaced in less than one million years, have caused severe environmental effects. Recent ^{40}K-^{40}Ar dating in the Mahabaleshwar Formation identified three volcanic pulses, a first minor one at ~67–68 Ma, a second major pulse at ~65 Ma and a last pulse occurring shortly after the KPB [*Chenet et al.*, 2007]. Nevertheless, a relative chronology of the catastrophic events that occurred in less than one million years is hard to reach using this method that suffers large systematic errors linked to inter-laboratory calibration, imprecise K and Ar isotopic standard data and incertitude of decay constants [e.g., *Renne et al.*, 2010]. Besides, biostratigraphic data from the intertrappean sediments of the Rajahmundry quarries of the Krishna-Godavari Basin indicated that the most massive Deccan trap eruption occurred near the KP mass extinction [*Keller et al.*, 2008]. However, in order to study the environmental impact of the Deccan traps in distal sections, other indirect (mineralogical) markers should be looked for.

[3] Here we test an original approach based on high-resolution environmental magnetic and mineralogical analyses in the Bidart section, France (Figure 1), in order to look for any environmental change before or after the KPB. Our results show that a horizon of very low magnetic susceptibility (MS), carried by an unknown Cl-bearing iron oxide for which magnetic properties are similar to hematite, precedes the KPB by some thousand years. Based on morphological and mineralogical criteria we interpreted this enigmatic Cl-rich iron oxide to correspond to modified hematitic dust transported by wind. The origin of the chlorine and the eventual links to the Deccan Traps volcanism are then discussed.

2. Geological Settings and Sampling

[4] The Bidart section is considered to be one of the most complete KPB sections in Europe and has been calibrated by magnetostratigraphic and biostratigraphic data sets [*Galbrun and Gardin*, 2004; *Alegret et al.*, 2004] (Figure 1). The entire sequence consists of hemipelagic to pelagic sediments deposited in a deep basin. The Maastrichtian is dominated by marls and calcareous marls while Danian sediments are composed by pink and white biogenic limestone beds. The KPB is easily identified by the typical iridium anomaly [*Bonté et al.*, 1984], well preserved in the section and located at the base of a thin dark clay layer containing the relics of the Chicxulub impact [*Apellaniz et al.*, 1997]. The sedimentation rate for the Maastrichtian is 4.3 cm/kyr but is unknown for the Danian. By analogy with the section of El Kef, Tunisia, a sedimentation rate of 1.4 cm/yr is suggested

[1]IDL, Universidade de Lisboa, Lisbon, Portugal.
[2]GET, UMR 5563, Toulouse, France.
[3]Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana, USA.
[4]HERCULES, Evora, Portugal.
[5]ISEL, DEC, Lisbon, Portugal.

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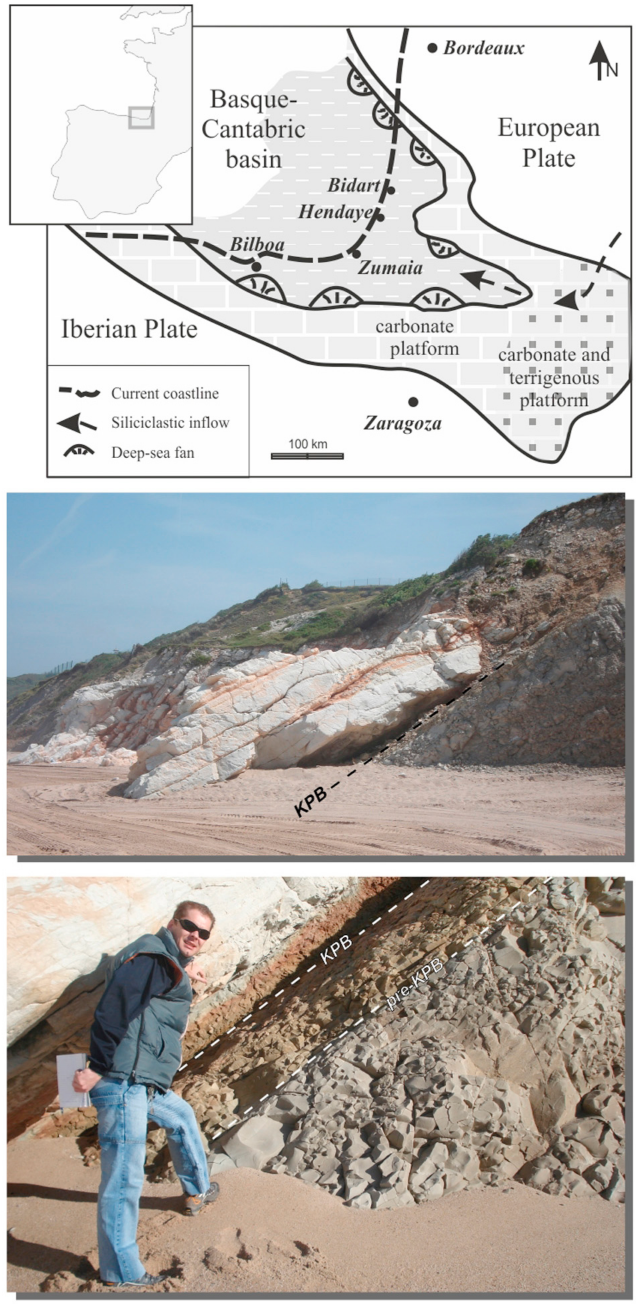

Figure 1. Paleoenvironmental context of the Bidart section [modified from *Alegret et al.*, 2004] and field photographs.

[*Vonhof and Smit*, 1997, and references therein]. Continuous sampling involved collecting oriented hand blocks in the field and subsequently cutting them in the laboratory into faceplates 1 cm in thickness.

3. Methods

[5] By coupling concentration (MS, SIRM) and grain-size/coercivity-dependent (χ_{ARM}/χ, $IRM_{-0.3T}/IRM_1$) magnetic proxies with mineralogical data, our aim was to characterize relative changes in the magnetic mineralogy that may result from local or global climatic/tectonic changes. More importantly, either a bolide impact or multiple volcanic pulses can be viewed as very rapid and abrupt phenomena that can be easily depicted by abrupt MS shifts within the stratigraphic column. MS was measured with a KLY-2 (AGICO) and reported relative to mass (m^3/kg). Selected samples were submitted to Anhysteretic (ARM) and Isothermal (IRM) measurement. IRM was acquired up to 2.5 T using an impulse magnetizer (IM-10-30) and subsequently analyzed using a cumulative Log-Gaussian function [*Kruiver et al.*, 2001]. ARM was induced with an AF field of 100 mT, biased with a DC field of 0.05 mT, using a LDA-3A demagnetizer coupled with an AMU-1A anhysteretic magnetizer. χ_{ARM} was then calculated dividing the values of the induced magnetization (A/m) by the DC field value. Thermomagnetic curves under low and high temperature were acquired using the MFK1 (AGICO) apparatus. For the characterization of the magnetic carriers, and particularly the newly discovered Cl-rich iron oxide, we observed small fresh rock fragments under Scanning Electron Microscope (SEM; Hitachi S-3700N) coupled to an Energy Dispersive Spectra (EDS; Bruker XFlash® 5010) detector.

4. Results

[6] Our results show that the KPB is characterized by an abrupt positive MS shift (Figure 2). High MS and Isothermal RM (IRM) values also span the dark clay level indicating an increase in the ferrimagnetic mineral content (Figure 3). Thermomagnetic, IRM and SEM-EDS analyses identified titanomagnetite of a detrital origin, and accessory hematite (less than 10%) of a secondary (pigmentary) origin. These data agree well with previous interpretations that the dark clay layer associated with the KPB corresponds to a period of intense continental erosion probably resulting from global climate modification following the Chicxulub impact or more likely Deccan volcanism [*Alvarez et al.*, 1980; *Vonhof and Smit*, 1997; *Ellwood et al.*, 2003]. The high MS signal of the dark clay layer is thus an excellent proxy in accurately locating the position of the KPB in distal marine sections.

[7] An abrupt decrease in MS values is depicted just below (~0.60 m) the KPB in Bidart (Figure 2). Such depletion in MS values in the uppermost Maastrichtian has been already observed in Bidart [*Galbrun and Gardin*, 2004] and in others KPB sections wide world [*Ellwood et al.*, 2003]. In Bidart, this transition is accompanied by a decrease in ferrimagnetic content (IRM_{1T}), an increase respective grain-size (Xarm/X), and dominance of the hard (i.e., high coercivity) over the soft (i.e., magnetite) mineral fraction ($IRM_{-0.3T}/IRM_{1T}$) (Figure 3). High coercivity and Curie temperatures around 680°C indicate the presence of hematite at this level (Figure 2). From a sedimentological point of view, this transition is associated with a change in the color of the sediment in Bidart, passing from greyish to reddish marls, with an abrupt decrease in the Ca content [*Apellaniz et al.*, 1997]. SEM observations provide evidence of many Cl-rich iron oxide occurrences of an unknown origin admixed to the detrital titanomagnetite phases (Figure 3). The crystals have a platy (specular) morphology and a typical size range from 2 to 10 μm that fits with the mean modal and median sizes of the present-day traveled Saharan/Sahelian dust (5–30 μm). It is also worth noting that this major global eolian dust source for the Quaternary (ca 50% of the emissions), although dominated by clays, is always characterized by a

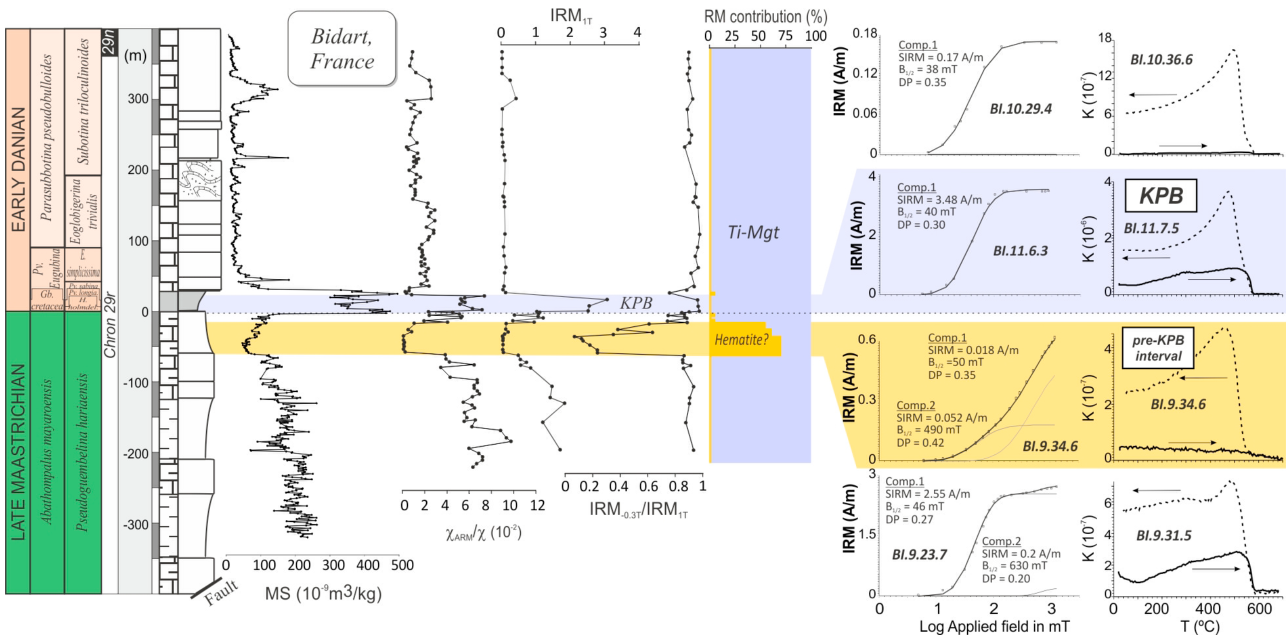

Figure 2. High-resolution magnetic data from the Bidart section showing that detrital titanomagnetite is the principal magnetic carrier, while the "pre-KPB" interval is dominated by a higher coercive iron oxide (hematite?).

hematite-goethite component [*Maher*, 2011]. Changes in fluxes, particle sizes and mineral proportions of this persistent source can be related to wind and, more generally, climate conditions.

5. Discussion and Conclusions

[8] The association of chlorine with iron oxides is very unusual in the terrestrial sedimentary record. Iron chloride phases are sometimes described in volcanic fumarolic environments [e.g., *Fulignati et al.*, 2002]. A low MS interval related to the same abrupt change in the magnetic mineralogy, also containing hematite, was observed in the uppermost Maastrichtian at Gubbio [*Lowrie et al.*, 1990]. These authors interpreted the occurrence of hematite at this level as a result of secondary (post-depositional) processes, such as the percolation of reducing fluids before the final consolidation of the sediment. However, the abrupt shift in magnetic properties at the pre-KPB event does not agree well with an overprint linked to downward fluid migrations. Moreover, the reducing character speculated for such fluids is in contradiction with the development of a Cl-bearing iron oxide. Therefore, we examined the samples corresponding to the interval of interest in Gubbio and found exactly the same mineral as in the Bidart section, i.e., specular, 2–10 μm in size and Cl-associated (Figure 3). Due to the fact that Bidart and Gubbio were separated by more than 1500 km during the late-Cretaceous, and that one section comes from the Atlantic and the other from the western Tethyan realm, we believe that this magnetic perturbation and its unusual mineral carrier may have global significance.

[9] The existence of a "pre-KPB" event is also evidenced using different methods at different locations (Figure 4). Paleotemperatures obtained on fossil plant material from North Dakota show an abrupt increase of 2–4°C beginning at ~500 kyr and ending at ~20–50 kyr before the KPB [*Wilf et al.*, 2003]. This coincides with an increase of species richness and the so-called "end-Maastrichtian warming event" (Figure 4). Stable carbon and oxygen isotopes from paleosol carbonates in Texas indicate the occurrence of two greenhouse episodes with atmospheric CO_2 levels between 1000 and 1400 ppmV, at 70 to 69 Ma and 500 kyr prior to the KPB, respectively. These are named the Mid- and Late-Maastrichtian events, and may have been due to Deccan volcanism [*Nordt et al.*, 2003]. A major drop in the marine $^{187}Os/^{188}Os$ record in chron 29r at different geographic locations suggests a correlation between the end-Maastrichtian warming event and the main Deccan Traps volcanism [*Ravizza and Peucker-Ehrenbrink*, 2003; *Robinson et al.*, 2009]. Despite uncertainties in the stratigraphic position and duration of the main Deccan volcanic pulses, there is some consensus that the main phase and largest lava volume production occurred just before the KPB [e.g., *Chenet et al.*, 2007; *Keller et al.*, 2008, 2009]. It is likely that the various records of a sudden paleoenvironmental change in the Upper Maastrichtian are indirect witnesses of this catastrophic volcanism.

[10] Explosive volcanism such as the 1991 Pinatubo eruption is known to produce climatic changes due to the large quantities of volcanic particles and aerosols that reach the stratosphere. The Deccan basaltic floods were also likely to have climatic consequences and recent physical modeling confirms this idea [*Kaminski et al.*, 2011]. Indeed, these huge basaltic emissions located in the southern tropical realm were likely responsible for penetrative atmospheric convection and rise of volcanic plumes into the stratosphere, with effects in both hemispheres, especially to the west due to prevailing trade winds. Among the volcanic gases emitted, SO_2, followed by HCl and HF, are the most important in volume [*Thordarson and Self*, 1996; *Self et al.*, 2006]. HCl is highly soluble in aqueous environments and wet deposition is expected in this case. However, in arid environments,

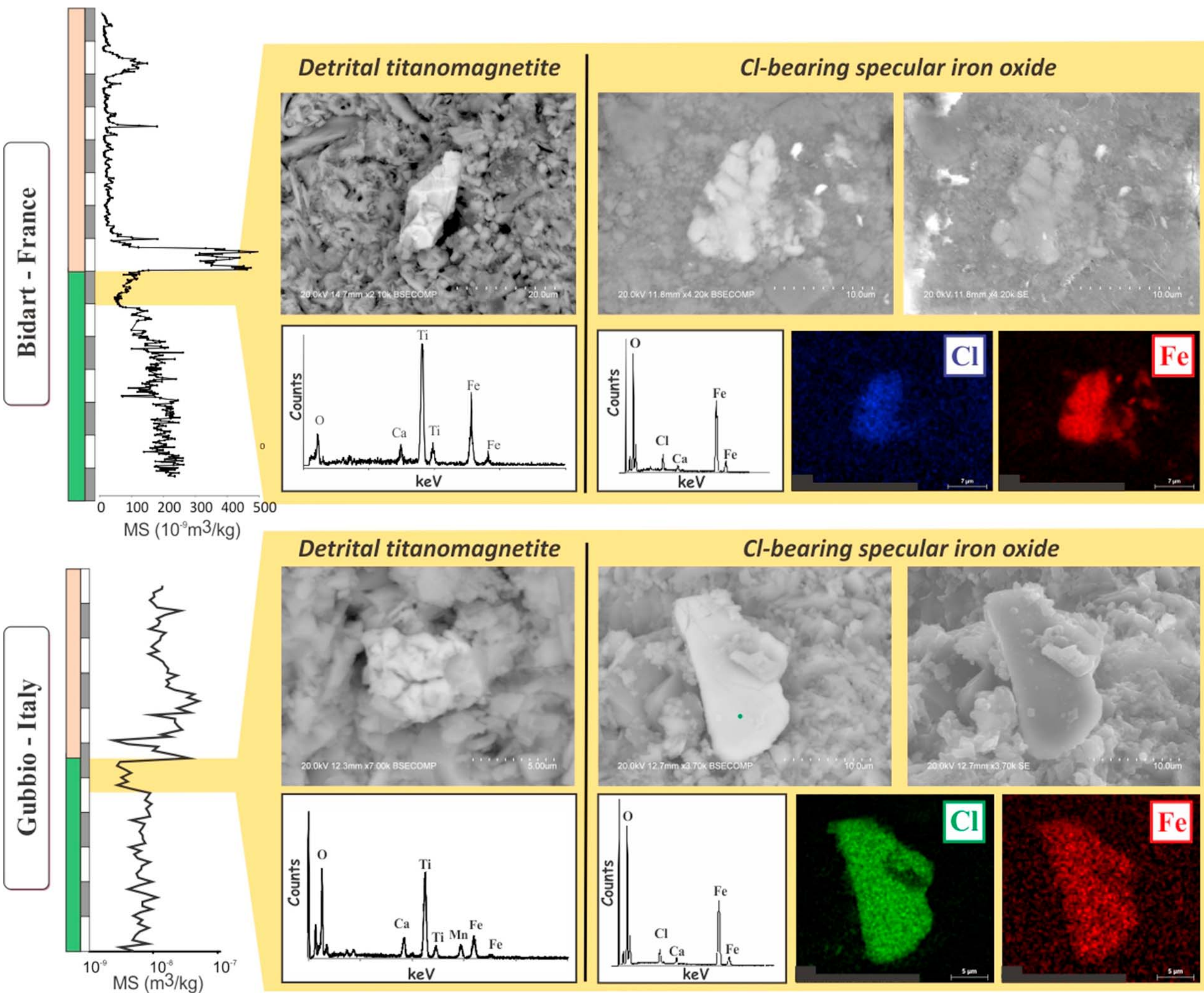

Figure 3. MS profiles of the Bidart (this study) and Gubbio [*Ellwood et al.*, 2003] sections and microscopic analyses (SEM-EDS) of the pre-KPB interval. The detrital component (i.e., titanomagnetite) contrasts with the newly discovered Cl-bearing iron oxide, which exhibits a well-preserved and plate-like shape with grain size in the range of 2–10 μm. SEM mapping (blue/green and red) shows that chlorine is always associated with iron and not in the matrix.

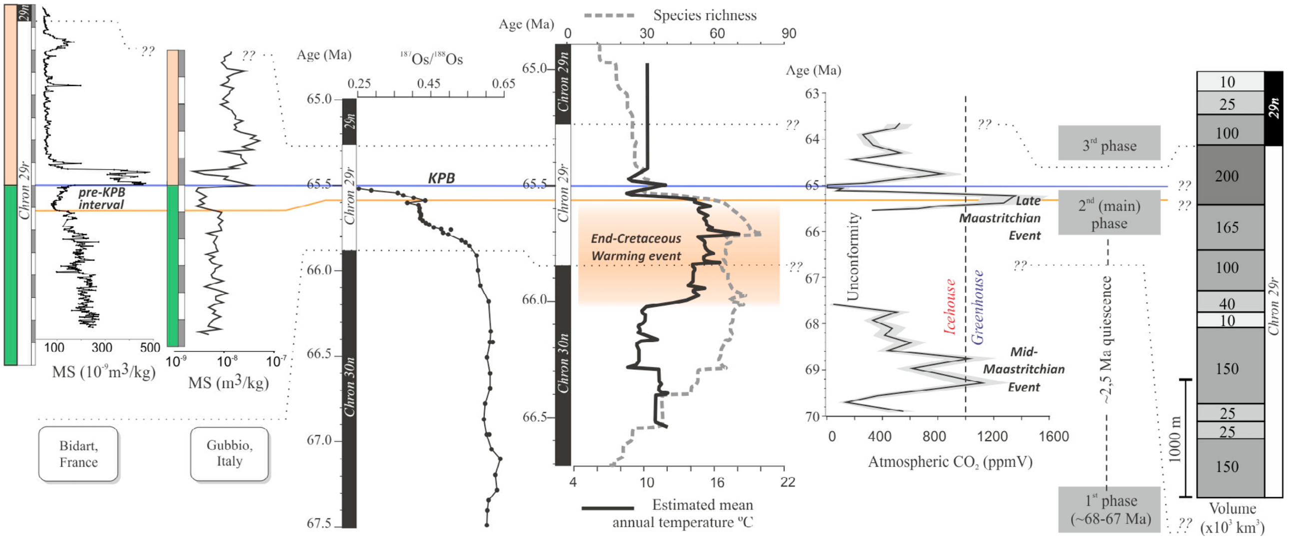

Figure 4. Global-scale correlations of the Bidart and Gubbio sections with paleoenvironmental proxies for referenced KPB sections worldwide. Profiles are anchored on the stratigraphic position of the KPB and, when available, on the Chron 29R/29N boundary (ages vary among authors). Relationships with volume of basalts from the Deccan Traps [*Self et al.*, 2006] are still ambiguous due to the unknown location of the KPB.

HCl can remain in the plume and transform to reactive species, e.g., ClO; OClO [*Lee et al.*, 2005]. Dusts typical of subtropical environments, including hematite crystals, rose in the volcanic plumes, at least periodically, and were easily transported upwards under these conditions. Due to the well-known affinity of chlorine and its reactive species for metals, heterogeneous reactions between volcanic gas and solid/aqueous aerosols are expected [*Aiuppa et al.*, 2007; *Kanari et al.*, 2010]. We thus contend that the Cl-bearing iron oxides that characterize the pre-KPB event in Bidart and Gubbio result from the volcanic origin of this environmental perturbation. They constitute an unprecedented piece of evidence indicating the acidification of the atmosphere as a consequence of the Deccan Traps main eruptive phase.

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B. B. Ellwood, Geology and Geophysics, Louisiana State University, Baton Rouge, LA 70803, USA.

E. Font, IDL, Universidade de Lisboa, P-1749-016 Lisboa, Portugal. (font_eric@hotmail.com)

J. Mirão, HERCULES, Largo Marquês de Marialva, 8, P-7000-809 Evora, Portugal.

A. Nédélec, GET, UMR 5563, Observatoire Midi-Pyrénées, 14, avenue Edouard Belin, Toulouse, F-31400, France.

P. F. Silva, ISEL, DEC, Conselheiro Emídio Navarro, N1 Lisboa, Lisboa P-1950-062, Portugal.