The Deccan Phase-2: an environmental magnetic approach

A fase 2 do Deccan: uma abordagem usando magnetismo ambiental

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Abstract: Environmental and climatic changes linked to Deccan volcanism are still poorly known. A major limitation resides in the paucity of direct Deccan volcanism markers and in the geologically short interval where both asteroid impact and volcanism occurred, making it hard to evaluate their contributions to the Cretaceous-Tertiary (KT) mass extinction. Here we present a short review about the environmental magnetic record of the Deccan Phase-2 in three reference KT sections (Bidart, Urrutxa and Gubbio). At Bidart and Gubbio, a change in colour of Maastrichtian sediments located just below the KT boundary is systematically associated to very low values of (low-field) magnetic susceptibility (MS). Rock magnetic properties shown that these very low MS values are the result of (reductive?) dissolution of iron oxides, namely magnetite and hematite. Akaganeite is systematically observed using scanning electron microscope in the low MS interval at Bidart, Gubbio and Urrutxa, but has never been observed in the rest of the stratigraphic section. The association of specular akaganeite and iron dissolution are discussed by evocating ocean acidification and aerosol deposition linked to the Deccan Phase-2.

Keywords: Akaganeite, Deccan volcanism, Mass extinction, Acidification, Rock magnetism.

Resumo: Os efeitos climáticos e ambientais relacionados as erupções vulcânicas da provincial do Deccan na Índia são ainda mal conhecidos. A maior limitação reside na ausência de marcadores sedimentares para o vulcanismo do Deccan e no curto intervalo geológico onde vulcanismo e impacto coexistem, sendo difícil de avaliar o impacto de cada um desses eventos na crise do Cretácico-Terciário (KT). Este trabalho apresenta uma revisão dos dados de magnetismo ambiental adquiridos nas sequências sedimentares de Bidart, Gubbio e Urrutxa. Em Bidart e Gubbio, a mudança de cor dos sedimentos maastrichtiano localizados logo abaixo do limite KT é associada a valores de suscetibilidade magnética (SM) muito baixo. As propriedades magnéticas indicam que estes valores de baixa SM resultam da dissolução dos óxidos de ferro, principalmente magnetite e hematite. Akaganeite é sistematicamente observada usando microscopia eletrônica de varrimento no intervalo de baixa SM, mas está ausente no resto da sequência sedimentar. A associação da akaganeite, e da dissolução dos óxidos de ferro é interpretada como o registo da acidificação do oceano e da deposição eólica de aerosóis relacionado com a fase 2 do Deccan.

Palavras-chave: Akaganeite, Deccan, Extinção em massa, Acidificação, Magnetismo de rocha.

1. Introduction

Paleoclimatic and paleoenvironmental effects of the Deccan volcanism are still badly known. One of the main challenges is to date precisely the age of the continental flood basalts from the Deccan Magmatic Province and the Cretaceous-Tertiary (KT) boundary recorded in marine sections by biostratigraphic data. Recently, three discrete Deccan volcanism phases with variable intensity have been dated based on magnetostratigraphy and 40K-40Ar ages (Chenet et al., 2007): Phase-1 (~67.5 Ma, 6% in volume), Phase 2 (~65 Ma; 80 % in volume) and Phase-3 (~64.5 Ma; 14% in volume). Biostratigraphic data showed dramatic changes in planktic foraminifera and macrofossils from the late Maastrichtian CF1-CF2 biozone leading up to the KT boundary, which is interpreted to record volcanism-induced high stress conditions worldwide (Keller et al., 2008, 2012). This short interval thus limits our ability to separate the main Deccan volcanic phase (i.e. phase-2) from the Chicxulub impact within resolvable 40K-40Ar ages (Chenet et al., 2007) and to separately evaluate the biotic effects of each catastrophic event and their contributions to the KT mass extinction.

Recent environmental magnetic data of several KT sections from the Biscay Bay and Tethys realm show peculiar changes in the mineralogy, colour and magnetic properties of the stratigraphic interval located below the KT boundary, and actually corresponding to the CF1 and CF2 biozone where Deccan Phase-2 is depicted. Here, we present a review of these recent insights and discuss their eventual links with ocean acidification and eruption of the Deccan Phase-2.

2. Iron oxide dissolution and akaganeite deposition: diagenesis or syn-depositional changes linked to Deccan Phase-2?

The upper part of the Maastrichtian at several KT sections from the Biscay Bay (Bidart, Sopelana, Urrutxa) and the Tethys (Gubbio) show abrupt changes in the colour, mineralogy and magnetic properties confined to the one meter below the KT boundary. The change in colour is
systematically associated to very low values of magnetic susceptibility (MS) at Bidart and Gubbio (Lowrie et al., 1990; Ellwood et al., 2003; Font et al., 2011). Magnetic susceptibility includes contributions from all minerals (diamagnetic, paramagnetic and ferrimagnetic) present in the sediment in proportion to their abundance and is very sensitive to the presence of ferromagnetic particles (i.e. magnetite). A useful method to identify the presence of ferromagnetic particles in sediment is represented by the analysis of Isothermal Remanent Magnetization (IRM) curves. IRM treatment by a cumulative log-Gaussian function (Kruiver et al., 2001; Robertson & France, 1994) further provide useful information about their concentration, coercivity (soft or hard) and compositional and grain size assemblages (Egli, 2004). Results show that the very low MS values result from the loss of soft (low to medium coercivity) iron oxides, which are identified at Bidart as magnetite by using thermomagnetic curves and microscopic observations (Font et al., 2011; Galbrun & Gardin, 2004). The high coercive components (hematite and/or goethite) either increase (at Bidart) or decrease (Gubbio) concomitantly, but are thought to be secondary in origin (pigment hematite and secondary goethite) (Fig. 1, 2). At Bidart, a medium coercive phase (component 2) is identified as corresponding to biogenic magnetite (henceforth "biomagnetite"), based on IRM and First Order Reversal Curves.

Reductive dissolution of iron oxides is a common diagenetic process in deep-sea sediments, where anoxic and reducing fluid are present (Cornell & Schwertmann, 2003; Abrajevitch & Kodama, 2011). Actually, a similar hypothesis has been proposed by Lowrie et al. (1990) who evoked reductive iron oxide dissolution in the white limestones below the KT boundary at Gubbio. The authors evoked reduction of hematite by downwards infiltration of reducing waters resulting from the large quantity of organic matter produced by the extinctions at the KT boundary. However, at Bidart, absence of pyrite, organic matter and dark colour as well as primary carbon isotopic signature are weakly compatible with reducing conditions acting during or after sedimentation at Bidart. The other way to dissolve iron oxides is acidity. Another plausible scenario is thus to evocate changes in the chemistry of the ocean linked to high CO$_2$ input and sulfuric acid aerosols from the Deccan Traps (Chenet et al., 2005; Self et al., 2006). For example, a weathering model of onland magnetite dissolution by acid rains showed that a pH of 4.6 (present day rain pH~5.6) is sufficient to dissolve more than 90% of the detrital magnetite (Font et al., 2014). In addition, dissolution (or lack) of biomagnetite in the low MS interval at Bidart (Font & Abrajevitch, unpublished data) and Gubbio (A. Abrajevitch, personal communication) suggests change in the anoxic/oxic boundary of the ocean as well. At Gubbio, the loss of biomagnetite below the KTB is compatible with the Lowrie et al. (1990)’s hypothesis, but not at Bidart where biomagnetite reappeared just after the low MS interval and just before the KTB (Fig. 1).

![Fig. 1. Magnetic data (magnetic susceptibility and isothermal remanent magnetization parameters) of the Bidart section (modified from Font et al., 2014). Log B$_{1/2}$ (mT) is the mean coercivity of each magnetic component. SIRM corresponds to IRM values at saturation. Component 1 and 2 correspond to detrital and biogenic magnetite, respectively, whereas component 3 is probably hematite. The low MS interval is featured by a loss in detrital and biogenic magnetite.](image-url)

Fig. 1.Dados magnéticos (susceptibilidade magnética e parâmetros de magnetização remanescente isotermal) da secção de Bidart (modificado de Font et al., 2014). Log B$_{1/2}$ (mT) é a coercividade média de cada componente magnética. SIRM corresponde aos valores de IRM a saturação. Componentes 1 e 2 correspondem a magnetite detrítica e biogênica, respectivamente, enquanto a componente 3 é provavelmente hematite. O intervalo de baixa susceptibilidade é caracterizado por uma diminuição da concentração em magnetite detrítica e biogênica.
In addition to the loss of detrital and biogenic magnetite, the low MS interval contains an enigmatic iron hydroxide identified under SEM as being akaganeite ($\beta$-Fe$_2$(OH)$_3$Cl) found at Bidart and Gubbio, suggesting a large-scale phenomenon as responsible for its precipitation. The composition of this mineral involves Fe, O and Cl. Due to its hollandite-type structure, akaganeite is the sole mineral that has enough space to incorporate the Cl atom in its crystalline system. Akaganeite is very rare in natural environments because its precipitation requires high content in Fe (II) and Cl (Reguer et al., 2007; Remazeilles & Refait, 2007, 2008; Yue et al., 2011). This is why akaganeite is generally found in peculiar environments like hypersaline lake (Emmerich et al., 2012), iron sulphide-rich environments (Bibi et al., 2011), fumaroles (Johnston, 1977), weathered (corroded) steel (Li et al., 2008) and weathered meteorites (containing Ni) (Bland et al., 1997). Natural and synthetic akaganeite have nanometric scale grain sizes and morphology called “rod-like” or “somatoidal” (cigar-shaped) (Cornell & Schwertmann, 2003; Yue et al., 2011; Zhang & Jia, 2014). Macro or specular akaganeite has never been documented. However, the akaganeite found at Bidart and Gubbio are significantly larger (~5-40 $\mu$m) and present unusual morphology which are plate-like, specular and semi-hexagonal. Crystal present smooth surfaces that strongly contrast with the eroded aspect of the detrital magnetite. Its grain size range and morphology rather evocate aeolian transport, similarly to the hematite dust currently transported by winds from the Sahara to Europe. By comparison, Cl-bearing solid volcanic aerosol forms particles in the 2-20 $\mu$m size range near the Masaya volcano in Nicaragua (Moune et al., 2010).

Actually, the Deccan Traps volcanic plume is an ideal environment to form akaganeite: it contains metal transported in the form of Cl-rich gas (NaCl, KCl, FeCl$_2$, ...), which rapidly reach the solid state during the cooling of the volcanic plume. FeCl$_2$ is highly soluble and rapidly reacts in the aqueous system with Fe(II) and Cl(II) (Remazeilles & Refait, 2007):

$$2\text{Fe}^{2+}_{(aq)} + 2\text{Cl}^{-}_{(aq)} + 3/2\text{H}_2\text{O} + 3/4\text{O}_2 = \beta\text{-Fe}_2(\text{OH})_3\text{Cl}_{(s)}$$

Penetrative convention by created by eruptive vent and spreading lava flows further provide transportation up to the stratosphere, giving an explanation for its deposition at Gubbio and Bidart (Fig. 3).
3. Conclusion

Environmental magnetism (i.e., the study of the variations in composition, concentration and grain-size of the mineral magnetic fraction in a sedimentary sequence) is an original and promising approach to evaluate the potential paleoclimatic and paleoenvironmental effect of the Deccan Traps eruptions. Our results highlight the presence of a peculiar stratigraphic interval, correlated in time by biostratigraphic (CF1, CF2) and isotopic (C and O) data to the Deccan Phase-2. The peculiarity of these strata reside in the presence of specular akaganeite and reductive dissolution of iron oxides just below the KTB and in reference geological sections from the Atlantic (Biscay Bay) and Tethysian realm (Gubbio). Here, we interpreted the loss of iron oxides as being the result of ocean acidification linked to the Deccan Phase-2 eruptions, while specular akaganeite deposition might be linked to interaction of volcanic aerosols with the stratosphere. These results provide new insight to identify the sedimentary signature of the Deccan Phase-2 in distal marine sections and to unravel it paleoclimatic and paleoenvironmental effects.

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