

Enriched mantle source for the Cretaceous alkaline lamprophyres from the Catalonian Coastal Ranges (NE Spain)

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During the Cretaceous, the opening of the Bay of Biscay led to a widespread alkaline magmatism in northeast Iberia [1]. This magmatism is recognised in the Pyrenees [2] and in the Catalonian Coastal Ranges [3]. In the latter sector, it is represented by lamprophyre sills, classified as camptonites. They are hypocristalline porphyritic rocks composed of large mafic crystals (clinopyroxene, kaersutite, olivine pseudomorphs and opaque minerals) set in a fine-grained groundmass. Most of the groundmass consists of microlites of feldspars and kaersutite; apatite is a common accessory phase.

The lamprophyres are basic and ultrabasic rocks enriched in incompatible elements (10 to more than 100 times over the primitive mantle). They show a Ti/V ratio over 50, similar to OIB-type rocks. In order to obtain petrogenetic information from the incompatible trace elements, only the most primitive samples (MgO > 7 wt. %) were considered. In addition, rocks with high volume fractions of large crystals were dismissed as their composition is strongly influenced by the accumulation of the crystals [4].

The primitive mantle-normalised multi-element patterns are very similar to each other, suggesting a common magma source. (La/Lu)_N values (14.9-17.3) indicate highly fractionated patterns. All the samples show positive anomalies for Nb-Ta and smaller ones for Ba; some of the samples also present a negative anomaly in Pb. These data point to an asthenospheric enriched mantle source similar to EM-1 [5]. Small differences are observed for K, which correlate with the proportion of kaersutite in the samples. Slight differences in P are probably related to the presence of apatite.

The εSr values define a wide variation range (-11.7 to +14.9). Given that these variations do not correlate with the SiO₂, MgO or Sr contents, crustal contamination can be ruled out. Therefore, a heterogeneous mantle source is inferred, as previously reported for the Permian and Triassic magmatisms in the Pyrenees [6].

In contrast, the εNd values (+3.1 to +4.4) and the Pb isotopic ratios (²⁰⁶Pb/²⁰⁴Pb: 19.06–19.46; ²⁰⁷Pb/²⁰⁴Pb: 15.65–15.70; ²⁰⁸Pb/²⁰⁴Pb: 39.28–39.82) show small variations. The low Pb ratios discard the involvement of a HIMU-type component. The Sr-Nd-Pb isotopic values support a heterogeneous, asthenospheric mantle source with the involvement of an EM-1 component [5].

The obtained T_{DM} ages are very consistent (0.55-0.60 Ga). They may reflect a Cadomian fractionation event in the mantle.

[1] Montigny *et al.* (1986) *Tectonophysics* **129**, 257-273. [2] Azambre *et al.* (1992) *Eur. J. Mineral.* **4**, 813-834. [3] Solé *et al.* (2003) *Cretaceous Res.* **24**, 135-140. [4] Ubide *et al.* (2012) *Lithos* **132-133**, 37-49. [5] Hofmann (1997) *Nature* **385**, 219-229. [6] Lago *et al.* (2004). *Geol. Soc. Sp. Publ.* **223**, 439-464.

Photodissociation origin of Archean S-MIF and dynamical sulfur cycling under highly reducing atmosphere

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Mass-independent fractionation of sulfur isotopes (S-MIF) demonstrated that Earth's atmosphere was virtually oxygen-free in the Archean [1], and is a key to understand chemistry of atmosphere and ocean before the rise of oxygen. However, the mechanism and factor controlling the S-MIF signal have been poorly understood yet. We newly determined higher resolution UV absorption cross sections of not only ³²SO₂, ³³SO₂ and ³⁴SO₂ but also ³⁶SO₂ within the two absorption bands: (1) 190 – 220 nm and (2) 250 – 320 nm. These data together with chemical reaction model allow us to predict isotopic compositions of photochemical product. The calculated photochemical fractionation pattern assuming broadband solar UV flux reproduce our previous work [2], though the effect of UV shielding by each atmospheric species including SO₂ itself differ from previously estimated trend. Nonetheless, almost all of the simulations result in Δ³⁶S/Δ³³S ratio of -0.9 ~ -1.1, generally reproducing those observed in Archean sedimentary rocks. Thus, we conclude that photodissociation of SO₂ was a primary MIF-yielding reaction in the Archean atmosphere. Our simulation predict, however, the remaining SO₂ after UV photolysis acquires positive Δ³³S as opposed to widely-accepted previous model where H₂SO₄ (-Δ³³S) and S₈ (+Δ³³S) aerosols carried "opposite" MIF signals into ocean and sediment [4,5]. We speculate the possibility that almost Archean sulfide deposits were produced by sulfate reduction. The new model requires relatively inert reducing form of sulfur reservoir. If the atmosphere was strongly reducing and contained high level of CO or CH₄, photolytically produced SO was finally transferred into OCS [2] or organo-sulfur compounds [6], respectively, which remained in the atmosphere and were not readily converted into sulfide. Occasional oxidation of the reducing sulfur pool enhanced sulfate concentration and deposited rare sulfate minerals with negative Δ³³S. The new dynamical sulfur cycle model may explain observed heterogeneity of S-MIF records in the basin to microscopic scale. If correct, this implies more reducing Archean atmosphere than previously thought.

[1] Farquhar *et al.* (2000) *Science*, **289**, 756-758. [2] Ueno *et al.* (2009) *PNAS* **106**, 14784-14789. [3] Danielache *et al.* (2008) *J Geophys Res* **113**, D17314. [4] Pavlov & Kasting (2002) *Astrobiology* **2**, 27-41. [5] Ono *et al.* (2003) *EPSL* **213**, 15-30. [6] Domagal-Goldman *et al.* (2011) *Astrobiology* **11**, 419-441.