

## U-Pb geochronology and source constraints for late S-type Variscan magmatism related to Sn-W metallogeny: The Logrosán granite pluton (Central Iberian Zone)

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S-type tin-bearing granites intruded along the Central Iberian Zone (CIZ) during syn- and late-kinematic stages of the Variscan orogeny. The Logrosán cupola belongs to the Central Extremadura Batholith (CEB) which crops out within the epizonal domains of the CIZ. This granitic body intruded the Neoproterozoic Schist-Greywacke Complex (SGC). The Logrosán cupola is a felsic, perphosphoric, and strongly peraluminous (ASI=1.2-2) tin-granite (Sn=11-67 ppm). The most evolved facies are well-exposed in the topographic heights at the centre of the granitic cupola. Major and trace element geochemistry (e.g. CaO, Rb, Sr) shows no fractional crystallization trends suggesting the input of felsic batches derived from a deeper magma reservoir. Besides, the Sr-Nd and Hf isotopic signatures indicate that the Logrosán granite was derived by partial melting of heterogeneous crustal sources (initial <sup>87</sup>Sr/<sup>86</sup>Sr ratios from 0.7134 to 0.7311; εNd between -4.3 and -4.0 and εHf(t) from 2.0 to -4.6 for Variscan zircons). An age for the granite emplacement of ca. 308 Ma (U-Pb Zrn & Mnz CA-ID-TIMS) indicates that the granite is coeval with other related plutons in the region. U-Pb LA-ICP-MS dating has identified a predominant group of Neoproterozoic inherited zircon with juvenile Hf-isotope composition (εHf up to +14.6; LA-MC-ICPMS data) similar to that of zircons from the SGC. This evidence suggests that the Logrosán granite was partially derived from melting a metasedimentary protolith similar to the Neoproterozoic SGC.

## Microaerophilic biological methane cycling 2.6-2.1 billion years ago

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We present a new and undescribed biogeochemical mechanism explaining the demise of the Archaean methane greenhouse atmosphere in the palaeoproterozoic using Cu, Fe, C<sub>org</sub> stable isotope systematics and microbial culture experiments. Based on Cu-Fe chemistry, we infer that oceanic Cu levels, hundreds to thousands of scales above that of modern oceans, orchestrated the transition into a previously unknown Cu-resistant microbial ecosystem after the rise of atmospheric oxygen. The associated Neoproterozoic emergence of Cu-dependent microaerophilic methanotrophy, ~2.8-2.5 Ga, provided a resilient biological filter against continuous catastrophic methane input into the Palaeoatmosphere, between ~2.6-2.1 Ga. Methane oxidation by this process peaked at ~50% increase by ~2.1 Ga, relative to the Neoproterozoic. We propose that microaerophilic Cu-dependent methane oxidation was the second most important process for primary productivity after H<sub>2</sub>-driven methanogenesis during the Palaeoproterozoic. It facilitated the accumulation of extremely low d<sup>13</sup>C<sub>org</sub> isotopic excursions and was intensely active from the start to the end of the Huronian glaciation, facilitating biospheric oxidation.