

## Paleoceanographic change associated with the Valanginian $\delta^{13}\text{C}$ excursion in the western Tethys

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Here we present phosphorus (P) and redox-sensitive trace-metal (TM) contents, coupled with organic matter analyses in a series of western Tethyan sections during the Valanginian positive  $\delta^{13}\text{C}$  excursion. We complement our analyses with samples of Valanginian age from the Pacific Ocean (Shatsky Rise) and a shallow strait connecting the Boreal and Tethyan realms (Wawal).

In all sections, the onset of the positive shift is marked by maximal values in phosphorus accumulation rates and minimal values during the shift. TOC data and palynological observations of the dark marly layers suggest characteristic features of an oxic pelagic setting (low TOC and low HI) in the western Tethys. At Shatsky Rise, three of the analysed samples show high TOC values, with HI/OI values characteristic of marine organic matter. In the section of Wawal, TOC-rich samples indicate a type-III origin. The stratigraphic distribution of TM shows no major excursions during the  $\delta^{13}\text{C}$  excursion in all the studied sections, except in the pre- $\delta^{13}\text{C}$  event 'Barande' layers and in the organic-rich levels of Shatsky rise, where TM show higher values.

Our results suggest that the onset of the shift is marked by an increase in continental input (high P values). We also show that sediments of the western Tethys lack evidence for the persistence of dys- to anaerobic conditions during the Valanginian  $\delta^{13}\text{C}$  excursion. Dys- to anaerobic zones were restricted to marginal seas of the opening Atlantic and eventually also to the Pacific.

## Developing models of disequilibrium magma degassing

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The noble gas composition of the mantle can inform issues ranging from recycling processes to events during the Earth's formation. However, the erupted samples used to determine this composition have undergone a degassing process which can alter their noble gas composition. An accurate model of this process is necessary if the original noble gas signature of the source mantle is to be determined. Knowledge of the solubility of the different noble gases allows degassing to be modelled under equilibrium conditions. However, under disequilibrium conditions, the relative diffusivity of the noble gases becomes important. [1] For example, heavier noble gases, which would usually be modelled as being preferentially lost, can be preferentially retained in the melt due to their lower diffusivity.

This study builds on Gonnermann and Mukhopadhyay's disequilibrium degassing model. [1] A key component is determining how to model the evolution of the major volatile concentrations over a number of open-system degassing steps. The major volatiles can be allowed to degas in equal proportions at each step, or allowed to degas based on the time available at each step; the difference in, for example, calculated He/Ne ratios can be several orders of magnitude and is also affected by the number of degassing steps.

We also investigate the model's sensitivity to temperature, initial major volatile concentrations, pressure, relative volatile diffusivity and degree of disequilibrium. The majority of these parameters can be estimated from sample location and composition but precise values are hard to determine; sensitivity tests are key to determining which can be estimated and which must be fitted from sample data. We find that the model is relatively insensitive to eruption temperature. In contrast, increasing the initial  $\text{CO}_2$  concentration from 0.17 wt% to 0.87 wt% can decrease final noble gas concentrations by more than an order of magnitude. Plausible variations in pressure, diffusivity and degree of disequilibrium can also affect results by an order of magnitude or more.

This study lays the groundwork for assessing the reliability of deriving the original mantle source noble gas composition from a suite of sample results.

[1] Gonnermann & Mukhopadhyay (2007) *Nature* **449**, 1037-1040.