

## Experimental study on As and Cd releases from anoxic sedimentary rock under anoxic and aerobic conditions

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The dissolution behaviors of As and Cd from the anoxic sedimentary rock and subsequent immobilization mechanism were investigated under anoxic and aerobic conditions.

Under aerobic condition, the decrease in pH and concomitant Cd release were attributable to oxidative dissolution of sulfide minerals, and 22 % of Cd in rock sample was dissolved out for 2 months. On the contrary, Cd concentration in the solution reacted under anoxic condition was maintained low level, and the contribution of dissolved Cd was only 0.14 %.

Arsenic was released as arsenite under both conditions. The As concentrations in extracts under both conditions was small, and the maximum contributions of As dissolution were about 1 %. The XANES spectra reveal that samples before the extraction contained the sulfide form As and As(V). Under aerobic condition, the As sulfide completely decomposed within a month and only As(V) existed in the samples after extraction.

The chemical state of As in samples oxidized under 100% humidity was changed to sulphide form to oxide and/or strongly sorbed ones. This experiment shows the change in chemical states of As within rock sample before the contact with water, and the result reveals that the oxidation of As sulfide did not lead to large amounts of As release. On the contrary, under anoxic condition, As and Cd concentrations were maintained low and the sulfate-rich acidic solution was not produced. Furthermore, the sulfide As were still remained in samples extracted for 2 months. These results indicate that the sulfide minerals containing As and Cd in anoxic sedimentary rock almost remained during extraction experiment for 2 months.

## The Mesozoic evolution of the West Iberian Margin as witnessed by magma geochemistry

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The main phases of the onshore West Iberian Margin (WIM) Mesozoic evolution were marked by the occurrence of 3 magmatic cycles separated by time lags of  $\approx 50$  Ma. The first cycle (202 - 198Ma) is linked to the initial stages of the Central Atlantic opening, being considered part of an important LIP: the Central Atlantic Magmatic Province. Magmatism produced low-Ti tholeiites characterized by  $(La/Yb)_n < 4$ ,  $(^{87}Sr/^{86}Sr)_0 > 0.7050$  and  $(^{143}Nd/^{144}Nd)_0$  down to 0.512268 which post-date the beginning of syn-rift sedimentation by  $\approx 20-30$  Ma. The second cycle (147 - 141Ma) was coeval of the westward rift axis migration from the Lusitanian Basin to the location where oceanization was successfully reached. Preserved rocks are hypabyssal with transitional affinities (moderately alkaline to subalkaline),  $6 < (La/Yb)_n < 12$ ,  $(^{87}Sr/^{86}Sr)_0 = 0.70403$  to 0.70456 and  $(^{143}Nd/^{144}Nd)_0 = 0.512531$  to 0.512664. The third cycle (94 to 72 Ma) was synchronous with the opening of the Bay of Biscay and of the rotation of the Iberia. It was characterized by the formation of abundant alkaline magmatism presenting  $(La/Yb)_n$  up to 21,  $(^{87}Sr/^{86}Sr)_0$  down to 0.702870 and  $(^{143}Nd/^{144}Nd)_0$  up to 0.512897. The geochemical evolution depicted by WIM magmas expresses the diminishing role of lithospheric sources. They prevailed during the first cycle, when magmas present fingerprints of supra-subduction processes probably developed in the lithosphere during the Upper Paleozoic Variscan orogeny.