# Cadmium enrichments in Jurassic carbonates: Causes and mechanisms

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Marine carbonate rocks represent a widespread lithology hitherto thought to be depleted in cadmium (Cd), a highly toxic trace metal that is transferred into the environment by weathering processes. However, we have identified middle and lower upper Jurassic carbonates outcropping in Switzerland, France, Spain and Italy as being considerably enriched in Cd, independent of their particular facies and correlated in time. Moreover, in one of the sections studied (Terminilletto/I), a positive correlation between Cd enrichments and the carbon isotope record has been observed.

The widespread occurrence of Cd anomalies in Jurassic carbonate rocks in western Europe and its correlation with the stable carbon isotope variations suggest that this enrichment was associated with a general change in the Cd cycle in the western Tethyan realm, probably related to contemporaneous global environmental changes that induced variations in the seawater composition. In this context, a direct incorporation inside the calcite lattice during carbonate precipitation is probable, although Cd transfer into carbonates during early diagenesis is also possible. Both experiments of sequential extraction (ICP-MS analyses) and maps of Cd repartition (micro X-Ray fluorescence analyses), that are underway, will allow us to better constrain the Cd bearing mineral phase and help us to elucidate the mechanism of Cd incorporation into carbonate rocks.

# Systematic spatial variations of Ba and Sr enrichments over ambient seawater values in saline, geothermal, submarine springs on the West Florida Shelf

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Several saline, geothermal, submarine springs are known to occur on the West Florida Shelf, at depths of 17-23 m and about 10 miles off shore. These have been shown to emit a constant flow of warm, saline water (t = 33 – 36 °C; S ~ 35), containing micromolar levels of sulfide. A model devised in the late 1960s proposes that seawater penetrates the Florida Plateau, most likely around the Florida Straits. This seawater is geothermally heated to a temperature of about 42 °C as it flows at 800 – 1000 m depth toward the axis of the Florida Plateau—roughly coinciding with the southern section of the West Florida Shelf—where it finally rises to the surface and emerges from a multitude of separate vents. This system is a rare example of warm seawater interacting extensively with a massive carbonate platform, rather than igneous rocks.

Detailed studies in the late 1970s revealed that the spring effluents have compositions nearly identical to that of sea-water, except for distinct Ca enrichments and Mg depletions probably resulting from dolomitization. The effluents are also highly enriched in Ra. During annual visits from 1996 to 2003, we collected high-purity effluent from four springs, using a syringe sampling technique performed by SCUBA divers. Filtered effluent was analyzed for major ions by ion chromatography and for Sr and Ba by ICP-MS. Major ion analyses confirm the seawater-like character of the effluents, as well as the Ca enrichment and Mg depletion. The alkaline earth elements Sr and Ba, like Ca and Ra, are enriched in the effluents by factors of 1.5 – 4 and 4 – 6, respectively. These Sr and Ba enrichments, while extremely stable over the 7-year sampling period, increase systematically from south to north, which may be indicative of the progressive interaction of warm seawater with the carbonate substrate, and hence of the direction of its flow deep underneath the Florida Plateau. Combined with a previous estimate of the flow rate from a single vent (~25 L/s), these results suggest that the springs may impart a pronounced chemical and thermal imprint on the coastal seawater of the West Florida Shelf.