



Origin and geochemical history of fluids in Gulf of Cadiz mud volcanoes: A multi-isotopic approach

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We report inorganic geochemical data from five submarine mud volcanoes (MVs) which are located on a transect spanning the Gulf of Cadiz from W to E at water depths between 3860 and 320 m. Inversely correlated δD and $\delta^{18}O$ values and, in part, pore water freshening point at clay mineral transformation and concomitant mineral dewatering as the major cause for overpressuring and thus fluid mobilization at depth. Differing trends for other pore water constituents however, suggest that additional processes have led to distinct geochemical signatures in the various MV fluids. This has important implications for the interpretation of their origin within the underlying sedimentary complex.

The easternmost, i.e. nearshore MVs (Captain Arutyunov MV and Mercator MV) are influenced by dissolution of evaporites, which is indicated by elevated concentrations of Na^+ , Cl^- and some other elements (e.g. K, Ca) as well as Na^+/Cl^- ratios close to one. Li is enriched with respect to seawater at all MVs, but the enrichment is highest at Captain Arutyunov MV and Mercator MV (up to 3350 μM). Mass balance calculations have shown that the excess Li cannot be derived from dissolution of evaporites or admixture of a primary brine. Instead, water/sediment or rock interactions, most likely at elevated temperatures, must be responsible for the extreme Li enrichments.

The $^{87}Sr/^{86}Sr$ values of the studied MV fluids increase from W (Porto MV: 0.7075) to

E (Mercator MV: 0.7106) indicating the transition from oceanic to continental crust.

To constrain the origin of the observed Li enrichments and to further characterize the above-postulated leaching processes we measured Li isotope variations in the MV fluids. The obtained $\delta^7\text{Li}$ values are throughout lighter than seawater suggesting a common process of Li mobilization.