



Barium in Black Sea sediments: a reliable indicator for marine primary productivity or the migration of the sulphate/methane transition zone?

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Sedimentary Ba profiles are often used to trace paleoproductivity since the decay of organic matter in the water column coincides with precipitation of “biogenic” barite. However, Ba is diagenetically overprinted if sediments are buried below the sulphate/methane transition zone (SMTZ). To gain insight into the geochemical behaviour and cycling of Ba in ocean areas characterized by an anoxic water column and a shallow sedimentary SMTZ, gravity cores from two sites in the northwestern Black Sea (GC 755, 501 m water depth and GC 214, 1686 m water depth) were examined. The main objective of this study was to evaluate the applicability of Ba as an indicator for marine primary productivity and/or migrations of the SMTZ in such exceptional (modern and ancient) environments. This is the first study that combines solid phase Ba data from the Black Sea with pore water Ba^{2+} profiles to identify current depths of diagenetic barite dissolution and precipitation. Within the uppermost ~ 1.5 m (above the current SMTZ) a positive correlation between solid Ba and total organic carbon (TOC) exists and suggests a contribution of “biogenic” barite to the bulk Ba concentration. In contrast, around the SMTZ and below, Ba and TOC are completely decoupled due to the diagenetic dissolution and reprecipitation of BaSO_4 . Authigenic barite fronts are indicated by pronounced peaks in particulate Ba slightly above the SMTZ (at about 1.7 and 1.5 m, respectively). The current zone of diagenetic barite precipitation corresponds to the overall solid-phase maximum of Ba at the shallow site (755), while at the deeper site (214) the current Ba^{2+} sink is situated some tens of centimetres above the distinct Ba maximum. This offset indicates an upward shift of the SMTZ at site 214 in the recent past, possibly induced by complete burial of the sapropel (stratigraphic Unit II) below the initial SMTZ depth and subsequent *in situ* methanogenesis within this TOC-rich section. Our findings indicate that the decoupling of TOC and solid phase Ba in Black Sea sediments results from diagenetic recycling of Ba at shallow sediment depths. This non-correlation between Ba and TOC is different to the one found in Mediterranean sediments, where the initial close positive correlation between these two components is affected by post-sedimentary aerobic degradation of TOC.

The numerical transport/reaction model CoTReM was used to simulate the downward migration of the SMTZ induced by the strong increase in bottom water sulphate concentrations after the Holocene intrusion of Mediterranean seawater into the formerly limnic Black Sea (~ 9 kyr BP). The simulation showed that the pore water system reached a steady-state situation (in terms of stable depth of the SMTZ) about 3.8 kyr after the first flooding. The diffusion of sulphate into the sediment column was faster than the burial of a particular horizon according to accumulation rates. Therefore, the SMTZ was located within the limnic deposits (Unit III) for several thousands of years. At both sites, the marine sapropel of Unit II was buried below the SMTZ only $\sim 1-2$ kyr BP, which confines the time available for barite recycling since the limnic sediments below probably did not contain significant concentrations of BaSO_4 .

Scanning electron microscopic analyses revealed the presence of two classes of barite in surface sediments at site 214: ellipsoidal “biogenic” and irregularly shaped “non-biogenic” particles. In addition to diagenetic and productivity-related barite formation, precipitation due to oversaturated deep water must therefore be taken into account. This study demonstrates that Ba cannot serve as a productivity tracer in the Black Sea or similar ancient marine environments, such as sediments deposited during Oceanic Anoxic Events (OAEs).