BARIUM IN BLACK SEA SEDIMENTS - REFLECTION OF PRIMARY PRODUCTIVITY OR EARLY DIAGENESIS?

S. Henkel [1]*, K. A. Bogus [2], C. Franke [3], E. Robin [4], A. Bahr [5], G. De Lange [6] and S. Kasten [1]
[1] Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany - susann.henkel@awi.de
[2] Department of Geosciences, University of Bremen, Germany
[3] Centre des Géosciences, Mines ParisTech, Fontainebleau, France
[4] Laboratoire des Sciences du Climat et de l'Environnement, Gif-sur-Yvette, France
[5] Leibniz Institute of Marine Sciences, IFM-GEOMAR, Kiel, Germany
[6] Institute for Earth Sciences, Utrecht University, Netherlands

Abstract

Barite is not restricted to reconstruction of paleoproductivity. If its sedimentary distribution underwent diagenesis, it can reflect changes in sedimentation rate, CH_4 and SO_4^{2-} fluxes. We present data from two cores retrieved in the Black Sea (BS). In contrast to Mediterranean sapropels, where Ba is used as tracer for organic matter accumulation, the primary Ba signal in the BS was lost in shallow sediment depths (>1.5 m). While Ba is inappropriate as a paloeproductivity proxy in the BS, it might serve as a tracer of the sulphate-methane transition (SMT). Migration of the SMT induced by the flooding of the BS was simulated using a numerical model. The results indicate that diagenetic $BaSO_4$ redistribution did not affect the top ~0.8 m of the cores. Steady state could have prevailed since 3.8 ka after the first intrusion of seawater.

Keywords: Black Sea, Sediments, Geochemistry

The Black Sea has experienced severe changes after the last deglaciation concerning its hydrological and geochemical conditions. Due to the flooding by Mediterranean waters, conditions developed from a lacustrine setting with an oxic water column to the largest modern marine anoxic basin in the world. These changes affected the geochemical zonation within the sediment column, pushing the SMT downward and enhancing organic matter (OM) preservation. In ocean basins, barite Ba concentrations in the sediment can be used to reconstruct paleoproductivity [1]. Particularly in the Mediterranean Sea, Ba is a helpful indicator for the original extent of sapropels, which have been affected by post-depositional "burn-down" [2]. However, in zones of sulphate depletion, $BaSO_4$ is subject to dissolution. This diagenetic overprint is decisive for Ba cycling in Black Sea sediments, where the SMT is located at shallow depths of 2-4 m. The authigenic $BaSO_4$ fronts that form at (or slightly above) the SMT potentially record the movement of the SMT [3]. This study is the first to present solid phase Ba data of Black Sea sediments in combination with pore water data. The main questions are: 1) Do distinct Ba/Al variations appear in the sedimentary record? If yes – 2) Does the Ba signal reflect productivity or diagenetic redistribution of $BaSO_4$? And 3) Can relict fronts be used to trace the movement ot the SMT and thus changes in sedimentation rate or the upward methane flux? Two gravity cores 755 (501 m water depth) and 214 (1686 m water depth) were retrieved west of the Crimean Peninsula during RV POSEIDON cruise 317/2 (2004) and RV METEOR cruise M72/1 (2007). In addition to wet geochemical analyses, scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were carried out on bulk sediments to identify the main Ba phases. Pore water profiles indicated barite dissolution below the SMT and precipitation of authigenic $BaSO_4$ fronts at the base of the sulphate zone (Fig.1). By SEM-EDS, barite crystals with sizes <3 µm were found in five samples above the current depth of the SMT. Most of those crystals were irregularly shaped and only a few grains showed morphologies characteristic of biogenic barites. The movement of the SMT since the Holocene flooding of the Black Sea was simulated using a numerical transport and reaction model. The results demonstrate that due to time constraints arising from sedimentation rates and the velocity of diffusion, the upper ~80 cm of the sediment column are not affected by diagenetic barite redistribution. A coupling of OM and Ba in these intervals can be recognised, although the correlation is still ambiguous. The sediments showed an opposite pattern to that in Mediterranean sapropels: OM is well preserved while $BaSO_4$ was efficiently remobilized. Ba is therefore not applicable for studying paleoproductivities in the Black Sea. These findings also suggest implications for the use of the Ba-proxy in analogue ancient settings.

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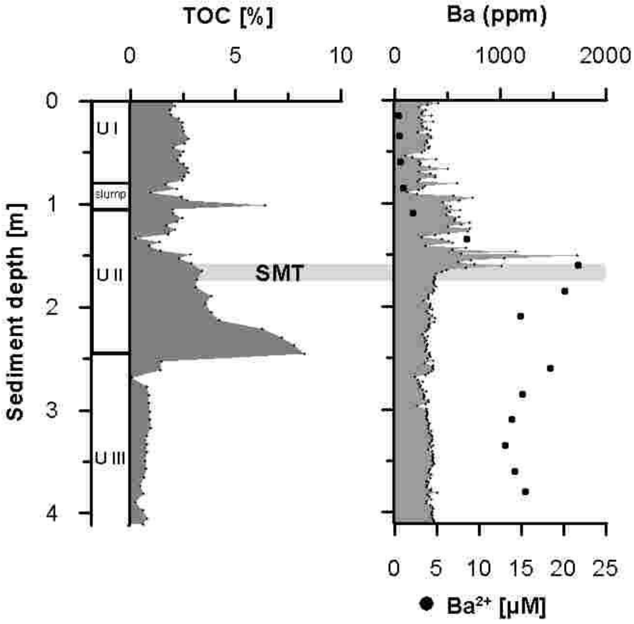

Fig. 1. Total organic carbon (TOC), solid phase and dissolved Ba of core 214. The stratigraphy (Units I-III) was established by Blumenberg et al. [4]. Dissolution of $BaSO_4$ and thus decoupling of Ba from the initial TOC input is observed below the SMT.

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