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Profiles of Particulate Barium in the Mediterranean Sea Coupled to Radium and Strontium Measurements

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In order to better understand the mechanisms leading to barite ($BaSO_4$) formation, a better understanding of the barium cycle is needed. The program BARMED was set up with this aim and five cruises were carried out between February and June 2003 in the western sector of the Mediterranean Sea, at the DYFAMED site. Our goal is to determine the seasonal variability of the barium distribution in the dissolved and all accessible particulate fractions (including phytoplankton, zooplankton and suspended matter) at this site. Radium and strontium, which are chemical analogues of barium, were also being investigated.

Suspended particles were collected in two ways: by filtration on 0.45 μm filters, in the lab, of small volumes of seawater sampled through Niskin bottles, or by in situ filtration on 0.8 μm filters of large seawater volumes using In Situ Pumps. Whereas the first method allowed a better resolution in the profiles of particulate Ba and Sr, the abundance of material collected through the second approach permitted that Ra activity be detected and sequential leachings be performed to discriminate between more or less refractory phases. Ba and Sr were measured using ICP-MS, while the activities of ^{226}Ra and ^{228}Ra were counted by Gamma Spectrometry. Suspended particles obtained from the lab filtration were also subjected to automated scanning electron microprobe analyses for the chemical identification and physical characterization of the barite crystals (cruises 1, 2 and 5 only). These analyses were combined with automated quantitative X-ray analyses of S, Ba and Sr allowing the determination of Ba-barite and Sr-barite concentration profiles in the water column.

Results display clear particulate Ba, ^{226}Ra and barite maxima around 200 m for the

five campaigns, suggesting a preferential formation of barite in sub-surface waters, which could however start upper in the water column in correspondence with the oxygen minimum. In situ Pumps measurements correlate fairly well with measurements performed on small volumes of seawater, except during the bloom period. Yet, although we expected the HCl 3% digestion to leach Ba-barite (Handbook of Chemistry, 1997) most of it was already released through gentler processes (Milli-Q water and HNO_3 1.5 M; Ganeshram et al., Geochim. Cosmochim. Acta 67, 2599-2605, 2003). On the opposite, analysis of plankton shows a significant fraction of Ba linked to barite, up to 75% during the bloom. Based on these preliminary results, we suggest that two separate mechanisms may initiate barite formation: indirect crystallization during organic matter degradation (the most favoured hypothesis as yet) and, of lesser importance, direct precipitation by living organisms.