On the comparison of redox-interfaces structure in Black Sea, Baltic Sea and Oslo Fjord

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Distributions of chemical parameters at the boundary between oxic and anoxic waters were studied at 3 stations; the Black Sea (northeast region), the Baltic Sea (Landsort Deep), and Oslo Fjord (Baerumsbassenget), on board RV 'Ashamba', RV 'Poseidon' and RV 'Uttern' respectively during July–August 2008. Dissolved oxygen (Winkler), hydrogen sulfide, phosphate, polyphosphate, nitrate, nitrite, ammonia and hydrogen sulfide were measured using standard methods. Manganese and iron sprceis were determined photometrically using the formaldoxime and ferrozine procedures respectively The joint analysis of manganese species distributions (dissolved Mn, particulate Mn, and bound Mn), enabled common features to be revealed that demonstrate the similarity in the mechanisms of pelagic redox-layer formation. Our investigations demonstrate that Mn bound in stable complexes with hypothetical P-containing compounds or organic matter (OM) is observed in the redox zones at significant (average: 0.5–1.0 μM) concentrations and is likely present as Mn (III), an intermediate product of Mn (II) oxidation. This bound Mn (III) can explain phosphate distribution in redox interfaces and the formation of the so-called 'phosphate dipole' with a minimum level above the sulfidic boundary, a maximum just below and a rapid increase in concentration within this range. This dipole structure serves as a geochemical barrier that decreases the upward flux of phosphate from the anoxic layer. An application of a coupled hydrophysical biogeochemical 1D RedOx Layer Model allowed to demostrate that the manganese cycle (formation of settling Mn (IV) particles and presence of dissolved Mn (III)) is the main cause of lack of oxygen and hydrogen sulfide contact. Modeling results show that the formation of the 'phosphate dipole' may be connected with manganese cycling and different factors (i.e. mixing, particle sinking rate, presence of Mn in the water column) should affect the peculiarities of the observed distributions at the different geographical locations.

Large MIF on O_2 photo-dissociation and its relevance to Earth wind

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Mass-independently fractionated oxygen have been reported on metal particles extracted from Apllo lunar soils [1, 2]. Ozima *et al*. [3] suggested that it was transported from the Earth's thermosphere to moon by Earth wind. We report the results of detailed quantum mechanical calculations of photo-dissociation of O_2, which showed considerable mass-independent isotopic fractionation of oxygen.

First principles reaction dynamics simulations were performed to compute the photolysis rate for the $B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ electronic transition, which corresponds to Schumann-Runge band. The Born-Oppenheimer approximation was employed in this paper; in the first step the time independent Schrödinger equation only for the electron-motion was solved, and in the second step we performed the wave-packet dynamics for the nuclei-motion in the potential energy curves. The theoretical photo-dissociation cross section as a function of wavelength of excitation light was estimated by the Fourier transform of the autocorrelation function, $\langle\phi(0)|\phi(t)\rangle$ [4]. Assuming the Boltzmann distribution for vibrational and rotational state, we summed up to get the total cross section.

The photolysis rate is calculated by integrating the product of the light intensity and the photo-dissociation cross section calculated above. We took the initial intensity as the black body radiation at 6000 K, and we considered the column density above the simulating altitude for atenuation of the light intensity. Using the Boltzmann distribution at 1000 K at the altitude of 300 km [5], we estimated that $\Delta^{17}O$ of dissociated O-atoms is 15.1 ‰, which is similar to the values observed in lunar metallic particles ($\Delta^{17}O \sim 30$ ‰) [1, 2]. This result encourages the Earth wind hypothesis [3].

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