

DEEP BASIN TURBIDITES AS A PREVIOUSLY UNRECOGNIZED SINK FOR HYDROGEN SULFIDE IN THE BLACK SEA

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Abstract

Speciation of sulfur and iron was investigated in the solid phase of Black Sea sediments (Unit 1 type and turbidites) collected during the R/V Knorr 2003 Black Sea expedition. Other than pyrite, solid phase sulfur in the upper Black Sea sediments existed as inorganic S(0) and acid-volatile sulfides (predominantly FeS) in the anoxic basin turbidites, and organic sulfur as humic sulfur in the uppermost 0-2 cm of the central basin sediments. A mathematical model was designed to simulate the temporal changes in the Fe-S chemistry in the anoxic basin turbidites, and successfully showed that turbidites were a previously unrecognized sink for sulfide in the Black Sea and can account for 14% of the annual burial of sulfur.

Keywords: Black Sea, Sediments, Geochemistry, Redox

Deep anoxic basin turbidites are a commonly reported feature of deep-basin Black Sea sediments [1, 2] but their chemical composition remained unexplored except for total elemental analysis. The recently found unexpected variability in the porewater chemistry [3] in the anoxic basin sediments could well be due to the differing solid phase compositions as a result of the presence of turbidites which were emplaced there after the 1999 earthquakes (mag. 7.4 and 7.2) in northwestern Turkey. In order to address these issues and to assess the impact of turbidites to Black Sea anoxic basin sulfur chemistry, detailed solid phase speciation of Fe and S will be reported and a mathematical model will be presented.

Pyrite – sulfur was the major phase in all anoxic basin cores [200-400 μmol (g dry wt)⁻¹]. However, zerovalent sulfur and humic sulfur also reached very significant levels: up to about 109 and 80 μmol (g dry wt)⁻¹, respectively [4]. Humic sulfur enrichment was observed in the surface fluff layers of the eastern central basin sediments where Unit-1 type depositional conditions prevail. Elemental sulfur accumulated as a result of porewater sulfide oxidation by reactive iron oxides in turbidities from the anoxic basin margin and western central basin sediments. The accumulation of elemental sulfur to a level close to that of pyrite-sulfur in any part of central Black Sea sediments has never been reported before and this finding indicates deep basin turbidites prevent the build-up of dissolved sulfide in the sediment. This process also contributes to diagenetic pyrite formation whereas, in the non-turbiditic parts of the deep basin, water column formed (syngenetic) pyrite dominates the sulfur inventory. Our study shows that the interactions between depositional patterns (Unit 1 vs. turbidite), redox state of overlying waters (oxic-suboxic-sulfidic) and organic matter content determine sulfur speciation and enable the accumulation of elemental sulfur and organic sulfur species close to a level of pyrite-S.

A time-variable mathematical model was constructed to further explore the non-steady-state diagenesis of Fe-S species in a turbidite mud emplaced on normal anoxic-sulfidic deep Black Sea sediments. The turbidite layer was 20 cm thick and initially contained 80 μmol (g dry wt)⁻¹ of Fe(III) in the form of goethite, which led to the rapid (1 day) oxidation and depletion of porewater sulfide and formation of solid phase sulfur intermediates such as S(0) and FeS. S(0) accumulated faster than FeS and was present in the sediment at high concentrations after 5-8 years following the deposition of the turbidite. Reduced iron was in the solid phase long after the consumption of all Fe(III), enabling the coexistence of S(0) and solid-phase reactive iron (which has not been sulfidized yet) for a long period of time. The porewaters had sub-micromolar concentrations of dissolved sulfide in the first 2 years after deposition with Fe (II) exceeding 1 mM. The turbidite layer served as a sink for the sulfide from the overlying waters for about 10 years after its deposition. These results agreed with the solid phase data for the western central station (30) and our suggestion that an earthquake-induced turbidity current could have transported iron oxides from the southwestern shelf/slope as far as 150 km in the western central Black Sea and caused massive oxidation of sulfide after the 1999 earthquakes in Northwestern Turkey.

Considering the ubiquity of the deep-basin turbidites found in the Black Sea and the dense tectonic activity on the Northern Anatolian Fault in Northern Turkey, an estimated 0.144 Tg sulfur / year could be buried as S₈ and FeS₂ due to the earthquake-induced turbidites. This value is about 14 % of the annual sulfur burial (as pyrite) and 3-5 % of the annual sulfide oxidation due to lateral injections of oxic Mediterranean waters to the anoxic-sulfidic Black Sea waters. It is highly likely that earthquake-induced turbidites and subsequent sulfide

oxidation in the deep basin represent a previously unrecognized sink in the budget of hydrogen sulfide in the Black Sea.

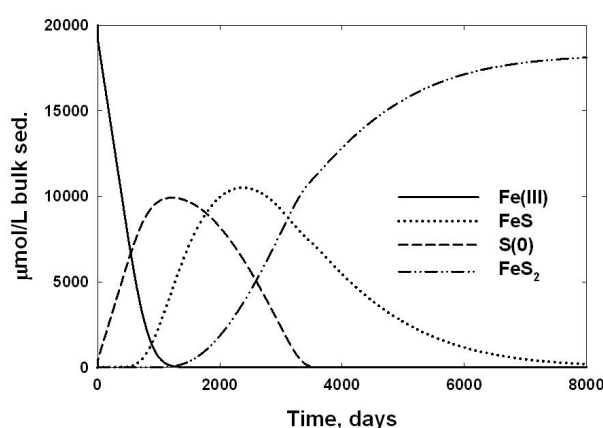


Fig. 1. Model output for the solid phase S-Fe species during the 8000 day simulation period. Time 0 indicates the deposition of the Fe(III) containing turbidite. Initially only dissolved sulfide and solid phase Fe(III) are present in the system. As the reactions progress sulfur intermediates, S(0) and FeS form in the solid phase. With time S(0), FeS and dissolved sulfide form pyrite, and the system reaches steady state after about 7000 days or 19.2 years.

References

- 1 - Jipa, D. C., 1974. Graded bedding in recent Black Sea turbidites: a textural approach. In *The Black Sea – Geology, Chemistry and Biology* (Edited by Degens, E. T. and Ross, D. A.). Published by The American Association of Petroleum Geologists, Tulsa, Oklahoma, U.S.A.
- 2 - Lyons, T.W., 1991. Upper Holocene sediments of the Black Sea: summary of the Leg 4 box cores (1988 Black Sea Oceanographic Expedition). In: *J. W. Murray and E. Izdar (eds.), Black Sea Oceanography*, NATO, Adv. Stud. Inst. Ser., Kluwer, Dordrecht, pp. 401-441.
- 3 - Kononov, S.K., Luther, G.W., and Yucel, M., 2007. Porewater redox processes and sediments in the Black Sea sediments. *Chemical Geology* **245**, 254-274.
- 4 - Yucel, M., Kononov, S. K., Moore, T., Janzen, C., Luther, G. W. (in press) Sulfur speciation in the upper Black Sea sediments, *Chemical Geology*.