

The characterization of sedimentary iron in the Gulf of Trieste (N Adriatic)

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The characterization of sedimentary iron is important from a variety of points of view in marine geochemistry. Mineralogically, there are two groups of Fe oxides in marine sediments which cannot be clearly distinguished from each other, i.e. amorphous iron oxyhydroxides, and various iron oxides. Fe can act as an electron acceptor in the microbial degradation of sedimentary organic matter in anoxic sediments (Froelich *et al.*, 1979). Besides dissimilatory reduction, the iron oxides are also reduced by organic acids (Luther *et al.*, 1992) and in the presence of other reduced electron acceptors, i.e. sulphides. Due to the particulate nature of Fe oxides, bioturbation and other bulk transport mechanisms are important regulators of Fe reduction (Canfield *et al.*, 1993). A major difficulty in quantifying bacterial Fe reduction lies in distinguishing it from competing non-enzymatic reactions with reduced inorganic compounds. The concentration of solid-phase iron

and its reactivity toward sulphide are limiting factors in the formation of pyrite in marine sediments (Canfield *et al.*, 1992).

In order to decode the complex role of iron during early diagenesis in coastal marine sediments in the Gulf of Trieste (N Adriatic), whose reduction was already shown to be significant component in anaerobic organic carbon degradation (Hines *et al.*, 1997), we used a combination of solid phase analyses of iron-containing sedimentary phases employing XANES and SEM-EDS analyses. Waters overlying these bioturbated sediments are often oxygen depleted in late summer and occasionally become anoxic due to strong vertical temperature and salinity gradients.

Materials and methods

Sediment cores (approx. 6 cm diameter) were taken by SCUBA at station F (45° 32' 43"N, 13° 33' 13"W)

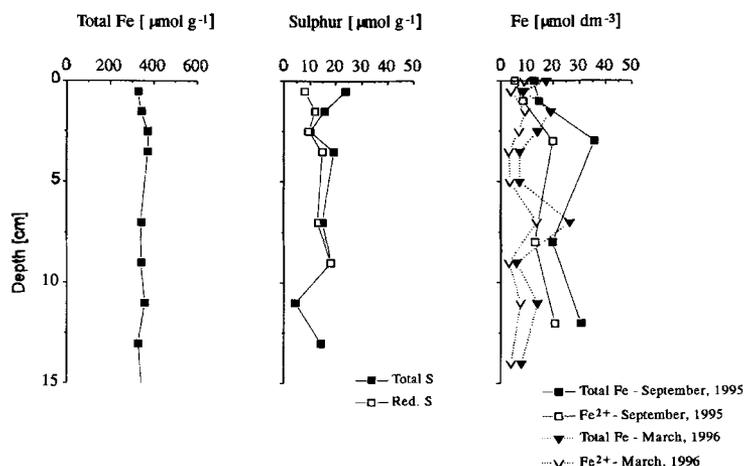


FIG. 1. Pore water and sediment chemistry of the site F in the Gulf of Trieste (N Adriatic).

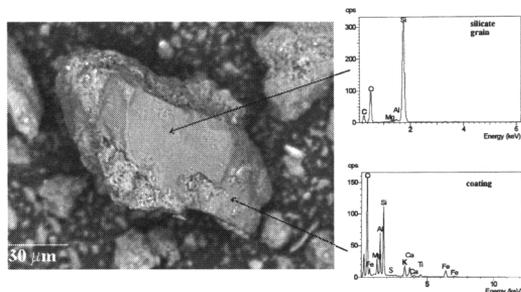


FIG. 2. SEM micrograph of a silicate grain and corresponding EDS spectra.

in the central part of The Gulf of Trieste. Sediment was extruded and sectioned in 1, 2 or 4 cm intervals in a N_2 -filled glove bag. Dissolved total Fe in pore water samples was determined by AAS, while the concentration of Fe^{2+} ions was measured spectrophotometrically using Ferrozine. Sediment samples were prepared by freeze drying and gentle grinding. The total iron content was obtained using an $HF/HClO_3/HNO_3$ dissolution scheme with final analysis by AAS. Total sulphur and reducible sulphur were determined with a CHNS analyser and by the chromium reduction method, respectively. Scanning electron microscopy was performed on a JEOL JSM 5800 SEM equipped with Link ISIS 300 EDS. EDS observations were made on graphite coated particles. XANES spectra at the Fe K-edge were measured at the EXAFS II station in HASYLAB at DESY (Hamburg, Germany). Synchrotron radiation from the DORIS storage was focused by a Ni-coated mirror on a Si(111) double-crystal monochromator with 1.5 eV resolution at 7 keV. Harmonics were effectively eliminated by detuning the monochromator crystal using a stabilisation feedback control. Powdered samples were prepared on multiple layers of adhesive tape. A Fe K-edge jump of only about 0.1 was obtained at the total absorption thickness of ~ 1.5 due to the low concentration of Fe in the sediment. Reference spectra on empty tapes were taken under identical conditions.

Results and discussion

Bulk sediment chemical analysis (Fig. 1), visual examination and mineralogy of the sediment indicate that the sediment in profile is practically uniform. The concentration of total dissolved Fe and Fe^{2+} increased with depth in both sampling periods (Fig. 1) indicating the reduction of iron oxide or iron hydroxide. The concentration of dissolved sulphide

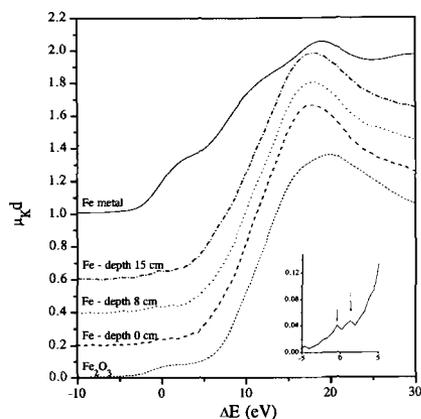


FIG. 3. Normalized Fe K-edge profiles, displaced vertically, for the sediment and reference samples. Energy scale is relative to the Fe K-edge in Fe metal (7112 eV). The average of the three spectra measured in sediment in the energy region of the pre-edge resonances (indicated by arrows) is shown in the inset.

was low ($< 1.0 \mu M$) in March 1996, while in September 1995 reached $25 \mu M$.

Using SEM, we observed that Fe minerals are dispersed on the surface of the sediment and bound to the surface of layered silicates (Fig. 2).

Normalised Fe K-edge XANES spectra of the sediment samples are shown in Fig. 3, together with the spectra of reference samples of Fe_2O_3 , and Fe metal. The K-shell contribution is obtained by removing the extrapolated pre-edge ($-250 \dots -50$ eV) trend. Spectra are normalized to a unit edge jump. The zero energy is taken at the first inflection point in the Fe metal spectrum at 7112 eV, which marks the 1s ionization threshold in the Fe metal. The Fe XANES spectra of the three sediment samples at the different depth exhibit identical edge structure, indicating that the local environment of Fe atoms is the same in all three samples.

The energy position of the edge is correlated with the valence state of the atom in the sample: with increasing oxidation state the edge is shifted to higher energies (Wong *et al.*, 1984). Energy shifts of the Fe K-edge of all three samples, taken at the edge inflection point, coincide with the energy position of the Fe K-edge in the reference Fe_2O_3 sample, indicating that average valence state of iron in the sediments is Fe^{3+} . The two resonances, separated by about 2 eV, are characteristic for octahedral coordinated Fe atoms (Petiau and Calas, 1983).