

Mössbauer spectroscopy and X-ray fluorescence studies on sediments from the methanic zone of the Helgoland mud area, North Sea

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Abstract ⁵⁷Fe Mössbauer spectroscopy (MS) and X-ray fluorescence spectroscopy (XRF) were used to determine the identity of iron(III) oxides in surface (top 30 cm) and sub-surface (>30 cm – 500 cm) sediments from the Helgoland mud area in the German Bight of the North Sea. A 500 cm-long sediment core was cut in 25 cm sections while only the top 10 cm of a 30 cm-long sediment core was sampled. Using a MIMOS spectrometer, MS spectra were recorded at 293 K (RT) in backscattering geometry. At 80 K and 5.5 K, MS analysis was carried out in transmission geometry. At RT and 80 K only illite was observed, but at 5.5 K lepidocrocite was revealed in the MS spectra. The relation between Fe(III) and Fe(II) doublets of illite did not significantly vary with depth, but the relative amount of lepidocrocite increased with depth reaching about 24 % of iron phases, as revealed by MS. XRF measurements showed that the amount of Fe in the sediments varied with depth but was always less than 4 % of total elemental composition. The main component of the sediment was silica and its depth profile alternated with those of other elements, especially

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aluminium and iron. It was observed that elevated concentrations of dissolved iron in the subsurface sediment of the Helgoland mud area correlated with the depth-wise distribution of distinct microbial populations presumably due to microbial reduction of excess bioavailable iron minerals such as lepidocrocite. These results are thus, important in the context of microbe-mineral interactions in marine sediments as iron oxides are an electron acceptor for microbial anaerobic respiration.

Keywords Marine sediments · Vertical distribution · Helgoland mud area · Mössbauer spectroscopy · X-ray fluorescence spectroscopy

1 Introduction

The Helgoland mud area in the German Bight of the North Sea extends over approximately 500 km² and has a water depth of less than 30 m [1]. It represents one of the few depocenters of fine-grained sediments in the North Sea. Between 750-1550 years ago, the average sedimentation rate was estimated to be high (13 mm/yr) and presently, it is at 1.6 mm/yr [1]. High sedimentation rates in the past, linked to the disintegration of substantial parts of the Helgoland Island, have been suggested to have facilitated the burial of reactive iron oxide phases.

Previously, we reported a study on the relationships between geochemical profiles and the distribution of microbial populations [2]. Pore water profiles of the sediments showed elevated concentrations of dissolved Fe(II) below the intersecting region between opposing fluxes of sulphate and methane (sulphate-methane transition, SMT) in the Helgoland mud area. Several mechanisms, mostly pointing towards microbial activities, were discussed to explain the observed deep reduction Fe (III) [2].

In order to determine the exact nature of the reactive iron mineral(s) present in the Helgoland mud area, Mössbauer spectroscopy was conducted, as this technique is known to be a powerful tool to investigate such Fe-containing materials as alloys, minerals and biological objects [3]. X-ray fluorescence analysis was also carried out to check the proportion of Fe in relation to other elements.

2 Experimental

Surface (top 30 cm) and subsurface (> 30 cm – 500 cm) sediments from the Helgoland mud area in the German Bight of the North Sea (54°5.01'N 7°58.01'E), were collected using a Multicorer (MUC) and a 5m long gravity corer (GC), respectively. The 500 cm-long sediment core was cut in 25cm sections while only the top 10 cm of the 30 cm-long sediment core was sampled. Therefore, 21 samples were obtained and each one was dry-frosted at about 200K and kept in glass containers.

⁵⁷Fe Mössbauer spectra of these samples were recorded at 293K in backscattering geometry using a MIMOS spectrometer [4] detecting 14.4 keV radiation with a ⁵⁷Co (Rh) source with an activity of about 80 mCi. Also, ⁵⁷Fe Mössbauer spectra were recorded at 80K and 5.5K, for selected samples covering the surface and deeper sediments [2], in transmission geometry with a 8 mCi ⁵⁷Co(Rh) source using a conventional

Table 1 Mean hyperfine parameters obtained from the fitting of spectra of sediment samples of the sediment core measured at temperatures of 293K, 80K and 5.5K

	IS(mm/s)	EQ(mm/s)	H(T)	Γ (mm/s)	%
T=293K					
Fe(III) illite	0.32(2)	0.61(2)	-	0.50(4)	70.8(20)
Fe(II) illite	1.13(1)	2.61(1)	-	0.45(3)	30.2(22)
T=80K					
Fe(III) illite	0.43(1)	0.60(2)	-	0.31(1)	70.1(8)
Fe(II) illite	1.24(1)	2.76(2)	-	0.35(1)	28.9(8)
T=5.5K					
Fe(III) illite	0.40(7)	0.78(8)	-	0.31(1)	55.8(11)
Fe(II) illite	1.29(8)	2.89(9)	-	0.36(1)	24.6(17)
Lepidocrocite	0.36(10)	0*	46.7(6)	0.69(1)	17.7(7)

*The parameter was fixed

IS, EQ, H, Γ are isomer shift, quadrupole splitting, magnetic field and full width at half maximum, respectively. IS is given relative to α -Fe at room temperature. % stands for the relative amount

constant-acceleration Mössbauer spectrometer (WissEL GmbH, Starnberg, Germany) equipped with a bath helium cryostat. The absorbers were prepared by placing the powdered samples of about 200 mg, taken from the first prepared glass containers, between acrylic platelets of a sealed sample holder. The fit of the spectra was done separately with two programs NORMOS, sold by WissEL, and RECOIL [5], and the results obtained compared between them. The fitting procedure was done using Lorentzian profiles and allowing all parameters being free except for equal line widths and intensities of each site. Isomer shifts are given relatively to iron metal at room temperature.

WD-X-ray fluorescence measurements were performed with a Phillips, MagiX Pro instrument working with 4kW and 125 mA. The mass of powdered samples was about 400 mg and the mass of flux material (LiBO_2) is about 5.2 g.

3 Results and discussion

Mössbauer spectra of sediments of all 20 samples of the 5 m long sediment core were recorded at 293K in backscattering geometry using MIMOS spectrometer. Some of the samples, from different depths, were also measured at 293K in transmission geometry, to confirm results obtained by backscattering geometry.

Figure 1 shows characteristic spectra obtained for a sediment sample at different temperatures. At room temperature the spectra, both backscattering and transmission) have two possible solutions. At 150K (spectra not shown) and especially at 80K (e.g. Fig. 1) one can see a shoulder on each spectrum at ca. -0.2 mm/s. It proves that the parameters obtained from the fitting procedure and shown in Table 1 are the correct ones. The parameters corresponded to illite [6, 7], which is a very common constituent of soils, clays, and shales.

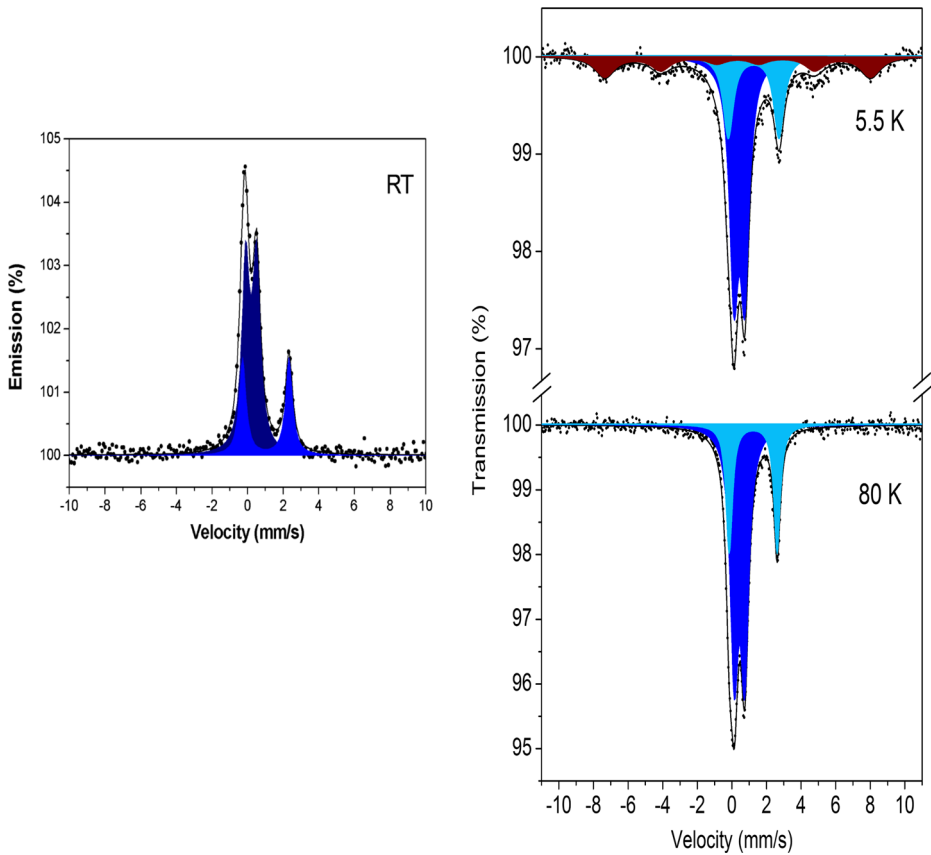


Fig. 1 Mössbauer spectra of a sediment sample from the 380–405 cm depth at different temperatures. Blue colours show the presence of illite while brown colour depicts the presence of lepidocrocite

It is defined as a clay-sized, nonexpanding, dioctahedral, aluminous potassium mica-like mineral.

Corroborating the solution obtained by fitting the spectra is the fact that the temperature dependence of isomer shift (IS) and quadrupole splitting (EQ) were in good agreement with theory [7]. IS of both doublets and EQ of Fe (II) doublet slightly increased with cooling, while EQ of Fe(III) doublet remained constant, within the error. The fraction of Fe(II) also remained constant with cooling (see Table 1).

At 5.5K, besides the two doublets corresponding to illite, we assigned lepidocrocite (γ -FeOOH) to the Fe(III) sextet (Fig. 1 and Table 1). The absence of magnetic sites at 293K and 80K spectra corroborates that this sextet was not an evidence of other iron oxides or hydroxides [8]. X-ray diffraction can not be used here to exclude the presence of ferrihydrite because of very small particle size of these minerals. It is known that ferrihydrite only exists as a fine grained and highly defective nanomaterial. The high abundance of lepidocrocite as an abundant iron (III) mineral is also consistent with results of sequential chemical extraction of iron minerals in the Helgoland mud area which showed high proportion of amorphous iron (III) mineral phases [2].

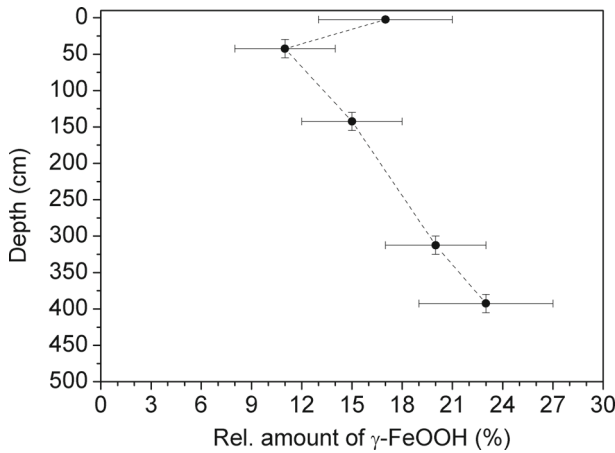


Fig. 2 Depth profile of lepidocrocite in sediment core of the Helgoland mud area

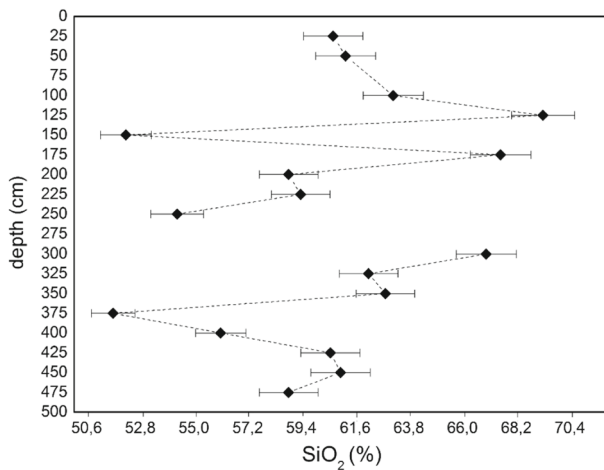


Fig. 3 Depth profile of silica in sediment core of the Helgoland mud area, as determined by XRF measurements

The amount of high-spin Fe(II) of illite did not change much with cooling down to 5.5K, but the amount of high-spin Fe(III) of illite decreased with cooling since γ -FeOOH is paramagnetic at 80K and magnetically ordered at 5K. So, part of the Fe(III) doublet observed at 293K and 80K appears as a sextet at 5.5K.

Although the relation between Fe(III) and Fe(II) doublets of illite did not change significantly with depth, the relative amount of lepidocrocite did vary with depth as seen in Fig. 2.

XRF was also applied to the 20 sediment samples obtained from the 5 m long sediment core in order to check the proportion of Fe in relation to other elements. Figures 3 and 4 shows the depth-wise variation in the amount of silica and different oxides. The main

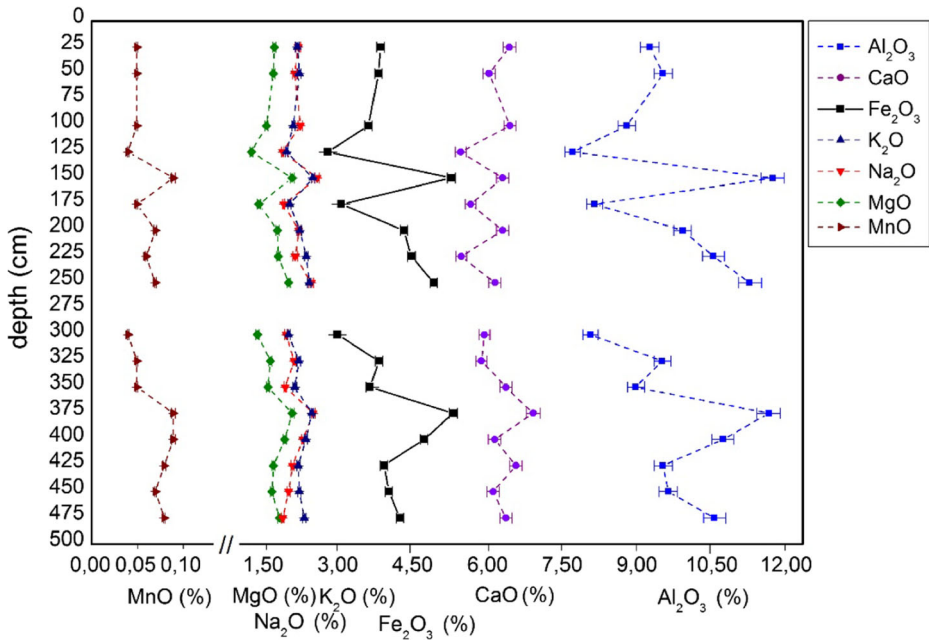


Fig. 4 Depth profile of several oxides in sediment core of the Helgoland mud area, as determined by XRF measurements

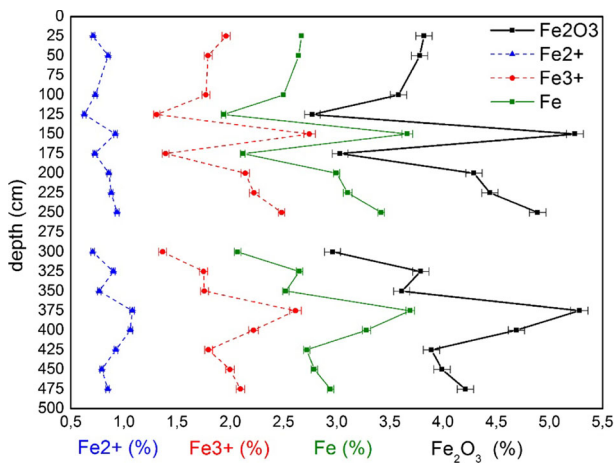


Fig. 5 Depth profile of total amount of Fe, Fe(II) and Fe(III) in sediment core (calculations done with Mössbauer analysis and XRF data) and depth profile of Fe_2O_3 , as determined by XRF data

component of the sediment is silica and its depth profile alternated with those of other elements, especially aluminium and iron.

From the analysis of Mössbauer spectra the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was obtained. Using XRF results for total amount of Fe_2O_3 for each sample, the total amount of iron was obtained. Figure 5 shows the Fe profile with depth, as well as Fe^{2+} , Fe^{3+} and Fe_2O_3 . The iron profile

obtained from XRF measurements is in accordance with that obtained from Mössbauer spectroscopy. The more iron exists (as seen by XRF) the more Fe^{3+} is observed by Mössbauer spectroscopy. It seems that if the amount of Fe is small it enters on the Fe^{2+} octahedral site of illite. If the total Fe amount increases, than Fe prefers to enter in tetrahedral sites of illite as Fe^{3+} because it is more energetically favourable due to its smaller ionic radius: 63 pm for Fe^{3+} (tetrahedral surrounding) in contrast with 92 pm for Fe^{2+} (high-spin octahedral surrounding). According to XRF results, excess Fe^{3+} substitutes Si in the charge state Si^{4+} .

4 Conclusions

By means of Mössbauer spectroscopy, the vertical distribution of iron species in the sediments collected from the Helgoland mud area in the North Sea was studied. At RT and 80K only illite was observed, but at 5.5K, the presence of lepidocrocite was revealed. The relation between Fe(III) and Fe(II) doublets of illite did not significantly vary with depth, but the relative amount of lepidocrocite increases with depth reaching about 24 % of iron phases, as revealed by MS. From XRF measurements, the amount of Fe in the sediments varies with depth but was always less than 4 %. The main component of the sediment was silica and its depth profile alternated with those of other elements, especially aluminium and iron.

This mineralogical characterization, especially the iron mineral phases, is a contribution in the ongoing effort to understand the mechanisms of iron reduction in the subsurface sediments of the Helgoland mud area. The observation that elevated concentrations of dissolved iron in the subsurface sediment of the Helgoland mud area correlated with the depth-wise distribution of distinct microbial populations [2], presumably due to microbial reduction of excess bioavailable iron minerals such as lepidocrocite is therefore important in the context of microbe-mineral interactions in marine subsurface sediments.

References

1. Hebbeln, D., Scheurle, C., Lamy, F.: *Geo-Marine Lett.* **23**, 81–90 (2003)
2. Oni, O., Miyatake, T., Kasten, S., Richter-Heitmann, T., Wagenknecht, L., Fischer, D., Blumers, M., Shylin, S., Ksenofontov, V., Costa, B.F.O., Klingelhöfer, G., Friedrich, M.W.: *Front. Microbiol.* **6**(365), 1–15 (2015)
3. Güttlich, P., Garcia, Y.: *Mössbauer Spectroscopy*, pp. 23–28. Springer, Berlin (2012)
4. Klingelhöfer, G., et al.: *JGR* **108**(8067), 8.1–8.17 (2003)
5. Lagarec, K., Rancourt, D.G.: *Nucl. Instrum. Methods Phys. Res. B* **129**, 266–280 (1997)
6. Murad E., Wagner U.: *Hyperfine Inter.* **91**, 685–688 (1994)
7. Murad E., Wagner U.: *Clay Minerals* **29**, 1–10 (1994)
8. Greenwood, N.N., Gibb, T.C.: in *Mössbauer Spectroscopy*, p. 240. Chapman and Hall Ltd, London (1971)