A Mössbauer spectroscopic study of the iron redox transition in eastern Mediterranean sediments

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Abstract—Fe cycling at two sites in the Mediterranean Sea (southwest of Rhodes and in the North Aegean) has been studied, combining the pore water determination of nutrients, manganese, and iron, citrate–bicarbonate–dithionite (CDB) and total sediment extractions, X-ray diffraction, and 57Fe Mössbauer spectroscopy (MBS). At the Rhodes site, double peaks in the CDB-extractable Mn and Fe profiles indicate non-steady-state diagenesis. The crystalline iron oxide hematite, identified at both sites by room temperature (RT) MBS, appears to contribute little to the overall Fe reduction. MBS at liquid helium temperature (LHT) revealed that the reactive sedimentary Fe oxide phase was nanophase goethite, not ferrhydrite as is usually assumed. The pore water data at both sites indicates that upon reductive dissolution of nanophase goethite, the upward diffusing dissolved Fe2+ is oxidized by Mn oxides, rather than by nitrate or oxygen. The observed oxidation of Fe2+ by Mn oxides may be more common than previously thought but not obvious in sediments where the nitrate penetration depth coincides with the Mn oxide peak. At the Rhodes site, the solid-phase Fe(II) increase occurred at a shallower depth than the accumulation of dissolved Fe2+ in the pore water. The deeper relic Mn oxide peak acts as an oxidation barrier for the upward diffusing dissolved Fe2+ thereby keeping the pore water Fe2+ depth. At the North Aegean site, the solid-phase Fe(II) increase occurs at approximately the same depth as the increase in dissolved Fe2+ in the pore water. Overall, the use of RT and cryogenic MBS provided insight into the solid-phase Fe(II) gradient and allowed identification of the sedimentary Fe oxides: hematite, maghemite, and nanophase goethite.

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1. INTRODUCTION

The geochemical cycle of iron is coupled to the cycles of many other elements in marine sediments through various reduction and oxidation reactions. Iron reduction may be coupled to the oxidation of reduced solutes such as sulfide (Pyzik and Sommer, 1981) or to the bacterial oxidation of organic matter (Lovley and Phillips, 1988). In addition to iron oxides, bacteria can directly couple the reduction of Fe(III) bound in smectites to organic matter oxidation (Kostka et al., 1999). The tan-green color transition in pelagic sediments is indicative of clay-bound Fe(II)/Fe(III) transition and the increase in the Fe(II) content with depth is in accordance with the increase in the absolute amount of reductive Fe(III) dissolution and liberation of dissolved Fe2+ in the pore water. Overall, the use of RT and cryogenic MBS provided insight into the solid-phase Fe(II) gradient and allowed identification of the sedimentary Fe oxides: hematite, maghemite, and nanophase goethite.

whereas direct detection methods such as X-ray diffraction (XRD) are often limited by the poor crystallinity or relatively low abundance of iron oxides in sediments. In a few instances, specific iron oxide minerals have been identified in marine sediments. For example, Slomp et al. (1996) identified poorly crystalline akageneite and ferrhydrite by differential XRD and showed that they play a dominant role in P binding in North Sea sediments. Drodt et al. (1997) demonstrated the presence of small amounts of hematite and goethite in Peru Basin sediments using Mössbauer spectroscopy (MBS). Van der Zee et al. (2003) have recently identified nanogoethite in several lake and marine sediments.

We applied 57Fe MBS to sediments from the Mediterranean Sea to examine iron speciation in terms of in situ redox conditions. The technique is sensitive to valence state, coordination, and magnetic properties of the iron phases. The information obtained from MBS was also combined with data obtained by other geochemical techniques: sediment extractions with citrate–dithionite–bicarbonate (CDB); whole sediment elemental analyses; pore water extraction; and XRD measurements. Our study shows that (1) the reactive iron oxide is nanophase goethite, (2) Mn oxides can be the predominant oxidant for upward diffusing Fe2+, and (3) the increase in solid-phase Fe(II) is not necessarily located close to the depth where reductive Fe(III) dissolution and liberation of dissolved Fe2+ occurs.

2. METHODS

2.1. Research Area

The sediment from a box core (SL48BC) and a gravity core (SL50GC) from a station southwest of Rhodes with a double Mn oxide
peak and a box core (SL78BC) from a station in the North Aegean with a high Mn content (up to 326 \( \mu \text{mol Mn g}^{-1} \)) were collected during the 1999 Smilable cruise in the Mediterranean Sea on the RV "Prof. Logachev." The high Mn concentrations in the sediment, more pronounced at the North Aegean than at the Rhodes site, indicate the influence of Black Sea water that is trapped in Mn and other phases during the North Aegean through the strait of Dardanelles (Zeri et al. 2000; Lykousis et al., 2002). The Rhodes site is located at 35.46°N, 27.34°E at a water depth of 706 m. The estimated sedimentation rate for the area is 30–35 cm ky\(^{-1}\) (Lykousis et al., 2002), but are subject to large uncertainty due to extensive slumping processes.

2.2. Sediment Handling and Pore Water Analyses

Sediment cores were sliced at in situ temperature (13°C) in a nitrogen-filled glovebox immediately after collection. Pore water was collected by squeezing (De Lange, 1992) for manganese and iron, and by centrifugation (15 min, 4400 g) filtration through Acrodisc polysulfone filters for nitrate, ammonium, and phosphate. All pore water samples were split under dry nitrogen into several portions. Subsamples for HPO\(_4^{2-}\), Fe, and Mn analyses were acidified to pH 1 (12 M HCl). The samples were immediately analyzed for NO\(_3^-\), NH\(_4^+\), and HPO\(_4^{2-}\) (Grasshoff, 1983) on-board using a Technicon TRAACS-800 autoanalyzer. Precision was better than 1.5% for NO\(_3^-\), 3% for NH\(_4^+\), and 1% for HPO\(_4^{2-}\). Diluted (10×) pore water samples were analyzed in triplicate for total Fe and Mn at Utrecht University using a Perkin Elmer 4100 ZL Zeeman atomic absorption spectrometer. Precision was better than 5% for Fe and 4% for Mn. Oxygen profiles were measured on deck in a separate subcore using a polarographic microelectrode (Brendel and Luther, 1995).

2.3. Solid-phase Chemical Analyses

Freeze-dried and ground sediment (Teflon mortar and pestle) was extracted with CDB (pH = 7.3, 8 h, 20°C); to 0.25 g sediment 20 mL of 0.3 M Na-citrate, 2.5 mL of 1 M NaHCO\(_3\), and 0.5 g Na\(_2\)S\(_2\)O\(_3\) was added. The sediment residue was washed once with 1 M MgCl\(_2\) (pH = 8, 30 min, 20°C). Additional details about this extraction procedure can be found in Ruttenberg (1992). The P, Mn, and Fe concentrations in the CDB extract were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The HPO\(_4^{2-}\) analyses of the MgCl\(_2\) rinse were performed colorimetrically on a Hitachi U-1100 spectrophotometer using the method of Strickland and Parsons (1972). Additional Mössbauer spectra were recorded for a number of reference materials, because all iron oxides including nanophase and poorly crystalline Fe oxides such as ferrihydrite are resolved at LHT but not at RT. The ferric doublets and collapsed sextets in the RT Mössbauer spectra split up into well-defined sextets with highly characteristic hyperfine parameters allowing easy identification of all the known iron oxides when the same samples are measured at LHT (Murad and Johnston, 1987). The source was kept at RT, whereas the sediment samples were measured in a flow type cryostat and kept at 4.2 K.

2.4. X-ray Diffraction

Bulk sediment from the 16.5–22.5 cm depth interval of the Rhodes site (gravity core) and the 2.4–3.4 cm depth interval of the North Aegean site were analyzed for their mineralogical composition by powder XRD (Philips X’pert PW3710 system, \(\theta\)-2\(\theta\) diffractometer with Kevex counter) using Cu-K\(_\alpha\) radiation. Scans were performed in step-mode from 5° to 70° with a step size of 0.02° and 7 s per step. The diffractometer was operated at 45 kV and 40 mA with an automatic divergence slit using a mask of 10 mm, a scatter slit of 1°, and a receiving slit of 0.2 mm. The sediment was packed in a filled trough, which was continuously spun during the scan. Mineralogical identifications were done with the JADE software package.

2.5. Mössbauer Spectroscopy

Transmission \(^{57}\)Fe Mössbauer spectra were recorded in constant acceleration mode with a velocity range of \(\pm 11\) mm/s. Both source and sample were kept at room temperature (RT). All center shifts are relative to an \(^{57}\)Fe-enriched \(\alpha\)-Fe absorber foil at RT. Data were collected with a 1024-channel analyzer and folded to obtain a flat background. The ideal absorber thickness (Rancourt et al., 1993) was estimated to be \(-150\) mg using the Mössbauer analysis software for windows Recoil (Lagarac and Rancourt, 1998). The folded RT spectra were analyzed with the Voigt-based fitting method (Rancourt and Ping, 1991) available in Recoil. Uncertainties were calculated from the covariance matrix.

Fe(III) and Fe(II) in high spin state can be easily distinguished due to the large difference in their center shifts (Rancourt, 1990). Fe(II) in pyrite is in low spin state and would have a similar center shift as high spin Fe(III). However, the sedimentary S content was always lower than 0.5 \(\mu\text{mol g}^{-1}\). Thus even if all S were bound in pyrite, the Fe in pyrite would be less than 0.1% of the total Fe and the error due to low spin Fe(II) in the percentage Fe(III) and Fe(II) estimates is negligible in these sediments.

Additional Mössbauer spectra were recorded at liquid helium temperature (LHT, 4.2 K) for selected sediment samples, because all iron oxides including nanophase and poorly crystalline Fe oxides such as ferrihydrite are resolved at LHT but not at RT. The ferric doublets and collapsed sextets in the RT Mössbauer spectra split up into well-defined sextets with highly characteristic hyperfine parameters allowing easy identification of all the known iron oxides when the same samples are measured at LHT (Murad and Johnston, 1987). The source was kept at RT, whereas the sediment samples were measured in a flow type cryostat and kept at 4.2 K.

The LHT spectra were analyzed with the extended Voigt-based fitting method (Lagarac and Rancourt, 1997) available in the Recoil software package.

A model was fit to the data with the least number of components necessary (see “Results”); components were only added to the model if this significantly reduced the chi squared of the fit. The percentage area of each model component in the spectrum (total area is 100%) is equal to the percent of the total Fe that is present in that component, assuming equal Mössbauer recoilless fractions for all Fe phases and species. The concentration of each component in a sample can be estimated by multiplying the percentage of iron in that specific component with the total Fe content of that sample obtained from the total sediment destruction analysis.

Mössbauer spectra were recorded for a number of reference materials. A 2-line ferrihydrite was synthesized by NaOH addition to a ferric sulfate solution at 60°C (start pH 1 and end point pH 4). The reaction was left to occur for \(-2\) h and was then quickly filtered, rinsed with distilled water, and oven-dried at 110°C. A 6-line ferrihydrite was synthesized following the recipe suggested by Cornell and Schwertmann (1996, p. 491). An As-rich ferrihydrite (97Y) was collected from an oceanic thermal vent near Papua New Guinea (Rancourt et al., 2001). A bulk hematite (PBH_3B) was purchased from GPR and is described in Dang et al. (1998). Nanophase hematite (nh4) was synthesized by addition of a ferric nitrate solution to heated water. After the addition the heater was turned off and the suspension was left to cool to RT. The suspension was subsequently filled into a dialysis tube, which was left in water with a pH of 4 (adjusted with HNO\(_3\)). The water was exchanged every 442 C. van der Zee et al.
2 days until the pH became constant. Finally, the suspension was freeze-dried. A microcrystalline hematite (L1) was synthesized by hydrothermal precipitation through oxidation of a ferrous sulfate solution at 160°C and is described in Dang et al. (1998). The high surface area (HSA) goethite and medium surface area (MSA) goethite are described in Roden and Zachara (1996).

3. RESULTS

3.1. Solid-phase and Pore Water Profiles

*Rhodes site.* The box core profiles agree well with those of the gravity core and therefore the data will be discussed as one core. Several features in the solid-phase profiles indicate that the sediment is not at steady state. Both the total Fe and the Fe/Al ratio show peaks at 26 and 37 cm depth, as well as an increase below 84 cm. The sediment Fe/Al ratio at 67 cm (64.5 to 69.5 cm depth interval) is depressed due to an enrichment with Al (Fig. 1). The nearby ash layer at 57.5–64 cm depth probably lowers the Fe/Al ratio and the CaCO$_3$ content in this interval. The total and CDB-extractable Mn profiles show two subsurface peaks at 10–14 and 23 cm depth. The first total and CDB-extractable Fe subsurface peak is located at ~26 cm depth.

![Fig. 1. Vertical profiles of solid-phase total Mn, total Fe (closed symbols), total Fe/Al ratio (open symbols), calcium carbonate, CDB-extractable manganese, iron, and phosphorus, and pore water profiles of oxygen, ammonium, nitrate, manganese, iron, and phosphate at the Rhodes site. The connected symbols are data from the box core and the single dots are data from the gravity core. Note the different depth scale for the oxygen profile.](image-url)
depth just below the deepest peak of Mn. The second total and CDB-extractable Fe peak is located at 37 cm depth. The Mn peaks are most likely due to Mn oxides, because the major part of the total Mn is CDB-extractable. The Fe-bound P concentration seems to increase slightly with increasing depth until the depth of the first CDB-extractable Fe peak after which it decreases with depth, although the profile data are scattered. The pore water species show the sequence predicted on the basis of the Gibbs free energy yield of the reactions between organic matter with oxygen, nitrate, manganese oxide, and iron oxide (Froelich et al. 1979). First, oxygen is depleted at ~5 cm, then nitrate at ~10 cm depth, below which ammonium starts to increase. Dissolved Mn$^{2+}$ appears in the pore water at a shallower depth than dissolved Fe$^{2+}$, which starts to accumulate at 20 cm depth close to the peak in Mn$^{2+}$. The phosphate concentration increases with depth throughout the profile.

North Aegean site. The CDB-extractable and total Mn profiles show a high Mn content at ~3 cm depth (Fig. 2). Although about two-thirds of the total Mn is CDB-extractable in the depth interval with the highest content of Mn, a significant amount of non-CDB-extractable Mn is also present. The latter Mn may be present as Mn carbonate. The total Fe and the Fe/Al ratio are relatively depth invariant. Both the CDB-extractable Fe and P contents are enriched at the sediment–water interface.

Fig. 2. Vertical profiles of solid-phase total Mn, total Fe (closed symbols), total Fe/Al ratio (open symbols), calcium carbonate, CDB-extractable manganese, iron, and phosphorus, and pore water profiles of oxygen, ammonium, nitrate, manganese, iron, and phosphate at the North Aegean site. Note the different depth scale for the oxygen profile.
and reach a maximum at ~10 cm depth. Pore water oxygen and nitrate are both depleted at ~2.5 cm depth, below which ammonium increases. Dissolved Mn\(^{2+}\) starts to accumulate between 2.2 and 2.9 cm depth, whereas the dissolved Fe\(^{2+}\) increase starts around 10 cm depth. Phosphate accumulates throughout the sampled interval and shows a small discontinuity in its profile around the depth where Fe\(^{2+}\) appears.

### 3.2. X-ray Diffraction

XRD measurements were done on sediments from the 16.5–22.5 cm depth interval of the Rhodes site and the 2.4–3.4 cm depth interval of the North Aegean site (Fig. 3). At the Rhodes site, the majority crystalline phases identified by XRD were calcite (Ca), halite (H), dolomite (D), albite (A), chlorite (C), mica (M), and lizardite (L).

![Fig. 3. XRD patterns of sediment samples from the N Aegean site (2.4–3.4 cm depth interval) and the Rhodes site (16.5–22.5 cm depth interval). The majority phases are indicated: quartz (Q), calcite (Ca), halite (H), dolomite (D), albite (A), chlorite (C), mica (M), and lizardite (L).](image)

Only at 67 cm depth at the Rhodes site the average quadrupole splitting (2.40 mm/s) and the line width (0.50 mm/s) of the Fe\(^{2+}\) doublet were different. Note, this is also the layer containing a lower Fe/Al ratio (Fig. 1).

The sextet in the RT spectrum is characteristic of hematite only; the average hyperfine field \(H\) at RT is 504.6 kOe at the North Aegean site and 503.3 kOe at the Rhodes site (Dang et al., 1998). The broad line centered near the middle of the x-axis is due to a collapsed sextet of superparamagnetic nanoparticle oxides that are not hyperfine split at RT. The center...
shift of the nanophase oxides component was frozen at 0.35 mm/s, and all other parameters were free in the model fit, except when the amount of hematite was very small. In this case the hematite parameters were also fixed using the values obtained from fits with larger amounts of hematite. At RT, it is not possible to discriminate between the ferric oxides with ordering temperatures below RT and ferric iron in clay minerals; the former will give rise to the broad line and partially contribute to the ferric doublet. The peak areas of the broad line and the ferric doublet overlap at RT, and estimates of their areas may therefore suffer from trade-off problems. The sum of peak areas of the ferric doublet and the collapsed sextet is, however, a robust number and represents the total amount of ferric iron minus the ferric iron in hematite. In the deepest sediment sample from the North Aegean site, a second small sextet was observed. Its hyperfine parameters suggest that the second sextet may be due to maghemite.

The contribution of Fe(II) to total Fe increases sharply at 12–14 cm depth at the Rhodes site (Fig. 5). From here, the percentage of Fe that is Fe(II) increases with depth and that of hematite and other Fe(III) phases decreases. At the North Aegean site, the percentage of ferrous iron increases below 5 cm mainly at the expense of ferric iron in the PM components and nanophase oxides (Fig. 5). Hematite decreases with depth from ~4% to ~3% of the total Fe.

3.4. LHT Mössbauer Spectroscopy

Mössbauer spectra at liquid helium temperature were recorded for samples from 28.7 cm (CDB-extractable Fe maximum), 54 and 110 cm depths of the Rhodes site, and sediments from 2.15 cm (CDB-extractable Fe minimum) and 9.9 cm (CDB-extractable Fe maximum) depths from the North Aegean site. An example of a LHT Mössbauer spectrum is given in Figure 6. The LHT spectra were fitted using a model composed of one ferric doublet with two gaussian components, two ferrous doublets and two sextets (Fig. 6). The ferric doublet is due to PM ferric iron, for example in clay minerals. One ferrous doublet, the sharp doublet, is due to ferrous iron that stays PM at LHT. The second (broad) ferrous doublet is due to ferrous iron in Fe-rich clay minerals that start to order magnetically, but are not completely ordered (Rancourt et al., 1994). The sextet with the smaller spectral area had one hyperfine field distribution (HFD) gaussian component, and the larger sextet had three HFD gaussian components. The smaller area sextet is due to hematite (Table 1). The model fit of the LHT spectra did not require a higher percentage of hematite than found in the RT measurements, and the total percentages of ferrous iron in RT and LHT measurements are conserved. Therefore, the amount of hematite and ferrous iron were fixed so that the percentage of iron found in the larger sextet was more constrained. The iron oxide that contributed to the ferric doublet and to the collapsed sextet at RT (i.e., the broad line at RT) has split up into the larger sextet of the two sextets at LHT, with hyperfine parameters characteristic of goethite at 4.2 K (Friedl and Schwertmann, 1996; Table 1).

The goethite content (in μmol Fe g⁻¹) is calculated by multiplying the percent area of the Fe in the goethite component of the LHT spectra (sum of all components in a spectrum is 100%) by the total Fe content (in μmol Fe g⁻¹) obtained from the sediment destruction analyses for each relevant depth interval. At the Rhodes site, the goethite content at the CDB-extractable Fe maximum (28.7 cm depth) is 26.1% of the total
From the spectral data, it is clear that the goethite content decreases deeper in the sediment (Fig. 7), but it is difficult to quantify due to its small amount and the broad width of the sextet lines. The estimated range of the goethite content is 8–17% of the total iron (49–103 μmol Fe g\(^{-1}\)) and 7–15% of the total iron (41–87 μmol Fe g\(^{-1}\)) at 54 and 110 cm depth, respectively. The lower values were estimated using one component for the goethite HFD and the higher values using fixed HFD parameters obtained from the 28.7-cm depth sample. At the North Aegean site, goethite accounts for 29.6% of the total iron.

Table 1. Hyperfine parameters for reference materials and the sextets of sediment samples at LHT.

<table>
<thead>
<tr>
<th>Material</th>
<th>CS (mm/s)</th>
<th>(e^b) (mm/s)</th>
<th>(H_{\text{peak}}) (kOe)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-line ferricydrite</td>
<td>0.46</td>
<td>-0.047</td>
<td>495</td>
<td></td>
</tr>
<tr>
<td>6-line ferricydrite</td>
<td>0.47</td>
<td>-0.057</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>As-rich ferricydrite</td>
<td>0.47</td>
<td>-0.024</td>
<td>468</td>
<td>Natural, yellow</td>
</tr>
<tr>
<td>Bulk hematite</td>
<td>0.47</td>
<td>0.179</td>
<td>539</td>
<td></td>
</tr>
<tr>
<td>Nanophase hematite</td>
<td>0.47</td>
<td>-0.088</td>
<td>530</td>
<td></td>
</tr>
<tr>
<td>Microcrystalline Hm</td>
<td>0.47</td>
<td>-0.117</td>
<td>530</td>
<td></td>
</tr>
<tr>
<td>HSA goethite</td>
<td>0.47</td>
<td>-0.143</td>
<td>501</td>
<td>211 m(^2)/g</td>
</tr>
<tr>
<td>MSA goethite</td>
<td>0.46</td>
<td>-0.140</td>
<td>503</td>
<td>39 m(^2)/g</td>
</tr>
<tr>
<td>Rhodes site 28 cm</td>
<td>0.45</td>
<td>-0.130 (+0.014)</td>
<td>497</td>
<td>Large sextet</td>
</tr>
<tr>
<td>Rhodes site 28 cm</td>
<td>0.49</td>
<td>-0.091 (+0.021)</td>
<td>533</td>
<td>Small sextet</td>
</tr>
<tr>
<td>Aegean site 2 cm</td>
<td>0.46</td>
<td>-0.130 (+0.010)</td>
<td>500</td>
<td>Large sextet</td>
</tr>
<tr>
<td>Aegean site 2 cm</td>
<td>0.47</td>
<td>-0.105 (+0.022)</td>
<td>535</td>
<td>Small sextet</td>
</tr>
<tr>
<td>Aegean site 10 cm</td>
<td>0.46</td>
<td>-0.138 (+0.007)</td>
<td>499</td>
<td>Large sextet</td>
</tr>
<tr>
<td>Aegean site 10 cm</td>
<td>0.45</td>
<td>-0.100 (+0.018)</td>
<td>533</td>
<td>Small sextet</td>
</tr>
</tbody>
</table>

\(a\) Average center shift.
\(b\) Average quadrupole shift; errors are given between brackets for the sediment samples and are 2SD errors; errors for reference materials are much smaller.
\(c\) Most probable hyperfine field of the HFD.
\(d\) HSA is high surface area.
\(e\) MSA is medium surface area. The HSA goethite is superparamagnetic at RT, whereas the MSA goethite is magnetically ordered at RT, giving rise to a sextet.
of the total iron or 197 µmol Fe g$^{-1}$ at 2 cm depth and 29.4% of the total iron or 216 µmol Fe g$^{-1}$ at the CDB-extractable Fe maximum at 9.9 cm depth.

4. DISCUSSION

4.1. Ferric Iron in the Solid Phase

The average center shift (0.36 mm/s), quadrupole splitting (0.83 mm/s Rhodes; 0.76 mm/s N. Aegean), and the quadrupole splitting distribution (QSD) standard deviation width (0.54 mm/s Rhodes; 0.48 mm/s N. Aegean) of the ferric doublet at RT (Fig. 4) are typical for Fe(III) in oxides, phyllosilicates, and other Fe(III)-bearing silicates. The ferric iron that remains paramagnetic at LHT could be from Fe(III) in chlorite, mica, and serpentine (see XRD results). At RT, ferric iron in nanophasic oxides will result in a doublet or broad line (collapsed sextet) in the Mössbauer spectrum due to the superparamagnetism of the nanoparticles. Consequently they cannot be resolved in contrast to larger iron oxide particles, such as the hematite in our sediments, which is hyperfine split at RT (Fig. 4). The hyperfine parameters for the sextet (Fig. 4) are diagnostic for hematite at RT (Dang et al., 1998): the average center shift is 0.35 (Rhodes) and 0.34 mm/s (N. Aegean); the quadrupole splitting is −0.087 (Rhodes) and −0.090 mm/s (N. Aegean); and the hyperfine field is 503.3 kOe (Rhodes) and 504.6 kOe (N. Aegean). Thus, the iron oxides identified at RT are hematite, which is present at all depths, and a small amount of maghemite that was observed at one depth interval only.

Mössbauer spectra at LHT were recorded for selected sediment samples (Figs. 6 and 7), because all iron oxides are resolved at 4.2 K including nanophasic iron oxides that are superparamagnetic at RT. The signal of superparamagnetic iron oxides will split up into a sextet when recorded at LHT. Each iron oxide can be identified at LHT due to their characteristic sextet which can be described with a few parameters. The center shift of the ferric iron in oxides is always around 0.47 mm/s at LHT and therefore not diagnostic for any iron oxide in particular. The quadrupole shift and hyperfine field are diagnostic. Under static circumstances, a distribution of hyperfine fields—characterized by the average hyperfine field, $<H>$, the most probable hyperfine field, $H_{peak}$, and the standard deviation, $\sigma_{HFD}$, of the hyperfine field distribution (HFD)—arises from the distributions of local chemical and magnetic environments in the mineral. The quadrupole shift parameter, $\varepsilon$, describes the effect of the local electric field gradient on the sextet pattern and has its own largely independent distribution characterized by the average $<\varepsilon>$. Additional Mössbauer spectra at LHT were recorded for relevant reference materials; different hematites, goethites, and ferrihydrites, because they are the most common oxides found in nature. Their hyperfine parameters are given in Table 1.

Two sextets are present in the Mössbauer spectra of the sediment samples at LHT (Figs. 6 and 7) indicating the presence of two different iron oxides. The smaller sextet, with its lines positioned towards the outside of the spectrum compared to the larger sextet, has hyperfine parameters diagnostic for hematite (Table 1) at LHT. The $H_{peak}$ values of hematite are large, $\sim$530 kOe, and characteristic only of hematites. Small particle hematites have a $<\varepsilon>$ around −0.1 mm/s, whereas bulk hematite has a positive $<\varepsilon>$ around 0.2 mm/s, because of the Morin transition. The larger sextet has hyperfine parameters characteristic of goethite (Table 1) at LHT, with $H_{peak}$ values of $\sim$500 kOe and $<\varepsilon>$ of about −0.14 mm/s. Spectra recorded at RT and LHT for two reference goethites are shown in Figure 8. The smallest reference goethite gives a doublet at RT and a sextet at LHT, whereas the larger reference goethite gives sextets at both RT and LHT. Morphologically, the reference goethites have a different appearance; the smaller one is rounded and the larger one is fibrous (Fig. 8). We found that synthetic nano-goethite reference materials are superparamagnetic at RT for sizes (mean diameters) 10.4 nm and smaller and hyperfine split (sextet) for sizes 14.4 nm and larger (Van der Zee et al., 2003), suggesting that our sedimentary nano-goethite...
is smaller than \( \sim 12 \) nm. Our results are in good agreement with those of Murad and Johnston (1987), who reported that the approximate critical size of goethite to give a doublet at RT is \( \sim 15 \) nm. If the sedimentary goethite were larger than the critical size it would be expected to give a sextet at RT, as does hematite. Thus, the sedimentary goethite is a nanophase oxide.

Based on the quadrupole shift parameter of the sextets, we conclude that ferrihydrite is not present in these samples. The disordered structures of ferrihydridites lead to near-zero values of \( e' \), where the \(-0.057\) mm/s of the 6-line ferrihydrite is the largest value associated with the most ordered occurrence of ferrihydrite. The less common magnetite, maghemite, lepidocrocite, and akaganeite oxyhydroxides are also eliminated on the basis of their hyperfine parameters (Murad and Johnston, 1987).

### 4.2. MBS and CDB Extraction

The nanogoethite content and the CDB-extractable Fe content decrease with depth at the same pace, but with an offset in absolute values at the Rhodes site (Fig. 9). At both sites, not all nanophase goethite is extracted with the CDB, suggesting that CDB-extractable Fe is not a precise measure of the total amount of sedimentary Fe oxides in our samples. On the other hand, it is not easy to fit the LHT spectra when the sextet peaks are so small and dynamic broadening occurs due to magnetic fluctuations related to superparamagnetism (Figs. 7 and 9).

The atomic \( \frac{P_{\text{CDB}}}{Fe_{\text{goethite}}} \) ratios of the 2-cm and 10-cm samples (Aegean site) are 27 and 33, respectively, similar to the \( \frac{P_{\text{CDB}}}{Fe_{\text{goethite}}} \) ratio of 33 of the upper sample at the Rhodes site (28.7 cm) decreasing to 14–30 and 11–23 deeper in the sediment (range of values due to maximum and minimum estimates of the goethite content). The higher loading of \( P_{\text{CDB}} \) per \( Fe_{\text{goethite}} \) atom deeper in the sediment is unexpected; generally freshly precipitated Fe oxides in the oxic layer will adsorb most phosphate, and with depth in the sediment first the easily reducible Fe oxides are dissolved, thereby releasing phosphate. Then crystalline Fe oxides, with lower sorption capacities for P, would remain deeper in the sediment, resulting in an increase in \( \frac{Fe_{\text{ox}}}{P_{\text{CDB}}} \)Ratio with depth. However, we observed high \( \frac{Fe_{\text{goethite}}}{P_{\text{CDB}}} \) ratios in the oxic layer and lower ones down core, indicating a higher loading of \( P_{\text{CDB}} \) per \( Fe_{\text{goethite}} \) atom. Also, we find the main iron oxide phase, nanogoethite, at all depths in the sediment. A reduction of the effective surface area by clumping together of freshly precipitated nanogoethite particles and the adsorption of other ions or organic molecules may occur. Alternatively, we may not extract all the iron-bound phosphorus in the surface sediment. These mechanisms provide an explanation for the apparent increase in the phosphate binding capacity of the nanogoethite with depth.

Reported phosphate adsorption capacities for synthetic and natural goethites approximate the theoretical value of 2.51 \( \mu \)mol P m\(^{-2}\) (Borggaard, 1983) of bidentate sorption to the hydroxyl groups on the (110) plane of the goethite. Using the same value for nanogoethite with an assumed specific surface area of 200 m\(^2\) g\(^{-1}\), we would expect an Fe:P atomic ratio for saturated goethite surfaces of 22. This estimation indicates that the nanogoethite deeper in the sediment may be saturated with phosphate in contrast with the nanogoethite close to the sediment–water interface. This may point at an extraction artifact in the surface sediment for iron-bound phosphorus.

### 4.3. Oxidation of Dissolved Fe\(^{2+}\) by Mn Oxide

At the Rhodes site, the dissolved Mn\(^{2+}\) and Fe\(^{2+}\) profiles show that the Mn and Fe oxide peaks, at \( \sim 12 \) and 26 cm depth respectively, are actively forming, whereas the deeper Mn and Fe oxide peaks probably are relics from older Mn and Fe redox
4.4. Ferrous Iron in the Solid Phase

The average center shift (1.14 mm/s), quadrupole splitting (2.57 mm/s), and QSD standard deviation width (0.37 mm/s) of the ferrous doublet at RT (Fig. 3) are typical for iron in phyllosilicates and other Fe(II)-bearing silicates. The presence of any ferrous iron–phosphate compound, e.g., vivianite, cannot be excluded, because corresponding Fe(II) nuclei have much larger quadrupole splitting values (~3 mm/s) (Mattieville and Danon, 1977; McCammon and Burns, 1980). Haese et al. (1997) identified siderite in sediment of the deep-sea fan of the Congo River (below 12.4 m), but no evidence for siderite was found in our sediment. The quadrupole splitting of siderite is typically 1.8 mm/s (Weaver et al., 1967), therefore a separate doublet due to siderite would have been observed in the spectra if it were present. Note that oxidation of very fine-grained siderite and vivianite cannot be completely ruled out, however. Drodt et al. (1997) identified the ferrous iron in a Peru margin core as redox active iron in the clay minerals chlorite, smectite, and illite. We conclude from the XRD and MBS results that chlorites and micas are the most important Fe(II)-bearing components in our sediments.

4.5. Fe Reduction

At the Rhodes site, the Fe(II) increases from ~25% of the total Fe at the sediment–water interface to ~35% deeper in the sediment (Fig. 5) without any sharp transition at the depths where oxygen or nitrate become depleted (6 and 10 cm depth, respectively) (Fig. 1). König et al. (1997) reported constant values of ~11% Fe(II) above the tan-green color transition at 20–23 cm depth in deep-sea sediments from the Peru margin and ~37% Fe(II) below this transition. There, the ferrous iron acts as an oxidation barrier for downward diffusing nitrate (König et al., 1999). We do not observe a sharply defined solid-phase Fe(II) gradient near the depth of nitrate penetration, although it is a likely oxidant. The solid-phase Fe(II) gradient appears to start at ~12 cm and continues until 67 cm depth (Fig. 5), whereas the steepest gradient in dissolved Fe(II) occurs between 25 and 35 cm depth (Fig. 1). The large depth separation, ~13 cm, between the onset of the solid-phase Fe(II) gradient and the dissolved Fe(II) gradient at the Rhodes site may be due to the presence of a relict Mn oxide peak at ~23 cm depth (Fig. 1). The pore water profiles indicate that this Mn
oxide peak is being reductively dissolved by Fe$^{2+}$ and that the resulting Mn$^{2+}$ oxidatively reprecipitates at shallower depth. Thus, the relict Mn oxide peak acts as a temporary oxidation front barrier for the upward diffusing Fe$^{2+}$ in the pore water. With time, we expect that the Mn oxide peak will be completely dissolved and then dissolved Fe$^{2+}$ can move upward until it is oxidized again, closer to the depth of the solid-phase Fe(II) gradient. At the North Aegean site, the percentage of ferrous iron increases from 15% in the oxic layer to 19% at 40 cm depth, with the most rapid change occurring between 5 and 15 cm depth (Fig. 5). It is difficult to determine whether oxygen and/or nitrate act as an oxidant for solid-phase ferrous iron, due to the small difference in the penetration depths of the two oxidants (Fig. 2). The solid-phase Fe(II) gradient (5–15 cm depth) occurs approximately at the same depth interval as the CDB-extractable Fe peak and the steepest gradient of Fe$^{2+}$ in the pore water (10–12 cm depth).

The increase in solid-phase Fe(II) is thought to result from the reduction of Fe(III) within the clay minerals as the novo formation of chlorite and mica is unlikely. The formation of Fe sulfides is unimportant because the S content is very low based on their quadrupole splittings. The formation of ferrous minerals such as vivianite and siderite can also be ruled out based on their quadrupole splittings. The formation of chlorite and mica are unlikely. Formation of Fe(III) within clay minerals as the novo reduction of Fe(III) within the clay minerals as the novo

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Hematite and nanophase goethite are the major iron oxides present in these Mediterranean sediments. Poorly crystalline iron oxides, such as ferrihydrite and lepidocrocite are generally thought to be most important in early diagenetic iron cycling, because they are more reactive towards sulfide than crystalline iron oxides (Canfield, 1989). Also, iron-reducing bacteria are most effective when the iron source is hydrous iron oxide; they can reduce it both faster and more completely than crystalline iron oxides. Very little of the iron in crystalline iron oxides (e.g., hematite and goethite) appears to be available for reduction by Fe-reducing bacteria under natural conditions (Lovley and Phillips, 1986, 1987, 1988). Furthermore, ferrihydrite is thought to be the first Fe oxide that forms, when aqueous Fe$^{2+}$ is oxidized. Ferrihydrite can be stabilized by phosphate (Schwertmann and Cornell, 1991; Benali et al., 2001) and, consequently, does not or very slowly transforms into more crystalline oxides such as hematite or goethite. The fact that the major iron phase extracted with the CDB-buffer is nanophase goethite implies that it is also the predominant P-binding oxide. This may then explain the persistence of Fe-bound P with depth in many sediments (Ruttenberg and Berner, 1993; Jensen and Thamdrup, 1993; Sølstrøm et al., 1996; Van der Zee et al., 2002) because poorly crystalline goethite is more slowly reduced than ferrihydrite and lepidocrocite (Larsen and Postma, 2001). The occurrence of nanophase goethite may be widespread as demonstrated by the present study and by Drodt et al. (1997) and Van der Zee et al. (2003).

5. CONCLUSIONS

The use of MBS in addition to pore water and solid-phase extractions in two Mediterranean sites has revealed a more complete and complex sedimentary iron geochemistry than would have been inferred from pore water chemistry and selective dissolution alone. The sedimentary iron oxides were identified as crystalline hematite and reactive nanophase goethite through a combination of RT and LHT MBS. No evidence was found for the presence of ferrihydrite, which is commonly assumed to be the dominant reactive sedimentary iron oxide. Nanophase goethite and hematite could not be identified by X-ray diffraction because of the nanocomposite nature of goethite and their low abundance compared to the majority phases in the sediment, whereas this is not a problem when using MBS because it is sensitive only to Fe. Mn oxide is the sole oxidant for upward diffusing Fe$^{2+}$ at both sites. At the Rhodes site,

<table>
<thead>
<tr>
<th>Station</th>
<th>Depth (cm)</th>
<th>PM Fe(III) RT$^a$</th>
<th>PM Fe(II) RT</th>
<th>Fe(III) in Hm</th>
<th>Fe(III) in Gt$^b$</th>
<th>Fe(III) in clay$^c$</th>
<th>CDB-Fe$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW Rhodes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>min-max</td>
<td>28.7</td>
<td>67</td>
<td>29</td>
<td>4</td>
<td>26</td>
<td>41</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>54</td>
<td>67</td>
<td>30</td>
<td>3</td>
<td>8–17</td>
<td>59–50</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>63</td>
<td>35</td>
<td>3</td>
<td>7–15</td>
<td>56–48</td>
<td>6</td>
</tr>
<tr>
<td>N Aegean</td>
<td>2.2</td>
<td>81</td>
<td>15</td>
<td>4</td>
<td>30</td>
<td>51</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>9.9</td>
<td>80</td>
<td>16</td>
<td>4</td>
<td>29</td>
<td>51</td>
<td>17</td>
</tr>
</tbody>
</table>

CDB = citrate–dithionite–bicarbonate; LHT = liquid helium temperature; MBS = Mössbauer spectroscopy; PM = paramagnetic; RT = room temperature.

$^a$ PM Fe(III) measured at RT includes Fe(III) in clays and Fe(III) in nanophase oxides. The sum of PM Fe(III) at RT, PM Fe(II) at RT, and Fe in hematite (Hm) is 100%.

$^b$ The Fe(III) in nanophase goethite (Gt) as determined by the LHT measurements.

$^c$ The difference between PM Fe(III) at RT and Gt Fe(III) at LHT gives the Fe(III) present in clays.

$^d$ The CDB-extractable Fe expressed as % of the total Fe.
dissolved Fe$^{2+}$ is oxidized by a relict Mn oxide peak and the released Mn$^{2+}$ reprecipitates at shallower depth in the sediment. The reduction of Fe(III) within clay minerals occurs $\sim$13 cm above the depth where reductive Fe(III) dissolution commences, as indicated by pore water Fe$^{2+}$ profiles, at the Rhodes site. At both sites, the solid-phase Fe(II) gradient is spread out over a larger depth interval than the pore water Fe$^{2+}$ gradient, indicating a slower Fe reduction rate of Fe(III) within clay minerals than Fe(III) in goethite. Although the non-steady-state conditions for deposition add uncertainty, the relative contributions of the ferric phases to Fe(III) reduction through the sediment column at the Rhodes site can be estimated as follows: 51% nanogoethite, 43% clay-bound Fe(III), and 6% hematite.

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