

ANALYSIS OF SOME LAKE SEDIMENTS FROM GREECE

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Résumé. — Des carottes de sédiment de six mètres de longueur prises dans trois lacs grecs ont été étudiées par spectroscopie Mössbauer et diffraction des rayons X. Le fer ferreux se trouve sous forme de chlorite ou de chamosite tandis que le fer ferrique se trouve sous forme d'illite, de smectite, d'oxydes et d'hydroxydes de fer pour la plupart mal cristallisés. Moins de 1 % du fer se trouve sous forme de magnétite, et 2 % environ sous forme d'haématite. Nous avons montré que dans les sédiments des lacs Vegorritis et Volvi en dessous d'une profondeur qui correspond à 2 000 ans d'âge 20 % du fer se trouve sous forme de sidérite. En outre nous avons remarqué que les extractions par l'oxalate d'ammonium acidifié du fer ferrique dans les oxydes éliminent aussi le carbonate ferreux.

Abstract. — Six-metre cores from Lakes Trikhonis, Vegorritis and Volvi have been studied by Mössbauer spectroscopy and X-ray diffraction. Ferrous iron is present in chlorite or chamosite, and ferric iron in illite or smectite and in ferric oxide and hydroxide phases which are poorly-crystallised in the main. Magnetite accounts for less than 1 % of the iron and haematite for ~ 2 %. A ferrous carbonate horizon below which some 20 % of the iron is present in siderite is found in Vegorritis and Volvi at a depth corresponding to 2 000 B. P. Acidified ammonium oxalate extractions designed to remove the ferric oxide phases, also eliminate the siderite.

1. Introduction. — Lake sediments interest workers in widely different scientific fields because they offer a continuous chronological record of events for thousands of years in the past. The inorganic fractions of the sediments may be regarded with fair accuracy simply as accumulations of material in the form in which it was washed into the lake. They are too young on a geological time scale to have suffered much transformation. If some way of reading it can be devised, the sediment record may provide information on past variations of the Earth's climate and magnetic field, and may bear the imprint of such diverse human practices as agriculture, industrialisation, sewage treatment or atomic bomb testing.

The application of Mössbauer spectroscopy to the analysis of lake sediments is a recent one [1-3]. It focusses attention on the iron in the sediments since ^{57}Fe is the only Mössbauer isotope with sufficient abundance in the Earth's crust. Luckily iron is a specially interesting element from a magnetic or geochemical point of view. In the previous work the ratio of ferrous to total iron in surface sediments from a set of Canadian lakes was found to be correlated with the water chemistry [1]. The iron-bearing mineral phases, some of them amorphous or poorly-crystallised, were

determined [1-3] and the change in their distribution with depth in an English post-glacial core was related to climatic and geochemical developments [2]. A ferric hydroxide horizon found in Lake Michigan was associated with the establishment of steel industry in the area [3].

In the present work, we have examined cores from three of the largest Greek lakes by Mössbauer spectroscopy and other techniques. The work was motivated by an interest in obtaining palaeomagnetic information from the cores [4, 5]. A knowledge of the variation of the Earth's magnetic field in Greece in antiquity would be interesting for its own sake, but might also open the possibility of archaeomagnetic dating of ancient ceramics.

The lakes studied were Trikhonis (Aetolia), Vegorritis (W. Macedonia) and Volvi (E. Macedonia). Dried homogenised samples from cores taken near the deepest part of each lake were used for the Mössbauer absorbers, with 90 mg/cm². One core from each lake, denoted as T3, B4 and V6 respectively, was sampled at approximately 50 cm intervals and a few samples were taken from other cores to corroborate the results. The cores themselves were taken using a 6 m Mackereth pneumatic corer [6] in the summer of 1975. The surface

sediment was disturbed by the corer, so the top of the recovered core corresponds to a depth, d , in the sediment of approximately 30 cm.

The main purpose of the present work was to identify the iron-bearing mineral phases. There turns out to be an unexpected variation with depth in some of the cores. A secondary aim was to determine the effectiveness of some of the chemical treatments described in the literature [7] for removing *free iron* from clay minerals. Two treatments were tried :

A. — Some 300 mg of dried sediment were shaken in several hundred ml of a mixture of 0.2 M ammonium oxalate and 0.2 M oxalic acid for 2 hours in the dark.

B. — The same procedure was used, except that u-v illumination was employed.

2. Results. — Some typical spectra for samples taken near the top and near the bottom of each core are shown in figure 1. All the spectra include a very broad

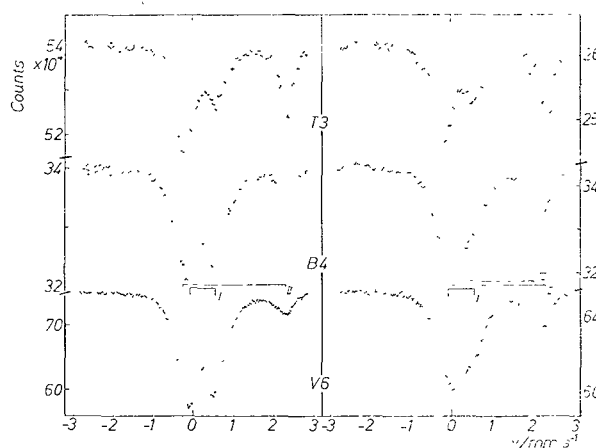


FIG. 1. — Room temperature Mössbauer spectra of sediments from Trikhonis (top), Vegorritis (middle) and Volvi (bottom). Those on the left are of samples taken near the top of the 6-metre core ; those on the right of the samples taken near the bottom. The positions of the doublets I, II and III are indicated above the V6 spectra.

ferric doublet, I, and a broad ferrous doublet II. In addition, another ferrous doublet with narrow lines, III, appears in samples taken near the bottom of cores from Vegorritis and Volvi. Magnetically-ordered iron

oxides accounted for less than 5 % of the total absorption in these sediments. The spectra were fitted to two or three doublets by the least-squares method, and the average parameter and their variation for each of the three cores are listed in table I. Only the linewidth of doublet III is sufficiently narrow for it to be identified with a single mineral phase with equivalent iron sites. From the values of δ and Δ it is certainly siderite, « FeCO_3 ». Doublet II is associated with ferrous iron in clay minerals. The parameter for Trikhonis and Vegorritis suggest that the Fe^{2+} is mainly present in chlorite, whereas those for Volvi suggest chamosite [8]. This attribution is supported by X-ray diffraction (see below). Doublet I is very broad, and besides ferric iron in the above clay minerals, any in illite or montmorillonite (smectite) will also contribute [8]. Furthermore, ferric iron in amorphous or poorly-crystallised iron oxide or hydroxide phases will absorb at the same velocities [9].

Doublet I is nearly always predominant in these sediments, showing that the iron is mostly oxidized. In figures 2 the normalized intensities of the three

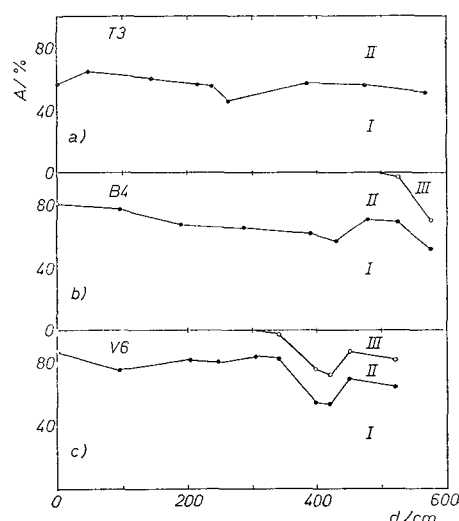


FIG. 2. — Relative absorption in the doublets I (Fe^{3+}), II (Fe^{2+}) and III (Fe^{2+}) as a function of a distance from the top of the cores from (a) Trikhonis (b) Vegorritis and (c) Volvi.

doublets are shown as a function of depth in the cores. The siderite makes its appearance below about 550 cm in Vegorritis and 350 cm in Volvi.

TABLE I

Average Mössbauer parameters for sediments from three Greek lakes

| Core | Doublet I | | | Doublet II | | | Doublet III | | |
|------|--------------|----------|----------|--------------|----------|----------|--------------|----------|----------|
| | δ (*) | Δ | Γ | δ (*) | Δ | Γ | δ (*) | Δ | Γ |
| T3 | 0.37 (1) | 0.68 (2) | 0.56 (2) | 1.14 (1) | 2.65 (1) | 0.36 (1) | — | — | — |
| B4 | 0.36 (1) | 0.65 (2) | 0.65 (2) | 1.13 (1) | 2.66 (2) | 0.39 (1) | 1.24 | 1.86 | 0.30 |
| V6 | 0.37 (1) | 0.64 (1) | 0.58 (2) | 1.13 (1) | 2.59 (3) | 0.43 (2) | 1.24 (1) | 1.85 (1) | 0.30 (1) |

(*) Relative to iron metal.

All are in mm/s. Standard variations are given in brackets.

The average iron content of the cores was evaluated roughly from the Mössbauer absorption as 2.8 wt % for T3, 3.6 wt % for B4 and 4.2 wt % for V6.

More information about the mineral phases present in the sediments was provided by X-ray diffraction. One diagram was taken in each case of the whole disoriented sample, and four of the oriented clay fraction ($< 2 \mu\text{m}$), untreated, after glycol ethylene and hydrazine treatments and after heating at 490 C. Some of the results are summarized in table II. Siderite was

TABLE II

Mineral phases in Greek lake sediments detected by X-ray diffraction

| Core Depth cm | T3 145 | | B4 96 574 | | V6 96 422 | |
|----------------------------|-----------|---|--------------|---|--------------|---|
| | — | — | — | — | — | — |
| Calcite | × | × | × | × | × | × |
| Siderite | | | × | | | × |
| Quartz | × | × | × | × | × | × |
| Plagioclase | × | | | × | × | × |
| Illite | × | | × | × | × | × |
| Talc | | × | × | | | |
| Chlorite | × | × | × | | | |
| Chamosite } Kaolinite } | | | | × | × | |
| Smectite | | | | × | × | |
| Interstratified Clays | × | × | × | × | × | × |

Relative abundances are indicated by the number of crosses.

identified in the samples where it was seen by Mössbauer spectroscopy, but not in the others. Its lattice parameter suggests some substitution by a larger cation, for instance $\text{Fe}_{0.9}\text{Ca}_{0.1}\text{CO}_3$. The small iron content of T3 (and B4 to a lesser extent) is explained by the admixture of large amounts of calcite and quartz to the clay phases where the iron is mainly located. The distribution of iron among mineral phases suggested on the basis of the Mössbauer data is essentially confirmed by the X-ray analysis: plagioclase, talc and kaolinite generally contain very little iron. The interstratified clays are composed of chlorite and smectite layers.

The influence of the chemical treatments «A» and «B» on the absorption in the three doublets in sediments from Volvi is shown in figure 3. From the curves before treatment, marked «I», it can be seen that the absorption in I and II remains more or less constant with depth and that Doublet III represents *additional* iron rather than iron obtained at the expense of one of the other components. Treatment A, which is supposed to remove only amorphous ferric hydroxide [10], decreases the intensity of Doublet I by $\sim 15\%$, and removes all the siderite. Treatment B, which should also attack crystalline ferric oxide phases reduces Doublet I by $\sim 30\%$, and also removes the ferrous carbonate. Neither treatment has much effect on Doublet II, the ferrous iron in the clay minerals, except in the carbonate zone. Similar results were obtained for the Vegorritis sediments.

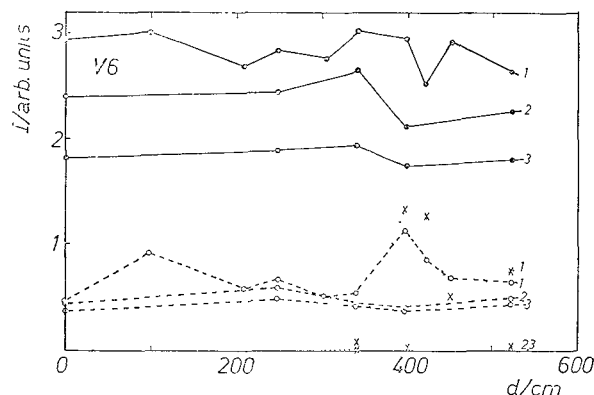


FIG. 3. — Removal of iron from sediments from the core V6 (Volvi) by chemical treatments. The symbols ●, ○ and × represent the intensities of the doublets I, II and III respectively. Curves 1, 2 and 3 represent the result before treatment, after treatment «A» and after treatment «B», described in the introduction.

3. Discussion. — The most interesting feature of the results is the ferrous carbonate horizon in the sediments. It was also found in a different core from Volvi, V2, though not in a different one from Vegorritis, B8, perhaps because of a greater sedimentation rate. Palaeomagnetic results for Volvi [11] indicate a date of about 1 500 B. P. at a depth of 350 cm. Pollen analysis has yielded a date of 2-3 000 B. P. for the bottom of the Volvi core, and a maximum of 3 000 B. P. for the bottom of the Vegorritis core B4. This places the ferrous carbonate horizon at about 2 000 B. P. in these two lakes. We have found no carbonate horizon in the more calcareous sediments of Trikhonis, despite a lower sedimentation rate. Radiocarbon dates of 2 400 B. P. and 6 600 B. P. have been determined for sediment from depths of 90 cm and 530 cm respectively in a Trikhonis core. Furthermore, a light-coloured band visible in the dried sediment at $d = 237$ cm in T3 may provide a unique marker in this and other southern Greek lakes. The natural remanent magnetization, high-field remanence and spontaneous magnetization all show a pronounced and narrow anomaly at this depth, increasing 3-4 fold. The band might be identified as an ash band caused by the cataclysmic eruption around 3 500 B. P. of Santorini, a volcano 400 km to the southeast. The position of the band is consistent with the radiocarbon dates, and implies a sedimentation rate only half as great as that of Volvi and Vegorritis. The ash band in Volvi and Vegorritis, if it occurs, would be below the bottom of our cores.

No definite interpretation of the ferrous carbonate horizon can yet be advanced. It could be a result of neoformation with the gradual approach to chemical equilibrium of the sediments and their interstitial waters, or else it may be inherited, reflecting the limnological parameters of the lake, pH, eH..., at the time of deposition, these parameters having subsequently changed, perhaps as a result of climatic variation. Some slight evidence for evolution of the sediment

in-situ may be adduced from the erratic variation of the direction and intensity of the natural remanence below the carbonate horizon in Volvi [11].

Some analysis of the iron oxide phases in the sediments may be made by combining magnetization and Mössbauer measurements. The average values of the spontaneous magnetization in the cores T3, B4 and V6 at room temperature are : 0.011, 0.025 and 0.023 emu/g. These give moments $M_s \sim 0.5$ emu/g of iron in the sediments. The moment must be carried almost exclusively by magnetite ($M_s \sim 130$ emu/g of iron) ; rather than *haematite* ($M_s \sim 0.7$ emu/g of iron) because at most 5 % of the iron was found to be present in magnetically ordered iron oxides. Less than a percent of the iron in the form of *magnetite* will suffice to explain M_s , yet escape detection in our spectra. In Volvi, one fifth of the high-field remanence disappears at the Morin transition, suggesting that ~ 2 % of the iron is present in *haematite* in accord with the above results. However, the fact that magnetite is the domi-

nant magnetite oxide does not mean that it dominates the weak *natural* remanence, roughly half of which disappears at the Morin transition.

Finally, we compare methods for distinguishing ferric iron in clay minerals and in poorly crystallised ferric oxide or hydroxide phases. For the sake of economy, acidified oxalate extractions were tried here in preference to recording spectra at two temperatures, room temperature and another, usually 4.2 K, below the blocking temperature of the hydroxide phases, yet above any magnetic ordering temperature of iron in the clay minerals. The extractions are very effective at removing ferrous carbonate, and show that some 30 % of the ferric iron in the sediments is present in the poorly-crystallised oxides, the rest probably remaining in the clay lattices. The ferrous iron in the clay lattices is barely touched by the treatment, except just below the carbonate horizon. However, a complete evaluation of its effectiveness in removing the ferric oxide phases will require spectra at 4.2 K.

References

- [1] COEY, J. M. D., SCHINDLER, D. W. and WEBER, F., *Can. J. Earth Sci.* **11** (1974) 1489.
- [2] COEY, J. M. D., *Geochem. Cosmochem. Acta* **39** (1975) 401.
- [3] PERLOW, G. J., PATZEL, W. and EDGINGTON, D., *J. Physique Colloq.* **35** (1974) C6-547.
- [4] MACKERETH, F. J. H., *Earth Planet. Sci. Lett.* **12** (1971) 322.
- [5] CREER, K. M., THOMPSON, R., MOLYNEUX, L. and MACKERETH, F. J. H., *Earth Planet. Sci. Lett.* **14** (1972) 115.
- [6] MACKERETH, F. J. H., *Limnol. Oceanogr.* **3** (1958) 181.
- [7] BLUME, H. P. and SCHWERTMANN, U., *Soil. Sci. Soc. Am. Proc.* **33** (1969) 438.
- [8] COEY, J. M. D., *Proceedings of the International Conference on Mössbauer Spectroscopy*, Cracow 1975 vol. 2 333.
- [9] COEY, J. M. D. and READMAN, P. W., *Earth Planet. Sci. Lett.* **21** (1973) 45.
- [10] LANDA, E. R. and GAST, R. G., *Clays and Clay Minerals* **21** (1973) 121.
- [11] READMAN, P. W. and PAPAMARINOPOULOS, S., *Proceedings of the Third European Geophysical Society Meeting*, Amsterdam, E. O. S. (1976).