

Mössbauer Spectroscopy applied to the study of some sediments samples from the Black Sea

by

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Summary

Marine sediments from 60 m and 200 m depth on the floor of the Black Sea, Romanian coast, for iron state valency by Mössbauer Spectroscopy between 77° K and 298° K have been analysed. Only Fe³⁺ at 60 m depth while two characteristic sublattices one for Fe³⁺ and another for Fe²⁺ at 200 m depth have been identified. The ratio Fe³⁺/Fe²⁺ is about 2.

Résumé

Des sédiments marins à 60 m et à 200 m de profondeur sur la plate-forme continentale roumaine, ont été prélevés en vue d'analyser l'état du fer, en appliquant la méthode de la spectrométrie Mössbauer. On a utilisé une installation du type ELRON et une source à ⁵⁷Co dans un réseau de cuivre. Les Spectres Mössbauer ont été effectués aux températures de 77° K et 295° K. Les données expérimentales ont été analysées à l'aide d'un computer IBM-370/135 dans le code FORTRAN IV. Les sédiments (nodules Fe-Mn) prélevés à 60 m de profondeur présentent seulement du fer trivalent, tandis que ceux de la zone anaérobie de la mer Noire à 200 m, sont caractérisés par deux sous-réseaux : un pour le Fe³⁺ et l'autre pour le Fe²⁺, le rapport Fe³⁺/Fe²⁺ \simeq 2. On n'a pas identifié d'environnements magnétiques au noyau du fer.

Introduction

In a previous work has been analysed for the first time by Mössbauer Spectroscopy the ferromanganese nodules collected in the oxidation zone of the Black Sea [1]. In this samples have been identified only Fe³⁺. The aim of this work was to extend our investigation in the reduction zone (anerobe) of hydrogen sulphide of the Black Sea, Romanian coast.

Methods and conclusions

Dried and powdered samples (100-200 mg) were taken for measurements at room and liquid nitrogen temperatures. The Mössbauer Spectra were performed with an ELRON type installation with a speed of 4.5 mm/s. and a ⁵⁷Co source embedded in a copper lattice. The experimental data have been computed in an IBM-370/135 computer in FORTRAN-IV code.

The following conclusions can be drawn :

1. — The sediments (Fe-Mn nodules) collected at 60 m depth from the Black Sea, have shown only Fe³⁺ quadrupolar splitting.

Rapp. Comm. int. Mer Médit., **23**, 7, pp. 37-38 (1976).

2. — The Fe-Mn nodules from 60 m depth, after carrying out the Mössbauer spectra between 77° K to 873° K, didn't show magnetic environment.

3. — The thermogravimetric analysis of the samples from 60 m depth, have proved small variation content of the mineralogical composition.

4. — Mössbauer Spectra carried out at room temperature, of the Black Sea sediments from 200 m depth have shown two sublattices : one for Fe²⁺ and another for Fe³⁺, but no magnetic environment. The ratio Fe³⁺/Fe²⁺ is about 2. The results were checked by chemical analysis.

5. — There was found 2.1 mg H₂S/l dissolved in the Black Sea water at 200 m depth.

Reference

- [1] GEORGESCU (I.I.) & NISTOR (C.), 1970. — Study of the iron chemical bond by Mössbauer Effect in the ferromanganese concretions of the Black Sea. *Rev. Roum. Phys.*, **15**, 7, pp. 819-823.

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Discussion

Question of M. Buljan : Why the authors have chosen the depth of 200 m for taking the samples? This is in Black Sea the transitory zone between oxydized layers of water and H₂S containing water strata. Taking samples from deeper bottoms the ratio Fe³⁺/Fe²⁺ would be probably much different.

Reply : The next year it will be taken sediments from different depths on the bottom of the Black Sea, and deeper than those presented here. But that technically is not easy to do.

Question of M. Fukai : How did you preserve your sample? Is there any possibility of oxidation of the sample after the collection?

Answer : The sediment sample was preserved without contact with air, so that the oxidation of the sediment after collection is estimated negligible.

The sediment sample hermetic has been packed between two thin glimmer foils (Mylar) of the Mössbauer ELRON type installation. The Mössbauer spectra carried out two times at an interval of five months, have not shown any difference between the characteristic areas of Fe³⁺ and Fe²⁺, such the ratio Fe³⁺/Fe²⁺ remained constant.

Questions of M. Macchi :

1. Do you made the chemical checking for the Fe³⁺/Fe²⁺ ratio in the mineral fractions, or in the entire sediment sample?

Answer : The ratio Fe³⁺/Fe²⁺ has been determined on the whole (entire) sediment sample, not in the mineral fractions.

2. Do you have an idea how much organic substances, sulphides and chlorides are present in your samples you measured with dichromate titration method?

Answer : The sediment samples were disaggregated in the presence of H₂SO₄ and HF in the absence of air and titration with K₂Cr₂O₇, when Fe²⁺ was oxidized to Fe³⁺. Our content in trivalent and divalent iron in the sediments by this method is in good agreement with that determined by Mössbauer spectroscopy in the limit of errors. By the acid method used for disaggregation is influenced only the organic matter. We didn't carry out measurement for organic matter, but this is not in great quantity because there was an agreement between Fe³⁺/Fe²⁺ by the both methods named before.

Question of M. Duursma : Is Fe³⁺ non-exchangeable Fe in the crystal structure and Fe²⁺ exchangeable Fe, sorbed on the sediment?

Answer : Has still to be studied.

In view to detect the iron exchange in the lattice crystal structure, the Mössbauer Spectra must be carried out not only at room, but also at N₂ liquid temperature on different thin slices cut off from the same sample.

Our Mössbauer Spectra represent the total Fe³⁺ and the total Fe²⁺ from the whole sediment sample taken under study.

Question of M. Skrivanic : Have you any data about pH and Eh of investigated sediments?

Answer : No, we have not yet studied this sediment from this point of view. It will be done on other samples in the next future.