ISSN 1028-334X, Doklady Earth Sciences, 2016, Vol. 469, Part 2, pp. 819–823. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © D.Yu. Rogozin, D.A. Balaev, S.V. Semenov, K.A. Shaikhutdinov, O.A. Bayukov, 2016, published in Doklady Akademii Nauk, 2016, Vol. 469, No. 4, pp. 470–474.

GEOCHEMISTRY

Magnetic Properties of Bottom Sediments from Meromectic Shira Lake (Siberia, Russia)

D. Yu. Rogozin[a, b*], D. A. Balaev[b, c], S. V. Semenov[b, c], K. A. Shaikhutdinov[c], and O. A. Bayukov[c]**

Presented by Academician A.G. Degermendzhi June 5, 2014

Received June 16, 2014

Abstract—Magnetic properties were studied in bottom sediments of saline meromictic Shira Lake by the methods of static magnetometry and resonance Mössbauer spectroscopy for the first time. All layers of bottom sediments contain nanosized single-domain magnetite particles produced by magnetotactic bacteria. The concentration of magnetite in bottom sediments decreased with depth, reaching a local minimum in the layer corresponding to the minimal level of the lake observed in 1910–1930. It is demonstrated that biogenic magnetite may indicate climate-related changes in the level of Shira Lake, in addition to the other biological and geochemical characteristics.

DOI: 10.1134/S1028334X16080067

The presence of magnetite (Fe_3O_4) in bottom sediments of natural water reservoirs is a common phenomenon. It is described in numerous papers ([1–3] and many others). The origin of magnetite may be purely geological (if rocks in the water drainage basin contain magnetite), as well as biogenic [2, 4]. Biogenic magnetite in sediments is produced by magnetotactic bacteria, which synthesize single-domain magnetite particles in the composition of intracellular inclusions (magnetosomes). Bacteria apply magnetosomes for orientation in space using the magnetic field of the Earth [5].

The saline undrained Shira Lake (54°30′ N, 90°11′ E) is located in the steppe zone of the northern part of the Minusa Basin (Khakassia Republic), 15 km from the regional center Shira Village. The area of the water surface is 35.9 km^2; the maximal depth is 24 m (2007–2012). Currently the lake is meromictic; its deep layers (monimolimnion) contain hydrogen sulfide [6].

It is known that the level of undrained lakes is sensitive to variations in climate humidity. Consequently, reconstruction of changes in the level of the undrained lake allows us to reconstruct the dynamics of variations in the budget of precipitates and evaporation in a certain area. Recent studies included dating of bottom deposits, estimation of the accumulation rate, analyses of the element composition, and the concentration of organics and photosynthetic pigments [7–9]. Here we report the first results of study of the magnetic properties of the upper part of bottom sediments in the lake. It is shown that sediments contain biogenic magnetite, which is an additional independent paleoindicator of variation of the redox conditions in the deep part of the lake.

Nineteen samples from the core in the upper part of bottom sediments with a depth up to 40 cm preliminarily dried at 105°C were selected for analysis of the magnetic properties. In addition, we analyzed magnetic properties of the sedimentary material collected using sedimentation traps in the lake, as well as of rocks surrounding the lake and stones on the shore (red and gray sandstones). Bottom sediments in similar cores were previously dated by the concentration of ^{137}Cs and ^{210}Pb and by visual calculation of the annual layers [9]. The upper boundary of the characteristic “white” layer in the core indicating 130 mm and corresponding to approximately 1945 [9] was used as the key point for correlation of various cores. The concentration of organics in bottom sediments was estimated as loss in weight of the samples dried at 105°C after ignition at 550°C.

The static (in a quasi-constant magnetic field) magnetic properties were studied on a vibrational

[a] *Institute of Biophysics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*
[b] *Siberian Federal University, Akademgorodok, Krasnoyarsk, Russia*
[c] *Kirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*
*e-mail: *rogozin@ibp.ru; **dabalaev@iph.krasn.ru*

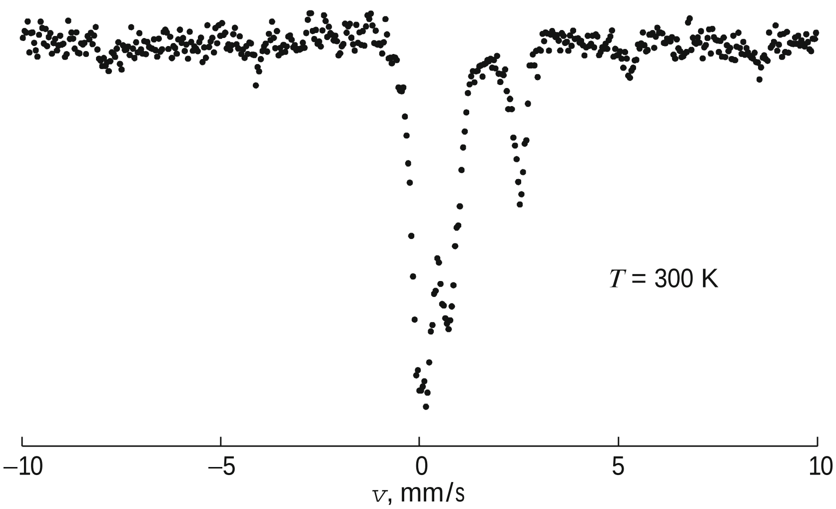

Fig. 1. Typical Mössbauer spectrum of the sample of bottom sediments of Shira Lake (depth of 65 mm).

magnetometer. Mössbauer studies were performed at room temperature on a MS-1104Em spectrometer with a $^{57}Co(Cr)$ source. It was established that preliminary drying of the samples did not result in changes to the magnetic properties.

Figure 1 shows an example of the typical Mössbauer spectrum of the sample from a depth of d = 65 mm. Comparison of the results of Mössbauer spectroscopy with the model spectra shows that the spectrum is characterized by the parameters typical of Fe atoms in hematite (35%), magnetite (8%), and paramagnetic ions Fe^{3+} (41%) and Fe^{2+} (16%); the portion (%) from the total content of Fe atoms is shown in parentheses. There is a small deviation in the parameters of Mössbauer spectra from the tabulated values for the corresponding volumetric materials due to the small particle size.

The method of static magnetometry confirms the magnetoactive phases registered by Mössbauer spectroscopy. The presence of paramagnetic ions Fe^{3+} and Fe^{2+} is observed in the low-temperature area, since the curve of magnetization of a paramagnetic material $M(H)$ may be described by the model Brillouin function:

$$B(J,H) = \left(\frac{2J+1}{J}\right)\coth\left[\frac{(J+1/J)g\mu_B H}{kT}\right] - (1/2J)\coth\left[\frac{g\mu_B H}{2kT}\right],$$

where J is the spin of 5/2 and 4/2 for Fe^{3+} and Fe^{2+}, respectively; g is the factor of ≈2 for Fe; μ_B is the Bohr magneton; k is the Boltzmann constant. The typical magnetization curve $M(H)$ for the sample of bottom sediments from Lake Shira at T = 4.2 K in the fields up to 60 kOe shown in Fig. 2 is described by the following equation:

$$M(H) = M_1 \times B(J = 5/2, H) + M_2 \times B(J = 4/2, H) + \chi H. \quad (1)$$

The values M_1 (≈2.95 emu/g) and M_2 (≈1.26 emu/g) reflect the quantitative proportions between the paramagnetic Fe ions (70% Fe^{3+}, 30% Fe^{2+}), which is in agreement with the results of Mössbauer study. The member $\chi \times H$ in (1) is typical of the antiferromagnetic phase, the constant χ is $\approx 2.5 \times 10^{-5}$ emu/g, which is in agreement with the value of antiferromagnetic susceptibility of α-Fe_2O_3 (hematite) [10] identified by Mössbauer spectroscopy. Increase in the magnetic moment $M(T)$ (Fig. 2, inset) in the low-temperature area reflects the paramagnetic contribution as well.

In addition, there is a clear anomaly at $T \approx 120$ K. There is only one candidate (magnetite Fe_3O_4), which is ferromagnetic, among the known natural magnetically ordered phases, including those in bottom sediments [2, 4]. The temperature $T_V \approx 120$ K corresponds to the structural transition in magnetite that is known as the Verwey point [11]. The hysteresis of magnetization $M(H)$ at T = 77.4 K typical of ferromagnetics and the contribution from paramagnetic ions at T = 77.4 K (under the given experimental conditions, the function $B(J, H)$ is linear by the field) are evident from Fig. 3. Deduction of the paramagnetic contribution from the dependence $M(H)$ for the sample provided the hysteresis dependence $M(H)$ from the phase of magnetite, which is characterized by magnetization of saturation M_S. Other parameters of the hysteresis loop (coercive force H_C and residual magnetization M_R) are shown in inset of Fig. 3.

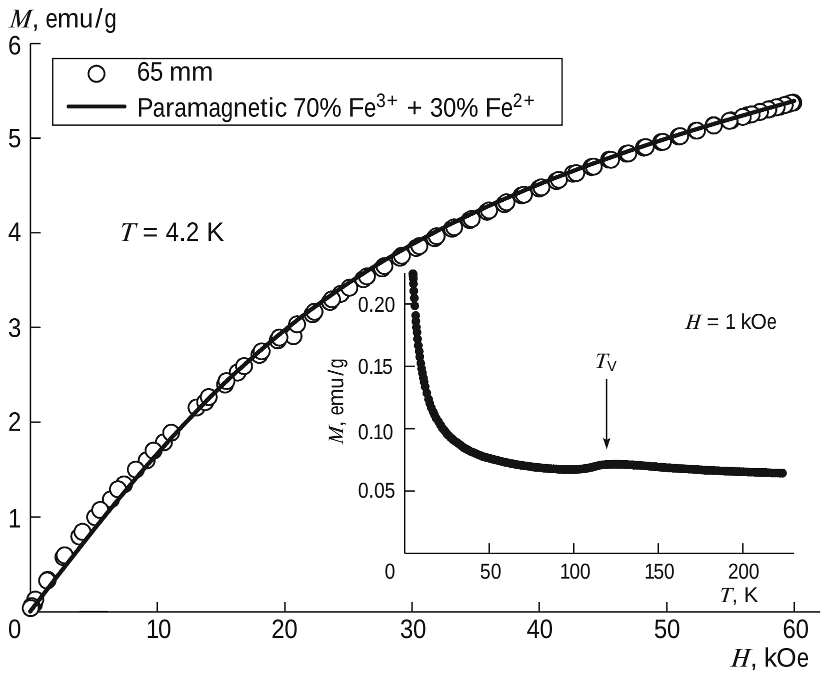

Fig. 2. Curve of magnetization $M(H)$ of the sample of bottom sediments from the depth of 65 mm (symbols) at T = 4.2 K. Solid lines indicate a model adjustment (1). The inset shows the behavior of $M(T)$ in the magnetic field H = 1 kOe.

It is established that the H_C values are ~200 Oe (77.4 K) and ~100 Oe (300 K), which exceeds the known H_C values for magnetite with large (~1 μm) granules (~30 Oe at T = 300 K) [12] and are typical of particles with a size from ~50 to several hundred nm [13]. At the same time, M_R/M_S at T = 77.4 and T = 300 K ranges from 0.1 to 0.25 for all samples studied. This allows us to consider that magnetite particles occur in the pseudo-single-domain state [13].

The M_S and M_R may be considered as "markers" of the concentration of the magnetite phase in bottom sediments (M_S(T = 300 K) for magnetite is ~92 emu/g [11]; according to our data, the portion of magnetite varies from ~1 to 0.1 wt % of the sample). The small size of magnetite particles and the pseudo-single-domain state allow us to assume their biogenic origin. It is known that the size of magnetic particles in bacterial magnetosomes is ~30–100 nm [2], i.e., similar to that in bottom sediments of Shira Lake. Correlation between the concentration of magnetite in bottom sediments and the content of organic materials (Fig. 4) provides indirect evidence for the biogenic origin of magnetite as well.

The tendency towards decrease in the magnetite concentration from the upper to the deeper layers shows that the source of magnetite occurs in the water column or in the uppermost layers of sediments (Fig. 4). The similar behavior and distribution with a maximum at the "water–bottom" boundary and decrease downwards the sediment is a typical phenomenon for lakes [2].

The presence of small portions of magnetite in sedimentation traps confirms that magnetite is produced in the water column of the lake. At the same time, magnetite was not registered in rocks around the lake.

Thus, magnetosomes of magnetotactic bacteria living in the lake are the most likely source of magnetite. It is known that bacteria synthesizing magnetosomes are mostly microaerophilic organisms; i.e., they live at the boundary between the hydrogen and sulfide-bearing waters in stratified water reservoirs [5, 14].

The "white" layer at a depth of 130–160 mm was accumulated in the 1910s–1930s, when the lake level decreased significantly (Fig. 4) [6, 8, 9]. It was previously shown that the low concentration of organic material, absence of hydrotroilite ($FeS^- \cdot nH_2O)^-$, and strong decrease in the concentration of okenone (specific pigment of purple sulfur bacteria) in the "white" layer in comparison with the overlying black layers provided evidence for the oxidized conditions in near-bottom waters of Shira Lake in that period [8, 9]. The local minimum in magnetite distribution at a depth of 130–160 mm registered in our study supports this hypothesis. Most likely, in that period the oxidized conditions inhibited development of anaerobic magnetotactic bacteria and, consequently, decrease the introduction of biogenic magnetite to the bottom sediments. In addition, it was shown that magnetite, especially forming nanoparticles, was very sensitive to oxidation by oxygen [3, 11]. Consequently, the rate of its degradation in sediments could be higher under the oxidized conditions. Although interpretation of the

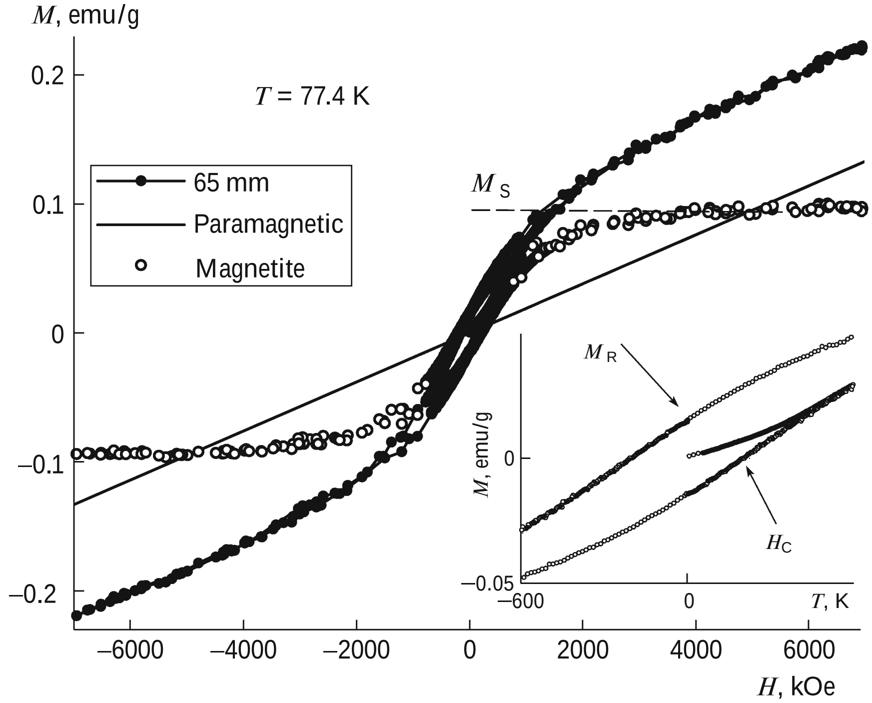

Fig. 3. Hysteresis curve of magnetization of the sample of bottom sediments at T = 77.4 K (full circles), paramagnetic contribution (solid line), and signal from magnetite (open circles). The inset shows the magnified signal from magnetite. The values of M_R, M_S, and H_C are given in the text.

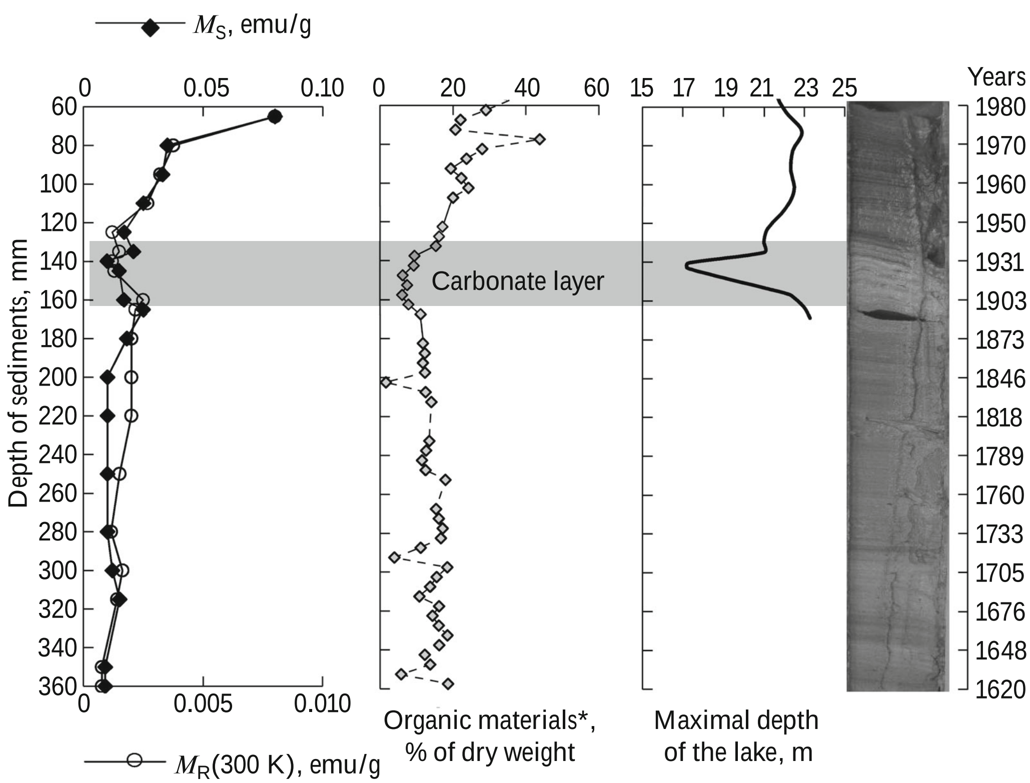

Fig. 4. Vertical distribution of magnetite and organic material in bottom sediments of Shira Lake, documented changes in the maximal depth (level) of the lake, and core photographs.

magnetite content in the bottom sediments should be accurate because of the strongly nonlinear responses of the concentration to different external factors [15], in this study, we confirmed that biogenic magnetite could be one of the paleoindicators of changes in the redox conditions of Shira Lake and, consequently, of climatically related changes in its level. This conclusion may be applied for interpretation of analyses of the older sediments aimed at paleoclimate reconstruction for the Late Holocene of South Siberia.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research and by the Krasnoyarsk Regional Foundation for Support of Scientific and Technical Activity (project no. 15-45-04272), as well as the Government Council on Grants of President of the Russian Federation for leading scientific schools (project NSh-9249.2016.5).

REFERENCES

1. F. Oldfield, C. Barnosky, E. B. Leopold, and J. P. Smith, Hydrobiologia **103**, 37–44 (1983).
2. I. F. Snowball, Earth Planet. Sci. Lett. **126**, 129–142 (1994).
3. Y. Pan, N. Petersen, A. F. Davila, L. Zhang, M. Winklhofer, Q. Liu, M. Hanzlik, and R. Zhu, Earth Planet. Sci. Lett. **232**, 109–123 (2005).
4. F. Oldfield and R. Wu, J. Paleolimnol. **23**, 165–174 (2000).
5. D. A. Bazylinsky and R. B. Frankel, Nat. Rev. Microbiol. **2**, 217–230 (2004).
6. D. Y. Rogozin, S. V. Genova, R. D. Gulati, and A. G. Degermendzhy, Aquat. Ecol. **44** (3), 485–496 (2010).
7. D. Yu. Rogozin, V. V. Zykov, I. A. Kalugin, A. V. Daryin, and A. G. Degermendzhy, Dokl. Biol. Sci. **439**, 228–231 (2011).
8. V. V. Zykov, D. Yu. Rogozin, I. A. Kalugin, A. V. Dar'in, and A. G. Degermendzhi, Sibir. Ekol. Zh., No. 4, 585–595 (2012).
9. I. A. Kalugin, A. V. Darin, D. Y. Rogozin, and G. A. Tretyakov, Quat. Int. **290/291**, 245–252 (2013).
10. S. T. Lin, Phys. Rev. B **116** (6), 1447 (1959).
11. R. Prozorov, T. Prozorov, S. K. Mallapragada, B. Narasimhan, T. J. Williams, and D. A. Bazylinsky, Phys. Rev. B **76**, 054406 (2007).
12. R. Day, M. Fuller, and V. A. Schmidt, Phys. Earth Planet. Inter. **13**, 260–267 (1977).
13. D. Sarkar, M. Mandal, and K. Mandal, J. Appl. Phys. **112**, 064318 (2012).
14. C. Moisescu, I. Ardelean, and L. G. Benning, Front. Microbiol. **5**, 49 (2014). doi: 10.3389/fmicb.2014.00049
15. R. Egli, Phys. Chem. Earth **29**, 869–884 (2004).

Translated by A. Bobrov