

Application of the EPR method in studying of the Mn behavior during the diagenesis of lacustrine carbonate sediments

Vosel Yulia S.^{1*}, Vosel Sergey V.^{2,3}, Stass Dmitriy V.^{2,3}

¹ Sobolev Institute of Geology and Mineralogy, SB RAS; ² Voevodsky Institute of Chemical Kinetics and Combustion SB RAS; ³ Physics department, Novosibirsk State University,

The processes of diagenesis play a significant role in the redistribution of microelements in sediments. Thus, the increase in uranium and the decrease in the manganese content downwards through the section of organic carbonate sediments is caused by the redox processes involving microorganisms. Manganese of oxide phases, being reduced in the lower layers, migrates with interstitial waters upwards through the section, where it is anew oxidized by oxygen and precipitated.

To determine the amount of oxides and hydroxides of Mn, a sequential leaching scheme is used. The disadvantage of the used scheme is that a large amount of manganese hydroxides is decomposed at the stage of carbonate dissolution. At the same time, this manganese is involved into redox processes. Hence, independent procedures are required, allowing one to separate Mn within the calcite from that in oxide phases. To do this, from the total amount of Mn released into solution during leaching, the amount of Mn present in calcite, determined by the EPR method, was subtracted.

Fig. 1 Scheme of measuring samples (Spectrometer Bruker EMX X-Band)

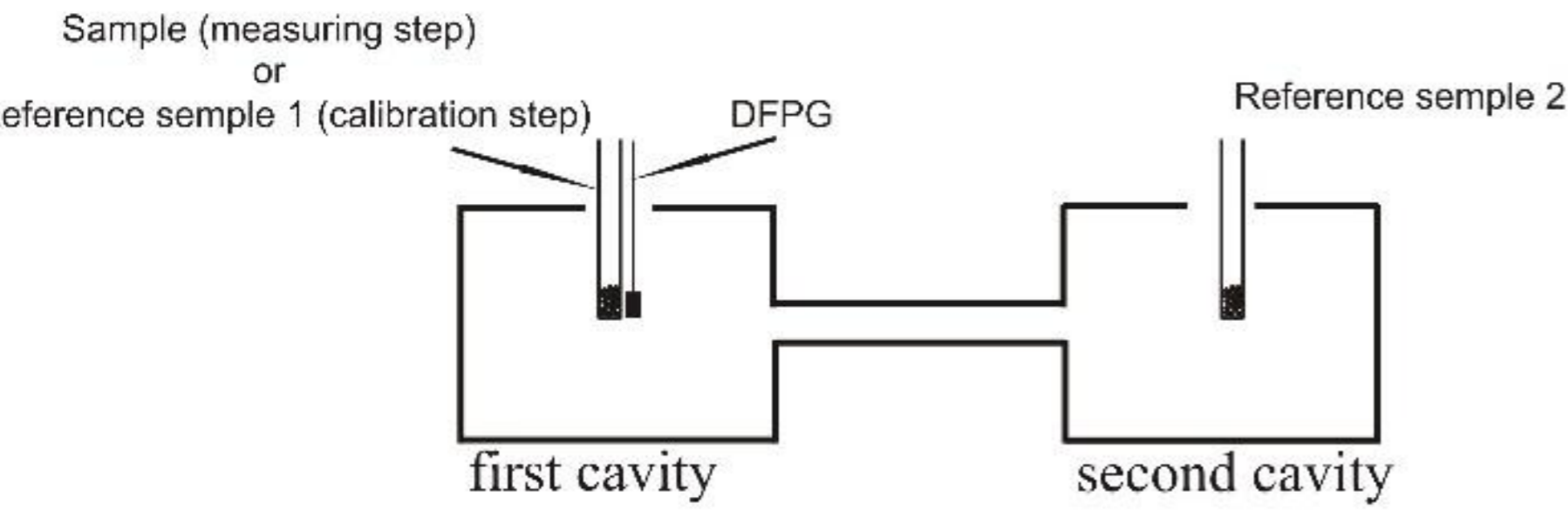
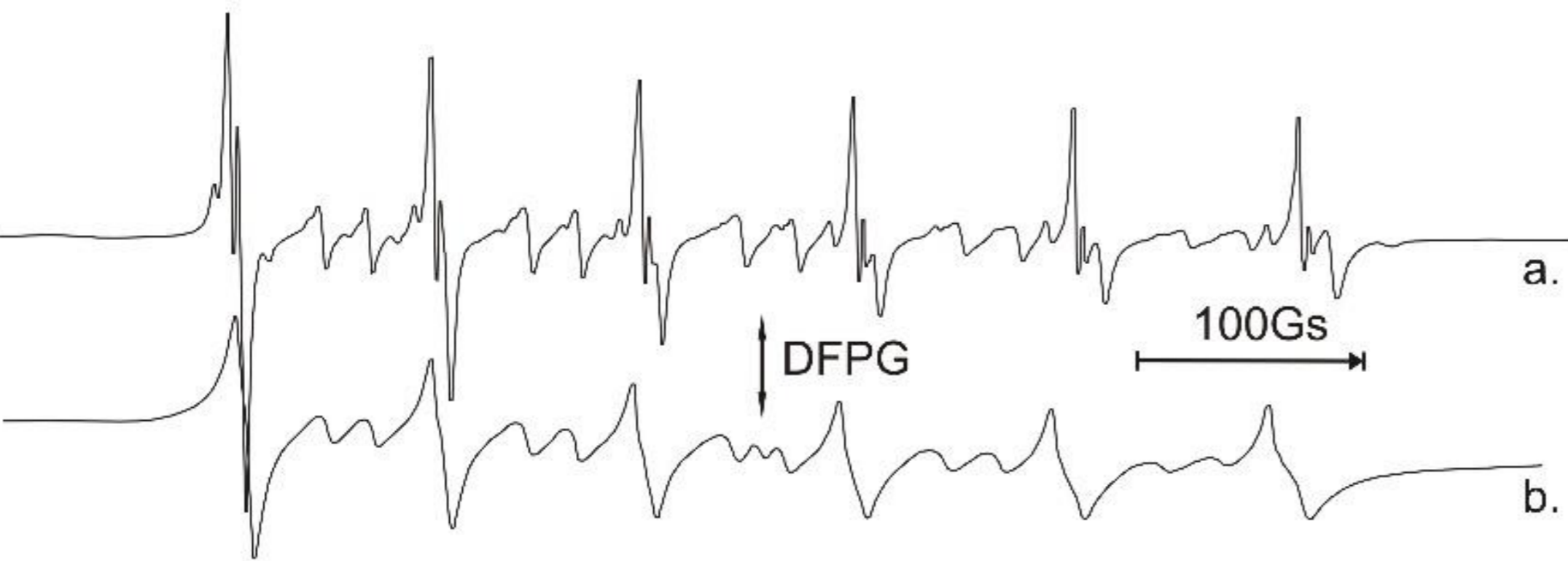


Fig. 2 ESR spectra of Mn in calcite, reference sample (a) sediments of Lake Alyaty (b)



The concentration (N, ppm) of impurity Mn²⁺ bounded to calcite contained in the sample is calculated using the formula:

$$N = \frac{N^* I_{int} P^* I^*}{I_{int}^* P I} \quad (1)$$

where *P* – the sample weight (mg); *I_{int}* – the integrated intensity of the low-field (doublet) line of the HFS of the EPR spectrum of Mn²⁺ in the calcite lattice of the sample; *I_{int}^{*}* – the integrated intensity of Mn²⁺ in calcite of the first reference sample, *N^{*}* (80 ppm) – concentration of Mn²⁺ in the first reference sample of calcite; *P^{*}* – weight of the first reference sample; *I* – the peak intensity of the low-field HFS line of the Mn²⁺ spectrum for the second reference sample (the sample is placed in the second cavity of the spectrometer to control its sensitivity), *I^{*}* – the peak intensity of Mn²⁺ of the second reference sample at the calibration step.

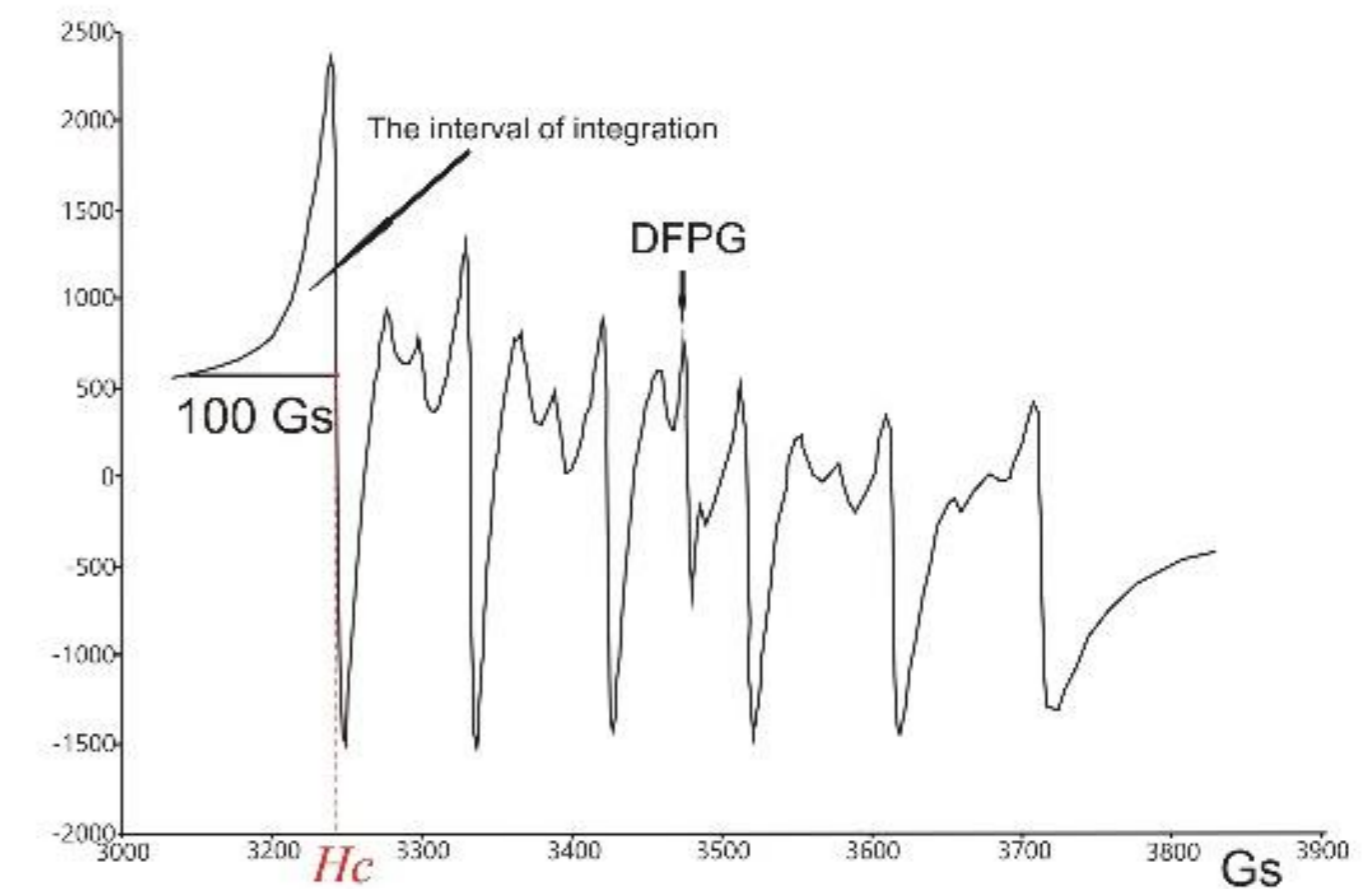
Table. 1 Scheme of sequential leaching (Giancoli Barelo et al., 2004)

Fractions	Chemical reagents	Phases with target ions
Step 1	1 M CH ₃ COONH ₄	exchangeable ions
Step 2	5 M CH ₃ COONH ₄ , HNO ₃ up to pH 5	carbonates
Step 3	0.1 M NH ₂ OH-HCl in 25% CH ₃ COOH	oxides and hydroxides of iron and manganese
Step 4	H ₂ O ₂ + HNO ₃ up to pH 1.5	organic matter
Residual	-	Residuals

Mn chemogenic
Mn(total)

A disadvantage of sequential extraction scheme is that the main quantity of Mn hydroxides dissolve on carbonate step. Therefore in addition the concentration of Mn²⁺ ions in the calcite was measured by ESR method.

Fig.3 ESR spectra of Mn in calcite of Lake Ordynskoye sediments



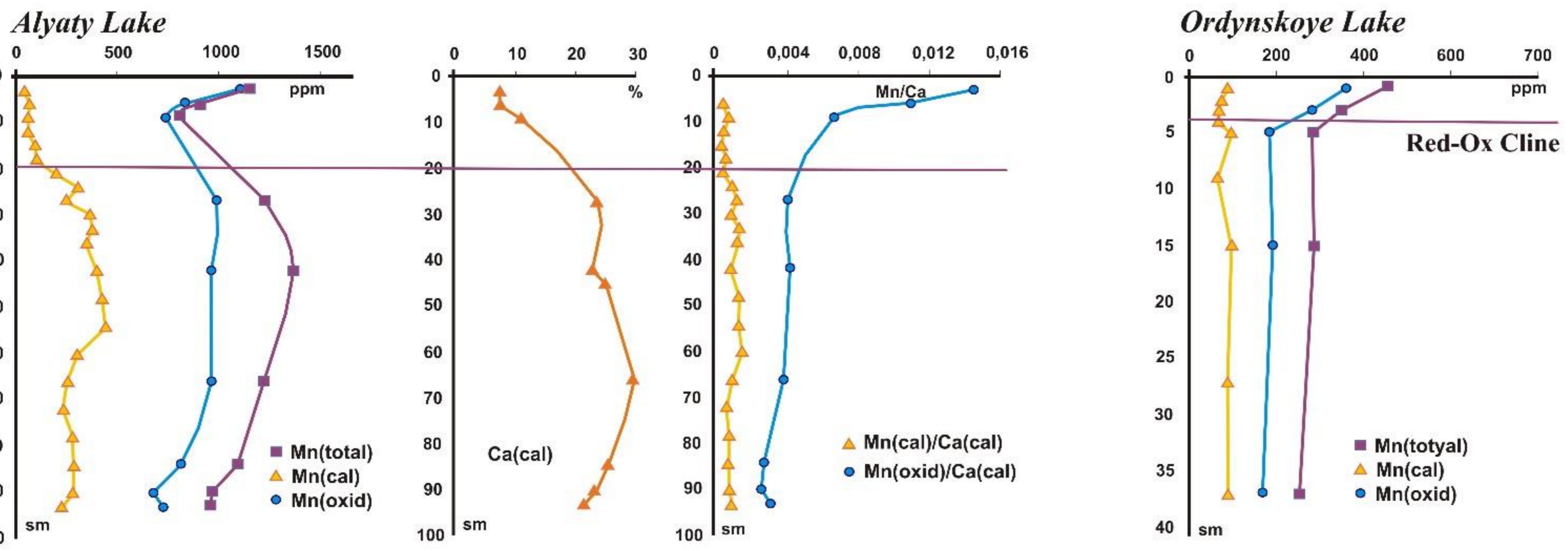
The integrated intensities were calculated by double integration on the segment from the center of the low-field doublet to a point on its left wing, located far enough from its center. Since the observed widths of the doublet lines in our samples are no more than 10 Gs, the used integration interval was 100 Gs. In addition to the boundaries of this segment, it was necessary to set the level of the zero line, *I₀*, from which the intensity of the ESR signal was measured. *I₀* was chosen so that the integral intensity of the ESR signal of ferromagnetic impurities ($\Delta I(H)$) vanishes upon double integration. Ferromagnetic Fe phases are always present in sediments. Since the widths of the spectra of ferromagnetic phases, are noticeably larger than 1000 Gs, the approximation was used that, over a short integration interval of 100 G, the impurities ESR signal intensity *I(H)* as a function of the magnetic field *H* changes linearly:

$$\Delta I(H) = I(H) - I_0 = a - bH, \quad (2)$$

The values of the constants *a* and *b* were determined based on the fact that at the ends of the integration interval the intensity of the observed signal is strictly equal to the intensity of the signal of the ferromagnetic impurities. As a result, the following expression was obtained for *I₀*:

$$I_0 = \frac{2I(Hc-100) + I(Hc)}{3} \quad (3)$$

Fig.4 The total amount of Mn released into solution and amount of Mn in calcite (ESR) in studied lakes



$$Mn(total) - Mn(cal) = Mn(oxid)$$