

Project Deliverable
D.3.3

Collaborative Project

ReCosy

REDOX PHENOMENA CONTROLLING SYSTEMS

Project Number: FP7 212287

D3.3.Buffer capacity and the redox kinetics of the systems investigated

Submitting organizations: II-HAS (Institute of Isotopes, Hungarian Academy of Sciences, project partner # 19)

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CO	Confidential, only for partners of the project	

The investigated system was the Boda Claystone, samples collected from different locations were analysed. Practically there were two types of locations from where the samples were obtained: i/ from boreholes drilled in an exploratory shaft in a depth of 1050 m, and ii/ from boreholes driven from the ground.

The mineral compositions of various Boda Claystone samples are known – several samples have been analysed and the obtained results have been published. Clay minerals represent a significant portion among the components (Árkai et. al (2000)).

A presumption was at the commencement of the recent studies that occurrence of redox changes most probably may be expected in the layered clay minerals. Further on, the Fe^{2+}/Fe^{3+} ratio in minerals was considered as a characteristic indicator of the redox state in the systems studied. A convenient way for the determination of the Fe^{2+}/Fe^{3+} ratio was the application of the Mössbauer spectroscopy.

1. First, the effects of *changes in the natural conditions* have been analysed.

In order to obtain information on the effects of changes having occurred in the natural conditions during the diagenetic and post diagenetic processes two types of samples have been analysed. First, a series of samples were collected from borehole Delta-9 in the depth of 1050 m. This borehole crosses a few meter thick reduction zone. In a second series samples collected from a borehole close to the surface were analysed (starting from 22.3 m depth – borehole BAT-14). (The Boda Claystone was covered here with Quaternary sediments of 22.3 m thickness - loess and marl).

1.1 Crossing a reduction zone

Typical Mössbauer spectra are shown in Fig 1.

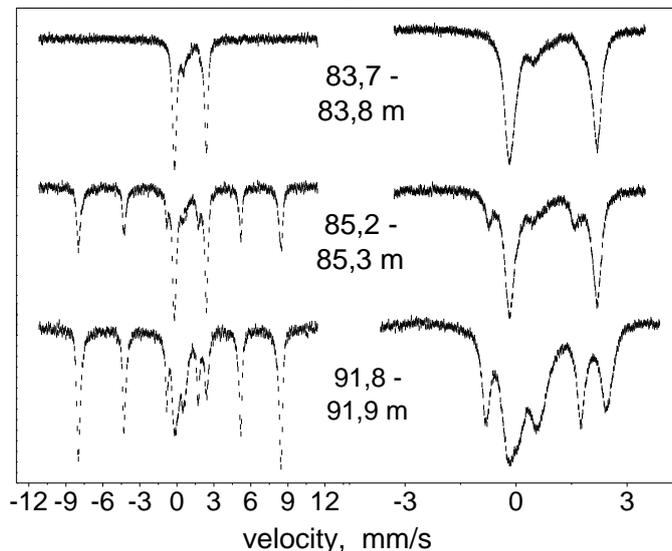


Figure 1. Mössbauer spectra of samples collected from Delta-9 borehole. Spectra were collected in two velocity ranges. The 12 mm/s range shows the whole spectrum (with sextet of hematite), the 4 mm/s range shows only the central part (only the two central lines are shown from the sextet of hematite). The top spectrum shows exclusive presence of ferrous iron whereas in the two bottom spectra presence of hematite is also apparent.

The spectra illustrates that in the centre of the reducing zone (83.7 m sample) iron occurs only in ferrous state dominantly in chlorite. In other samples collected from more or less oxidized strata presence of ferric oxide (hematite) is apparent. Simultaneously, presence of ferric iron can also be revealed in the chlorite mineral in the bottom spectrum. Further details, interpretations of these measurements are described in (Lázár et al. (2009)).

1.2. Effect of weathering

The effect of weathering can be deduced from Mössbauer spectra of Fig. 2. Hematite is present in each sample, showing that during the formation of this thick strata of claystone the oxidative environment was prevailing. However, the Fe^{2+}/Fe^{3+} ratio in the clay minerals (chlorite, illite-muscovite and montmorillonite) was changing with the depth. Close to the surface the Fe^{3+} forms of minerals were dominant, whereas in a few m distance from the surface the ferrous component also appears in the chlorite and its proportion starts to grow with the depth.

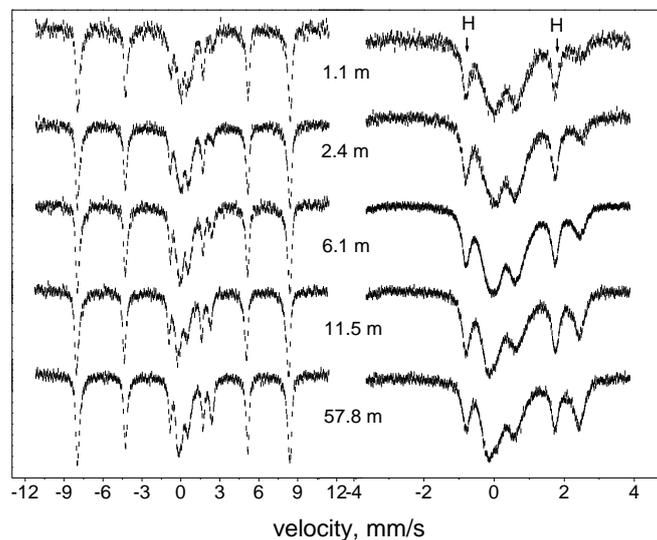


Figure 2. Mössbauer spectra of samples collected from different depths of BAT-14 borehole. Left side: full velocity scale (12 mm/s range), right side: central part (4 mm/s range). The increase of the portion of Fe^{2+} component is apparent with the increase of the depth (the very right peak belongs to Fe^{2+} component)

Further details, interpretations of these measurements are described in (Lázár et al. (2009)).

Here a short estimation for the **buffer capacity** can also be presented. Considering e.g. the samples of BAT 14 in an undisturbed region e.g. in the 57.8 m (bottom spectrum of Fig. 2), the amount of Fe^{2+} present in the clay minerals can be estimated. The mineral composition of the sample is known, it contains clay minerals in ca. 50%. From the Mössbauer spectra the Fe^{2+}/Fe^{3+} ratio in the layered clay minerals can also be estimated (with the exclusion of hematite). This ratio is close to 1 (Lázár et al. (2009)). Combining all these data together approximately 1 mmol / 1 g sample redox buffer capacity can be estimated, with assuming an one electron, $Fe^{2+} \leftrightarrow Fe^{3+}$ redox process in the clay minerals.

2. Treatments of samples with **oxidizing and reducing agents** in aqueous phase (artificial conditions)

In a further stage of studies a set of samples were treated with strong oxidizing and, in another series and another set of samples, with strong reducing agents.

2.1 Treatments with strong oxidizing agents

Samples collected from borehole Delta-9 (84.9 m) were selected for these treatments. These samples were situated in the reducing zone of formation – similar to those mentioned in paragraph 1.1 (Fig. 1, top spectrum). 800 mg of samples were treated with aqueous solutions of perchlorate, hypochlorite and hydrogen peroxide agents. The amounts of the oxidants were applied in 4 – 5 fold excess as compared to the amount necessary to reach a ferrous → ferric oxidation of the iron component present in the stone. The oxidizing solutions were equilibrated with the crushed samples for 10-15 days. Figure 3. shows the results. It is clearly seen that the oxidizing agents did not have any detectable effect: the prevailing ferrous oxidation state have not been changed during treatments.

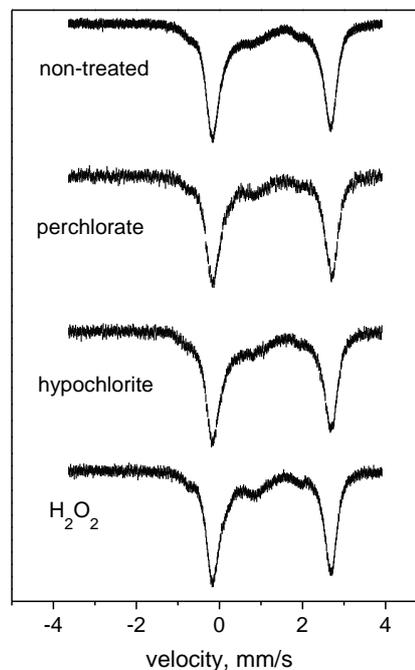


Figure 3. Mössbauer spectra of samples taken from the reducing zone of Delta-9 borehole treated with different oxidative agents in aqueous media.

2.2. Treatments with reducing agents

Samples were selected from the same borehole but from another location (91.9 m). At this location the oxidizing conditions were dominant during formation, i.e. samples contained hematite in significant amounts and ferric iron was also present in the layered clay minerals (Fig. 4.) Various reducing agents were applied: hydroxylamine hydrochloride, formaline, hydrazine and dithionite. The conditions were the same as in the previous case: the agents were applied in 4-5 fold excess, and they had been equilibrated with the crushed samples in aqueous media for 10 – 15 days. The results with the first three agents were same as in the previous case:

no influence of the treating agents on the oxidation state of iron could be detected. The fourth case, treatment with dithionite, was an exception, the shape of the detected Mössbauer spectrum has been changed. The decomposition revealed that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio did not change in the layered clay minerals in this case, either. Instead, the hematite component was reductively dissolved, this process resulted in the change of the shape of the spectrum.

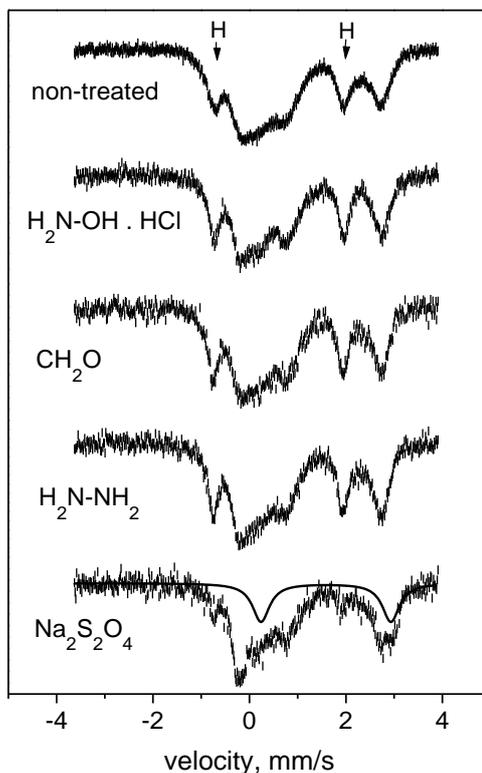


Figure 4. Mössbauer spectra of samples taken from an oxidative region of Delta-9 borehole and treated with various reducing agents in aqueous media. In the bottom spectrum the solid line represents a new component formed in the course of the treatment with dithionite.

In short, the results of the treatments both with oxidizing and reducing agents can be summarised that no influence of the treatments could be revealed on the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of the layered clay minerals.

Further experimental details of these oxidation/reduction treatments and interpretation of the treatment with dithionite are reported in (Lázár et al. (2010)).

Finally, it should be mentioned that Boda Claystone samples collected from borehole Delta-9 and BAT-14 were also characterised with **voltammetric measurements**. In voltammetry the iron containing different minerals gave different signals thus, they can also be distinguished by this method. The results could be correlated with those of Mössbauer spectroscopy. Further details of voltammetric characterisation of Boda Claystone samples can be found in the poster presented at the 3rd AWS (Perdicakis et. al (2011)).

References

Árkai P., Balogh K., Demény A., Fórizs I., Nagy G., Máthé Z., (2000), Composition, diagenetic and post-diagenetic alterations of a possible radioactive waste repository site: the Boda Albitic Claystone Formation, *Acta Geologica Hungarica*, **43**, 351-360.

Lázár K., Máthé Z., Földvári M., (2009), Redox transitions in Boda Albitic Claystone under natural conditions: Variations in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of clay minerals, in: 1st Annual Workshop Proceedings, 7th EC FP- Recosy CP, Ed: G. Buckau et al., Forschungszentrum Karlsruhe, FZKA 7466, 131-137.

Lázár K., Megyeri J., Máthé Z., (2010), Lack of redox response in some cases on Boda Claystone samples as reflected in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in minerals, in: 2nd Annual Workshop Proceedings, 7th EC FP- Recosy CP, Ed: G. Buckau et al., Karlsruhe Institute of Technology, KIT Scientific Reports, 7557, 193-200.

Perdicakis M., Xu Y-L., Lázár K., Máthé Z., (2011) Voltammetric characterization of Boda Albitic Claystone: Comparison with Mössbauer spectroscopy data, Poster, presented at the 3rd AWS ReCosy, Balaruc-les-Bains, France, 21-24 March.