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Mössbauer study of dissimilatory reduction of iron contained in glauconite by alkaliphilic bacteria

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Abstract ^{57}Fe Mössbauer investigations of glauconite and new solid phases formed during the process of the bacterial growth in alkaline environment were carried out at room temperature, 78 K and 4.8 K. The magnetically ordered phase formed during bioleaching of glauconite by *G. ferrihydriticus* in pure culture or in combination with *Cl. alkalicellulosi* represented as a mixture of off-stoichiometric magnetite and maghemite. In case of combined binary bacterium culture growth the relative content of magnetically ordered phase was more than for the *G. ferrihydriticus* growth.

Keywords Mössbauer spectrometry · Glauconite · Alkaliphilic bacterium · Iron reducing bacterium

1 Introduction

Soda deposits are formed at the final stages of continental CO_2-weathering. It could occur under alkaline conditions either chemically or stimulated biotically. There are two main groups of alkaliphilic microbial agents that act in anaerobic conditions on the water-rock contact: a) fermentative hydrolytic decomposers of particulate organic matter, e.g. cellulose, capable to produce organic acids as the products of metabolism; b) respiratory anaerobes, utilizing dissolved compounds with external electron acceptors. The aim of our work was to study the interactions between representatives of this two group of alkaliphilic anaerobes and glauconite $[K_{<1}(Fe^{3+}, Fe^{2+}, Al, Mg)_{2-3}[Si_3(Si, Al)O_{10}]\ [OH]_2 \cdot nH_2O]$ by Mössbauer spectroscopy.

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2 Experimental

Two alkaliphilic anaerobic bacteria were used in the work. Bacteria *Clostridium alkalicellulosi* (strain Z-7026) [1] was isolated from the sediments of soda lake Verhnee Beloe (Buryatia, Russian Federation), it is hydrolitic decomposer. The growth conditions are: pH 8.0–10.2 (pH_{opt} 9.0); $T = 18 - 39°C$ (T_{opt} 35°C). NaCl 0–30 g/l ($NaCl_{opt}$ $10 - 20$ g/l). This strain is able to fermenting cellulose producing lactate, acetate, ethanol, formate and $H_{2.}$. Bacteria *Geoalkalibacter ferrihydriticus* (strain Z-0531) [2] was isolated from the sediments of soda lake Khadyn (Tuva, Russian Federation), it is respiratory anaerobe. The growth conditions are: pH 7.8–10.0 (pH_{opt} 8.6); $T = 18 - 39°C$ (T_{opt}35°C). NaCl 0–50 g/l ($NaCl_{opt}$0 g/l). The strain Z-0531 utilizes acetate, formate, lactate, ethanol, H_2 with ferrihydrite as an electron acceptor. Siderite [$FeCO_3$] and/or magnetite [Fe_3O_4] are the main reduced solid products [2, 3].

For the experiment 70 ml of carbonate buffered anaerobic medium (total mineralization 15 g/l, pH 9.5) in 120 ml flasks with 200 mg of micas were used. Microcellulose (MCC) (10% w/v) either acetate (2 g/l) were added as substrates. Time of exposition was 165 days at 35°C.

^{57}Fe Mössbauer investigations of solid phase samples obtained during the process of the bacterium growth were carried out at room temperature, 78 K and 4.8 K. The program SpectrRelax from MSTools Complex was used for spectra processing.

3 Results and discussion

Mössbauer spectra of initial glauconite, glauconite in cultivation medium in sterile conditions, solid phases obtained as a result of biotic alkalinolysis of glauconite by *Cl. alkalicellulosi with MCC*,*G. ferrihydriticus* with acetate and combined alkalinolysis of glauconite by binary culture of *Cl. alkalicellulosi* and *G. ferrihydriticus* with MCC as organic substrate are shown in Fig. 1. Spectra were recorded at room temperature and at 78 K. Room temperature spectra were paramagnetic type spectra. In (d) and (e) spectra small intensity sextet with broaden lines was observed.

There are some different models for glauconite spectrum fitting [4–6] (four-doublet or three-doublet models) due to the different possible distribution of ferric and ferrous atoms in different position M1 and M2 of glauconite. The octahedral sheet of glauconite contains three structurally-independent positions: one trans-octahedron (M1) and two cis-octahedra (M2) differing in positions of the OH groups. However according to X-ray and oblique-texture electron diffractions, and EXAFS spectroscopy [7] only the *cis*-sites are occupied by cations. Therefore the presence of more than one quadrupole doublets in the spectra is not due to the occupation of both types of positions but such factors as charge and type of neighboring octahedral cations, distribution of Al and Si in tetrahedral.

Room temperature Mössbauer spectrum of initial glauconite (Fig. 1a) was satisfactory fitted by a superposition of four quadrupole doublets corresponding to ferric and ferrous ions: $\delta_1 = 0.36 \pm 0.01$ mm/s, $\Delta_1 = 0.47 \pm 0.01$ mm/s; $\delta_2 = 0.49 \pm 0.04$ mm/s, $\Delta_2 = 1.37 \pm 0.06$ mm/s; $\delta_3 = 1.16 \pm 0.02$ mm/s, $\Delta_3 = 1.73 \pm 0.03$ mm/s; $\delta_4 = 1.15 \pm 0.01$ mm/s, $\Delta_4 = 2.74 \pm 0.02$ mm/s. For 78 K spectrum two quadrupole shift distributions were extracted – one for Fe^{3+} atoms and one for Fe^{2+}. Comparison

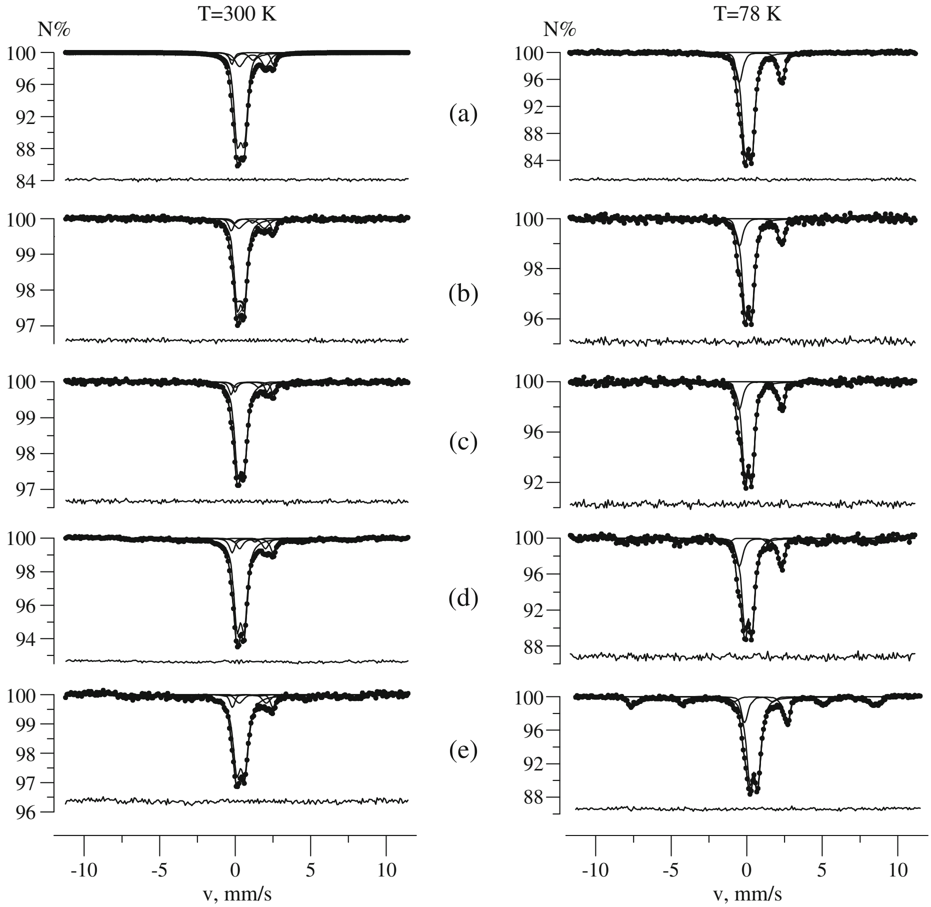

Fig. 1 Mössbauer spectra recorded at room temperature and at 78 K of initial glauconite (**a**), initial glauconite in cultivation medium in sterile conditions (**b**), solid phases obtained during the growth of *Cl. alkalicellulosi* with MCC and glauconite (**c**), *G. ferrihydriticus* with acetate and glauconite (**d**), binary culture of *Cl. alkalicellulosi* and *G. ferrihydriticus* with MCC and glauconite (**e**)

of (a) and (b) spectra in Fig. 1 showed that these spectra did not virtually differ. So a cultivation medium in sterile conditions did not significantly affect on initial glauconite. Similar results were observed when comparing (a) and (c) spectra. Thus *Cl. alkalicellulosi* did not reduce Fe^{3+} during its biotic alkalinolysis of glauconite. In the samples obtained as a result of *G. ferrihydriticus* growth with acetate and glauconite (Fig. 1d) the formation of magnetically ordered phase (about 5%) was observed. In 78 K spectrum the relative intensity of sextet reached 15%. In case of combined growth of *Cl. alkalicellulosi* and *G. ferrihydriticus* (Fig. 1e) the relative intensity of sextet increased and for 78 K spectrum was 22%. Thereby the content of synthesized magnetically ordered phase was more in case of combined binary bacterium culture growth. The increase in Fe^{2+} atoms content in solid phases obtained as a result of *G. ferrihydriticus* (d) and binary culture growth (e) occurred due to a decrease of Fe^{3+} atoms content and besides this decrease observed for

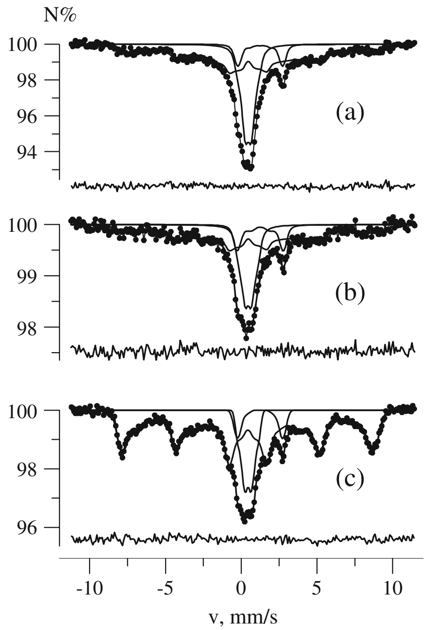

Fig. 2 Mössbauer spectra recorded at 4.8 K of initial glauconite (**a**), initial glauconite in cultivation medium in sterile conditions (**b**), binary culture of *Cl. alkalicellulosi* and *G. ferrihydriticus* with MCC as organic substrate and glauconite (**c**)

the position which corresponded to second doublet with larger quadrupole splitting. Moreover the intensity of the third doublet which corresponded to Fe^{2+} atoms also decreased.

Mössbauer investigations were carried out at 4.8 K (Fig. 2) to determine the magnetically ordered phase formed during binary culture growth. In 4.8 K spectrum of glauconite sextet with relative intensity 59 ± 3% appeared. The hyperfine magnetic field corresponding to maximum distribution was 491 ± 17 kOe which correlated with data obtained in [8]. These measurements also showed that spectra of initial glauconite and glauconite in cultivation medium did not virtually differ. In case of binary culture growth the intensity of sextet significantly increased. The difference between intensities of two sextets in (b) and (c) spectra which was equal to the relative intensity of the magnetically ordered phase was 19 ± 3% that corresponded to the results obtained at 78 K. The model fitting of the spectrum (c) showed the presence of Fe^{2+} atoms in magnetically ordered phase. The analysis of hyperfine parameters of this sextet made us conclude that magnetically ordered phase was a mixture of off-stoichiometric magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3).

4 Conclusions

Biotic alkalinolysis of glauconite by *G. ferrihydriticus* in pure culture or in combination with *Cl. alkalicellulosi* leaded to formation of new magnetically ordered phase containing magnetite and maghemite. While *Cl. alkalicellulosi* was inactive in enchancing weathering, binary combination of *G. ferrihydriticus* resulted in predominant synthesis of magnetically ordered phase.

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