

Experimental and thermodynamic study of silicate minerals interaction with gases of C–O–H system

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The interaction of carbon dioxide with minerals and rocks is important for both fundamental and applied geochemistry. Carbonation reactions are significant for description of hydrothermal processes, weathering, metamorphic processes, as well as for description of atmospheric gases interaction with rocks of the terrestrial planets' surface. In recent years much attention is paid to study the interaction of carbon dioxide with minerals and rocks in connection with the environmental issue on greenhouse gases sequestration in geological structures. By the present time numerous experimental studies are carried out [Lackner, *et al.*, 1995; O'Connor, *et al.*, 1999; Gerdemann, *et al.*, 2007; Huijgen, Comans, 2003; Huijgen, *et al.*, 2006; Oelkers, *et al.*, 2008; Soong, *et al.*, 2005; Xu, *et al.*, 2005; Zevenhoven, Kavaliauskaite, 2004], there are even pilot projects to inject carbon dioxide in various geological structures in situ [Gislason, *et al.*, 2010; Matter, *et al.*, 2007; McGrail, *et al.*, 2006].

The aim of the study is experimental and thermodynamic simulation of carbon dioxide interaction with silicate minerals at hydrothermal conditions (100–150°C).

Several series of experiments on the interaction of high-Mg olivine with carbon dioxide (source of which was foody dry ice) were carried out. Natural olivine from alkaline basalts of Shavaryn Tsaram (Mongolia) was used in experiments. Monofraction of the mineral was separated by hand using a binocular microscope and was treated in aqueous solution of HCl (HCl: H₂O = 1: 2) for removal of possible impurities. The olivine grain size in various experiments varied from 0.071 mm to 0.5 mm. The experiments with duration from 10 to 50 days were conducted with both pure CO₂ and addition of distilled water in stainless steel autoclaves with teflon liners inside, as well as in titanium autoclaves at temperatures of 100°C and 150°C by quenching.

X-ray powder diffraction and Raman spectroscopy were used for the analysis of experimental solid products.

The interaction of olivine with pure CO₂ (dry conditions) was carried out in first two series of experiments at temperature of 100°C and pressures of 100 and 150 bar with different olivine grain sizes. According to the results of X-ray diffraction and Raman spectroscopy (Fig. 1) carbonate phases was not detected. The composition of olivine from reaction products corresponded to the composition of initial olivine which was used in experiments.

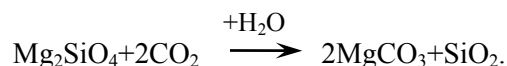
Thus, the formation of carbonate phase in dry system does not occur or occurs too slowly.

The interaction of carbon dioxide with rocks in dry system is of great practical importance for technologies of CO₂ sequestration in ultramafic rocks. If the injection of carbon dioxide in geological structures results in the formation of gas cap, CO₂ in it will be bad fixed in mineral form.

Further experiments on olivine interaction with carbon dioxide and water were carried out at the temperature of 150°C and CO₂ pressure of 105–165 bar. The duration of experiments varied from 10 to 50 days. The magnesium carbonate, magnesite, was already formed in reaction products of the 10-day experiment. The carbonate phase was identified by Raman spectroscopy (Fig. 2).

Also amorphous SiO₂, hematite and undecomposed olivine were detected in reaction products by this method (Fig. 2).

Thus, the reaction of olivine carbonation goes as follows:



Implementation of experimental study is labor-consuming enough and not always allows to answer to all formulated questions.

In this connection we carried out thermodynamic simulation using software package HCh developed by Yu.V. Shvarov at MSU. HCh includes the program Gibbs needed for the calculation of chemical equilibria in systems of arbitrary phase composition and the thermodynamic data bank Unitherm, which covers large part of geologically important substances and wide range of conditions.

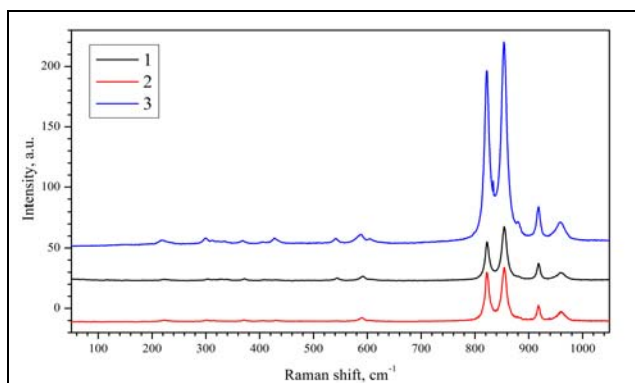


Fig. 1. Raman spectra of experimental products in dry system. Identification of olivine; 1 – experiment: olivine+CO₂, T=100°C, P=100 bar, 2 – experiment: olivine+CO₂, T=100°C, P=150 bar, 3 – initial olivine which was used in experiments

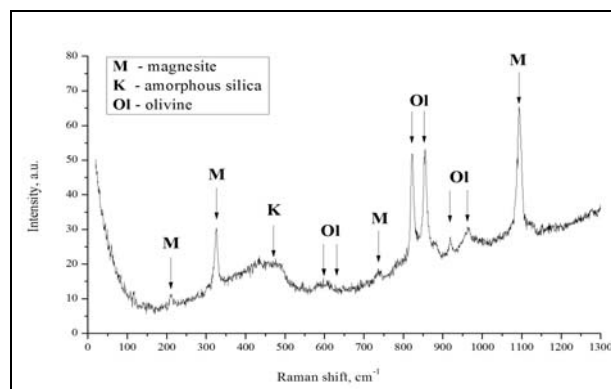
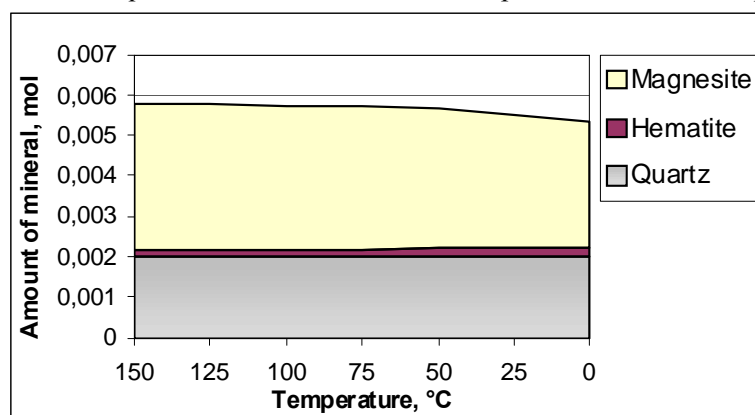


Fig. 2. Raman spectrum of reaction products of the experiment on olivine interaction with carbon dioxide and water, T = 150°C, P = 115 bar, 10 days duration

For more accurate description of the gas mixture obtained at simulating of C–O–H gases interaction with minerals and rocks we used data for real gases (H₂O, CO₂, H₂, O₂, CH₄, CO) during the creation of a model. Absent in the thermodynamic data bank information for the real gas CO was added to the standard data bank. Mixing of gases in the gas mixture was described by PRSV equation (Peng-Robinson-Stryjek-Vera, Peng-Robinson equation of state modified by Stryjek and Vera) [Stryjek, Vera, 1986] with using the additional parameters of imperfection – the coefficients of gases mixing with each other. The information for them was taken from literature [Roberts, Tremaine, 1985; Alvarez. et al., 1988; Peng Ding-Yu, Robinson, 1976; Mironenko, Kosorukov, 1990].

Also in a thermodynamic system oxygen was taken into account for more accurate simulation of autoclave filling conditions.

First the thermodynamic simulation of olivine interaction with carbon dioxide and water was implemented in accordance with conducted experiment. The initial composition of the thermodynamic system corresponded to the composition of experimental one. The calculation was carried out in the range of temperatures from 150°C to 0°C, the pressure was 115 bar. As a result the mineral association: magnesite-hematite-quartz was obtained. This corresponds to the reaction products obtained in the experiment (Fig. 3).



Verification	
Products of experiments	Result of calculation
Magnesite	Magnesite
Hematite	Hematite
Amorphous SiO ₂	Quartz

Fig. 3. Thermodynamic simulation in the system olivine+CO₂+H₂O at equilibrium conditions, T = 150–0°C, P = 115 bar. Verification according to experiments

For verification of thermodynamic calculations at higher temperatures and pressures we used the results of experimental studies from article [Dufaud, et al., 2009], in which experiments on the interaction of different minerals (olivine, chrysotile and orthopyroxene) with carbon dioxide and water were described. The

source of volatile matter in these experiments was the oxalic acid, the temperature and pressure of experiments were 400–500°C and 1 kbar, respectively. All conditions in our thermodynamic calculation corresponded to experimental conditions described in the article. The initial composition of the system took into account compositions of initial minerals used in experiments.

As a result we calculated polythermal diagrams on the interaction of each mineral with oxalic acid at temperature range from 500°C to 0°C with 50°C step.

The most significant result of this simulation is that the main reaction product obtained in the experiments – magnesite – in the calculation occurs only at temperatures < 500°C (Fig. 4). As temperature decreases the amount of formed magnesite increases and reaches the constant value at 400°C. Thus, at temperature of 400°C more magnesite is formed than at 500°C that corresponds to the results of conducted experiments.

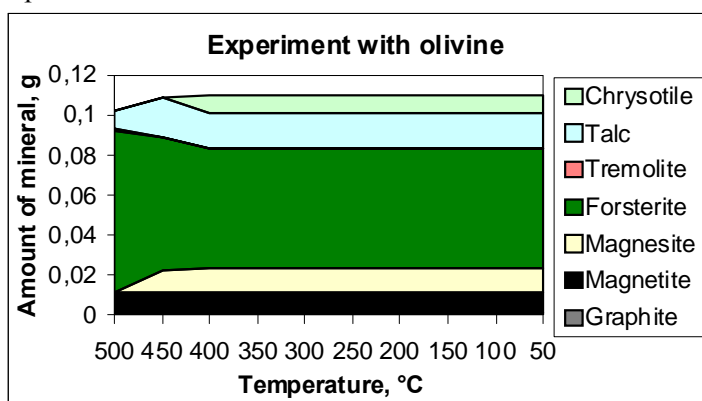


Fig. 4. Thermodynamic simulation based on literature data at the system olivine+oxalic acid at equilibrium conditions, T=500–0°C, P=1 kbar

Implemented study shows that the verification of thermodynamic models according to the experimental study is a challenge. However it allows not only to confirm the quality of calculation of reaction products composition but also to answer the question which wasn't raised – the dependence of the carbonation efficiency on temperature.

Next, the thermodynamic simulation on the olivine interaction with carbon dioxide in dry conditions was implemented. The conditions of calculation corresponded to the conditions of dry experiment. The temperature was 100°C, the pressure varied in a wide range. Two variants were considered: with increasing (from 1 to 100 bars) and with decreasing (from 1 to 10^{-10} bars) of the pressure. The simulation showed that under equilibrium conditions in dry system the formation of carbonate phase is possible (Fig. 5). Moreover, the magnesite is already formed at CO₂ pressure of 0.001 bar.

The discrepancy of simulation results and results of experiments in dry conditions indicates that there was not enough time in experiment for the formation of magnesite and the process in dry system is probably very slowly.

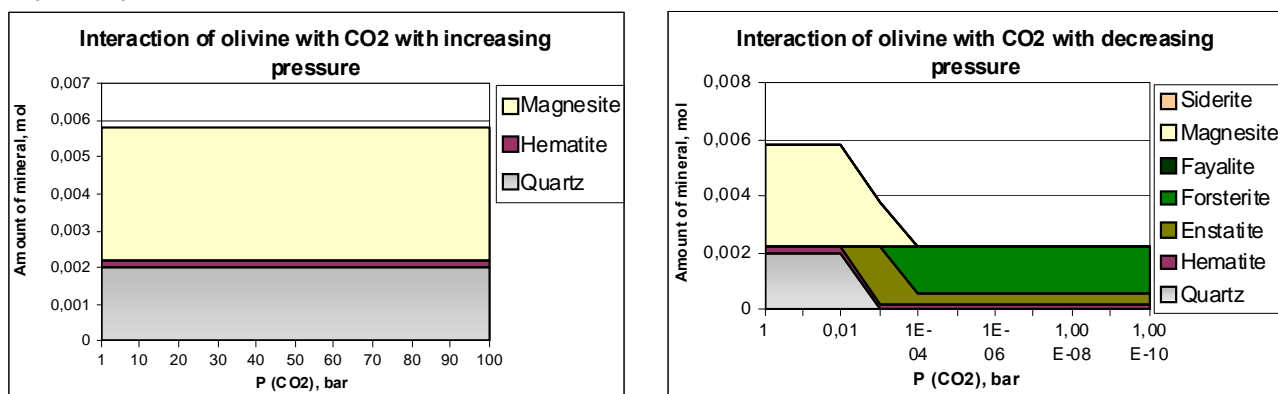


Fig. 5. Thermodynamic simulation in dry system under equilibrium conditions with variable pressure, T = 100°C

Conclusions

1. The experimental study of the olivine interaction with carbon dioxide in dry system at not high temperatures and pressures showed that the rate of carbonates formation is very low. For effective carbonation of olivine at moderate temperatures the presence of liquid water is necessary.
2. The thermodynamic model on «olivine – C–H–O fluid» interaction was developed. The model is verified according to the results of own and published in literature experimental data in a wide range of conditions.
3. The stability zone of magnesite in the reaction products is limited by the isotherm of 500°C at the pressure of 1 kbar.
4. The contradiction in the results of calculations and experiments on the interaction of olivine with carbon dioxide in dry system is caused by kinetic factor. This indicates to the importance of experimental studies as a control factor of simulation, especially for solving applied issues.
5. The comparison of thermodynamic and experimental results allows to make much deeper interpretation of obtained data.

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