KINETICS OF EXCHANGE REACTION WATER-CO_2 IN STRUCTURAL CHANNELS OF CORDIERITE

Bul'bak T.A., Shvedenkov G.Yu.[*], Sverdlova V.G., Ripinen O.I.
Institute of Mineralogy and Petrography SB RAS, [*]Novosibirsk State University
taras@uiggm.nsc.ru, Fax: +7-3832-332792
[*]shved@nsu.ru, Fax: +7-3832-302242

Key words: Fe-Mg cordierite, fluid, isotope exchange

Using of cordierite as a sensor of fluid environment of metamorphogenic minerogenesis predetermines the necessity of evaluating of keeping degree of fluid components in structural channels of cordierite under regressive changing of P-T parameters. In the decision of this problem the important place is borrowed with the characteristic of the diffusion process of exchanging between contents of structural channels and external fluid. It creates a basis for quantitative evaluating of changes in the fluid contents of cordierite channels during geological processes. In present work the definition of water diffusion factors in cordierite in conditions close to equilibrium is done on the basis of experiments studying the kinetics of an isotope exchange between water contents in cordierite channels and D_2O in surrounding fluid. The idea of experiments was: to place cordierite, previously saturated by water, to nonequilibrium conditions, thus to initiate partial reset of H_2O and to ensure an opportunity of exchanging between components contained in it's structural channels and surrounding fluid.

Starting Mg-cordierite was received by hydrothermal synthesis in gold ampoule at $P_{H_2O} = 275$ MPa and T=595 °C during 52 hours from dried out $2MgO\text{-}2Al_2O_3\text{-}5SiO_2$ gel. Starting Fe-bearing secanianaite with ferruginosity $F = \frac{Fe^{2+}}{Fe^{2+} + Mg} \cdot 100 = 97{,}7\%$ was hydrothermally synthesized from ferrous stehiometric gel of appropriate composition under conditions of $P_{H_2O} = 200$ MPa and T=650 °C during 240 hours with using of start-up pieces which were previously made from 75% Fe-bearing cordierite with using traditional two-ampoule technology with P_{O_2}-buffer. Further magnesian and ferriferous samples with the average size of crystalline grains 37±2 μm were affected with various time expositions by heavy water and carbon dioxide under pressures P=50, 100, 150, 200 MPa and temperatures varying from 700 up to 200 °C.

On the basis of the experimental studying of kinetic characteristics of exchange reactions $H_2O \rightarrow D_2O$ and $H_2O \rightarrow CO_2$ in structural channels of cordierite there were determined the "closing" parameters of the system (Mg, Fe^{2+})-cordierite - water-carbon dioxide fluid. With the rise of total pressure from 50 to 200 MPa in the temperature interval of 200-350 °C the exchanging of fluid components between water from cordierite and external fluid ends outside of the stability field of Mg- and Fe-cordierites.

As migration of fluid molecules in cordierite most likely occurs along its structural channels, it's quite applicable for this case the solving of one-dimensional differential equation of diffusion in the cylinder [1]. Average values of the water diffusion coefficient at T=700-200 °C in Mg-cordierite are located in the interval (2, 49±1, 15)*10^{-12} – (2, 62±0,618)*10^{-15} cm^2/sec, and the activation energy is appreciated as 16, 54±0, 99 kcal/mol H_2O, the frequency factor D_0 = (2, 71±0, 34)*10^{-8} cm^2/sec. For secaninaite the water diffusion coefficient are determined as (1, 13±0, 33)*10^{-12} – (5, 60±0,336)*10^{-15} cm^2/sec in the temperature interval of 700-300 °C, activation energy makes 17, 35±1, 87 kcal/mol H_2O, D_0 = (1, 29±0, 76)*10^{-8} cm^2/sec.

The activation energy of diffusion in this work coincides in the limits of accuracy with the energy of activation of the cordierite hydration reaction defined by Mirwald et al (13±2,5 kcal/mol H_2O) [2]. It means, that the major factor which determines the speed of reaction of hydration, is diffusion mobility of water in structural channels of cordierite. In confirmation of the results of Mirwald et al [2] the values of diffusion coefficients determined in present work are a little bit below the effective values, determined by Lepezin and Osorgin [3, 4] for conditions of dehydration .

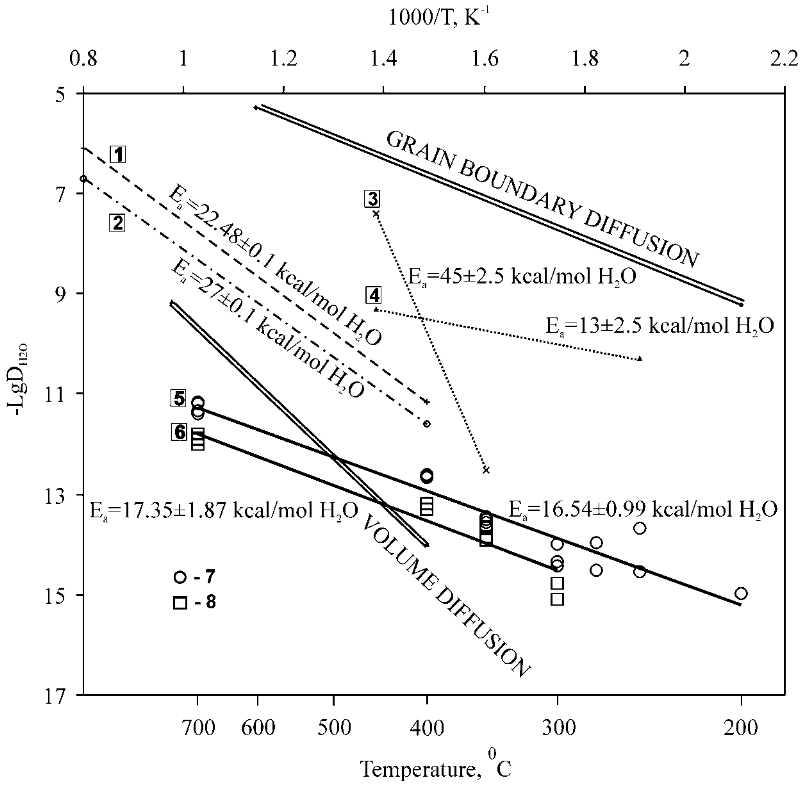

Fig.1. Definition of activation energies of water diffusion in cordierite based on experimental data: 1 – theoretical calculation based on the model of diffusion from the cylinder; 2 – theoretical calculation based on the model of diffusion from sphere; 3 – dehydration of Mg- cordierite; 4 - hydration of Mg- cordierite; 5, 6 – this work's definitions based on the data of an isotope exchange for magnesium cordierite and secaninaite, accordingly. 7, 8 – definition diffusion coefficients of water based on isotope exchange for magnesium cordierite and secaninaite.

The grain boundary diffusion and volume diffusion are specified by [2].

The research was made possible in part by Award No. NO-008-XI, Y1-CG-08-06 of the U.S. Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CDRF) and was financially supported by Ministry for Education of the Russian Federation within the Program "Basic researches and higher education" and by grants: 03-05-65076 from the Russian Foundation for Basic Research; E3H 3H-116-00, E3H 3H-018-00 from Ministry for Education of the Russian Federation; НШ-225.2003.5 from the President of the Russian Federation for support of young Russian scientists and leading scientific schools of Russian Federation and 2003-88 the Siberian Branch of the Russian Academy of Science for young scientists.

References

1. *Aramanovich I.G., Levin V.I.* The equations of mathematical physics // M.:Nauka, 1969, 288 p. (in Russian).
2. *Mirwald P.W., Jochum C., Maresch W.V.* Rate studies on hydration on and dehydration of synthetic Mg-cordierite // Materials Science Forum, 1986. V.7. PP. 113-122.
3. *Lepezin G.G., Osorgin N.Yu.* The kinetics of degasation of natural cordierites: the definition of water diffusion coefficients under isothermal conditions // Dokl. RAN, 1994. V.339. № 5. PP. 658-661 (in Russian).
4. *Osorgin N.Yu.* The kinetics of degasation of (H_2O and CO_2) cordierites and its role for metamorphic petrology // Ph.D.Thesis, Novosibirsk, 1991, 163 p. (in Russian).

Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(22)'2004
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2004
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2004/informbul-1_2004/mineral-30e.pdf
Published on July, 1, 2004