EXPERIMENTAL STUDY OF THE MECHANISMS OF CALCITE AND DOLOMITE MELTING AT HIGH FLUID PRESSURES

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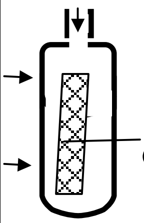
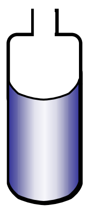
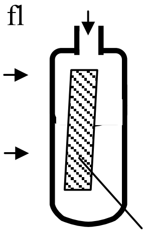
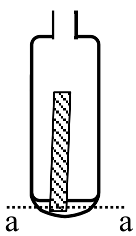
Key-words: carbonates, melting, high pressures apparatus, fluid, mechanism

Melting experiments on natural calcite crystal and natural Si-poor dolomite at 1 kbar pressures of fluid of different composition (Ar, Ar + H_2O, CO_2, CO_2 + H_2O) and at the temperature up to 1310°C were carried out to understand the effect of fluid composition on the mechanisms of calcite and dolomite melting. A unique high gas pressure apparatus has been used for the experiments. The apparatus is composed of an internally heated pressure vessel that is equipped with an internal device [1]. The device involves a special modified piston cylinder-type separator-equalizer [2].

The experimental study of calcite (Cal) and dolomite (Dol) melting under 1 kbar pure and dried CO_2 and Ar pressures and at the temperature 1310°C was carried out for the first time. The results obtained indicated that calcite (pure icelandic crystal) incongruently melted at T= 1310°C ± 10°C and carbonatite melt (92.3Cal + 7.7CaO, in wt %, calculated) formed, the weight loss of this sample was 5.27 wt %. This result is consistent with the calculated data for the calcite incongruent melting at 1 kbar CO_2 pressures [3].

Table 1. Experimental conditions and results of calcite and dolomite melting at P_{fl} = 1 kbar

Sample No.	T, °C	Fluid composition, (wt %); oxygen buffer	The design of Pt capsules: start	The design of Pt capsules: after run	Run duration (min.)	Weight loss of carbonate (CO_2 wt %)
1575/1 (No. 1)	1150	97Ar + 3H_2O; HM	fl  Cal		5	3.7 ***5.27
1604/1 (No. 14)	1260	97Ar + 3H_2O; HM			120	12.8 12.3 (calculated)
1576/5 (No. 13)	1280-top 1300-bottom	98CO_2 + 2H_2O; HM			120	13.1 12.3 (calculated)
1604/2 (No. 15)	1260	97Ar + 3H_2O; HM	fl  Dol	 a a	120	36.5 36.2=23.98* +12.3 (calculated)
1576/4 (No. 3)	1280-top 1300-bottom	98CO_2 + 2H_2O; HM			120	36.4 36.2=23.98* +12.3 (calculated) **47.72

Abbreviations: * The reaction of partial decomposition of dolomite:
$MgCa(CO_3)_2 = MgO + CaCO_3 + CO_2$ (The CO_2 loss is 23.98 wt %);
** The reaction of full dolomite decomposition: $MgCa(CO_3)_2 = MgO + CaO + 2CO_2$ (The CO_2 loss is 47.72 wt %);
*** The full incongruent melting of calcite (The CO_2 loss is 5.27 wt %)
HM is the hematite/magnetite oxygen buffer; Dol - dolomite; Cal - calcite

Dolomite sample was partly decomposed at T > 800°C to form periclase (Per) + Cal + CO_2, and formed Cal is incongruently melted in full at T= 1310°C. The CO_2 loss of that sample was 29.25 wt %

in sum. Periclase, calcite and the assemblage of CaO + Cal were found in this quenched sample using microprobe analyses.

A quite different result has been obtained in the runs with a water-bearing CO_2 and Ar fluids (up to 3 wt %). In these cases the icelandic crystals start to melt at T=1150^{o}C (samples No. 1, Table 1), and they melted in full at moderate temperature shown at the table (samples No. 14 and 13, Table 1). The assemblage of CaO + Cal and separated calcite phases have been determined in quenched samples. The CO_2 loss at high temperatures is about 13 wt %. The incongruent melting of calcite can not explain such a full melting because in this case the CO_2 loss should be just 5.27 wt % as indicated above. Based on the data obtained and the results of mass-balance calculations (Table 1) as well as on experimental data on melting in the system portlandite (Prd)+Cal [4], the following mechanism has been proposed.

Calcite must be partly react with water to form (Prd) at the temperatures up to 680^{o}C and then the system of a eutectic melt (56Prd + 44Cal, in wt %) + solid Cal should be formed at the moderate temperatures. At the temperatures higher than 1150^{o}C the mentioned system should melt in full with formation of a carbonatite melt (82Cal + 18CaO, in wt %, calculated) and 12.3 wt % CO_2 released in sum. Formed water must be extracted on a fluid too because water solubility in carbonatite melts is very small at such high temperatures [3].

The dolomites (samples No. 15 and No. 3, Table 1.) are partly decomposed and formed Cal melted in full by the mentioned above mechanism. The weight loss of these samples is inconsistent with the reaction of the full decomposition of Dol (Table 1), and on the contrary, it is consistent with the results of mass-balance calculations for the proposed mechanism as well as with experimental data obtained (Table 1). The melt formed is mostly separated from dolomite and it is accumulated at the bottom of the Pt capsule and formed a differentiated crust around a mostly periclase core (Table 1). Using microprobe analyses we found mostly periclase and a small amount of calcite in a periclase-rich restite and calcite, separated CaO and the assemblage of Cal + CaO in the formed melt (the crust of this sample). The CO_2 loss in this case must be about 37 wt % in sum (Table 1). It is interesting that all the admixture elements of dolomite such as Al_2O_3, SiO_2 and P_2O_5 are concentrated in the formed melt.

This result is the first experimental evidence that a rapid heating of dolomite at the 1 kbar water-bearing fluid pressures caused the decomposition it into periclase + calcite, releasing much CO_2 and then quantitatively melting of calcite by the proposed mechanism. A periclase-rich restite was left behind after the extraction of a low density, low-viscosity carbonatite melt.

Financial support was provided by the Russian Foundation for Basic Researches,
RFBR grant 03-05-64808 to E.S. Persikov

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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/term-5e.pdf
Published on July, 1, 2004