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Water solubility in carbonatite melts

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ABSTRACT

Water solubility in Ca-Na-Mg carbonate melt was measured at 900 °C from 0.25 to 2.25 kbar using a modified double-capsule technique and rapid-quench cold-seal vessels. The data can be described by the empirical relationship $W = 8.705\ P^{0.635}$, where W is water solubility in weight percent and P is pressure in kbar. The relative error in water solubility calculated by this equation is estimated to be about 15%. Already at 1 kbar, water solubility reaches nearly 10 wt%, which is two to three times the value observed for most silicate melts under similar conditions. The exceptionally high water solubility in carbonatite magmas together with the preferential partitioning of alkalis into a coexisting fluid phase may explain the massive aqueous metasomatism (fenitisation) usually observed around intrusive carbonatite bodies.

INTRODUCTION

Carbonatites are rare rocks on the Earth's surface, but they are believed to be important agents of mantle metasomatism. Moreover, some economically important deposits of the rare-earth elements and niobium are hosted by carbonatites (Bell 1989). Although there is no doubt that the ultimate source of carbonatites is in the mantle, a variety of processes may be involved in their formation and differentiation. Carbonatite magmas may be generated by partial melting of a carbonated mantle, by liquid immiscibility, or by fractional crystallization of silicate melts (Bell 1989; Bell et al. 1999, and references therein).

Water is an important agent to be considered in carbonatite genesis. First, water is able to depress the melting point of carbonatites to geologically reasonable temperatures (Wyllie and Tuttle 1960). Second, water may be crucial for the differentiation of carbonatite magmas. Fluid inclusion data suggest that water saturation was reached during the crystallization of many intrusive carbonatite bodies (Rankin 1977; Samson et al. 1995; Bühn and Rankin 1999). Although carbonatites exposed in the field usually consist of calcite and dolomite, with virtually no alkali carbonates, experimental evidence suggests that the primary carbonatite melts contains significant amounts of Na and K (e.g., Wallace and Green 1988; Lee and Wyllie 1994, 1998). A plausible explanation for this apparent contradiction could be a combination of crystal fractionation and alkali partitioning into an evolving aqueous fluid phase, leading to the formation of calcite or dolomite cumulates surrounded by zones of alkali metasomatism. Such a model would be consistent with field observations (Bell 1989; Bell et al. 1999; and references therein), fluid inclusion data (e.g., Bühn and Rankin 1999), and results from partitioning experiments (Veksler and Keppler 2000). It has even been suggested recently that the natrocarbonatite lavas of Oldoinyo Lengai, Tanzania are actually a condensate from an aqueous vapor phase rather than a product of normal magmatic fractionation or liquid immiscibility (Nielsen and Veksler 2002).

Despite the importance of water for carbonatite magmatism, water solubility in carbonatite melts is essentially unknown. Water solubility might be very high, because Koster van Groos (1990) observed complete miscibility in the Na_2CO_3-H_2O system above 500 °C and 1.5 kbar. Carbonatite melts are highly reactive and, usually, they cannot be quenched to glasses (Genge et al. 1995). Therefore, standard methods for measuring water solubility in silicate melts (Ihinger et al. 1994) cannot be applied. In this paper, I describe measurements of water solubility in carbonatite melts using a modified double-capsule technique (compare Ryabchikov et al. 1989; Veksler and Keppler 2000). In principle, this method also could be used to measure water solubility in other melts that cannot be quenched to a glass. A melt composition consisting of 40 wt% $CaCO_3$, 40 wt% Na_2CO_3, and 20 wt% $MgCO_3$ was chosen for the measurements, because Ca and Na, together with Mg are major constituents of most carbonatite melts. The compositions of the hydrous fluids coexisting with such a melt were studied by Veksler and Keppler (2000). Essentially, the fluids consist of water with some dissolved carbonates.

EXPERIMENTAL METHODS

Experiments were carried out in rapid-quench cold-seal vessels made of Nimonic 105 super alloy with water as a pressure medium. These vessels operate in a vertical position with the hot spot at the top of the vessel. The sample is placed on top of a filler rod, which can be moved between the hot spot and a water-cooled zone by an external magnet. Samples can be quenched to room temperature within 1–2 s.

Starting material for all experiments was a mixture of 40 wt% $CaCO_3$, 40 wt% Na_2CO_3, and 20 wt% $MgCO_3$ prepared from high-purity chemicals. Experiments were carried out in several steps:

(1) About 70 mg of the carbonate mixture were sealed into a platinum cap-

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sule of 3.5 mm diameter and 2.5 cm length. This capsule was run above the liquidus at 1 kbar and 900 °C for several days. Upon quench, the melt solidified to a massive block of carbonate inside the capsule.

(2) A tiny pinhole of about 200 µm diameter was drilled into the uppermost end of the capsule obtained in step 1. This capsule was then sealed into a larger platinum capsule (5 mm diameter, 3.5 cm length) together with 10 to 50 mg of distilled water. A rapid-quench autoclave was preheated to 900 °C and the desired pressure, with the capsule being in the cold part of the vessel. Once the final temperature was reached, the double capsule was elevated into the hot spot. During this experiment, the double capsule was always kept vertical, with the pinhole of the inner capsule pointing upward. Accordingly, the molten carbonate could not flow out of the inner platinum container. After a few hours, the charge was quenched to room temperature within 1–2 s. The double capsule was removed from the vessel within five minutes. Afterward, the outer capsule was opened and removed. Visual inspection showed that small amounts of carbonate were usually extruded from the inner capsule. The inner capsule was usually filled with a massive block of quenched carbonate up to the pinhole. Runs that showed some cavity behind the pinhole were discarded.

(3) The inner capsule was cleaned with a tissue, weighed, and immediately sealed into a larger platinum capsule (5 mm diameter, 3.5 cm length) to avoid any loss of water before measurement.

(4) Water contents were measured by coulometric Karl-Fischer-Titration (Eberius 1958). This method is based on the reaction $SO_2 + I_2 + 2\ H_2O = 4\ H^+ + 2\ I^- + SO_4^{2-}$. The platinum capsule was pierced immediately before the measurement and placed in a furnace where it was slowly heated to 1300 °C. The water released was transported into the titration cell by a stream of purified argon. Any CO_2 released from the sample would not affect the measurement.

In order to calculate water solubility, the mass of water measured by Karl-Fischer titration was divided by the total mass, M_C, of quenched hydrous carbonate melt present in the capsule. M_C is given by $M_C = A - (B - C)$, where A is the mass of dry carbonate originally loaded into the capsule in step 1, B is the total weight of the capsule prepared in step 1, and C is the weight of the same capsule as determined in step 3. The difference, $B - C$, is due to the dissolution of water in the carbonate melt and the extrusion of some of the carbonate from the inner capsule during the experiment in step 2.

RESULTS AND DISCUSSION

Experimental results are compiled in Table 1. In order to establish the time necessary to reach equilibrium, a series of experiments was carried out at 900 °C and 1 kbar for various run durations (Fig. 1). Apparently, equilibrium is reached within a few hours. Moreover, a series of experiments at 1 kbar and 900 °C with a variable weight ratio of water/carbonate ranging from 0.3 to 1.3 revealed no systematic variation of water solubility. Figure 2 shows the water solubility in the Ca-Na-Mg-carbonate melt at 900 °C and from 0.25 to 2.25 kbar. The data can be described by the empirical relationship

$$W = 8.705\ P^{0.635}$$

where W is water solubility in weight percent and P is pressure in kbar. The relative error in water solubility calculated by this equation is estimated to be about 15%. The scatter in the data may partially be due to the absorption of traces of water on the surface of the inner capsule retrieved in stage 3 of the experimental procedure. Because of the very low viscosity of carbonate melts, the presence of gas bubbles in the melt at high temperature is very unlikely. Indeed, after the experiments, the inner capsule always contained a massive block of fine-grained carbonates with the textural characteristics of quench crystals. Only in experiments at a pressure of 0.25 kbar were a few larger crystals of carbonate found in the charge, which may indicate that the charge was not yet completely molten under these conditions.

If compared to typical values for water solubility in silicate melts (e.g., Behrens 1995), the data presented here suggest exceptionally high water solubility in carbonatite melts. Al-

TABLE 1. Experimental results on water solubility in carbonatite melt at 900 °C

Run	*P* (kbar)	Duration (hours)	Weight ratio water/carbonate	Water content (wt%)
C15	1	1	5:7	9.68
C17	1	4	5:7	8.61
C18	1	8	5:7	10.12
C19	1	16	5:7	10.17
C21	1	2	5:7	10.24
C31	0.5	18	1:2	7.19
C33	1	19	1:2	11.19
C34	1.5	17	1:2	12.56
C35	1.25	3	1:2	8.22
C36	1.5	3	1:2	10.52
C38	2	4	1:2	13.03
C39	2.25	4	1:2	14.39
C41	0.5	3	1:2	6.45
C42	0.75	3	1:2	5.31
C43	1	4	1:2	9.42
C44	1.25	4	1:2	11.41
C45	0.25	2	1:7	2.64
C46	0.5	2	1:2	5.60
C48	1	2	1:2	8.13
C50	1.25	2	1:2	8.19
C52	1.75	2	1:2	9.12

Note: The weight ratio water/carbonate refers to the initial ratio of pure water to anhydrous carbonate at the beginning of the experiment.

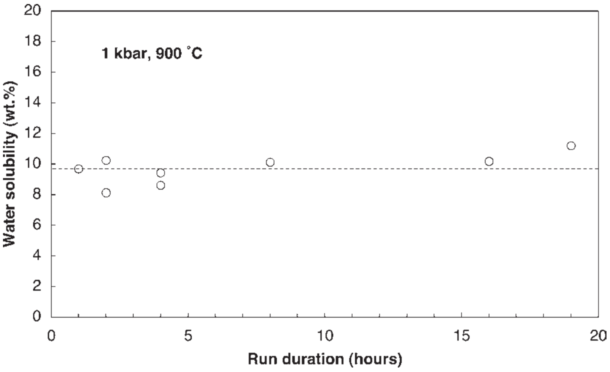

FIGURE 1. Measured water solubility in a Ca-Na-Mg carbonate melt at 1 kbar and 900 °C as a function of run duration.

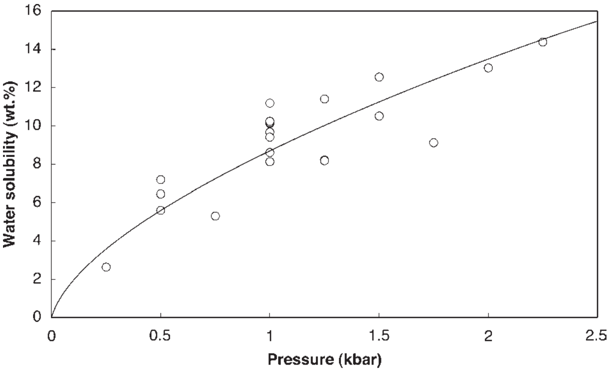

FIGURE 2. Water solubility in a Ca-Na-Mg carbonate melt as a function of pressure at 900 °C.

ready at 1 kbar water solubility reaches nearly 10 wt%, two or three times the value observed for most silicate melts. As fluid inclusion evidence suggests water saturation during the crystallization of many carbonatites (Rankin 1977; Samson et al. 1995; Bühn and Rankin 1999), the water contents of these melts must be very high. It is therefore not surprising that hydrothermal alteration is particularly strong around intrusive carbonatite bodies (Bell 1989), and that major mass transfer of alkalis occurs upon the evolution of a hydrous fluid phase during the last stages of carbonatite crystallization.

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