The properties of carbonated fluids in the systems Na_2CO_3-H_2O and K_2CO_3-H_2O to 1000°C and 20 kbar

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Fluids and melts are generally accepted to be the principle agents of metasomatism in the Earth's crust and upper mantle. In the lithospheric mantle, for example, they are assumed to be responsible for the 'cryptic' enrichment in light *REE* and large-ion lithophile elements of many peridotite xenoliths hosted by alkali basalt (e.g. Harte *et al.*, 1987) and for modal metasomatism linked to the production of phlogopite, amphibole and Fe-Ti rich phases in xenoliths found in kimberlites (e.g. Dawson, 1987). In the mantle wedge overlying subduction zones hydrous fluids or melts appear to transport material with high B, U/Th and Pb/Ce (Brenan *et al.*, 1995) while CO_2-rich fluids and melts have been connected with enrichment in the rare earth elements without concomitant enrichment in their high field strength elements (Ti, Zr, Nb, Ta etc.). In practice, however, these ideas about the effects of fluids are based mainly on petrographic and geochemical evidence; they are empirical and of dubious validity. The problem of how elements, particularly incompatible trace elements, are transported in the mantle and in the lower crust is geologically very important because these elements are the ones used to deduce temperatures and patterns of melting beneath mid-ocean ridges, island arcs and ocean islands (e.g. McKenzie and O'Nions, 1992). If the stabilities of the fluids and melts and their potential to transport material are poorly known, then deductions about the melting processes are poorly constrained.

Natural and synthetic carbonate melts appear to produce strong metasomatic enrichment in the light *REE* and Ba, high Zr/Hf and low Ti/Eu (e.g. Rudnick *et al.*, 1993). However, little is known about the nature of carbonate melts in the Earth's mantle and crust. In this study phase relations of the carbonate-H_2O fluids are presented.

Results

Here we present the properties of the systems Na_2CO_3-H_2O and K_2CO_3-H_2O. The study was undertaken in a diamond-anvil cell (up to 20 kbar and 1000°C), where the formation of fluids and crystals can be observed *in situ* under the microscope. The results are surprising, but confirm observations on synthetic fluid inclusions (Wilkinson *et al.*, 1996). On the K_2CO_3-H_2O join (90–96 wt.% H_2O) at 8.5 kbar, one fluid exists below 250°C. Upon heating the fluid exolves to two fluids. For simplicity, the second fluid will here be referred to as 'melt'. At about 350°C crystals are observed within the melt. *In situ* synchrotron XRD measurements revealed these crystals to be Na_2CO_3. Upon further heating crystals grow at the expense of the melt until no melt is observed and the crystals are present with a fluid. At about 700°C the crystals melt again, and fluid and melt are observed together to about 800°C. Above this temperature only one fluid is present. The Na_2CO_3-H_2O join exhibits similar behaviour, displaced to about 100°C higher temperature. Very similar phase relations are observed for the Na_2CO_3-H_2O and K_2CO_3-H_2O system at 18 kbar, displaced to about 50°C higher temperature. At low pressure the complete miscibility between Na_2CO_3 and H_2O at high pressure and temperature is replaced at low pressure (1.5 kbar) by a fluid and a melt (Koster van Groos, 1990) with a wide miscibility gap. Carbonate melt have a high dielectric constant and are thus likely to form stable complexes with many incompatible elements which can be transported within the mantle and crust without the involvement of water. These results show that carbonate melts can exist in a variety of pressures, as low as 1.5 kbar and as high as 18 kbar. Their presence can account for metasomatism observed in a variety of settings, where no traces of water are observed and cast doubts on any suggestions that CO_2-rich fluids exist as metasomatic agents.

This study provides the first step in understanding the relative capacities of aqueous fluids and carbonate melts to transport alkali, alkaline earth and high field strength elements and to produce metasomatism in the Earth's crust and upper mantle.

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