

Experimental study of phase relations in the systems $\text{Na}_2\text{O}+\text{CO}_2+\text{H}_2\text{O}\pm\text{SiO}_2$ and the solubility of pyrochlore at high pressures and temperatures

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The system $\text{Na}_2\text{O}+\text{CO}_2+\text{H}_2\text{O}$ is a relatively simple model for fenitising fluids and natrocarbonatites. Very little is known about the phase diagrams at high pressures and temperatures (mostly from differential thermal analysis [1]), and on the solubility of pyrochlore, the predominant Nb ore mineral in carbonatites, in alkali carbonate fluids. Here, we used a hydrothermal diamond-anvil cell to gain information on phase relations for the bulk compositions $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}=\text{H}_{20}\text{CO}_{13}\text{Na}_2$ (see figure, the phase diagram determined at quartz saturation is similar), $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}=\text{H}_2\text{CO}_4\text{Na}_2$, NaHCO_3 , and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}+\text{quartz}$, by visual observation and in situ Raman spectroscopy.

Decompression at high temperatures resulted in unmixing of two aqueous fluids, a dilute solution and the other rich in silica species (Q^0 , Q^3 , Q^4) and carbonate. For $\text{H}_2\text{CO}_4\text{Na}_2$, the natrite liquidus was observed at 794 °C, ~460 MPa in the presence of aqueous fluid, and showed a positive dP/dT slope. For HCO_3Na , it was located at 787 °C, ~100 MPa, in the presence of two aqueous fluids. In contrast to sodium hydrogen carbonate, heating of sodium carbonate hydrates does not generate detectable CO_2^0 .

Based on integrated Raman band intensities Nb–O, Si–O, and C–O stretching vibrations, the Nb concentration released from pyrochlore at 600 °C was by two orders of magnitude higher if quartz was present. In a quartz-free run at 600 °C, 623 MPa, the aqueous sodium carbonate liquid reacted with pyrochlore contained about 60 ppm Nb. At 600 °C, 1456 MPa, it contained about 1% Nb if quartz and pyrochlore were present. The Raman band from Nb–O stretching vibrations resembles that observed in carbonate-free alkali silicate glasses and is interpreted as Q^2 species (chains of NbO_6 octahedra and SiO_4 tetrahedra).

We discuss implications of the experimental data with respect to pyrochlore formation in carbonatites and in the light of Raman spectroscopic and LA-ICP-MS data for carbonate inclusions in mineralized carbonatites.

[1] Koster van Groos, A.F. (1990) *American Mineralogist* 75, 667–675.

Figure. P - T diagram, bulk composition $\text{H}_{20}\text{CO}_{13}\text{Na}_2$. Nat – natrite Na_2CO_3 , Aq – aqueous fluid, V – vapor, c.p. – critical point, diamonds – this study, squares – Koster van Groos (1990), triangle – Ravich (1974).

