Experiments on the stability of cancrinite in the system Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$-CO$_2$-H$_2$O

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ABSTRACT

The synthesis and upper thermal stability of cancrinite were investigated experimentally in the system Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$-CO$_2$-H$_2$O at 2 kbar and in the presence of a mixed H$_2$O-CO$_2$ fluid. Cancrinite could only be formed under water-rich conditions in this system. The breakdown of cancrinite to nepheline + calcite occurred at decreasing temperatures with increasing $X_{CO_2}$ as expected for a dehydration reaction of the form cancrinite = nepheline + calcite + $n$H$_2$O. Partial melting and the formation of melilite was observed at the highest temperatures and for the most H$_2$O-rich fluid compositions.

The molecular water content of the cancrinite formed at various $T$-$X_{CO_2}$ conditions was evaluated with a combined infrared (IR)-thermogravimetry (TG) technique. Results suggest (within analytical error) a decrease in the water content of cancrinite toward the breakdown reaction and an apparently constant water content along the breakdown curve. Thermodynamic analysis combining the compositional and phase-equilibrium data from this study was performed and yielded a value of $\Delta f' H = -14722 \pm 147$ kJ and $S^\circ = 981 \pm 118$ J/K at 298 K and 1 bar for synthetic cancrinite of the composition Na$_6$Ca$_{1.5}$[Al$_6$Si$_6$O$_{24}$](CO$_3$)$_{1.5}$·$1.1(\pm0.4)$H$_2$O. This study demonstrates the important role that water plays in controlling the stability of cancrinite in igneous and metamorphic rocks.

INTRODUCTION

Cancrinite crystal chemistry

Cancrinite-group minerals are framework aluminosilicates (feldspathoids) characterized by a network of (Al,Si)O$_4$ tetrahedra having fully ordered Al and Si cations. Their structure consists of parallel six-membered rings of alternating AlO$_4$ and SiO$_4$ tetrahedra (Jarchow 1965; Grundy and Hassan 1982). The hexagonal symmetry ($P6_3$) results from the stacking of these six-membered rings in an ABAB... sequence. This stacking gives rise to large continuous channels parallel to the $6\bar{3}$ axis and chains of smaller undecaedral (elevenfold) cages along the threefold axes. The large channels contain extra-framework cations (Na$^+$, Ca$^{2+}$, K$^+$), anions (CO$_3^{2-}$, OH$^-$), and H$_2$O molecules whereas the undecaedral cages hold [Na·H$_2$O]$^+$ clusters (Hassan and Grundy 1991; Hassan and Busseck 1992).

Phoenix and Nuffield (1949) defined the cancrinite group of minerals as (Na,K,Ca,Al)$_{n_0.5}$(Si$_n$Al$_{1.5}$O$_{10.5}$)(SO$_4$,CO$_3$)$_{0.5}$.1–5H$_2$O, and proposed an ideal formula for the carbonate end-member of cancrinite as Na$_6$Ca$_{1.5}$[Si$_6$Al$_6$O$_{24}$](CO$_3$)$_{1.5}$·3H$_2$O. They recognized the difficulties of dealing with the chemistry of this mineral, due to numerous possible substitutions, vacant positions, and variable zeolitic water content. Given the role that the carbonate salts play in the chemistry of cancrinite, Eitel (1922), Edgar and Burley (1963), and Watkinson and Wyllie (1971) proposed phase diagrams and mineral reactions emphasizing the role of carbonates and CO$_2$ in cancrinite phase relations without explicitly considering its water content. The present study draws attention to the role that water plays in the formation and stability of the carbonate end-member of cancrinite. The hydroxyl group is a possible constituent in both natural and synthetic cancrinites. A hydroxyl-rich (basic) cancrinite has been synthesized (e.g., Edgar 1963; Hassan and Grundy 1991) and also has been found occurring as a rare natural variety (Nadezhina et al. 1991).

The zeolitic character of the water in cancrinite was demonstrated by the continuous weight loss observed during the TG study performed by Buhl (1991), who showed that water was released in the interval 80–430 °C for two synthetic cancrinites. At higher temperatures (730–880 °C), the release of water present as hydroxyl groups accompanied by the release of CO$_2$ took place in a strong endothermic reaction. In a detailed TG and structural study, Hassan (1996) showed the complete thermal behavior of a well-characterized sample from Bancroft, Ontario, with an ideal formula expressed as Na$_6$Ca$_{1.5}$[Si$_6$Al$_6$O$_{24}$](CO$_3$)$_{1.5}$·2H$_2$O. The water loss continued up to ~860 °C, followed by a rapid release of CO$_2$ between 924 and 940 °C. Although the overall weight loss and the exact intervals of dehydration and decarbonation might vary in different thermal studies of cancrinite because of compositional differences, the general shape of the TG and differential thermal gravimetry (DTG) curves remain the same, partitioned into two main steps for dehydration and decarbonation respectively (Buhl 1991; Hassan 1996; Barrer et al. 1970; Liu et al. 1993).