American Mineralogist, Volume 83, pages 339–347, 1998

High-temperature multi-nuclear NMR investigation of analcime

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ABSTRACT

Two analcimes of hydrothermal and diagenetic origin were investigated by in situ ^{29}Si, ^{27}Al, and ^{23}Na NMR from room temperature to 550 °C, and by TGA and DSC. The two samples dehydrate at different temperatures, and the high-temperature NMR behavior is closely related to the dehydration. The diagenetic analcime (CR-6) has higher surface area, and thus its dehydration starts and is completed at lower temperatures than the hydrothermal analcime (Hilaire). The ^{29}Si chemical shifts and ^{27}Al peak maxima become first more shielded and then less shielded with increasing temperature and are related to changes in the Si-O-Si and Si-O-Al bond angles caused by thermal expansion, distortion of framework due to H_2O loss at high temperature, and the decreased bond length caused by rigid unit modes (RUMs). Changes in the ^{27}Al NMR peak widths are also correlated to H_2O loss at high temperature and are due to the increased mobilities of H_2O and Na. Paramagnetic impurities and motion of H_2O and Na play important roles in the T_1 relaxation of ^{27}Al. The ^{23}Na NMR peak maxima become first more negative and then less negative with increasing temperature, with the most negative values occurring near the temperature of maximum H_2O loss. The ^{23}Na peak width decreases, increases, and then again decreases with increasing temperature. These results are best interpreted as due to Na undergoing exchange between the 24(c) Na sites and other sites, possibly the 16(b) H_2O sites, combined with collapse of the cages. The less negative ^{23}Na peak and increasing and then decreasing ^{23}Na peak widths at high temperature are due to the effects of motional averaging of the intensity due to the ($\pm$½, $^3/_2$) satellite transitions.