The kinetics of dehydration and order-disorder of molecular H$_2$O in Mg-cordierite

CIRIACO GIAMPAOLO 1 and *ANDREW PUTNIS 2

1. Dipartimento di Scienze della Terra, Universita di Roma “La Sapienza”, P.le A. Moro 5, 00185 Roma, Italia
2. Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, England

Abstract: The kinetics of water loss in synthetic, hydrated Mg-cordierite has been studied between 336 °C and 687 °C by thermogravimetry. Analysis of the rate data shows that water loss is controlled by two thermally activated processes, one with activation energy, $E_a$ of 39 kJ/mole, the other with $E_a$ 135.5 kJ/mole. The lower $E_a$ process, which may be associated with the loss of disordered, loosely-bound H$_2$O, operates in the early stages of the dehydration, the proportion of water being lost by this process increasing markedly with temperature. The higher $E_a$ process, associated with the loss of ordered, strongly-bound H$_2$O, decreases in importance at high temperatures where most of the channel water is disordered. The kinetic data is used to define the temperature dependence of the change in structural state of H$_2$O molecules from ordered Type I (with H-H vector parallel to the $c$ axis) to disordered.

Key-words: kinetics, dehydration, Mg-cordierite, thermogravimetry, H$_2$O disorder.

Introduction

Hydrated magnesium cordierite, Mg$_3$Al$_2$Si$_5$O$_18$.nH$_2$O, has a framework structure of corner sharing SiO$_4$ and AlO$_4$ tetrahedra in which six-membered rings of tetrahedra are interconnected laterally and vertically by other tetrahedra (Gibbs, 1966). The rings define channels, parallel to the $c$ axis, which can contain a variety of constituents, the most important of which is H$_2$O (Schreyer, 1986). The channels pinch to “bottlenecks” (= 2.5 Å diameter) or swell to large “cages” (= 5.5 Å diameter in the $ab$ plane) (Armbruster and Bloss, 1982). This suggests a maximum of one H$_2$O molecule per cage ($n = 1$), corresponding to 2.99 wt.% H$_2$O, although experimental measurements (Mirwald and Schreyer, 1977) indicate that slightly higher water contents are possible. The hydration state is continuously variable depending on P(H$_2$O) and T.

The molecular water content of cordierite has a profound effect on many equilibria involving this phase (Newton and Wood, 1979). The H$_2$O-solubility data of Mirwald and Schreyer (1977) have been fitted to an ideal solid solution between hydrous ($n = 1$) and anhydrous end-members, yielding values of $\Delta H^0 = -38.55$ kJ and $\Delta S^0 = -96.44$ J/K for the hydration reaction (Helgeson et al., 1978; Kurepin, 1979). Newton and Wood used $n = 1.2$ for the hydrous end-member and obtained values not greatly different per mole of H$_2$O absorbed (Newton, 1987). The partial molal entropy of H$_2$O in the cordierite structure is almost the same as that for free H$_2$O at the same conditions, a result in keeping with the assumptions of the ideal solid solution model i.e. water molecules disordered and free to move within the channels.