In situ observation of the thermal decomposition of weddelite by heating stage environmental scanning electron microscopy

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ABSTRACT

The morphological and chemical changes occurring during the thermal decomposition of weddelite, CaC2O4·2H2O, have been followed in real time in a heating stage attached to an Environmental Scanning Electron Microscope operating at a pressure of 2 Torr, with a heating rate of 10 °C/min and an equilibration time of approximately 10 min. The dehydration step around 120 °C and the loss of CO around 425 °C do not involve changes in morphology, but changes in the composition were observed. The final reaction of CaCO3 to CaO while evolving CO2 around 600 °C involved the formation of chains of very small oxide particles pseudomorphic to the original oxalate crystals. The change in chemical composition could only be observed after cooling the sample to 350 °C because of the effects of thermal radiation.

INTRODUCTION

Oxalates play an important role in medicine (calcium oxalate–urinary calculi) (Petrov and Soptrajanov 1975; Schubert and Ziemer 1981) and as secondary minerals in lichens, e.g., Ca (weddelite and whewellite), Mg (glunshinskite), Fe (humboldtine), and Cu (moolooite), which live on rocks containing these elements (Chisholm et al. 1987; Clarke and Williams 1986; Cowgill 1989; Wilson et al. 1980). Pyrolysis of oxalates is an important way to synthesize oxodic materials, e.g., superconductors (Andrade and Machado 1992; Chen and Tseng 1990) and certain ceramic materials (e.g., PbO, BaTiO3, and PbTiO3) (Bhattarcharjee et al. 1992; Fang and Lin 1989; Munson and Riman 1991), because it forms homogenous powders at relatively low temperatures.

The thermal decomposition of weddelite, CaC2O4·2H2O, and other oxalates is well known (Dollimore 1987; Dollimore et al. 1963; Dollimore et al. 1970; Jordanovska et al. 1992; Li et al. 1992) and often used for both teaching purposes (Stucki and Boldtine), and Cu (moolooite), which live on rocks containing these elements (Chisholm et al. 1987; Clarke and Williams 1986; Cowgill 1989; Wilson et al. 1980). Pyrolysis of oxalates is an important way to synthesize oxodic materials, e.g., superconductors (Andrade and Machado 1992; Chen and Tseng 1990) and certain ceramic materials (e.g., PbO, BaTiO3, and PbTiO3) (Bhattarcharjee et al. 1992; Fang and Lin 1989; Munson and Riman 1991), because it forms homogenous powders at relatively low temperatures.

The thermal decomposition of weddelite, CaC2O4·2H2O, and other oxalates is well known (Dollimore 1987; Dollimore et al. 1963; Dollimore et al. 1970; Jordanovska et al. 1992; Li et al. 1992) and often used for both teaching purposes (Stucki and Bish 1990) as an example and as a standard in thermal analysis. The decomposition of weddelite shows three major mass-loss events. The first around 120 °C corresponds to the dehydration reaction:

\[ \text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + 2 \text{H}_2\text{O} \text{(gas)} \quad (1) \]

The second mass loss around 425 °C results from the reaction of the dehydrated oxalate to carbonate:

\[ \text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}_2 \text{(gas)} \quad (2) \]

In the final reaction, around 600 °C, the carbonate breaks down to the oxide:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \text{(gas)} \quad (3) \]

In addition to thermal analysis, a limited number of papers have reported on the crystallographic changes based on X-ray diffraction (XRD), infrared emission and Raman spectroscopy. However, so far no one has observed in situ the transformation taking place during the decomposition of minerals. The use of an environmental scanning electron microscope (ESEM) allows one to observe samples under pressures up to a maximum of 20 Torr (2670 Pa). This means that small amounts of gas produced during the heating of a sample on a heating stage in the electron microscope chamber do not hinder the observation of a sample.

This instrumentation opens up a whole new area of research, allowing not only mineralogists but also materials scientists to observe changes like thermal expansion, decomposition, calcination, sintering etc. taking place in their materials when heated (Belenli et al. 1995; Foitzik et al. 1997; Habesch et al. 2001; Maroni et al. 1999; Srinavas 2002). In this paper, we describe for the first time the in situ observation of the thermal decomposition of a mineral by heating stage scanning electron microscopy.

EXPERIMENTAL METHODS

The synthetic weddelite was prepared by slowly mixing stoichiometric amounts of sodium oxalate and calcium chloride at 0 °C. The resulting material was filtered and washed with deionized water until free of chloride (checked by the silver nitrate method). After drying, phase identification was conducted by Queensland University of Technology using a Philips wide-angle PW 1050/25 vertical goniometer applying CuKα radiation. The sample was measured at 50% RH in stepscan mode with steps of 0.02 °2θ and a scan speed of 1.00° per minute from 5 to 75° 2θ. XRD of the oxalate sample showed the presence of only crystalline weddelite plus a small amount of amorphous material. The amount of amorphous material, which was later identified as calcium oxalate monohydrate, was so small that it did not interfere with the observations of the thermal decomposition of the weddelite.

Scanning electron microscope (SEM) images were obtained using a FEI Quanta 200 Environmental Scanning Electron Microscope (FEI Company, USA) operated at an accelerating voltage of 20 kV Queensland University of Technology. The microscope was fitted with an FEI water-cooled 1000 °C specimen heating.