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Note

Thermal decomposition of dolomite (calcium magnesium carbonate) studied by ^{25}Mg solid-state nuclear magnetic resonance

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Abstract

^{25}Mg MAS NMR indicated that in the thermal decomposition of dolomite, MgO is formed long before it can be detected by XRD and without the formation of intermediate $MgCO_3$ in this case.

The thermal decomposition of the mixed magnesium calcium carbonate dolomite is of practical importance in the manufacture of basic refractories from this material. This decomposition is also the subject of considerable dispute. In CO_2 (i.e. a self-generated atmosphere), two distinct thermal reactions occur [1]. The first, at about 550–760°C, results in the appearance of $CaCO_3$ and MgO, apparently without the formation of intermediate $MgCO_3$ [2], although thermogravimetric measurements have been taken to suggest that the $CaCO_3$ contains 5–10 mol% $MgCO_3$ in solid solution [3]. The second thermal reaction, at about 900–960°C, involves the decomposition of the $CaCO_3$ [2]. In air, these reactions overlap into one broad, continuous event [2], while under reduced pressure, both carbonates are reported to decompose simultaneously, the product being an equicomposition oxide solid solution with a rock salt structure, which subsequently undergoes spinodal unmixing into Mg-rich and Ca-rich oxide phases [4]. In-situ decomposition of dolomite by the electron beam of a transmission electron microscope [5] indicated that under these reaction conditions, the initial equicomposition oxide solid solution is topotactically related to the dolomite *c*-axis, but the oriented domains subsequently become unoriented, passing through an amorphous state before the randomly-oriented MgO and CaO crystallites are formed.

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Solid-state nuclear magnetic resonance with magic-angle spinning (MAS NMR) has proved useful in studying the behaviour of the Al and Si during thermal decomposition of a number of aluminosilicate minerals, but although ^{25}Mg MAS NMR has been shown to be possible for several Mg compounds [6], that preliminary survey suggested that only those compounds with Mg in well-defined and extremely symmetrical sites have usefully sharp Mg spectra. Thus, the ^{25}Mg MAS NMR spectrum of MgO has been reported [6], but not the spectra of dolomite, or magnesite (magnesium carbonate). This communication contains the first report of the ^{25}Mg spectrum of dolomite, which is sufficiently well resolved to permit a study of the behaviour of the Mg during the thermal decomposition of this mineral, especially in the rather narrow temperature range in which the transformation occurs.

The dolomite was a natural mineral from NW Nelson, New Zealand, containing <0.5% Fe, and essentially equimolar proportions of CaO to MgO. X-ray powder diffraction showed it to be crystalline dolomite with a very small trace of calcite impurity. Thermal analysis in a static self-generated atmosphere (Perkin-Elmer DTA 1700) and thermogravimetry in 1.5 ml min^{-1} flowing Ar (Stanton Redcroft TG770), both at a heating rate of 10°C min^{-1} (Fig. 1) indicated that in both experiments the sample is experiencing a self-generated CO_2 atmosphere, with the two decomposition events resolved. The slight temperature differences in the DTA and DTG traces reflect the difference in the atmosphere dynamics of the thermobalance and DTA cells. Both the DTA and DTG results (Fig. 1, curves A and C) suggest that the higher-temperature endotherm is composed of two overlapping reactions, but since this reaction involves the calcium component, ^{25}Mg NMR does not shed further light on this observation.

Samples for XRD and NMR study were prepared by heating for 15 min at temperatures dictated by the thermal analysis results, in platinum-lined boats in an electric muffle furnace. Since the isothermal heating regime and atmosphere conditions within this furnace are different to those of the thermal analysis experiments, the two sets of experiments will not be completely comparable.

X-ray powder diffraction (Philips PW 1700 computer-controlled goniometer with Co Kα radiation and graphite monochromator) indicates the abrupt appearance of reaction products (MgO and $CaCO_3$) at 770°C, corresponding with the almost total loss of the dolomite reflections. By 800°C some CaO has appeared, co-existent with $CaCO_3$ and MgO. Full conversion of $CaCO_3$ to CaO has occurred by 900°C, the crystallinity of this phase and the MgO improving on heating to higher temperatures. A small degree of hydration of the CaO is also apparent from the presence of a portlandite, $Ca(OH)_2$. These changes are shown semi-schematically in Fig. 1, part D.

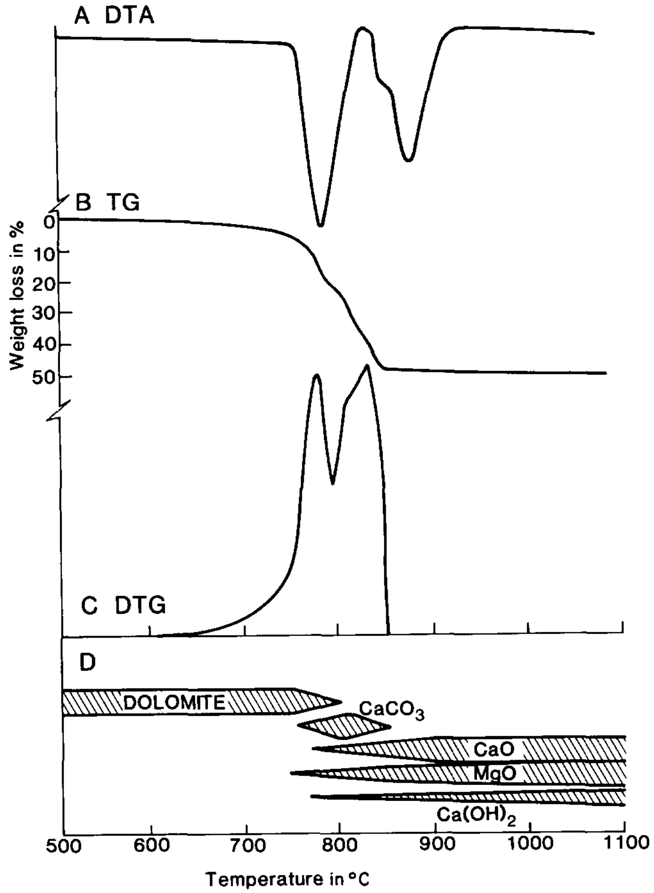

Fig. 1. Curves A–C, thermal analysis traces for Nelson dolomite, with (D) semi-schematic X-ray phase compositions as a function of heating temperature.

Measurements of the cell dimensions of the MgO and CaO throughout this temperature range were made using silicon as the external angular reference material. Comparison with the cell dimensions for MgO and CaO solid solutions [7] indicate that solid solutions were not formed at any stage during the present experiments.

The ^{25}Mg MAS NMR spectra were obtained at 11.7 T using a Varian Unity 500 spectrometer and Doty 5 mm probe at 10 kHz spinning speed. The spectra were acquired at 30.584 MHz using a 90° (solids) pulse of 3 μs with a recycle delay of 0.3 s. A gaussian line broadening of 15 or 60 Hz was applied after acquisition of several thousand transients. The chemical shifts were referenced to a saturated solution of $MgSO_4$.

The ^{25}Mg MAS NMR spectra of unheated and heated dolomite samples are shown in Fig. 2. Unheated natural dolomite has a reasonably sharp ^{25}Mg resonance centred at −8.8 ppm (Fig. 2, curve A) which is largely unaltered

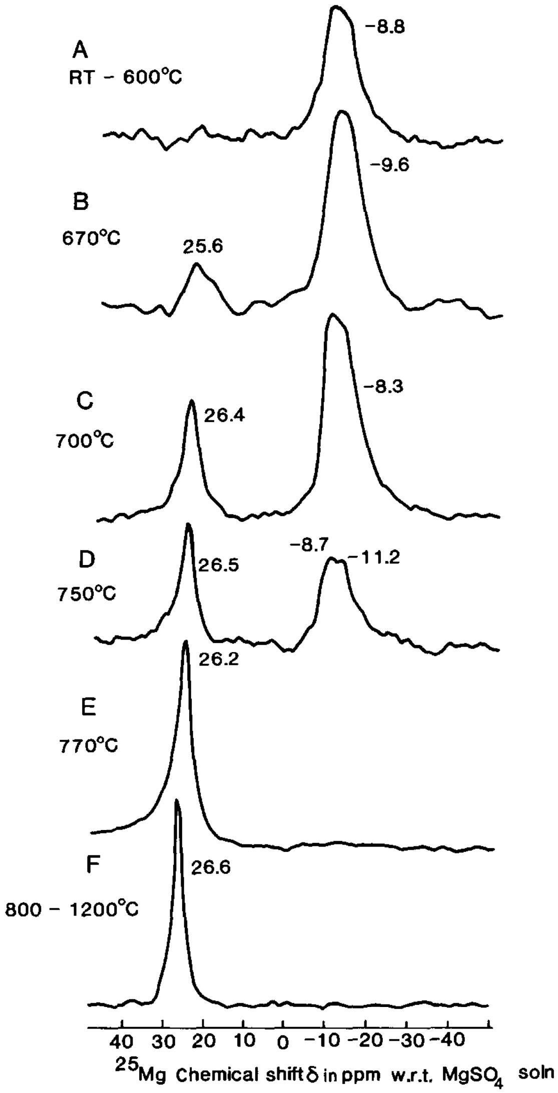

Fig. 2. ^{25}Mg NMR spectra of unheated and heated Nelson dolomite. Line broadening 60 Hz.

by heating to 600°C. The shape of this resonance, and those of the heated samples, may be due either to electric field gradient (EFG) effects, or to the partitioning of the Mg into some of the more distorted Ca sites in the dolomite structure [8].

EFG calculations indicate that both the heated and unheated spectra can be reasonably simulated by assuming the following values: nuclear quadrupole coupling constant $e^2qQ/h = 0.9$ MHz, EFG tensor asymmetry parameter = 0, with a gaussian line broadening of 90 Hz. The simulated spectrum is shown in Fig. 3, curve B, together with observed spectra of dolomite, unheated and heated to 700°C.

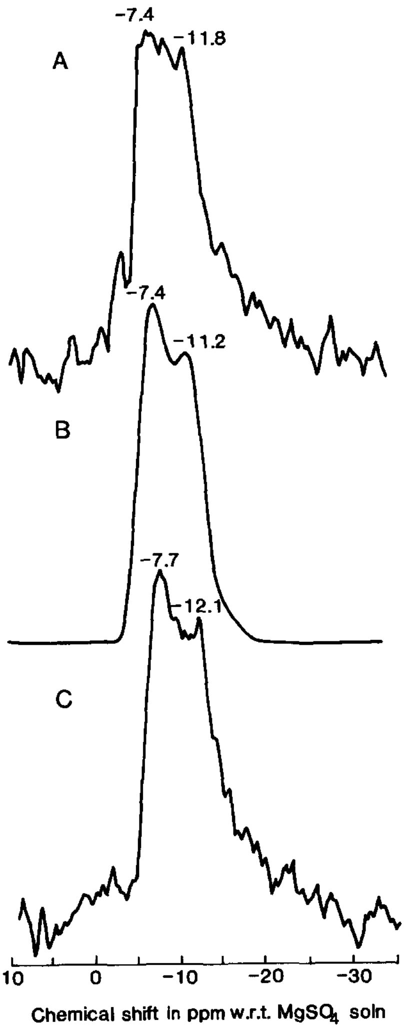

Fig. 3. Observed and simulated ^{25}Mg MAS NMR spectra of dolomite. Curve A, observed spectrum, unheated sample, line broadening 15 Hz; curve B, spectrum simulated using parameters as in text; curve C, observed spectrum, sample heated at 700°C, line broadening 15 Hz.

These calculations indicate that the observed spectra can be understood in terms of a single Mg site with an EFG splitting which is largely unchanged during thermal decomposition, and with a chemical shift, after correction for EFG effects, of −4.3 ppm. Thus, these Mg spectra can be interpreted without invoking mixing of the Mg atoms on the more distorted Ca sites [8], for which there is no evidence in the present spectra. However, the environment of the magnesium in dolomite is different to that in pure magnesite (magnesium carbonate), in which an EFG split spectrum is also

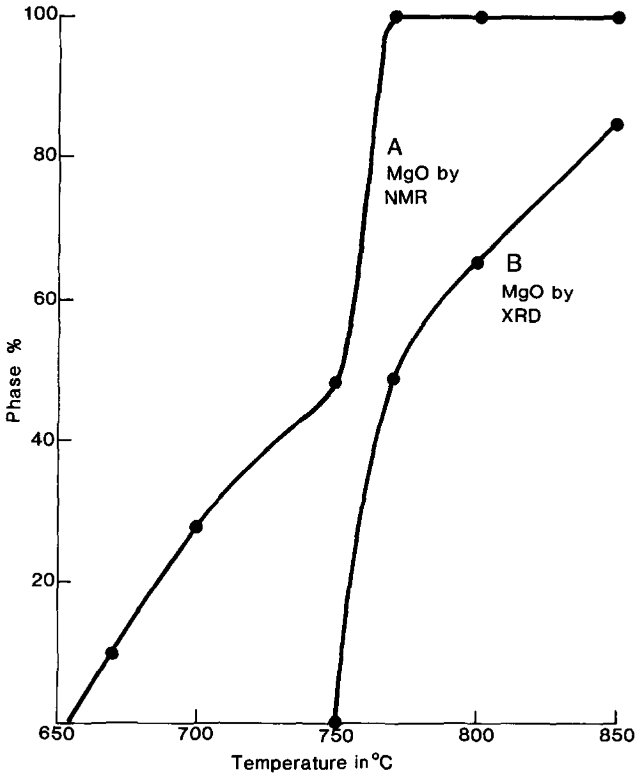

Fig. 4. Development of MgO from Nelson dolomite. Curve A, % Mg as MgO, from NMR; curve B, % MgO, estimated from XRD peak heights, relative to sample heated to 1200°C, assumed to contain 100% MgO.

observed, with a corrected chemical shift of about +4.8 ppm and a much larger nuclear quadrupole coupling constant (2.5 MHz) [9].

At 670°C, the temperature at which weight loss begins to occur, a small resonance at 25.5 ppm accompanies the dolomite peak (Fig. 2, curve B); the new peak corresponds to MgO [6], its broadness (65 Hz) suggesting a lack of crystallinity. This temperature at which the MgO first appears in the NMR spectrum is 100°C below the temperature at which the phase is detected by XRD. At 700°C, the MgO spectrum has grown, but is still broad (Fig. 2, curve C) and the dolomite resonance shows increased signs of EFG splitting, which becomes even more pronounced at 750°C as the structure becomes progressively degraded (Fig. 3, curve D). No indication is found of $MgCO_3$ as a discrete transitory phase. By 770°C, the dolomite resonance has disappeared, but the MgO resonance is still broad (69 Hz) by comparison with its eventual width (35 Hz), which it achieves by 900°C. Changes in the calcium phases above 770°C are not reflected in the Mg spectra.

A striking feature of this study is the way in which ^{25}Mg NMR detects regions in which the characteristics of MgO have developed, long before these localized regions have coalesced into structures identifiable as MgO by XRD (Fig. 4). This result indicates that the formation of X-ray amorphous MgO proceeds much more readily and completely than previously realized from X-ray studies, and originates in many very small nuclei randomly distributed throughout the bulk of the crystal. Crystalline MgO begins to be detected by XRD only when the formation of these regions is complete (Fig. 4). Under the present experimental conditions, the reaction is simpler than previously suggested, with no evidence of the formation of $MgCO_3$, either as a discrete phase or in solid solution, nor of oxide solid solutions.

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