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The thermal reactions of talc studied by ^{29}Si and ^{25}Mg MAS NMR

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Abstract

Solid-state ^{29}Si and ^{25}Mg MAS NMR spectroscopy, in conjunction with thermal analysis and X-ray powder diffractometry, indicates that the thermal decomposition of talc is an essentially simple reaction in which the loss of structural water is concomitant with the atomic rearrangements involved in the formation of orthoenstatite with silica separation. The ^{25}Mg MAS NMR spectra of talc, enstatite and partially converted materials suggest no major differences in the octahedral cation environments of these phases, and provide no evidence for the incorporation of Mg into the amorphous silica phase. Neither the ^{29}Si nor the ^{25}Mg spectra indicate the formation of a reaction intermediate such as a pyribole, which, if formed, may however have characteristics which are too similar to the talc and pyroxene units from which it is composed to be distinguished by NMR.

Keywords: Co-ordination; DTA; DTG; EDAX; MAS NMR; NMR; Talc; TG; XRPD

1. Introduction

Talc, $Mg_6Si_8O_{20}(OH)_4$ is a common 2:1 layer lattice silicate, the structure of which consists of two tetrahedral silicate sheets separated by an octahedral Mg–O(OH) sheet, i.e. it is the trioctahedral magnesian analogue of pyrophyllite, $Al_4Si_8O_{20}(OH)_4$. Among its many uses, talc is an important raw material for magnesium ceramics (steatites, cordierite, enstatite and forsterite products). As a

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ceramic raw material, its thermal decomposition behaviour is of considerable interest.

Thermal analyses of talc suggest a simple reaction; endothermic dehydroxylation occurs at 870–1050°C with about 4% weight loss [1]. Recrystallization of the product phase enstatite ($MgSiO_3$) is virtually immediate, and is accompanied by the separation of a silica-rich phase, but no DTA exotherm. When first formed, the silica is X-ray amorphous and may not necessarily be completely free of Mg [2], but on further heating, it recrystallizes to cristobalite. Nakahira and Kato [3] established the topotactic relationships between the talc and its enstatite decomposition product, thus supporting an inhomogeneous thermal reaction mechanism such as previously suggested by Ball and Taylor [4], in which 8 protons are lost from the talc unit cell during dehydroxylation, balanced by counter-migration of 4 Mg^{2+} to regions which become enstatite. The Si-rich regions thus formed by depletion of Mg become cristobalite. Although the reaction involves the formation of a chain silicate from a layer silicate, only small local movements of oxygen ions are involved, and even the cation movements between different coordination positions are small [5]. Electron-optical studies of the reaction in fibrous talc [6] have confirmed and extended the topotactic relationships reported by Nakahira and Kato [3], and suggested the formation of an anhydrous intermediate phase at 800–900°C. A more recent high-resolution electron-optical study [7] has suggested that the disordered phase initially formed by heating talc has the structure of disordered pyribole. The concept of pyriboles or biopyriboles [8] provides a convenient means of describing structures built up from mica (or talc) and pyroxene (e.g. enstatite) units (called M and P units respectively). Under this nomenclature, pyriboles can be of two types, of general formula $M_{(n-1)}P$ and $M_nPM_{(n-1)}P$, where n is a positive integer. Where $n = 1$ in the second type of structure, an MPP sequence would result, consisting of alternating single and double chains (called a (21) sequence). The disordered pyribole intermediate identified in heated talc [7] is reported to consist of an MPP structure with regions containing 4–6 repeat units of (21) sequence. The topotactic formation of disordered pyribole regions during the thermal decomposition of talc is thought to proceed with the simultaneous formation of amorphous silica [7]; when the transformation is complete, the adjacent double chains depolymerize to form enstatite. A parallel reaction is also envisaged [7], in which the talc transforms directly to enstatite and silica, these phases intergrowing with the pyribole regions.

Solid-state nuclear magnetic resonance with magic-angle spinning (MAS NMR) has proved to be a very useful technique for examining the thermal transformations of the related 2:1 layer-lattice silicate minerals pyrophyllite [9] and montmorillonite [10]. Although the ^{29}Si MAS NMR spectrum of talc has been reported by several groups (see, for example Weiss et al. [11]), the thermal reactions of talc have not been followed by ^{29}Si MAS NMR. Neither the ^{25}Mg MAS NMR spectrum of talc nor its thermal decomposition products have been previously reported, although our recent work [12] indicates that reasonable ^{25}Mg MAS NMR spectra of these and other minerals can be obtained using high fields and high spinning speeds.

The aim of the present work was therefore to apply ^{29}Si and ^{25}Mg MAS NMR to a reinvestigation of the thermal reaction sequence of talc, with particular attention to the formation of pyribole intermediates, or other previously unreported phases.

2. Experimental

The talc used in this study was a massive sample from Three Springs, Western Australia. EDAX analysis showed the only impurity to be iron, present at a concentration of about 0.2%. X-ray diffractometry indicated monophase crystalline talc with a pattern almost identical to JCPDS card no. 13-558. Thermal analysis was carried out in air at a heating rate of 10°C min^{-1}, using a Perkin-Elmer DTA 1700 differential thermal analyser and a Stanton-Redcroft TG770 thermobalance. Powdered samples for NMR studies were heated to various temperatures for 15 min in platinum-foil-lined ceramic boats in a pre-heated electric muffle furnace. After cooling, the samples were examined by X-ray powder diffractometry (Philips PW1700 computer-controlled diffractometer with graphite monochromator and Co $K\alpha$ radiation).

The ^{29}Si MAS NMR spectra were recorded at 4.7 T (Varian XL-200 spectrometer), using a Doty probe spun at 4–5 kHz and a 90° pulse of 6 μs with a delay of 0.5 s. The ^{29}Si spectra were referenced to tetramethylsilane (TMS). The ^{25}Mg MAS NMR spectra were obtained at 11.7 T (Varian Unity 500 spectrometer), using a 3.5-mm high-speed Doty probe with zirconia rotor at spinning speeds of 19.5–20 kHz. T_1 measurements using a saturating comb gave a value of 0.207 ± 0.032 s; the present spectra were therefore acquired at 30.584 MHz using a 90° (solids) pulse of 3 μs with a recycle delay of 0.3 s. Gaussian line broadening of 200 Hz was applied after acquisition of several thousand transients. The ^{25}Mg chemical shifts are quoted with reference to a saturated solution of $MgSO_4$.

3. Results and discussion

The thermal analysis curves for the talc are shown in Fig. 1.

The curves for talc are as expected with a single dehydroxylation weight loss of 3.6% beginning at 875°C. The associated DTA endotherm is composed of two events, at 880 and 950°C (Fig. 1, curve C). Such a double endotherm might indicate the presence of an impurity such as calcite or dolomite [1], but it is not paralleled by the TG and DTG curves, nor are these impurity phases present in sufficient amount to be detected by elemental analysis or X-ray diffractometry. Alternatively, both endotherms may be associated with the dehydroxylation process; a similar but less well-resolved double endotherm has been observed in the 1:1 magnesiosilicate chrysotile [13]. X-ray diffractometry indicates a relatively slow transformation from talc to enstatite over the temperature range of dehydroxylation; at 900°C, the sample contains talc and a small amount of enstatite, which increases in relative concentration at 950°C. By 1000°C, the talc basal spacing has disappeared, but the X-ray trace is otherwise not very different from that at 950°C, containing broad

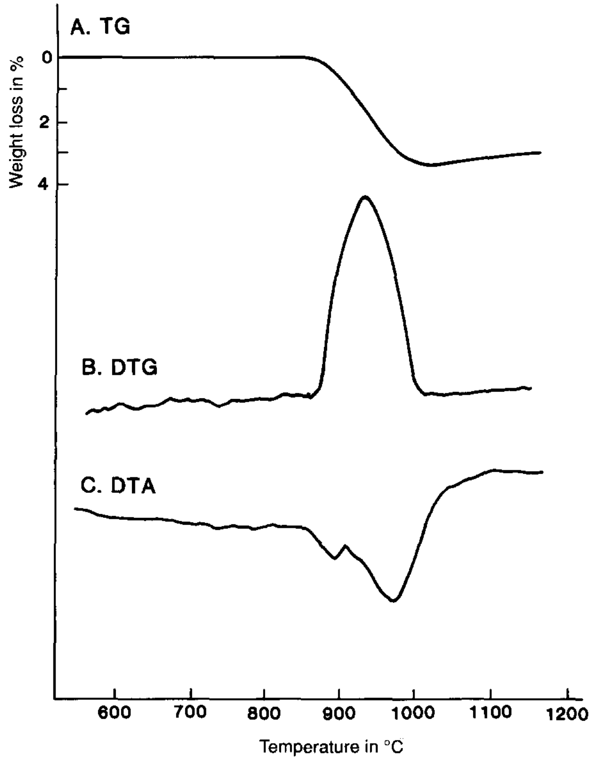

Fig. 1. Thermal analysis traces of Three Springs talc, in flowing air (150 ml min^{-1}), heating rate 10°C min^{-1}.

peaks corresponding to poorly crystalline enstatite. Heating to 1300°C improves the crystallinity of the enstatite, and produces a small amount of crystalline cristobalite.

3.1. ^{29}Si MAS NMR

The ^{29}Si MAS NMR spectra of talc heated to various temperatures are shown in Fig. 2.

The spectrum of unheated talc (Fig. 2, curve A) is identical to those published by many previous workers (see, for example Weiss et al. [11]) with a chemical shift within the range of previously reported values (−97 to −98.1 ppm). Heating to 850°C produces the first hint of an enstatite-like chain structure, with the appearance of a small shoulder at about −82 ppm (Fig. 2, curve B). Although XRD shows no sign of enstatite development at 850°C, this is approximately the temperature of the first DTA endotherm; the change in silicate configuration is thus associated with the onset of dehydroxylation. By 900°C, enstatite is detected by XRD, and its ^{29}Si NMR resonance is clearly resolved at −84 ppm, together with the first indication of the separation of silica (the shoulder at about −110 ppm

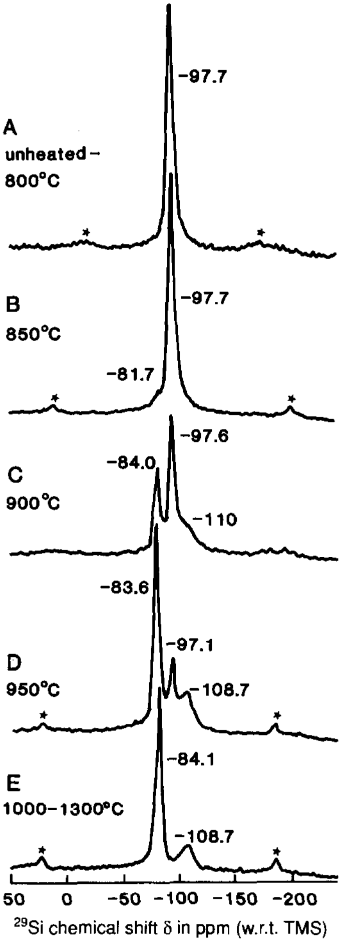

Fig. 2. ^{29}Si MAS NMR spectra of talc, unheated and heated to various temperatures. Field strength 4.7 T. Spinning side bands indicated by *.

(Fig. 2, curve C)). On heating to 950°C, the enstatite resonance grows at the expense of the talc, and the amorphous silica resonance becomes better defined (Fig. 2, curve D). By 1000°C the spectrum consists of only enstatite and silica (Fig. 2, curve E). The single enstatite resonance corresponds better with that reported for orthoenstatite [14] than for clinoenstatite, which has two peaks, at about −81.8 and −84.2 ppm [15]. The ^{29}Si NMR spectra provide no explanation for the double endotherm, and suggest that the reaction involves the progressive conversion of the Q^3 phyllosilicate structure directly to a Q^2 pyroxene chain structure, with no evidence of an intermediate dehydroxylate phase. There remains, however, the question of the existence of the postulated pyribole intermediate, for which no ^{29}Si NMR spectrum has been reported because the natural mineral containing this MPP structure has yet to be discovered. However, a ^{29}Si NMR study has recently been reported of the transformation between amphibole and a triple-chain (MMP) silicate in the synthetic Na–Mg–Si system [16], in which the MAS NMR spectrum was found to be quantitatively composed of the individual spectra of the two intergrown phases. Further, the ^{29}Si NMR spectra of the synthetic sodium clinojimthompsonite MMP phase and its related amphibole are very similar, as would be expected from a comparison of the known structure of the related pyribole jimthompsonite [17] with those of pyroxenes and amphiboles, which reveals strong similarities in the general features of the silicate chain structures. The ^{29}Si chemical shifts for amphiboles such as tremolite are typically −88 and −91 ppm for the T2 and T1 sites respectively [15], whereas those for pyroxenes fall in the range −81.8 to −91.8 ppm [18]. Thus, by analogy with the recent biopyribole study [16], the NMR spectrum of the pyribole intermediate formed in the transformation of talc should consist of the spectra of the component phases, and fall in the range −82 to −92 ppm, i.e. under the envelope of the developing pyroxene resonance. Thus, the present spectra are consistent with the previous limited NMR results for biopyriboles, the spectra of which behave like a physical mixture of the intergrowing components [16], but for this reason provide no additional structural details of this intermediate phase.

3.2. ^{25}Mg MAS NMR

The ^{25}Mg MAS NMR spectrum of unheated talc (Fig. 3, curve A) shows a single unresolved resonance at 4.0 ppm. This is probably broadened due to electric field

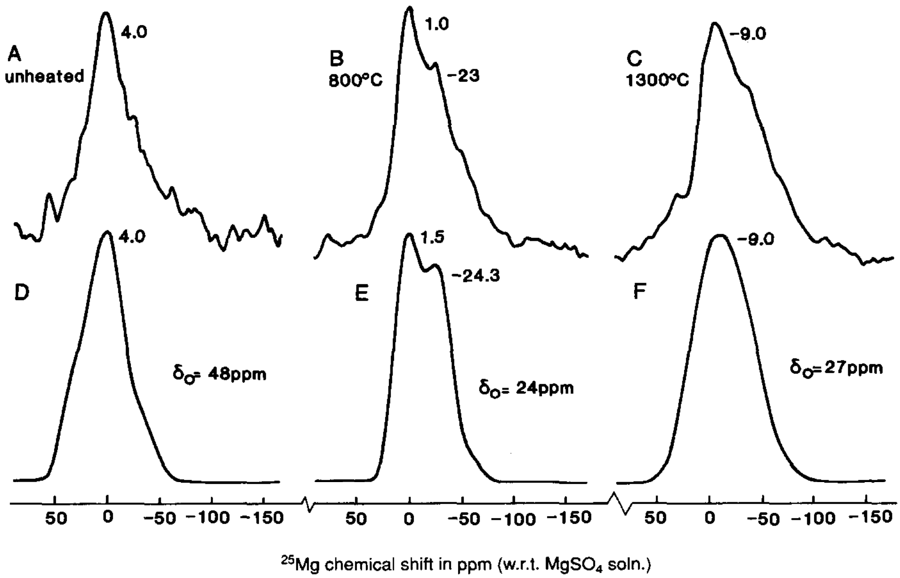

Fig. 3. Curves A–C, observed ^{25}Mg MAS NMR spectra of talc, heated as marked. Field strength 11.7 T. Spectrum C corresponds to pure enstatite. Curves D–F, corresponding spectra simulated using parameters as in text.

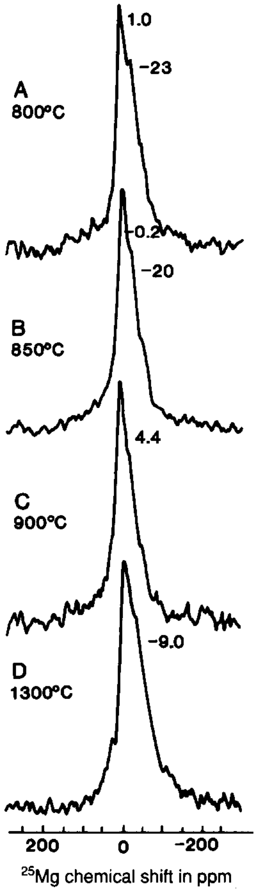

Fig. 4. ^{25}Mg MAS NMR spectra of talc heated to various temperatures. Field strength 11.7 T.

gradient (EFG) effects, which can be more clearly distinguished in the sample heated to 800°C (Fig. 3, curve B) (in which the talc structure is still preserved, according to XRD and ^{29}Si MAS NMR). A reasonable simulation of the unheated talc spectrum can be achieved (Fig. 3, curve D) by assuming a nuclear quadrupole coupling constant (χ) of 2.4 MHz, an EFG tensor asymmetry parameter (η) of 0.7, with a gaussian line broadening of 20 Hz. Comparison of the observed and calculated spectra indicates a value of 48 ppm for δ_0, the chemical shift corrected for EFG effects.

The ^{25}Mg MAS NMR spectra heated to various temperatures in its decomposition range are shown in Fig. 4. The spectra change very little in shape or in relative intensity throughout the reaction, reflecting the considerable similarity in the resonances of the starting material and the final product enstatite (Fig. 4, curve D). A reasonable simulation of the 800°C spectrum can be obtained by setting $\chi = 2.4$ MHz and $\eta = 0.2$, with a gaussian line broadening of 20 Hz (Fig. 3, curve E). The resulting value of δ_0 (24 ppm) suggests that this heat treatment has changed the environment of the Mg sites even though the talc structure is still intact. The spectrum of enstatite (Fig. 3, curve C) has a shape which is difficult to simulate, but an approximation can be achieved by setting χ in the range 2.4–2.5 MHz, η in the range 0.2–0.4, and the gaussian line broadening at 35–40 Hz (Fig. 3, curve F). The resulting value of δ_0 is 27 ppm.

The ^{25}Mg MAS NMR results suggest that such changes as occur in the octahedral environment of the Mg have taken place by 800°C, before any significant change in the silicate structure has begun. The crystal structure of talc contains two octahedral Mg sites [19], for which an angular distortion index DI can be calculated from the relationship [20]

$$\mathrm{DI} = \left(\sum_{i=1}^{12} |\Theta_i - \Theta_\mathrm{m}| \right) \Big/ 12\Theta_\mathrm{m} \qquad (1)$$

where Θ_i and Θ_m are the observed and true (undistorted) octahedral angles respectively. The calculation indicates that the DI of the M1 and M2 octahedral sites in talc are equal (0.057), providing a possible explanation for the appearance of a single resonance. A similar calculation for orthoenstatite, from the crystallographic data of Ohashi [21], indicates that the M1 and M2 sites have different degrees of distortion ($\mathrm{DI} = 0.048$ and 0.099 respectively). It is not clear whether this difference in distortion between the two sites would be sufficient for their distinction in the NMR spectra; partial resolution may however explain the unusual shape of the enstatite spectrum, and the difficulty encountered in simulating its shape by EFG calculations.

Neither the ^{29}Si nor the ^{25}Mg MAS NMR spectra provide evidence for the incorporation of Mg into the amorphous silica phase formed during the reaction, nor any evidence for the formation of an anhydrous intermediate as proposed by DeSouza Santos and Yada [6]. If either this type of intermediate or a pyribole is formed, its constitution must be too similar to those of the reactants and products to be distinguished by NMR.

References

[1] R.C. MacKenzie (Ed.), The Differential Thermal Investigation of Clays, Mineralogical Soc., London, 1957, Chapt. 6.
[2] H.F.W. Taylor, Clay Miner. Bull., 5 (1962) 45.
[3] M. Nakahira and T. Kato, Clays Clay Miner., 12 (1964) 21.
[4] M.C. Ball and H.F.W. Taylor, Mineral. Mag., 33 (1963) 467.
[5] G.W. Brindley, in J.E. Burke (Ed.), Progress in Ceramic Science, Vol. 3, Pergamon, Oxford, 1963, p. 1.
[6] H. DeSouza Santos and K. Yada, Clays Clay Miner., 36 (1988) 289.
[7] H. Konshi and J. Akai, Phys. Chem. Mineral., 17 (1991) 569.
[8] J.B. Thompson, Am. Mineral., 63 (1978) 239.
[9] K.J.D. MacKenzie, I.W.M. Brown, R.H. Meinhold and M.E. Bowden, J. Am. Ceram. Soc., 68 (1985) 266.
[10] I.W.M. Brown, K.J.D. MacKenzie and R.H. Meinhold, J. Mater. Sci., 22 (1987) 3265.

[11] C.A. Weiss, S.P. Altaner and R.J. Kirkpatrick, Am. Mineral., 72 (1987) 935.
[12] K.J.D. MacKenzie and R.H. Meinhold, Am. Mineral., 79 (1994) 250.
[13] K.J.D. MacKenzie and R.H. Meinhold, Am. Mineral., 79 (1994) 43.
[14] M. Magi, E. Lippmaa, A. Samosan, G. Engelhardt and A.-R. Grimmer, J. Phys. Chem., 88 (1984) 1518.
[15] N. Janes and E. Oldfield, J. Am. Chem. Soc., 107 (1985) 6769.
[16] M.D. Welch, J. Rocha and J. Klinowski, Phys. Chem. Mineral., 18 (1992) 460.
[17] D.R. Veblen and C.W. Burnham, Am. Mineral., 63 (1978) 1053.
[18] B.L. Sheriff, H.D. Grundy and J.S. Hartman, Eur. J. Mineral., 3 (1991) 751.
[19] B. Perdikatsis and H. Burzlaff, Z. Kristallogr., 156 (1981) 177.
[20] W.H. Baur, Acta Crystallogr. Sect. B, 30 (1974) 1195.
[21] Y. Ohashi, Phys. Chem. Mineral., 10 (1984) 217.