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# Role of Water in the Mechanochemical Reactions of MgO–SiO$_2$ Systems

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**The products of mechanochemical activation of mixtures in the magnesia–silica system ground in a planetary pot mill for up to 20 h. were found to depend on the water content of the siliceous starting materials. Mixtures containing silica gel produced no new products detectable by XRD and $^{29}$Si MAS NMR, but their thermal reaction to form forsterite at 890°C was slightly enhanced by grinding. In contrast, mixtures containing more highly hydrated silicic acid produce a layer-lattice magnesium silicate with an 8.4-Å basal spacing and a $^{29}$Si MAS NMR spectrum similar to that of the product obtained when the same mixture is subjected to hydrothermal reaction conditions. A possible explanation in terms of a mechanochemically induced hydrothermal reaction mechanism is discussed.** © 1998 Academic Press

## 1. INTRODUCTION

Grinding of solid mixtures of inorganic compounds is a basic technique in solid-state mechanochemical synthesis (1). The grinding can be carried out under either wet or dry conditions; dry grinding is expected to be influenced by the presence of water or hydroxyl groups in the starting materials (2–4). The influence of water or hydroxyl groups on mechanochemical reactions (soft mechanochemical reactions) (4) has been studied extensively and systematically by Senna and co-workers (4–11). Mechanochemical reactions of hydroxides or hydrous compounds have also been reported (12–14). Avvakumov *et al.* reported (15, 16) that mechanochemical reactions in mixtures of hydrated oxides occur faster than those in anhydrous oxide mixtures. The acceleration of soft mechanochemical reactions by water or hydroxyl groups has been interpreted in terms of acid–base reactions between oxides (4–6, 8, 9, 11, 16).

Liao and Senna (5, 6) reported the formation of an amorphous phase during reaction of amorphous SiO$_2$ with magnesium hydroxide. They suggested that the solid-state reaction between Mg(OH)$_2$ and SiO$_2$ begins at the contact points between these dissimilar particles through solid state charge transfer, i.e., between basic hydroxide and acidic oxide. However, previous studies of the mechanochemical reaction of hydrated mixtures of Mg(OH)$_2$ and SiO$_2$ have not been reported.

The aim of the present investigation was to examine the mechanochemical reactions of three mixtures (magnesium hydroxide/silica gel, magnesium hydroxide/hydrous silicic acid, and magnesium oxide/silicic acid) to elucidate the effect of hydration water on the mechanochemical interaction in these systems. The mechanochemical product obtained in this study was shown by XRD and solid-state MAS NMR to have the characteristics of a layer-lattice magnesium hydroxysilicate, and its similarity to the products of hydrothermal reaction of magnesium hydroxide with silicic acid was noted.

## 2. EXPERIMENTAL PROCEDURE

The starting materials were silica gel, silicic acid, and magnesium oxide (Wako Pure Chemical Industries, Ltd) and magnesium hydroxide (Kanto Chemical Co., Inc). The average particle sizes ($d_{50}$) of the magnesium hydroxide, silicic acid, and silica gel measured with a laser analyzer (Nikkiso, Microtrac) were 3, 12.4, and 20 μm, respectively, and the specific surfaces of these reagents, determined by the BET method in nitrogen at 77 K, were 23.5, 142, and 580 m$^2$ g$^{-1}$, respectively. Thermogravimetry of the starting materials up to 1200°C showed that Mg(OH)$_2$ loses its structural water at 400°C, the associated mass change of 32.3% being satisfactorily close to the theoretical loss (31%). The mass loss of the silica gel (17.4%) occurred at 88–140°C, representing the removal of surface adsorbed water. The silicic acid was in a hydrated form, SiO$_2 \cdot n$H$_2$O, and had an ignition loss of 46%, most of which (the hydration water) was lost below 150°C with a further small continuous loss up to 1200°C due to the dehydroxylation of silanol groups. Before use, the magnesium oxide was

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annealed at 500°C for 2 h to remove the hydrated surface phase, and showed no tendency toward rapid atmospheric rehydration or carbonation. The ground mixtures $Mg(OH)_2$–$SiO_2$,$Mg(OH)_2$–$SiO_2 \cdot nH_2O$ and MgO–$SiO_2 \cdot nH_2O$ are denoted TM1-*t*,TM2-*t*, and TM3-*t*, respectively, where -*t* indicates the grinding time in minutes. The molar ratio of MgO to $SiO_2$ in all mixtures was 1:1. Grinding was carried out in a laboratory planetary pot mill (Itoh Co., Ltd., La-PO.1) using a 3.15-g charge, ground in air at a rotation speed of 400 rpm. Both the pot and milling medium were of silicon nitride and the weight ratio of balls to powder was 20 : 1. Hydrothermal synthesis of magnesium silicate was carried out using 3.15 g of mixture M2 suspended in 15 ml distilled water, sealed in a container and heated at 80°C for 24 h. After heating, the slurry was evaporated at room temperature and examined, together with the ground samples, by powder XRD (Rigaku, Geigerflex, with monochromated Cu*K*α radiation), $^{29}$Si MAS NMR spectroscopy at 11.7 T (Varian Unity 500 spectrometer with Doty probe spun at 10–12 kHz), and DTA-TG (Rigaku, Thermoplus TG 8120 thermal analyzer). The crystallized materials, heated in the DTA cell to above the exotherm temperature, were analyzed by XRD. The infrared spectra were recorded using an IR spectrometer (Japan Spectroscopic Co., J-0033) with the samples suspended in KBr disks pressed at 1.3 MPa.

## 3. RESULTS AND DISCUSSION

### *3.1. X-ray Diffraction Data*

XRD patterns of samples ground for various times are shown in Fig. 1. With increasing milling time the XRD intensity of $Mg(OH)_2$ decreased and broadening was observed in all samples, indicating a reduction in crystallite size and increase in lattice strain induced by milling. Figure 1a shows that no crystalline products were formed in ground mixture TM1 [$Mg(OH)_2$ and silica gel]. In TM2 [$Mg(OH)_2$ and silicic acid], the intensity of the $Mg(OH)_2$ peaks decreased with milling time but broadening of these peaks did not occur (Fig. 1b). Concomitant with the decrease in $Mg(OH)_2$ peak intensity in TM2, new broad peaks appeared at $2\Theta° = 10°$–13°, 20°–22°, 24°–27°, 35°–39° and 60°–62°, respectively, which indicate the formation of a poorly crystalline layered magnesium silicate hydrate phase by a mechanochemical reaction between $Mg(OH)_2$ and silicic acid. A similar reaction also occurs between MgO and silicic acid Fig. 1c. In the latter system, a large amount of $Mg(OH)_2$ was observed in the unground mixture that was formed during the preliminary mixing of the components, resulting from the release of a large amount of adsorbed water in the silicic acid during mixing. This preliminary mixing also results in the appearance of amorphous silica, evidenced by the broad XRD baseline hump at about 25°2*θ*

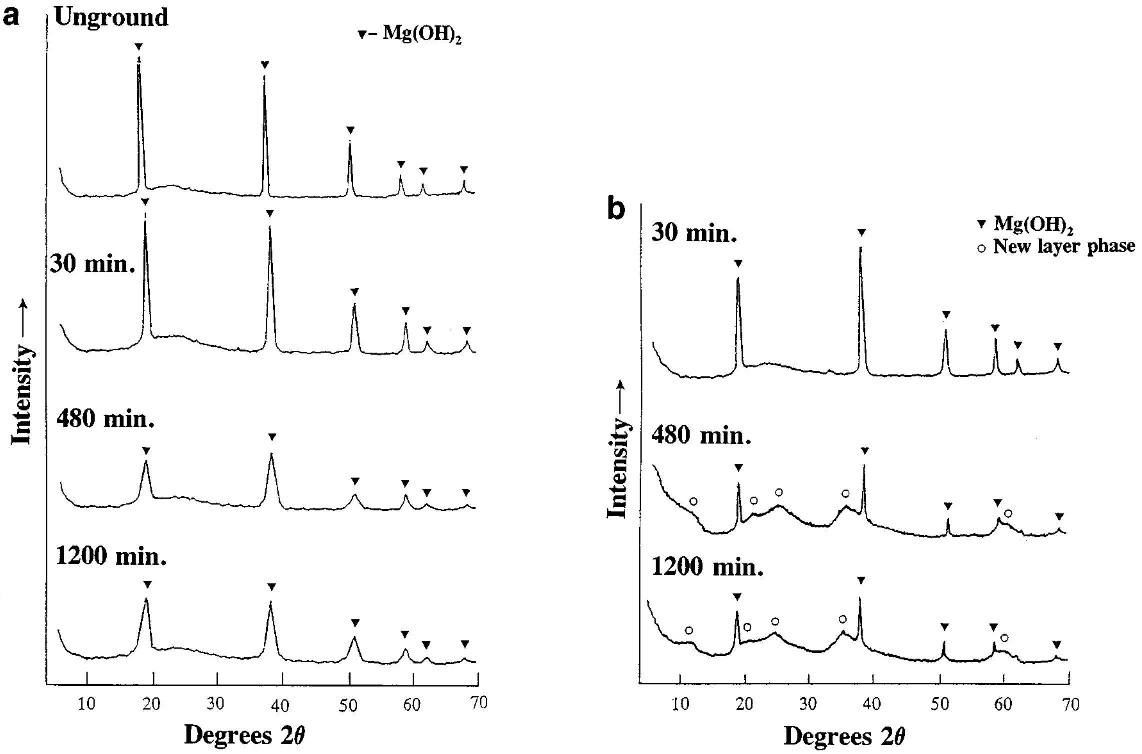

**FIG. 1.** XRD patterns of samples ground for varying times. (a) TM1, (b) TM2, (c) TM3.

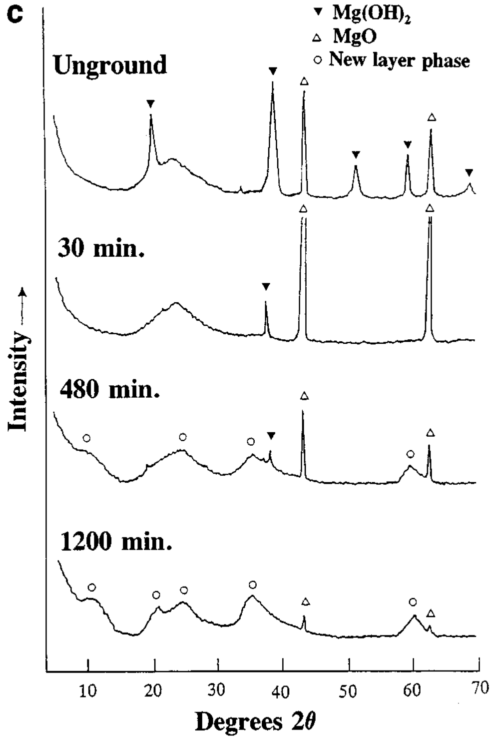

FIG. 1—*Continued*

(Fig. 1c). The formation of the new layered phase occurs more intensely in TM3 than in TM2, possibly because of the ready hydration of the MgO powder to form magnesium hydroxide. The freshly formed $Mg(OH)_2$ is also highly reactive, facilitating formation of the new layered phase that has an XRD pattern similar to that of the magnesium silicate formed by interaction of hydrous silicic acid and magnesium hydroxide on grinding (Fig. 1b).

### *3.2. Thermal and Crystallization Behavior*

The thermal behavior of the three ground samples is shown in Fig. 2. The DTA and TG curves of TM1 (Fig. 2a) did not change significantly with increased milling times, with only a slight increase in the height of the exothermic peak noted, together with a decrease in the exothermic peak temperature from 865 to 852°C at longer milling times. By contrast, the DTA curves of TM2 and TM3 showed sharp exothermic peaks at around 850–860°C.With increased milling time the intensity of the endothermic dehydroxylation peak of $Mg(OH)_2$ at 365°C decreased almost to zero and, at the same time, shifted to slightly higher temperatures. In TM2, the weight loss due to dehydration of adsorbed water below 150°C increased slightly with increased milling time. In other words, the mechanochemical dehydroxylation of $Mg(OH)_2$ was not accompanied by a large increase in adsorbed water, suggesting that the disappearance of the endothermic peak at longer grinding times may be associated with the change of the brucite structure to a hydrous magnesium silicate of typically layer structure. The DTA-TG conclusions are consistent with the XRD results. The exothermic peak intensity in the TM2 DTA trace increases with grinding, but in TM3 it decreases; the reason for this difference is presently unclear.

The crystallized phases formed in the exothermic reactions were examined by XRD in samples heated in the DTA cell up to 890°C (Fig. 3). On heating to 890°C, the ground TM1 mixtures contained forsterite and periclase (Fig. 3a); the DTA exotherm is therefore assigned in TM1 to forsterite formation resulting from solid-state reaction between MgO and $SiO_2$. Forsterite formation is reported to be thermodynamically more favored than formation of enstatite (17). The increase in the rate of forsterite formation with increased milling time indicates an increased homogeneity and intimacy of mixing in the powders, and represents a thermal reaction distinctly different from that of TM1 and TM2, in which enstatite is also formed. In contrast to the results of Liao and Senna (5, 6) we did not observe mechanochemical formation of amorphous magnesium silicate that crystallized to the form of enstatite in the TM1 mixtures, possibly because our experimental conditions were milder than those of Liao and Senna, who ground 1-g. samples using 100 steel balls of 6-mm diameter in a vibration mill.

Mixtures TM2 and TM3 both show thermal behavior different from that of TM1; each contains a significant amount of enstatite and only a small amount of forsterite and periclase after heating to 890°C. The amount of periclase decreased and the enstatite increased with increasing milling time, the intensities of enstatite peaks being generally a little smaller in TM3. The large amount of clinoenstatite formed in TM2-1200 and TM3-1200 fired at the exothermic peak temperature can be understood in terms of the formation of a local arrangement of $MgSiO_3$-like chain structure in the ground samples. The thermal analysis results therefore suggest that the exothermic reaction in TM1 reflects the solid-state formation of forsterite, in contrast with the exotherms in TM2 and TM3, which result predominantly from the formation of enstatite, a typical thermal decomposition product of layer-lattice hydrous magnesium silicates such as talc (18).

### *3.3. IR Spectra*

As shown in Fig. 4a the IR spectra of the TM1 samples showed only slight changes on grinding, indicating relatively little chemical interaction between brucite and silica gel. These IR results agree with the XRD and DTA-TG data. By contrast, the TM2 samples show clear changes in the IR spectra on grinding (Fig. 4b). The silicic acid shows absorption bands at 1095, 800, and 470 $cm^{-1}$, typical of

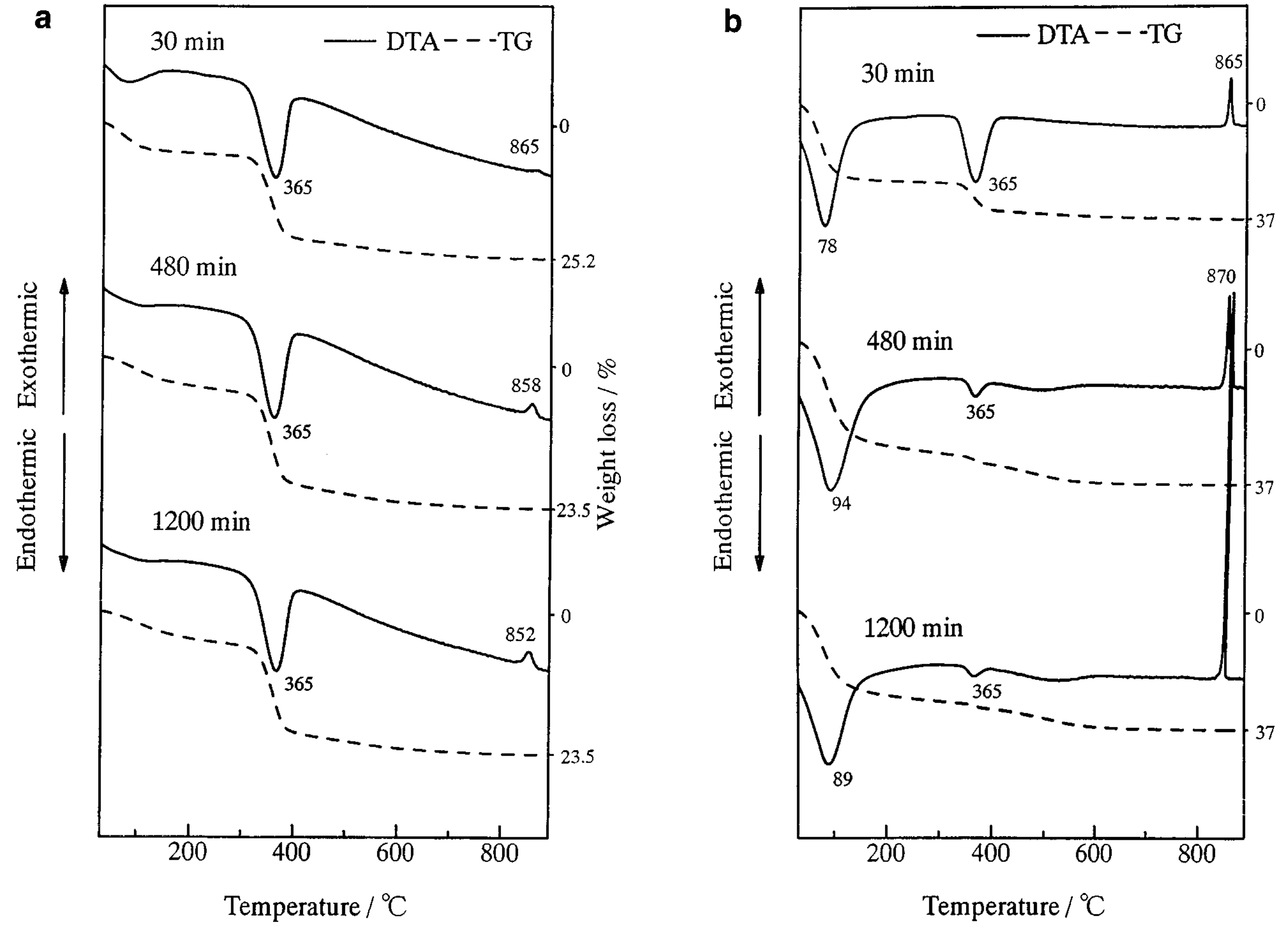

**FIG. 2.** DTA-TG curves of the samples ground for varying times. (a) TM1, (b) TM2, (c) TM3.

four-coordinated silica. The band at 3750 cm$^{-1}$ was assigned as the O–H stretching band of $Mg(OH)_2$ and the medium-intensity band at 950 cm$^{-1}$ arises from the stretching vibration of silanol groups (Si–OH) (19). The IR spectra of the ground TM2 and TM3 samples were similar, resembling the spectra of layer magnesium silicate hydrates, such as talc and serpentine (19). With increasing milling time the absorption bands due to four-coordinated silica changed to the band of layer structure magnesium silicate, e.g., the centre-of-gravity of the band at 1095 cm$^{-1}$ shifted towards 1010 cm$^{-1}$ and the 800 cm$^{-1}$ band almost disappeared. A new band appeared at 630 cm$^{-1}$, which can be assigned as the bending vibration of Mg–OH in layer-structure magnesium silicate (19). With increasing milling time, the intensity of the $Mg(OH)_2$ at 3750 cm$^{-1}$ decreased and almost disappeared. Slight differences were observed in the IR spectra of mixtures TM2 and TM3; sample TM3-0 showed no absorption band at 950 cm$^{-1}$ characteristic of the Si–O stretching of the Si–OH group, suggesting that the formation of $Mg(OH)_2$ is related to the disappearance of the Si–OH groups.

The weak absorption band at 910 cm$^{-1}$ in the TM2-1200 and TM3-1200 samples may be attributed to the interlayer Si–OH group of layered magnesium silicate hydrate. The increase in the adsorbed water bands at 3500 and 1630 cm$^{-1}$ during grinding is consistant with mechanochemical dehydroxylation of $Mg(OH)_2$ and/or polycondensation of $Mg(OH)_2$ with Si–OH.

### 3.4. $^{29}$Si MAS NMR Spectra

A selection of $^{29}$Si MAS NMR spectra of the starting silicic acid, ground TM2 and TM3 samples, and the product of a hydrothermal reaction are shown in Fig. 5. The hydrothermal sample shows an XRD pattern (not shown here) similar to those of $M2$ and $M3$, but with the broad reflection at 10–13° 2Θ shifted to 5–6° 2Θ, suggesting a slightly different structure for the layered magnesium silicate

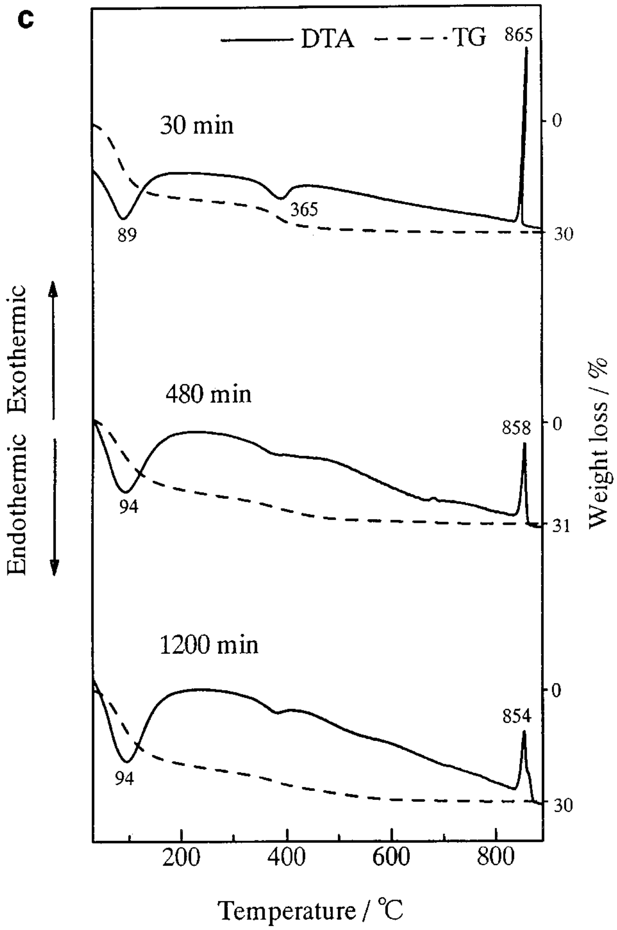

**FIG. 2**—*Continued*

product. On the basis of literature chemical shift data, the $^{29}Si$ peaks can be assigned to the various silicate structures, denoted as $Q^n$ where ($n$) indicates the number of bridging oxygens. The peak and shoulder at $-111$ and $-100$ ppm in silicic acid (Fig. 5A) were assigned as $Q^4$ and $Q^3$ units, respectively. The TM2-1200 and TM3-1200 spectra (Figs. 5B,5C) contain two distinct peaks at $-84$ and $-91$ ppm and a small peak at $-111$; the new resonances at about $-84$, and $-91$ ppm are in the region expected for the $Q^2$ and $Q^3$ units present in magnesium silicate (20, 21). Alternatively, the $Q^3$ peak at $-91$ ppm may be associated with a silicon site bearing two OH groups ($Q^2$), but previous studies (22) of mechanochemically treated amorphous silica showed that protonation of the $Q^4$ framework results in an increased $Q^3$ signal at $-102$ ppm. In such a protonated system, the $Q^2$ signal at $-91$ ppm was insignificant, suggesting that this peak in our TM2-1200 and TM3-1200 samples probably does not correspond to the $Q^2$ signal of silica.

Since the $Q^2$ peak cannot be identified with any crystalline phase in the XRD patterns of the ground samples, it must be present in an amorphous compound in which the local Si environment cannot bear any similarity to forsterite, since this phase shows a strong, characteristic $^{29}Si$ resonance at $-61.6$ ppm (23) which is absent from all the present $^{29}Si$ MAS NMR spectra. The $Q^3$ peak does not correspond precisely with the known crystalline layer structure magnesium silicates (talc and serpentine), suggesting it may arise from a poorly crystalline phase. The $^{29}Si$ spectrum of hydrothermally synthesized magnesium silicate (Fig. 5D) shows similarities to the MAS NMR spectra of the $M2$ and $M3$ samples, but with the $Q^2$ and $Q^3$ peaks shifted slightly to $-86$ and $-93$ ppm, respectively. The shift at $-93$ ppm is more typical of serpentine (21), although the XRD pattern of this sample shows a basal reflection of 15–16°A usually associated with saponite-like minerals.

In summary, therefore, the mechanochemical behavior of TM1 [$Mg(OH)_2$ + silica gel] is different from that of TM2 [$Mg(OH)_2$ + silicic acid] and TM3 (MgO + silicic acid). Grinding promotes only slight reaction in TM1, as evidenced by the lack of XRD evidence of new phases, little change in the IR spectrum, and the formation of only forsterite by solid-state reaction at 890°C. In contrast, samples TM2 and TM3, in which the silica source is considerably more hydrated, show XRD, IR, and $^{29}Si$ MAS NMR evidence of the formation of a layer-lattice hydrous magnesium silicate after mechanochemical treatment. The characteristics of this product phase, including its thermal transformation to enstatite rather than forsterite, are consistent with a layer-lattice silicate such as can be formed by hydrothermal reaction between silica and magnesia. The mechanochemical formation of this phase appears to depend on the hydration state of the silica rather than the structural water associated with the magnesian component, since it forms from anhydrous MgO (TM3) but not with a less hydrated form of silica (TM1).

### *3.5. Possible Mechanochemical Reaction Mechanisms and the Nature of the Layer-Lattice Silicate Product*

Mechanochemical activation of reacting solid-state systems promotes the formation of defects, especially at regions of contact between the reactant grains, where the formation of amorphous forsterite-like material might be expected in the present mixtures. However, the $^{29}Si$ MAS NMR results suggest that such a mechanochemical solid-state reaction is unlikely, since the diagnostic forsterite resonance at $-61.6$ ppm, which is sensitive and independent of long-range atomic order (crystallinity), is not observed in any of the ground samples.

Mechanochemical processing is reported (1) to produce local spot temperatures as high as 1000 K for short times; bulk temperature rises an order of magnitude lower may well occur in the sample during grinding, but would not be sufficient to induce solid-state reactions and would not in

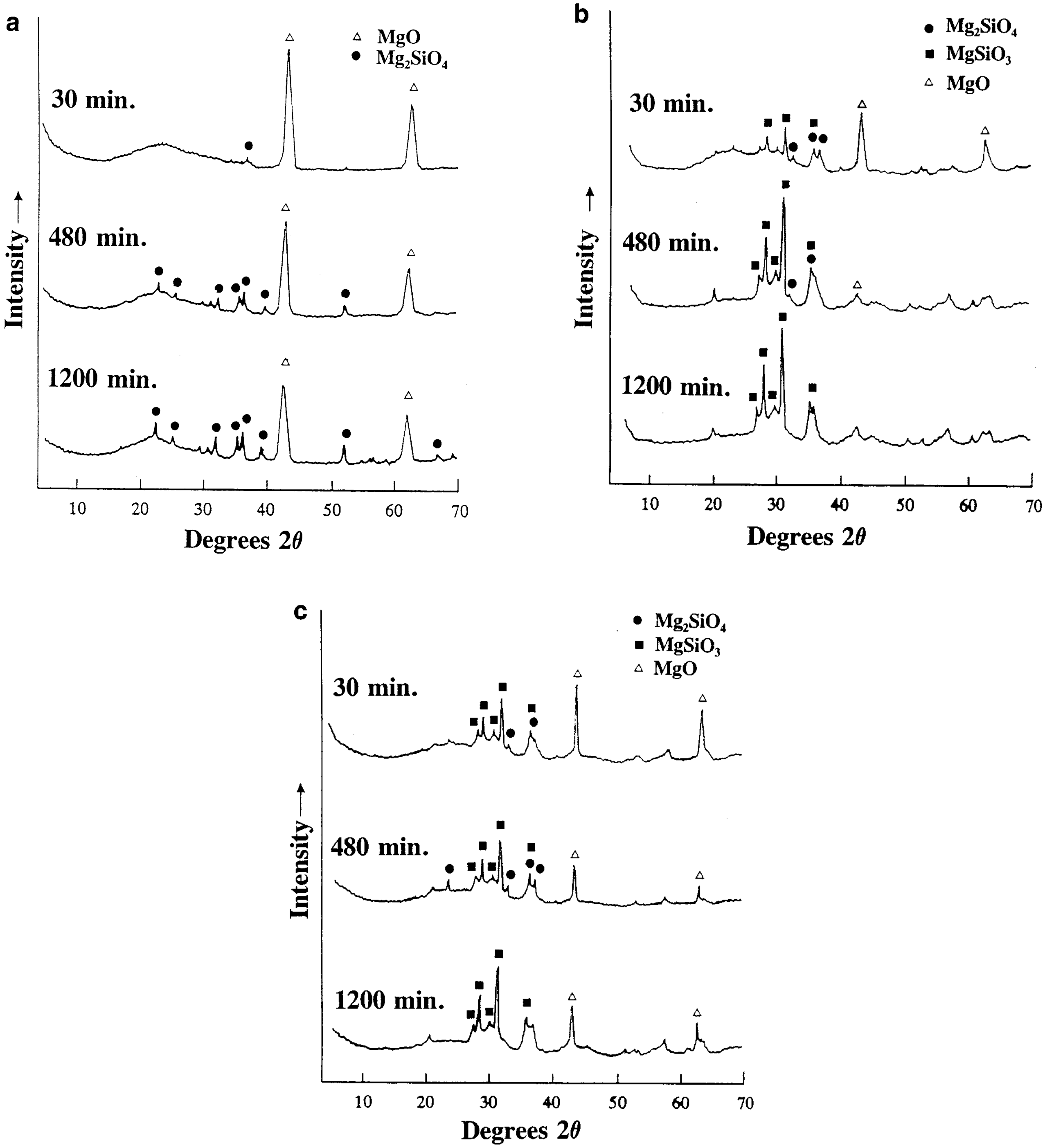

**FIG. 3.** XRD patterns of the samples fired up to 890°C after grinding various times. (a) TM1, (b) TM2, (c) TM3.

itself explain the key role played in the formation od the layer-lattice structure by the water present in the siliceous starting material.

The beneficial effect of free water on mechanochemical reactions of oxides has been reported previously. Longo and Voight (24) suggested that the increased solubility of the components in the thin water films at the grinding surface could account for their rapid reaction rate. Boldyrev (25) reported the hydrothermal formation of calcium silicate during grinding of a stoichiometric mixture of calcium oxide

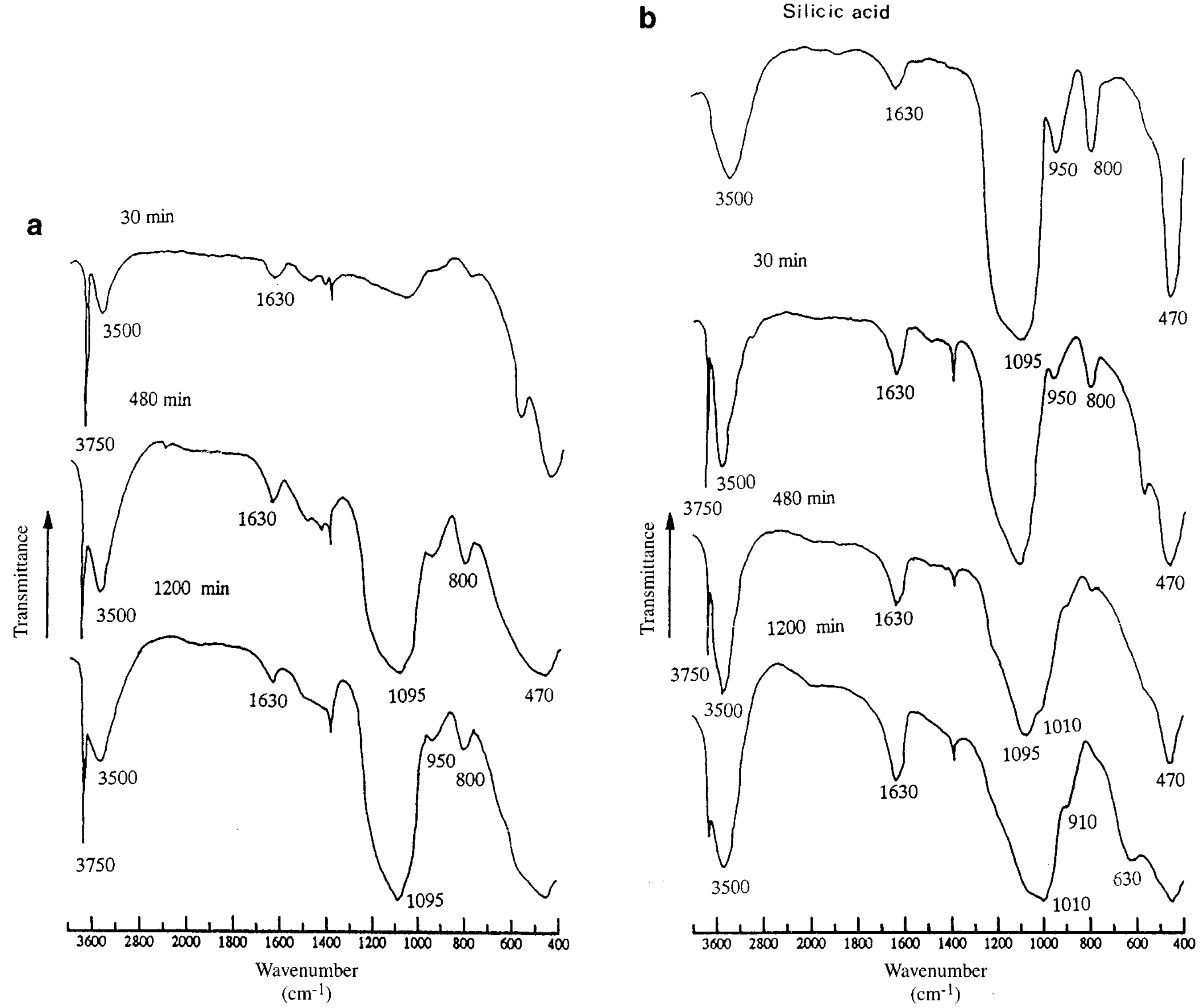

**FIG. 4.** IR spectra of the samples. (a) ground TM1, (b) silicic acid and ground TM2, (c) unground and ground M3.

and silicon dioxide. On the other hand Watanabe *et al.* (9) showed that calcium silicate can be formed mechanochemically in an acid–base reaction between $Ca(OH)_2$ and fumed silica without the addition of free water. Avvakumov *et al.* (16) reported that the reaction rate of CaO with various oxides depends on the amount of added water, achieving a maximum rate at the optimal water content. Avvakumov (26) has discussed the influence of the acid–base properties of the reactants in "mild mechanochemical syntheses" and noted that the reaction of silica with $Al(OH)_3$ to form amorphous aluminosilicate is enhanced by the use of more acidic (highly hydrated) forms of silica. Although acid–base considerations are clearly relevent to the present system, they do not explain the formation of a layer-lattice product with silicic acid and not silica gel; both reagents contain labile hyration water.

Boldyrev (25) has made a theoretical analysis of a number of mechanisms for transfer of energy from the milling medium to the reacting material under mechanochemical reaction conditions. In addition to his treatment of processes involving friction, particle deformation, and crack formation/comminution (25), Boldyrev also addresses liquid–solid reaction systems which appear to be more relevant to the present case, in view of the observed importance of the silicic acid water content in the formation of a layer-lattice hydrous product. If the reactant particles are considered as a porous matrix containing liquid, mechanical energy may be transferred to the reactant as a result of adiabatic com-

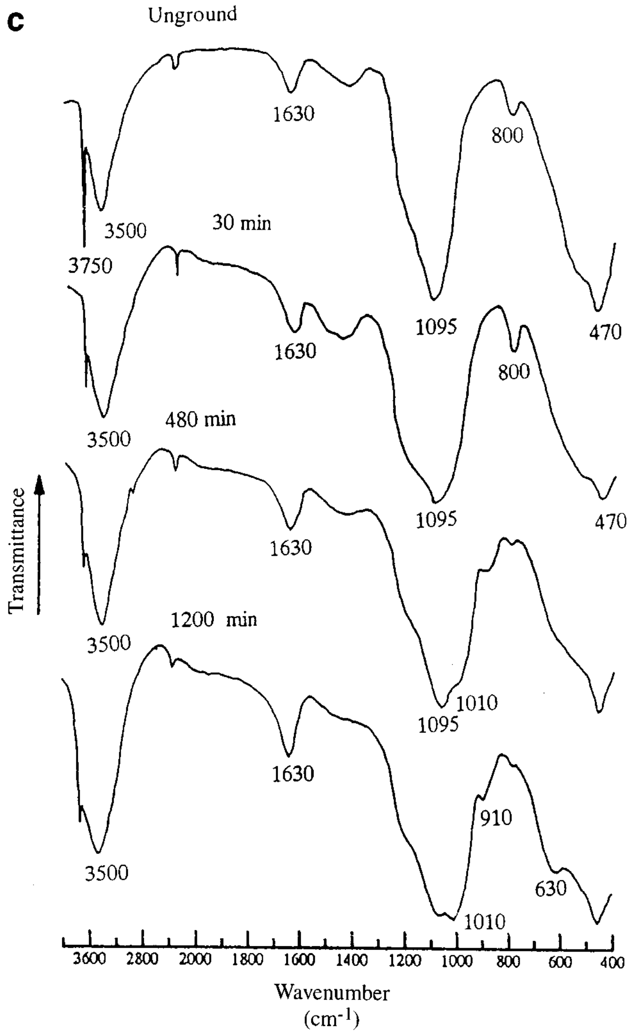

**FIG. 4**—*Continued*

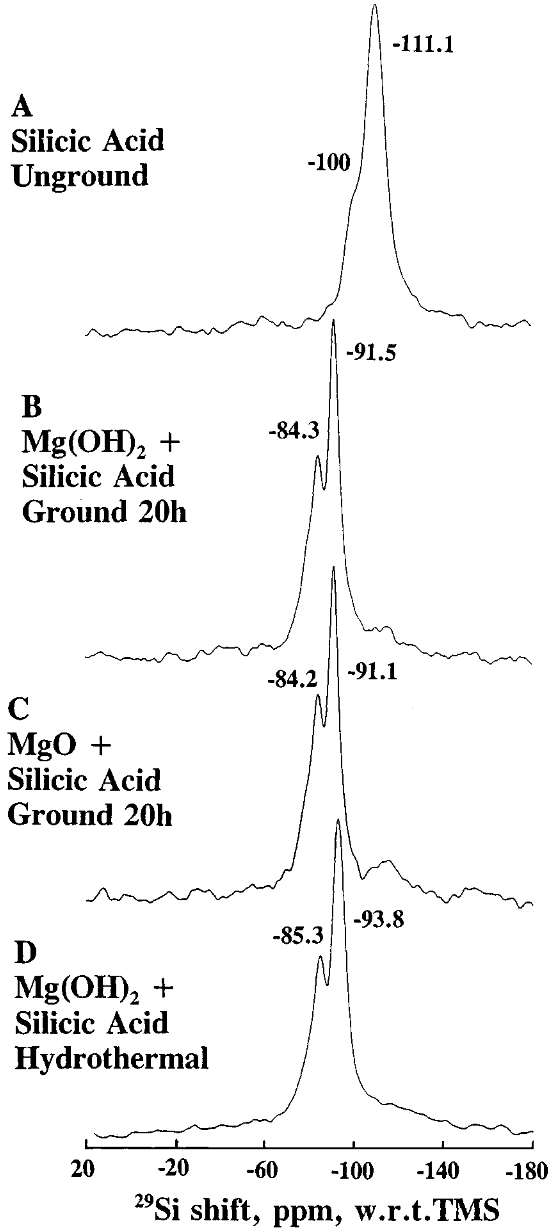

**FIG. 5.** $^{29}$Si MAS NMR spectra of the starting materials and reaction products.

pression of the liquid present, especially if it contains gas bubbles, and as a result of liquid flow through the pores (25). Temperatures and pressures in such a system have been estimated (25) to rise to 500–700°C and 500–600 atm, respectively, i.e., well into the range for hydrothermal reactions to occur via material transport in the liquid state. Boldyrev (25) cites two examples of typical hydrothermal reactions that have been carried out by mechanochemical activation in the presence of water (the synthesis of hedenbergite and of calcium silicate). The present results suggest that we may have identified another example of such a mechanochemically induced hydrothermal reaction. In the present system, water is supplied by very rapid release of hydration water from the silicic acid component of mixtures TM2 and TM3 during grinding, producing essentially a water–silica–magnesia closed system. The difference in behavior observed with the two forms of silica may be due both to differences in the amount of labile water available for release and to the increased acidity of the more highly hydrated silicic acid.

Hydrothermal reactions within the water–magnesia–silica system were studied by Yang (27) and Kalousek and Mui (28). Yang (27) reported two phases resembling chrysotile and talc in the ternary system $MgO–SiO_2–H_2O$ at 100 to 300°C. Kalousek and Mui (28) studied reactions of mixtures with a $MgO : SiO_2$ ratio of 0.5 : 1 to 2.0 : 1, at 75 to 350°C for various reaction times. They observed the formation of product phases intermediate to those of talc and chrysotile, remarkably similar to the present grinding products. Both

Yang (27) and Kalousek and Mui (28) reported that $Mg(OH)_2$ reacted more slowly than MgO, again consistent with our findings. The composition of our mixtures ($MgO:SiO_2 = 1$) would not lead solely to talc or chrysotile. The reported hydrothermal products showed basal reflections of 9.4 and 7.37 Å in the talc-like and chrysotile-like materials, respectively (28). The layered magnesium silicate formed in the present study had a basal spacing of 8.4 Å, possibly representing a mixture of talc-like and chrysotile-like products. When mixture TM2 was ground with a large excess (400%) of free water, no reaction occurred because the thermal energy needed for the reaction between magnesia and silica was absorbed by the excess water. The mechanochemical production of a typically hydrothermal product from mixtures TM2 and TM3, which release significant but not excessive water, suggests that these mechanochemical reactions may proceed by a similar hydrothermal mechanism. Systems such as TM1 that cannot generate the necessary hydrothermal conditions during grinding show only a slight degree of mechanochemical activation and do not form the typically hydrothermal products.

## 4. CONCLUSIONS

1. Silica–magnesia mixtures containing silicic acid behave differently under mechanochemical activation from a mixture containing less hydrated silica gel. In the latter, new crystalline phases are not observed, but the slight improvement in the solid-state formation of forsterite on heating at 890°C is probably due to improved interparticle contact and conminution induced by the grinding.

2. Mechanochemical activation of mixtures containing silicic acid produces a new phase, identified by XRD and $^{29}$Si MAS NMR as a layer-lattice magnesium silicate with a basal spacing of 8.4 Å. This material forms predominantly enstatite on thermal reaction at 890°C, and possibly represents a mixture of talc-like and chrysotile-like products. The formation of this mechanochemical product is independent of the presence of structural water in the magnesian reactant, being formed from both $Mg(OH)_2$ and MgO.

3. A product with comparable XRD and $^{29}$Si MAS NMR characteristics was formed by hydrothermal reaction of the present unground TM2 mixture at 80°C for 24 h. The formation of a typically hydrothermal product by mechanochemical activation of mixtures containing the more hydrated silicic acid suggests the possible operation of a hydrothermal mechanism, shown by Boldyrev (25) to be theoretically and experimentally feasible during mechanochemical processing of such hydrous systems.

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