Properties of magnesium silicate hydrates (M-S-H)

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Abstract

Investigations of synthetic magnesium silicate hydrate (M-S-H) samples have shown that M-S-H aged for 1 year can exhibit variable compositions with molar Mg/Si ratios in the range $0.7 \leq \text{Mg/Si} \leq 1.5$. At lower Mg/Si ratio, additional silica is present whereas brucite is observed for $\text{Mg/Si} \geq 1.3$. FT-IR and ^{29}Si NMR data reveal a high degree of silicate polymerisation, indicating the formation of silicate sheets. TGA shows the presence of bound water and of hydroxyl groups bound to Mg and as silanol groups in the M-S-H, in accord with $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS and high-speed ^1H NMR measurements. Raman and XRD data suggest that the M-S-H structure is related to a disordered talc precursor at low Mg/Si and to a serpentine precursor at high Mg/Si ratio. Solubility products for M-S-H phases were calculated on basis of the compositions of the aqueous solutions and a solid solution model was suggested.

Keywords: MgO – D; Magnesium silicate hydrate (M-S-H); Solubility; clay-cement interface; Spectroscopy – C.

26 1. Introduction

27 There is a growing interest for using magnesium silicate hydrate (M-S-H) as potential
28 low-pH cements for e.g. nuclear-waste encapsulation [1]. M-S-H may also form on the
29 surface of cement in contact with ground water containing magnesium sulphate [2, 3]
30 and in the interaction zone between cement and clays [4, 5], *i.e.*, under conditions
31 important for CO₂ storage in deep reservoirs and for disposal of radioactive wastes in
32 underground repositories. Recent investigations have shown that the decrease of pH
33 near the cement – clay interface and the diffusion of magnesium ions from the clay
34 towards the cement can lead to a magnesium enriched zone at the interface [6, 7]. In
35 these magnesium enriched zones magnesium silicate hydrates, which exhibit a gel-like
36 structure with little or no aluminium, are observed. Although analyses of solid M-S-H
37 phases have been reported in the literature, the properties, conditions of formation and
38 solubility of such M-S-H phases are not well investigated. M-S-H synthesized at room
39 temperature has been characterised showing evidence for low crystalline structure
40 consisting of silicate sheets [8-10]. Hydrothermal synthesis routes for M-S-H lead to the
41 formation of crystalline talc at low Mg/Si [11-14] and of crystalline serpentine at high
42 Mg/Si [14, 15] for temperatures above 200 °C. But it is neither known how much Mg can
43 be incorporated in such M-S-H phases nor its thermodynamic solubility constants.

44 In the present paper the composition and structure of M-S-H prepared from MgO and
45 SiO₂ at room temperature is investigated. The composition of the aqueous solutions is
46 determined and used to calculate tentative solubility products. The solid phases are

analysed by combining conventional methods (XRD, TGA, IR, Raman, ^1H , and ^{29}Si MAS NMR) with innovative ^{25}Mg NMR spectroscopy. ^{25}Mg NMR is employed for the first time in studies of cement phases to characterize the local structural environments of the Mg^{2+} ions.

2. Materials and methods

2.1 M-S-H synthesis

The M-S-H samples were synthesised by mixing appropriate quantities of MgO (Merck, pro analysis, >97 wt.% MgO, <1.5% CO_2 and < 0.1% CaO) and silica fume (SiO_2 , Aerosil 200, >99.8% SiO_2). Samples targeting six different Mg/Si molar ratios (0.4; 0.6; 0.8; 1.0; 1.3 and 1.7) were prepared and equilibrated at 20°C for one year. All samples were prepared in polyethylene (PE) containers with a water/solid ratio of 45 to ensure the availability of sufficient water. The synthesis and sample handling was performed in a N_2 filled glove box to minimize CO_2 contamination. The samples were placed on a horizontal shaker (100 rpm) during the reaction time of 1 year. After 1 year, the samples were filtered (0.45 μm Nylon filter), rinsed first with approximately 50 mL of 1:1 water - ethanol solution and then with 50 mL 94% ethanol solution in a N_2 filled glove. The solids were freeze dried for seven days, ground in an agate mortar and then stored in N_2 filled desiccators over a saturated aqueous CaCl_2 solution at approximately 30% relative humidity until analysis.

68 2.2 Analyses of the solid phases

69 A Mettler Toledo TGA/SDTA 8513 instrument was used for thermogravimetric analysis
70 (TGA). Samples of 30 to 40 mg were heated in a nitrogen atmosphere at 20°C/min from
71 30 to 980°C. The amount of brucite was quantified from the weight loss between 330
72 and 480°C using the tangential method [16].

73 X-Ray Diffraction (XRD) data were collected using a PANalytical X'Pert Pro MPD
74 diffractometer in a θ - 2θ configuration, applying $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) with a fixed
75 divergence slit size of 0.5° and a rotating sample stage. The samples were scanned
76 between 5° and $75^\circ 2\theta$ using a step size of $0.017^\circ 2\theta$ with the X'Celerator detector.

77 The infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer
78 using the ATR technique (attenuated total reflection) on bulk material and a step size of
79 1.9 cm^{-1} . The data are reported in wavenumbers (cm^{-1}).

80 The Raman spectra were measured with a Bruker Senterra instrument of 5 cm^{-1}
81 spectral resolution, using a 532 nm laser (20mW) at room temperature. The spectral
82 acquisition time was 10 seconds and 5 spectra were accumulated for each sample in
83 the frequency ranges of $110 - 1560 \text{ cm}^{-1}$ and $2700 - 3800 \text{ cm}^{-1}$.

84 The single-pulse ^{29}Si MAS NMR spectra were acquired at 79.49 MHz on a Bruker
85 Avance 400 NMR spectrometer using a 7 mm CP/MAS probe, a spinning speed of $\nu_R =$
86 4500 Hz, a 30° excitation pulse of $2.5 \mu\text{s}$ ($\gamma B_1/2\pi = 33 \text{ kHz}$), a relaxation delay of 60 s,
87 and ^1H TPPM decoupling ($\gamma B_2/2\pi = 42 \text{ kHz}$) during acquisition. The $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS
88 NMR spectra were recorded on a Varian-Unity 400 spectrometer using a CP/MAS NMR

probe for 5 mm o.d. rotors, a spinning speed of $\nu_R = 4.0$ kHz, and rf field strengths of $\gamma B_1/2\pi \approx \gamma B_2/2\pi = 33$ kHz for the CP transfer with contact time of 1.5 ms, and $\gamma B_2/2\pi = 62$ kHz for the subsequent ^1H TPPM decoupling during acquisition. The chemical shifts of the ^{29}Si MAS NMR spectra were referenced to an external sample of tetramethylsilane (TMS). The ^{29}Si MAS NMR spectra were analysed by least-squares fitting of a combination of Gaussian and Lorentzian peak shapes to the experimental spectra. The amount of nanosilica/silica fume was estimated from the intensity of the Q^4 peak at -110 ppm.

The ^{25}Mg MAS NMR spectra were obtained on a Varian Direct Drive VNMR-600 (14.1 T) spectrometer using a home-built CP/MAS NMR probe for 5 mm o.d. zirconia/ Si_3N_4 rotors and a spinning speed of $\nu_R = 12$ kHz. The spectra were acquired with the Hahn spin-echo pulse sequence, employing quadrupolar $\pi/2$ - and π -pulses with pulse widths of $2.4\ \mu\text{s}$ and $4.8\ \mu\text{s}$, respectively ($I = 5/2$, $\gamma B_1/2\pi = 35$ kHz), and evolution/refocusing delays of $83\ \mu\text{s}$ ($= 1/\nu_R$). ^1H TPPM decoupling ($\gamma B_2/2\pi = 42$ kHz) was applied during the spin-echo period and acquisition. A relaxation delay of 4 s was used and typically 60,000 scans were accumulated. The ^{25}Mg chemical shifts are referenced to an aqueous 1.0 M solution of $\text{Mg}(\text{NO}_3)_2$, using solid MgO ($\delta(^{25}\text{Mg}) = 26.05$ ppm) as a secondary reference.

The ^1H MAS NMR experiments were obtained on a Varian Direct Drive VNMR-600 (14.1 T) spectrometer using a Varian FastMASTM triple-tuned NMR probe for 1.6 mm o.d. zirconia rotors. The experiments employed a spinning speed of $\nu_R = 40$ kHz, a pulse width of $\tau_p = 1.9\ \mu\text{s}$ for $\gamma B_1/2\pi = 130$ kHz, and a 10-s relaxation delay. The ^1H

NMR spectra are referenced to TMS using a solid sample of adamantane ($\delta(^1\text{H}) = 1.77$ ppm) as a secondary reference.

2.3 Analyses of the pore solutions

The pH measurements were carried out immediately after filtration using small aliquots of the pore solution with a Knick pH meter (pH-Meter 766) equipped with a Knick SE100 electrode. The pH electrode was calibrated with CertiPUR[®] buffer solutions from Merck (pH 4.01 with potassium hydrogen phthalate, pH 7 with KH_2PO_4 / Na_2HPO_4 and pH 12.00 with $\text{NaOH}/\text{Na}_2\text{HPO}_4$). The pH measured in the filtered solutions were 0.3pH units lower than the pH values measured directly in the suspensions as charge balancing anions such as hydroxides can be removed during filtration [17]. The reported pH values are corrected to refer to the H^+ activity in the unfiltered solutions. Another part of the liquid phase was diluted in ratios of 1:10, 1:100 and 1:1000 with MilliQ H_2O immediately after filtration and used for ionic chromatography (IC) analysis. The dissolved concentrations of Mg and Si were quantified using a Dionex DP series ICS-3000 ionic chromatography instrument. The IC analyses are associated with a measurement error of $\leq 10\%$.

2.4 Thermodynamic modelling

Thermodynamic modelling was carried out using the Gibbs free energy minimization program GEMS [18]. GEMS is a general-purpose geochemical modelling code which

computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. Chemical interactions involving solids, solid solutions, aqueous electrolytes and gas phases are considered simultaneously. The speciation of the dissolved species as well as the kind and amount of solids precipitated are calculated at 20 °C by computing the Gibbs free energy of each species for 20°C using the thermodynamic data as given in the PSI-Nagra [19, 20] and the SUPCRT database [21]. The thermodynamic data for aqueous species as well as for many solids were taken from the PSI-Nagra thermodynamic database [19, 20]. Additionally, for the calculations of saturation indices for talc, chrysotile and antigorite data from the SUPCRT database [21] have been used. It is important to mention that a wide range of thermodynamic data for talc and chrysotile is reported in the literature (see Table 1) as the thermodynamic data have been derived from measurements at high pressure and temperatures. The datasets of Holland and Powel [22] and of Melekhova et al. [23] for example would indicate a 6 to 8 log units higher solubility of talc and a 5 log units more soluble chrysotile than the SUPCRT database [21].

Table 1: Chemical composition, fraction of silicon present in Q^3 and Q^2 sites, and thermodynamic properties of different magnesium silicate hydrates at 25 °C for comparison.

Chemical	$Q^3:Q^2$	$\log K_{s0}^b$	V°	density
formula ^a			[cm ³ /mol]	[g/cm ³]

Brucite [19, 20]	MH	-	-11.16	24.6	2.37
Jimthompsonite	$M_{3.33}S_4H_{0.67}$ ^c	2:1	-	136.1	2.84
Talc [21]	M_3S_4H	4:0	-62.9	136.3	2.78
<i>Talc [22]</i>	M_3S_4H		-54.5	136.3	
<i>Talc [23]</i>	M_3S_4H		-56.2		
Chrysotile [21]	$M_3S_2H_2$	2:0	-52.9	108.5	2.55
<i>Chrysotile [22]</i>	$M_3S_2H_2$		-48.2	107.5	
Antigorite [21]	$M_{2.8}S_2H_{1.8}$ ^d	2:0	-51.0	102.9	2.59
<i>Antigorite [22]</i>	$M_{2.8}S_2H_{1.8}$ ^d		-50.8	103.2	
SiO _{2,am} [19, 20]	S	-	-2.71	29.0	2.07

^a The short-hand cement notation is used: H =H₂O; M = MgO; S = SiO₂.

^b All solubility products refer to the solubility with respect to the species Mg²⁺, SiO₂⁰, OH⁻, or H₂O.

^c Rescaled formula from M₅S₆H to ease comparison with talc;

^d Rescaled formula from M₄₈S₃₄H₃₁ to ease comparison with chrysotile.

The measured compositions of the solutions were used to calculate ion activity products (IAP) and saturation indices (SI) with respect to amorphous SiO₂, brucite and talc and to derive tentative solubility products (K_{S0}) for M-S-H. Saturation indices offer the possibility to assess independently which solid phases could potentially form from a thermodynamic point of view. The saturation index (SI) with respect to a solid is given by log(IAP/K_{S0}), where the IAP is calculated from activities derived from the concentrations determined in the solution and K_{S0} denotes the solubility product of the respective solid. A positive saturation index implies oversaturation whereas a negative value reflects

under-saturation with regard to the respective solid. All calculated saturation indices refer to the solubility products of the solids as given in Table 1.

3. Results and Discussion

3.1 Solid phase Analyses

3.1.1 XRD and TGA

The powder X-ray diffraction (XRD) patterns in Figure 1 show that the M-S-H syntheses lead to low crystalline phases with the same broad humps at 19.7, 26.7, 35.0 and 59.9° 2θ as reported earlier for M-S-H [1, 8]. The broad humps at ~20° and 27° 2θ overlap with the signal from unreacted silica gel at ~ 21.5° 2θ for Mg/Si molar ratios ≤ 0.8 (silica gel is detected by ²⁹Si NMR, FT-IR and Raman spectroscopy, see below). The formation of brucite is observed for the high Mg/Si samples (Mg/Si = 1.3 and 1.7). The broad peaks in Figure 1 are very similar to the main reflections from talc at 9.5, 19.5, 28.6, 36.1 and 60.5° 2θ (PDF 01-083-1768) [24]. Jimthompsonite with main reflections at 10.0, 19.5, 23.2, 28.8, 32.6 and 35.1 (PDF 98-011-0925 [25]) fits less well with the diffractograms in Figure 1. Alternatively, the broad peaks may reflect the formation of serpentine such as antigorite (19.6, 24.6, and 35.1° 2θ [26], PDF 98-006-7465) and lizardite (12.1, 19.3, 24.5 and 35.9° 2θ [RUFF R060006]) as proposed by Walling et al. [27] or other phyllosilicates such as stevensite ((Ca_{0.5},Na)_{0.33}(Mg,Fe)₃Si₄O₁₀(OH)₂·nH₂O) or hectorite (Na_{0.3}(Mg,Li)₃Si₄O₁₀(OH)₂). Experimental findings and structural modelling from Roos et al. [10] are suggesting that the investigated M-S-H samples are nano-

crystalline and turbostratic Mg-Si phyllosilicates that cannot be straightforwardly be related to any known mineral.

The main peaks of talc related to the interlayer distance (9.4 Å) are observed at 9.5° (001) and 28.6° 2θ (003), according to PDF 01-083-1768 [24]. These peaks are very broad in the case of M-S-H and shifted to slightly lower angles than those reported for talc, which could be caused by a larger basal spacing for M-S-H than for talc or be an effect of M-S-H nanocrystallinity as suggested by [10]. In accordance with our observations, a large basal spacing has been observed at ambient temperatures for M-S-H (Mg/Si = 0.75), while synthesis at 180 °C and above resulted in M-S-H with a smaller interlayer distances and the formation of talc [11, 12, 14]. In addition, the shift to higher 2θ for this first peak indicates a smaller basal spacing for high Mg/Si than for low Mg/Si M-S-H.

199

200 Figure 1: XRD diffractograms for the synthetic M-S-H samples with varying Mg/Si ratios.

201 B: brucite; M: M-S-H; S: unreacted SiO₂.

202

203 The TGA data (Figure 2) show multi-step weight loss curves for the synthetic M-S-H,
 204 which is in good agreement with earlier reported TGA results for M-S-H [28]. The first
 205 weight loss at 30°C to 280°C is most likely related to loosely bound interlayer water,
 206 while the remaining weight losses between 280°C to 750°C result from hydroxyl groups
 207 bound to Mg²⁺ ions and present as silanol groups in the M-S-H between 750°C to
 208 840°C. A clear relation between bound water and the magnesium content can be
 209 observed.

Figure 2: Thermogravimetric analysis of the synthesised M-S-H samples with varying Mg/Si ratios. The asterisks indicate the dehydroxylation peak for brucite.

The TGA/DTG data reveal, in accordance with the XRD results, the presence of brucite in the samples with Mg/Si ratios ≥ 1.3 , as observed by the well-defined weight loss at 410°C related to the dehydroxylation of $\text{Mg}(\text{OH})_2$ to MgO and H_2O . This result indicates an upper limit of the Mg/Si molar ratio in M-S-H equilibrated for 1 year which is close to 1.3. The molar fraction of magnesium present in brucite was quantified to be 4% and 20% for the samples with Mg/Si ratios of 1.3 and 1.7, respectively.

Differential thermal analysis (DTA) of the M-S-H samples reveals a distinct exothermic transition around 840 - 860 °C, which is attributed to the decomposition of amorphous M-S-H and the recrystallization to SiO₂ and enstatite (MgSiO₃) [11, 12] or SiO₂ and forsterite (Mg₂SiO₄) for high Mg/Si ratios [29]. The dehydroxylation of the phyllosilicate sheets in talc (Mg₃Si₄O₁₀(OH)₂) and the transformation to SiO₂ and enstatite occurs at slightly higher temperatures of 850 to 950 °C [11, 12]. The lower dehydroxylation temperature of M-S-H compared to talc is consistent with a less crystalline structure [11, 12].

3.1.2 FT-IR and Raman spectroscopy

In accordance with the results from XRD and TGA analyses, the FT-IR spectra (Figure 3) reveal the presence of brucite by the sharp band at 3692 cm⁻¹ [30] in the samples with Mg/Si ratios of 1.3 and 1.7. Additionally, the bands at 800, 1090 (shoulder) and 1190 cm⁻¹ (shoulder) for the samples with Mg/Si molar ratios ≤ 0.8 are assigned to unreacted silica gel [31]. Furthermore, very weak bands from CO₃²⁻ ions are observed in the range 1400 - 1500 cm⁻¹ and at 875 cm⁻¹ (this is most pronounced for the samples containing free brucite) [32, 33]. Generally, the IR spectra of the samples show bands related to M-S-H between 800–1200 cm⁻¹, originating from asymmetric and symmetric Si-O stretching vibrations, and a band at around 665 cm⁻¹, corresponding to Si-O-Si bending vibrations [33]. In all samples a band with increasing intensity for increasing Mg/Si ratios is observed around 1635 cm⁻¹ which is attributed to H-O-H bending vibrations of molecular bound H₂O. There is a small shift to lower wavenumbers with increasing Mg/Si ratios for the main band due to Si-O vibrations of the Q³ tetrahedra at

244 950 - 1100 cm^{-1} . The intensity of the 870-920 cm^{-1} band, related to Si-O vibrations of Q^2
245 tetrahedra, increases with increasing Mg/Si ratio. Both observations point towards a
246 stepwise depolymerisation of the silicate network with increasing Mg/Si ratio. A
247 systematic decrease in intensity of the band related to Si-O-Si bending at $\sim 665 \text{ cm}^{-1}$ is
248 observed in the order Mg/Si: 1.0 > 0.8 and 1.3 > 1.7 and 0.6 > 0.4, which is most likely
249 attributed to a simple dilution effect of M-S-H caused by the presence of brucite and
250 silica. The band at 3678 cm^{-1} (shoulder for samples with Mg/Si ratio of 1.3 and 1.7; see
251 inset in Figure 3) is assigned to OH stretching of M-S-H.

252 The band at 3678 cm^{-1} and the main bands from Si-O stretching and Si-O-Si bending
253 (M-S-H 0.8: 1005 and 662 cm^{-1} , respectively) are in excellent agreement with the
254 vibrational modes observed for the mineral talc (3677, 1018 and 670 cm^{-1} [34]),
255 indicating a structural similarity of M-S-H and talc. However, these bands could be also
256 indicative for a sepiolite-like structure, as it has been proposed by Gunnarsson et al.
257 [35], or at higher Mg/Si also for serpentine like antigorite (3700, 990 and 620 cm^{-1} [36]).

258

Figure 3: FT-IR spectra of the synthetic M-S-H samples with varying Mg/Si ratios. The spectra were scaled to ease comparison. The dotted lines indicate the infrared bands for the mineral talc.

In accordance with the XRD and FT-IR results, the Raman spectra (Figure 4) of the M-S-H samples with $\text{Mg/Si} \geq 1.3$ show bands characteristic for brucite at 270, 436 and 3651 cm^{-1} (high wavenumber region not shown) [37]. Furthermore, samples with $\text{Mg/Si} \leq 0.6$ show Raman bands at 500 cm^{-1} and a broad band from 900 to 1550 cm^{-1} resulting from unreacted silica. Seven major bands, visible in all investigated samples and located at 175, 220, 361, 439, 668, 882 and 3686 cm^{-1} , are assigned to

270 M-S-H. These bands are all in reasonable agreement with Raman spectra of the mineral
271 talc (197, 232, 366, 435, 456, 471, 679, 795 and 3675 cm^{-1} [34]) at lower Mg/Si ratios or
272 minerals from the serpentine group (chrysotile, antigorite or lizardite) [38] and the
273 smectite-class (hectorite) [39]. The position of the typical bands of antigorite (230, 375,
274 520, 683, 795 and 1044 cm^{-1} [38]) show a reasonably good agreement with high-Mg/Si
275 M-S-H. However, due to the broad Raman bands of poorly ordered M-S-H the bands
276 could also be related to chrysotile and lizardite [38] as proposed by Walling et al. [27].
277 The peaks for M-S-H 0.4 are broader and at slightly higher wavenumbers, which could
278 be related to a poorer ordering and possibly to a different local ordering of the M-S-H. In
279 general, the Raman peaks of M-S-H show a distinct redshift, i.e. they are shifted to
280 lower wavenumbers compared to the crystalline talc or antigorite peaks. Such a redshift
281 could be explained by small particle sizes in the nm range compared to bulk crystalline
282 material as detailed in [16] for SiO_2 nanoparticles. The Raman spectra indicate that two
283 different M-S-H structures are present in M-S-H, a low- and a high-Mg/Si M-S-H, both
284 with a phyllosilicate-like structure.

Figure 4: Raman spectra of the synthetic M-S-H samples with varying Mg/Si ratios and for comparison spectra of talc and antigorite. B: brucite; M: M-S-H; S: unreacted SiO₂.

3.1.3 NMR spectroscopy

The ²⁹Si MAS NMR spectra of the M-S-H samples (Figure 5) contain resonances in the range -78 ppm to -98 ppm, which are assigned to the M-S-H phase. In addition, two broadened peaks at roughly -101 ppm and -111 ppm are observed for the M-S-H 0.4 and M-S-H 0.6 samples, which reflect the presence of unreacted silica in the form of silica surface sites, (SiO)₃Si^{*}-OH, and fully condensed (SiO)₄Si^{*} sites, respectively, following earlier ²⁹Si MAS and CP/MAS NMR studies of silica gels [40]. This assignment is supported by ²⁹Si{¹H} CP/MAS NMR spectra of the M-S-H 0.4 sample (Figure 6),

297 where the peak at -102 ppm is clearly observed whereas the -111 ppm resonance is
298 absent. A small amount of unreacted silica is also observed for the M-S-H 0.8 sample,
299 which accounts for 4.7 % of the total ^{29}Si NMR intensity. This indicates that the lower
300 Mg/Si limit in M-S-H is ~ 0.8 , as also observed by the IR spectra (Figure 3). The narrow
301 resonance at -85.4 ppm originates from a Q^2 site with a chemical shift close to the value
302 for a similar Q^2 site in enstatite (MgSiO_3 , $\delta(^{29}\text{Si}) = -83$ ppm [41]). The low-intensity peak
303 at -78 ppm is observed at 7 ppm to higher frequency compared to the Q^2 resonance,
304 which is a characteristic shift for a lowering in the degree of silicate polymerization [42],
305 and thus, this peak is ascribed to a Q^1 site. Three overlapping resonances at lower
306 frequency are also observed, with chemical shifts of -92.4 ppm,
307 -94.6 ppm, and -96.7 ppm, which are assigned to three different Q^3 sites. These
308 chemical shifts are similar to the value, $\delta(^{29}\text{Si}) = -97.0$ ppm, reported for crystalline talc
309 [43] and the value of -93.1 ppm reported for antigorite [44], indicating the presence of a
310 silicate sheet structure. The observed broad Q^3 signal could be explained by structural
311 deformations as discussed in [10]. Alternatively, the Q^3 sites may reflect branching
312 silicate chain sites, as observed in xonotlite (-97.8 ppm [42]) as well as 9Å- and 11Å-
313 tobermorites (-96.4 to -97.8 ppm [45]). The three Q^3 sites contain 63 – 70% of the total
314 intensity for the Mg/Si = 0.4 – 0.8 samples, when the contribution from the silica gel is
315 disregarded, whereas their intensity decrease from 55% to 40% for the Mg/Si = 1.0 – 1.7
316 M-S-H phases. This observation strongly suggests that silicate sheets are a principal
317 constituent of the M-S-H structures. $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra of the M-S-H 1.0
318 sample (Figure 6) show that all resonances associated with the M-S-H phase originate
319 from Si sites with hydrogen in their near vicinity (*i.e.*, within the second or third

320 coordination spheres). Comparison of the spectra acquired with different CP contact
321 times (τ_{CP}) reveal a stronger $^1H - ^{29}Si$ CP intensity enhancement for the Q^1 and Q^2 sites
322 at low CP contact times relative to the Q^3 sites, for which the largest CP transfer
323 appears at longer contact time ($\tau_{CP} \geq 5.0$ ms). These observations strongly suggest that
324 the Q^1 and Q^2 sites include hydroxyl groups, $Si-O-Si^*-OH$ and $(Si-O)_2-Si^*-OH$ sites,
325 respectively, whereas 1H is present in further distant coordination spheres for the
326 silicons in the Q^3 sheets, e.g., hydroxyl groups bonded to Mg^{2+} ions or interlayer water
327 molecules. The presence of hydroxyl groups bonded to Mg is also found in the
328 structures for talc, antigorite and other phyllosilicates.

329 The single-pulse ^{29}Si MAS NMR spectra (Figure 5) have been deconvolved, employing
330 resonances for the different ^{29}Si sites mentioned above, as illustrated for the spectrum of
331 the M-S-H 0.6 sample in Figure 7. The relative intensities from the deconvolutions are
332 listed in Table 2 along with the calculated Q^3/Q^2 ratios for the M-S-H phases. At
333 $Mg/Si \leq 0.8$ a Q^3/Q^2 ratio of ≈ 2 (Table 2) is observed. This ratio decreases with
334 increasing Mg/Si content. Talc and antigorite exhibit sheet structures, corresponding to
335 $Q^3/Q^2 \gg 1$, whereas a triple-chains structure of SiO_4 tetrahedra, such as found in
336 jimthompsonite, would have a ratio $Q^3/Q^2 = 2$ at infinite chain length. Smaller values for
337 Q^3/Q^2 may reflect a conversion of the triple chains into double chains, where some of
338 the Si-O-Si bonds of the branching tetrahedra are broken. For example, a double-chain
339 structure where the Si-O-Si bond in every second branching site is broken will have the
340 ratio $Q^3/Q^2 = 0.50$, as found in the xonotlite ($Ca_6Si_6O_{17}(OH)_2$). Alternatively very small
341 coherent regions of sheet silicates could result in a high fraction of Q^2 units at the edge
342 of the silica sheets and thus, $Q^3/Q^2 = 2$ could be obtained as recently suggested by

343 Roosz *et al.* [10]. It is apparent from both the XRD analysis and the ^{29}Si NMR spectra
344 that the M-S-H samples are not highly ordered and the clear observation of a significant
345 fraction of Q^1 sites (Table 2) reflect a disordered structure with several vacancies or
346 broken chains in the polymerized silicate network. An overall layer structure, where the
347 silicate sheets are connected by layers of octahedrally coordinated Mg^{2+} ions and similar
348 to the structure of talc, antigorite or jimthompsonite, will also imply that the Q^3 sites are
349 further distant from hydroxyl groups than the Q^2 and Q^1 sites, associated with the
350 defects mentioned above. Thus, the $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra support this model
351 since optimum CP transfer is observed for short CP contact time for the Q^1 and Q^2 sites
352 and longer times for the Q^3 sites, reflecting these are further distant from the hydroxyl
353 groups. In talc, antigorite and jimpthompsonite all hydroxyl groups are bonded to Mg^{2+}
354 ions which would result in long optimum $^1\text{H} - ^{29}\text{Si}$ CP contact times, considering that the
355 $^1\text{H} - ^{29}\text{Si}$ dipolar interaction is inversely proportional to the cube of the internuclear
356 distance.

357

358 Figure 5. ^{29}Si MAS NMR spectra (9.4 T, $\nu_R = 4.5$ kHz) of the synthesized M-S-H
 359 samples with Mg/Si ratios ranging from 0.4 to 1.7.

360

Figure 6. $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra (9.4 T, $\nu_R = 4.0$ kHz) of the M-S-H 0.4 and M-S-H 1.0 samples acquired with three different CP contact times (τ_{CP}). The spectra for the two samples are shown on identical vertical scale.

Table 2: ^{29}Si NMR chemical shifts (ppm) and relative intensities (%) from deconvolution of the ^{29}Si MAS NMR spectra for the M-S-H phases.

initial Mg/Si	²⁹ Si chemical shifts - ppm (relative peak intensities - %)							Q ³ /Q ^{2(*)}
	M-S-H					unreacted SiO ₂		
	Q ¹	Q ²	Q ^{3a}	Q ^{3b}	Q ^{3c}	Q ³	Q ⁴	
0.4	-78.3 (1.3)	-85.4 (21.6)	-92.4 (23.9)	-94.6 (8.1)	-96.7 (7.1)	-100.9 (7.8)	-110.7 (30.1)	1.78
0.6	-78.3 (3.3)	-85.4 (22.6)	-92.4 (25.5)	-94.6 (19.2)	-96.7 (10.0)	-100.9 (4.6)	-110.7 (14.7)	2.39
0.8	-78.3 (3.2)	-85.4 (25.9)	-92.4 (29.3)	-94.6 (14.8)	-96.7 (22.1)	-100.9 (1.1)	-110.7 (3.6)	2.54
1.0	-78.3 (4.5)	-85.4 (40.8)	-92.4 (15.2)	-94.6 (25.7)	-96.7 (13.8)	-	-	1.34
1.3	-78.3 (12.5)	-85.4 (44.2)	-92.4 (22.6)	-94.6 (7.8)	-96.7 (13.0)	-	-	0.98
1.7	-78.3 (11.7)	-85.4 (48.1)	-92.4 (18.5)	-94.6 (10.9)	-96.7 (10.7)	-	-	0.84

(*) Calculated Q^3/Q^2 ratio, $I(Q^3)/I(Q^2)$ for the M-S-H where $I(Q^3) = I(Q^{3a}) + I(Q^{3b}) + I(Q^{3c})$.

368
 369 Figure 7. (a) ^{29}Si MAS NMR spectrum (9.4 T, $\nu_R = 4.5$ kHz) of the M-S-H 0.6 and (b) the
 370 optimum deconvolution, employing the peaks shown in part (c), which exhibit the
 371 intensities listed in Table 2.

372
 373 Figure 8. Spin-echo ^{25}Mg MAS NMR spectra (14.1 T, $\nu_R = 12.0$ kHz) of the M-S-H
 374 samples shown on identical intensity scales.

Figure 9. Spin-echo ^{25}Mg MAS NMR spectra (14.1 T, $\nu_R = 12.0$ kHz) of (a) M-S-H 1.7, (b) $\text{Mg}(\text{OH})_2$ and (d) a mineral sample of talc. Subtraction of the $\text{Mg}(\text{OH})_2$ spectrum from the spectrum of M-S-H 1.7, using a scaling factor of 1/5 for $\text{Mg}(\text{OH})_2$, as used in part (b), gives the difference spectrum shown in part (c).

Spin-echo ^{25}Mg MAS NMR spectra of the M-S-H samples, obtained with ^1H decoupling during both the evolution and detection periods (Figure 8), all include a broadened

asymmetric centerband resonance ranging from roughly 0 ppm to -250 ppm, which intensity increases with increasing Mg/Si ratio. Indications of distinct peaks at -5 ppm and -52 ppm are observed in the lineshapes for the M-S-H 1.3 and 1.7 samples. The XRD analysis showed that these samples contain a small amount of $\text{Mg}(\text{OH})_2$ and thus, the ^{25}Mg MAS NMR spectra of M-S-H 1.7 and a pure sample of $\text{Mg}(\text{OH})_2$ are compared in Figure 9. The ^{25}Mg MAS NMR spectrum of $\text{Mg}(\text{OH})_2$ shows the characteristic features of second-order quadrupolar lineshape for a single ^{25}Mg site. Simulation of this lineshape results in the isotropic chemical shift, $\delta_{\text{iso}}(^{25}\text{Mg}) = 10.0$ ppm, and the quadrupole coupling parameters, $C_Q = 3.08$ MHz and $\eta_Q = 0.0$, in good agreement with earlier reported values [46] and the crystal structure for brucite [47]. Moreover, the two singularities of the quadrupolar lineshape match the peaks observed in the ^{25}Mg MAS NMR spectra of M-S-H 1.3 and M-S-H 1.7. TGA indicated that the M-S-H 1.7 sample contains 20 wt.% $\text{Mg}(\text{OH})_2$ and subtraction of the experimental ^{25}Mg NMR spectrum of $\text{Mg}(\text{OH})_2$ from the spectrum of M-S-H 1.7, using a scaling factor corresponding to a $\text{Mg}(\text{OH})_2$ content of 20 wt%, gives the difference spectrum shown in Figure 9c. The asymmetric lineshape in this spectrum resembles the spectra observed for the M-S-H samples with lower Mg/Si ratios, thereby indicating that the environments of the Mg^{2+} ions in the different M-S-H samples are very similar and independent of the Mg/Si ratio. Moreover, comparison of ^{25}Mg MAS NMR spectra, acquired with and without ^1H decoupling, shows a small line-narrowing effect of ^1H decoupling, suggesting the presence of ^1H atoms in the near vicinity, either as Mg-OH or solid water very close to the Mg layers. Figure 9 also includes a spectrum of a pure mineral sample of talc, which contains a centerband resonance with a much smaller width than those observed for the

406 M-S-H samples and $\text{Mg}(\text{OH})_2$. The asymmetric form of the centerband observed for the
 407 M-S-H samples is typical for a distribution in quadrupolar coupling parameters [48, 49],
 408 reflecting variation in the local environments for the Mg^{2+} sites. This agrees well with the
 409 disordered nature of the M-S-H phases observed by ^{29}Si NMR.

410

411

412 Figure 10. ^1H MAS NMR spectra (14.1 T, $\nu_R = 40.0$ kHz) of three selected M-S-H
 413 samples. The asterisks indicate resonances from impurity phases, i.e., the CH_2 and CH_3
 414 groups of ethanol at 3.8 and 1.3 ppm, respectively.

415 ^1H MAS NMR spectra, recorded with a high spinning speed ($\nu_R = 40.0$ kHz), have be
 416 obtained for all M-S-H samples and allow distinction of the resonances from water

molecules in the structure and hydroxyl groups. Selected spectra are shown in Figure 10, where the broad resonance at 4.8 – 5.1 ppm can be assigned to ^1H in solid water. A second broad resonance is observed in the range 0 – 1 ppm with a lineshape that indicate the presence of two overlapping resonances. These resonances originate from hydroxyl groups, potentially two different types of Mg-OH sites, considering the ^1H chemical shifts of 0.3 ppm and 0.5 ppm observed in similar high-speed ^1H MAS NMR experiments for $\text{Mg}(\text{OH})_2$ and the talc sample, respectively, in accordance with literature values for these samples [50, 51]. In addition, two narrow resonances at 3.8 and 1.8 ppm are present in all spectra (Figure 10). These peaks are ascribed to the CH_2 and CH_3 groups of ethanol or ethoxy groups bonded to the M-S-H structure, and reflecting that the samples have been washed with ethanol prior to drying. The ^1H MAS NMR spectra have been deconvolved using resonances for water, the hydroxyl groups, and ^1H in ethanol, resulting in the relative ^1H NMR intensities listed in Table 3. The molar $\text{H}_2\text{O}/\text{OH}$ ratios, calculated from these intensities, decrease with increasing Mg/Si ratio. We note that these ratios are slightly underestimated since the ^{29}Si NMR and XRD analyses have shown that the M-S-H 0.4 and 0.6 samples contain a small fraction of unreacted silica gel, including $(\text{Si-O})_3\text{Si-OH}$ sites (Table 2), and that $\text{Mg}(\text{OH})_2$ is present as an impurity phase in the M-S-H 1.3 and 1.7 samples. The hydroxyl groups from these additional phases contribute with intensity to the resonance at 0.5 – 0.7 ppm, resulting in a lowering of the molar $\text{H}_2\text{O}/\text{OH}$ ratio for the M-S-H phases.

Table 3. ^1H chemical shifts and relative intensities of the resonances from water and hydroxyl groups, obtained from ^1H MAS NMR spectra of the M-S-H samples, along with the total bound water and molar total water content per silica in M-S-H from TGA.

Mg/Si	$\delta(\text{H}_2\text{O})$ (ppm)	$\delta(\text{OH})$ (ppm)	$I(\text{H}_2\text{O})^{\text{a}}$	$I(\text{OH})^{\text{a}}$	Molar $\text{H}_2\text{O}/\text{OH}$	TGA weight loss (wt.%) ^b	Weight loss/Si ^c	H_2O /Si ^d
0.4	4.75	0.57	79.9	20.1	1.99	16.2	0.82	0.66
0.6	4.82	0.60	77.7	22.3	1.74	19.7	1.15	0.89
0.8	4.85	0.72	74.2	25.8	1.44	21.9	1.44	1.07
1.0	4.82	0.70	69.0	31.0	1.11	23.1	1.67	1.15
1.3	5.0	0.74	68.0	32.0	1.06	24.8	2.08	1.45
1.7	5.10	0.74	62.6	37.4	0.84	24.6	2.42	1.69

^a Relative intensities from deconvolution of the ^1H MAS NMR spectra, excluding the contribution from the impurity resonances.

^b TGA weight loss from 40 to 950°C including loosely bound H_2O and water loss from dehydroxylation of hydroxyl groups.

^c Weight loss per Si in M-S-H corrected for the presence of brucite (TGA) and unreacted SiO_2 (NMR).

^d $\text{H}_2\text{O}/\text{Si} = \text{weight loss}/\text{Si} \cdot I(\text{H}_2\text{O})/100$;

3.1.4 M-S-H composition

Based on the TGA and the deconvolution of the ^{29}Si NMR spectra, the solid Mg/Si molar ratios as well as the total content of hydroxyl groups together with the bound interlayer water of the precipitated M-S-H can be calculated. The values for the Mg/Si molar ratios range from 0.7 to 1.5 (see Table 4 for details). Two obvious trends are noticeable with increasing Mg/Si ratio in synthetic M-S-H:

a) an increase in the interlayer water which could possibly be related to the depolymerisation of the silicate network which makes it more hydrophilic and

b) an increase in the number of hydroxyl groups which are most likely bound within the octahedral MgO sheet and to lesser extend in form of silanol groups.

By comparison of the proposed stoichiometry of the different M-S-H samples (Table 4) with the Q^3/Q^2 silicon environments obtained by NMR (Table 2), the synthesised samples can be divided in three different sets: a) The samples with an initial Mg/Si molar ratio ≤ 0.8 , b) the M-S-H with an initial Mg/Si molar ratio of 1, and c) the M-S-H samples with an initial Mg/Si ratio ≥ 1.3 . The first set is characterised by high Q^3/Q^2 ratios ranging from 1.78 to 2.54, similar Mg/Si ratios as well as similar contents of hydroxyl groups and interlayer water. The last set with an initial Mg/Si ratio ≥ 1.3 is comprised of M-S-H with low Q^3/Q^2 ratios, i.e. < 1.0 , high Mg/Si ratios and high contents of hydroxyl groups and loosely bound water. The data for these solid phase would be consistent with (i) the formation of a M-S-H with a variable composition in the range, $M_{0.64}SH_{0.78}$ to $M_{1.4}SH_{2.4}$, or (ii) the presence of two immiscible solids $M_{0.64}SH_{0.78}$ and $M_{1.42}SH_{2.42}$ where both are present at Mg/Si = 1.

Table 4: Summary of the experimentally determined Mg/Si molar ratios, content of hydroxyl groups and interlayer water of the synthesised M-S-H.

Initial Mg/Si	M-S-H Mg/Si	H ₂ O/Si ^b	Si-OH/Si ^c	Mg-OH/Si ^d	composition	
0.4	0.64	0.66	0.24	0.01	$Mg_{0.64}O_{0.52}(OH)_{0.25}SiO_2 \cdot (H_2O)_{0.66}$	$M_{0.64}SH_{0.78}$
0.6	0.74	0.89	0.29	0.18	$Mg_{0.74}O_{0.51}(OH)_{0.47}SiO_2 \cdot (H_2O)_{0.89}$	$M_{0.74}SH_{1.13}$

0.8	0.84	1.07	0.32	0.41	$\text{Mg}_{0.84}\text{O}_{0.47}(\text{OH})_{0.73}\text{SiO}_2 \cdot (\text{H}_2\text{O})_{1.07}$	$\text{M}_{0.84}\text{SH}_{1.44}$
1.0	1.00	1.15	0.50	0.54	$\text{MgO}_{0.48}(\text{OH})_{1.04}\text{SiO}_2 \cdot (\text{H}_2\text{O})_{1.15}$	$\text{MSH}_{1.67}$
1.3	1.25	1.45	0.69	0.57	$\text{Mg}_{1.25}\text{O}_{0.58}(\text{OH})_{1.26}\text{SiO}_2 \cdot (\text{H}_2\text{O})_{1.45}$	$\text{M}_{1.25}\text{SH}_{2.08}$
1.7	1.42	1.69	0.72	0.74	$\text{Mg}_{1.42}\text{O}_{0.52}(\text{OH})_{1.46}\text{SiO}_2 \cdot (\text{H}_2\text{O})_{1.69}$	$\text{M}_{1.42}\text{SH}_{2.42}$

^a Calculated from the initial Mg/Si, the amount of brucite (TGA) and unreacted SiO₂ as given in Table 2.

^b H₂O/Si = weight loss/Si · I(H₂O)/100; from Table

^c Silanol groups: Si-OH/Si = 2(weight loss/Si · I(OH)/100 · (2I(Q¹)+I(Q²))/100);

^d Magnesium hydroxide Mg-OH/Si = 2(weight loss/Si - H₂O/Si - ½Si-OH/Si)

3.2 Solution Analyses

3.2.1 Dissolved Concentrations and Saturation Indices

The composition of the solutions in equilibrium with the synthesized M-S-H phases is given in Table 5. At low Mg/Si ratios where amorphous SiO₂ persisted even after 1 year, the silica concentrations remained at 1-2 mM and pH values near 9 were observed. At Mg/Si >1 the measured Si and Mg concentrations decreased while the pH values increased up to 10.5 at Mg/Si = 1.7 (Table 5). A similar strong effect of the Mg/Si ratio on the pH values has been reported previously [52, 53].

Thermodynamic modelling based on the measured concentrations revealed saturation indices for amorphous SiO₂ near 0 for low Mg/Si ratios (see Table 5). This indicates that the solutions were near saturation and consequently supporting the experimental observation of unreacted silica in the precipitated samples. At high Mg/Si ratio, the pore solutions were in all cases clearly undersaturated with regard to amorphous SiO₂,

consistent with the absence of amorphous SiO₂. At Mg/Si ≥ 1.3, the solutions were near saturation with respect to brucite, which is in accordance with the experimental results.

Table 5: Measured dissolved concentrations in the solutions in equilibrium with the synthesized M-S-H samples and calculated saturation indices at 20 °C.

Mg/Si total	Mg/Si Solid	Si mM	Mg mM	OH ⁻ mM	pH	<i>saturation indices</i>		
						SiO ₂ ^a	brucite	talca
0.4	0.64	0.81	0.14	0.003	8.6	-0.3	-4.1	5.6
0.6	0.74	0.67	0.13	0.002	8.5	-0.4	-4.3	4.9
0.8	0.84	1.51	0.18	0.002	8.6	-0.1	-4.1	6.8
1.0	1.00	0.25	0.17	0.005	8.9	-0.9	-3.4	5.5
1.3	1.25	0.009	0.087	0.110	10.2	-2.8	-0.8	5.0
1.7	1.42	0.011	0.055	0.190	10.5	-2.9	-0.3	5.5

^a Amorphous SiO₂.

3.2.2 Derivation of Solubility Products for M-S-H

If the composition of the solid phase is known and equilibrium between aqueous and solid phase is attained, solubility products can be obtained from measured aqueous concentrations; e.g. for an M-S-H with a talc like composition $K_{S0} (M_3S_4H_5) = \{Mg^{2+}\}^3 \cdot \{SiO_2^0\}^3 \cdot \{OH\}^6 \cdot \{H_2O^+\}^2 / \{M_3S_4H_5(solid)\}$, where {} indicates activity. The solubility product can be shortened to $K_{S0} (M_3S_4H_5) = \{Mg^{2+}\}^3 \cdot \{SiO_2^0\}^4 \cdot \{OH\}^6 \cdot \{H_2O^+\}^2$ as the activity of a pure phase equals to 1 by definition. As in the present study equilibrium was approached from oversaturation only, equilibrium might not yet have been reached after 1 year of experiments and the derived “solubility products” should be considered as tentative only.

In the case of M-S-H, the definition of the solid phase composition is complicated as the experimental findings show that the Mg/Si ratio of the synthesised magnesium silicate hydrates varies from approximately 0.7 to 1.5. The solubility of such low-crystalline solids with variable composition can either be described

(i) by defining for each possible composition a separate solubility product, which can lead to a large number of different solubility products (see e.g. [54]), limits the possible solid phase and liquid phase composition to the M-S-H compositions actually synthesized and results in a stepwise description of the aqueous concentrations as shown by the dotted lines in Figure 11b or

(ii) by a solid solution approach, as has been done successfully for calcium silicate hydrates (C-S-H) [55], which also have a highly variable composition. Instead of defining a solubility product for each of the solid phase compositions, only the solubility products of end-members solids (e.g. a high and a low Mg/Si ratio M-S-H) are defined, while the solubility of any intermediate M-S-H composition can be derived from these two end-members. For details on the definition of solid solutions and its applications, see for example refs. [55-57]. As our knowledge about the possible structure of M-S-H is very limited, the most simple solid solution approach was chosen to describe M-S-H solubility: an ideal solid solution between magnesium-silicate-hydrates with a high and low Mg/Si ratio as shown in Figure 11a, b. However, more appropriate solid solution models might be developed in the future if we will know more about M-S-H structures.

Although the structure of M-S-H is not known, the observation of mainly Q³ units by ²⁹Si NMR, the presence of ~20% bound water, associated most likely with a magnesium hydroxide layer, and the variation of the Mg/Si ratio from 0.7 to 1.5 indicate a structure similar to that of talc (3MgO·4SiO₂·H₂O) with additional H₂O and Mg(OH)₂ in the interlayer or to the presence of talc- and serpentine(3MgO·2SiO₂·2H₂O)-like precursors. Consequently, these two compositions were used as endmember compositions for the solid solution.

Table 6: Compilation of solubility products at 20°C of the two solid solution endmembers (M₃S₄H₅ and M₃S₂H₅) for the samples equilibrated for 1 year.

Mg/Si total	Mg/Si Solid	<i>log K_{so} at 20 °C</i>	
		M ₃ S ₄ H ₅ ^a	M ₃ S ₂ H ₅ ^b
0.4	0.64	-57.7	-51.5
0.6	0.74	-58.4	-52.1
0.8	0.84	-56.5	-50.8
1.0	1.00	-57.8	-50.5
1.3	1.25	-58.3	-47.1
1.7	1.42	-57.7	-46.5

solubility products (±0.8) refer to:

The measured aqueous concentrations given in Table 5 were used to calculate a solubility product for both end-member compositions for each of the experiments as shown in Table 6. If in fact a solid solution can be used to describe M-S-H solubility, the solubility products calculated for the samples which contain M-S-H only, should vary with the Mg/Si ratio, while the solubility products in mixtures where both silica fume plus

M-S-H or M-S-H plus brucite are present, should be constant and relate directly to the solubility of the end-members. Thus, for $M_3S_4H_5 \Leftrightarrow 3Mg^{2+} + 4SiO_2^0 + 6OH^- + 2H_2O$ a mean $\log(K_{so})$ of -57.6 ± 1 was obtained using the data for the Mg/Si 0.4 to 0.8 samples, where the calculated solubility products show no significant trends as the presence of silica limits both the aqueous silicon concentration and the theoretical Mg/Si ratio in the M-S-H. The calculated $\log(K_{so})$ values for $M_3S_2H_5 \Leftrightarrow 3Mg^{2+} + 2SiO_2^0 + 6OH^- + 2H_2O$, where the composition of high Mg/Si M-S-H is limited by the presence of brucite, is around -47 for Mg/Si = 1.3 and 1.7 but clearly lower at Mg/Si <1. Such apparent decrease is consistent with the expected stabilisation due to the formation of a solid solution. Based on the limited structural information available, a tentative $\log(K_{so})$ of -47.1 ± 2 was calculated for a high-Mg/Si M-S-H: $M_3S_2H_5 \Leftrightarrow 3Mg^{2+} + 2SiO_2^0 + 6OH^- + 2H_2O$ at 20 °C, as summarised in Table 7.

Table 7: Tentative thermodynamic properties for M-S-H at 20 °C:

		$\log K_{so}$	$\Delta_r G^\circ$	V° ^c	Density
		$\pm \sigma$	[kJ/mol]	[cm ³ /mol]	[g/cm ³]
$3MgO \cdot 4SiO_2 \cdot 5H_2O^a$	$M_3S_4H_5$	-57.6 ± 1	-6436.9	189.8	2.38
$3MgO \cdot 2SiO_2 \cdot 5H_2O^b$	$M_3S_2H_5$	-47.1 ± 2	-4709.5	148.6	2.23

^a $3MgO \cdot 4SiO_2 \cdot 5H_2O \Leftrightarrow 3Mg^{2+} + 4SiO_2^0 + 6OH^- + 2H_2O$, ^b $3MgO \cdot 2SiO_2 \cdot 5H_2O \Leftrightarrow 3Mg^{2+} + 2SiO_2^0 + 6OH^- + 2H_2O$. Molar volume calculated based on the volume of talc or chrysotile and the volume of water bound in brucite (13.38 cm³/mol H₂O).

Comparison of the calculated solubility product for low-Mg/Si M-S-H, $M_3S_4H_5$, with crystalline talc shows that talc is more stable than M-S-H, as indicated by the lower solubility product of talc of -63.3 at 20 °C [21] (or comparable to talc depending on the dataset used -54.9 [22], -56.5. [23] at 20 °C). Similarly, the solubility of the high-Mg/Si M-S-H is 3 - 5 log units higher than the solubility of crystalline antigorite ($M_{2.8}S_2H_{1.8}$, -51.3 [21]) or chrysotile ($M_3S_2H_2$, -53.2 [21]; or comparable depending on the dataset used -48.8 [22] at 20 °C. The comparability of the (tentative) solubility products derived for M-S-H with the solubility of crystalline talc or antigorite underlies that we are near a (meta)stable equilibrium after 1 year.

The solubility products of $M_3S_4H_5$ and $M_3S_2H_5$ at 20 °C, obtained in Table 7, were used to calculate the dissolved Mg and Si concentrations and the Mg/Si ratio in the M-S-H as a function of pH (Figure 11). After 1 year, the low-Mg/Si (0.4, 0.6 and 0.8) M-S-H samples showed all a pH value of ~8.3 and very similar concentrations, consistent with the presence of two solids, M-S-H and amorphous SiO_2 . However, in the calculations the measured Mg concentrations are somewhat underestimated. At higher Mg/Si, where only M-S-H is present, the calculations indicate a decrease of silica concentrations with increasing pH which agrees with the measurements as shown in Figure 11. Although brucite has been observed experimentally in the high Mg/Si experiments, the measured samples were clearly undersaturated with respect to brucite. The dissolution of brucite seems to be kinetically hindered in these samples and equilibrium is not yet reached after year.

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595 Figure 11: Mg/Si ratio in M-S-H (triangles), Si (squares) and Mg (circles) concentrations

596 a) as a function of the pH values and b) as a function of the Mg/Si ratio in the solid

597 phase. Dashed lines indicate the solubility of amorphous SiO₂ and brucite. For the598 calculations, i) a solid solution between M₃S₄H₅ and M₃S₂H₅ (see Table 7) was assumed

599 (solid lines) and for comparison ii) single solids (dotted lines) with the composition as

600 determined in Table 4 and using the following solubility products at 20°C (M_{0.64}SH_{0.78} -

13.0; $M_{0.74}SH_{1.13}$ -14.4; $M_{0.84}SH_{1.14}$ -16.0; $MSH_{1.67}$ -18.0; $M_{1.25}SH_{2.08}$ -20.8; $M_{1.42}SH_{2.42}$ -
22.7; referring to Mg^{2+} , SiO_2^0 , OH^- and H_2O) have been used.

4. Conclusions

The present contribution shows that M-S-H prepared from MgO and silica fume is the main hydration product after one year of curing at 20°C. The Mg/Si ratio in synthetic M-S-H varies between 0.7 and 1.5, for lower ratios unreacted silica remained and for higher ratios brucite precipitated. Thermogravimetric analyses revealed a multistep weight loss for synthetic M-S-H. Up to 280°C, the sample loses its loosely bound molecular water followed by a stepwise dehydroxylation of Mg-OH and Si-OH. FT-IR as well as ^{29}Si NMR investigations showed a higher polymerization degree of the Si network in M-S-H compared to C-S-H, eliminating a single chain-like structure like in C-S-H. A sheet-like structure as in phyllosilicates or a double (triple) chain-like structure like in anthophyllite seems highly possible with stepwise depolymerisation for increasing Mg/Si ratios in M-S-H. Raman and XRD investigations support our hypothesis that the M-S-H structure could be related to talc at low Mg/Si and to serpentine at higher Mg/Si. Solubility products for M-S-H calculated on the basis of the aqueous concentrations were used to illustrate the changes observed in the measured concentrations.

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