



## Crystal structure of magnesium silicate hydrates (M-S-H): The relation with 2:1 Mg–Si phyllosilicates



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### ABSTRACT

Two magnesium silicate hydrates (M-S-H) with structural magnesium/silicon ratios of  $0.57 \pm 0.08$  and  $1.07 \pm 0.13$  were synthesized at room temperature, with one year of synthesis duration. Their structure was clarified by considering results from X-ray diffraction, TEM,  $^{29}\text{Si}$  MAS NMR spectroscopy, TGA, and EPMA. A modeling approach appropriate to defective minerals was used because usual XRD refinement techniques cannot be used in the case of turbostratic samples, where coherency between successive layers is lost. M-S-H with Mg/Si ratio of  $\sim 0.6$  appears to be structurally close to nanocrystalline turbostratic 2:1 Mg–Si phyllosilicates. The increase of the Mg/Si ratio from 0.6 to 1.2 occurs by increasing the occurrence of defects in the silicate plan. The layer-to-layer distance evolves from 9.46 Å to 14 Å under air-dried and ethylene glycol conditions, respectively. Crystallites have a mean size of 1.5 nm in the **ab** plane, and 2.4 nm along **c**<sup>\*</sup>.

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### 1. Introduction

The occurrence of magnesium silicate hydrates (M-S-H) has been mentioned in many environments: carbonate successions [1], contaminated soils [2], glass alteration [3], phyllosilicate synthesis [4–6], concrete formulations [7,8], and cement clay interactions [9–11]. In all these studies, M-S-H were described as low crystalline phases due to the low intensity and broad X-ray diffraction (XRD) signals. Characterizations of these poorly crystalline Mg-silicates suggest a 2:1 magnesium phyllosilicate-like structure with short range stacking order, and may be described as a talc-like structure [12]. The talc structure as described in these previous studies is in agreement with the characteristics of synthesized talc after short equilibration times [5]. In that case, the M-S-H particles display a low crystallinity and a small particle size [5].

In the framework of a radwaste disposal in a deep geological repository, the disposal facility will imply large amounts of concrete in close contact with the surrounding clayrock. In this context, low pH cementitious materials are considered, especially for sealing requirements, in order to minimize chemical reactions at the interfaces between cement materials and the clay surrounding rock formations

and/or engineered clay materials. The target is to reach a pH of the concrete pore solution (pH–10–11) more compatible with the clay materials or rock formation (pH–7–7.5). Recent studies [13–15] have proposed low-pH formulations based on ternary and quaternary mixes of Portland cement with supplementary cementitious materials (SCMs). The addition of SCMs induces pozzolanic reactions such as the precipitation of calcium silicate hydrates (C-S-H) with low Ca/Si (C/S) ratios.

However, if the hydration products are well characterized in Ordinary Portland Cement (OPC) and/or standard concrete formulations with constrained kinetic/thermodynamic models [16], the mineralogical control of elements in solution has to be discussed for low pH formulations, because of their higher aluminum and magnesium contents [17]. Considering in particular the hydration of MgO, that is mainly introduced by the blast furnace slag (BFS), if some hydrates are proposed to control the higher contents of aluminum and magnesium, like C-A-S-H, hydrotalcite, hydrogarnet or straeltingite [18], another product of reaction has been identified as a magnesium silicate hydrate (M-S-H) phase [7,19]. Zhang et al. [8] have also mentioned the precipitation of brucite ( $\text{Mg}(\text{OH})_2$ ) which reacted with the silica fume to produce such M-S-H. The calculated pH in equilibrium with this mineralogical assemblage is around 10.5 that satisfies the requirement of low pH condition.

Some authors have tried to explain the precipitation of such Mg-silicate hydrates according to Ca/Mg isomorphic substitution in the

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calcium silicate hydrates (C-S-H) [20,21]; however this uptake of magnesium by C-S-H by an exchange of calcium does not explain the presence of M-S-H [20,21].

Despite this abundance of evidences for M-S-H formation, their structure is not well known. The present study aims to define the nature of M-S-H (cement phase or phyllosilicate) and to determine their structure. Two low temperature syntheses of M-S-H with an Mg/Si ratio of 0.6 and of 1.2, close to the talc composition ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) and consistent to the Ca/Si of the C-S-H phases, have been studied. The structure of M-S-H was determined by combining electron probe micro-analysis (EPMA), TEM, NMR and powder X-ray diffraction. The XRD patterns were modeled according to the Drits and Tchoubar matrix approach [22]. They provided meaningful and accurate structural information, including structure defects, despite the weak modulation of the profiles. A full structural model is thus proposed for M-S-H.

## 2. Material and methods

### 2.1. Sample synthesis preparation

All samples used for this study were made by mixing magnesium oxide (MgO – Merck) and amorphous silica ( $\text{SiO}_2$  – Aerosil 200, Degussa). Ultrapure water (Milli-Q 18 M $\Omega$ ), heated to 100 °C for 1 h and cooled under a  $\text{N}_2$  flux for 2 h prior to its introduction in the glove-box, was used.

Samples of synthetic M-S-H were made by precipitation, in glove-box under nitrogen, at 22 °C. Two Mg/Si ratios (0.6 and 1.2) were tested. Thereafter, these samples are respectively labeled M-S-H 0.6 and M-S-H 1.2. The homogenized reactants were mixed with distilled and  $\text{CO}_2$ -free water at a water/solid ratio of 50. After the dissolution of the reagents, each sample was shaken in tightly closed PE-vessels for one year at 22 °C.

After centrifugation and filtration (0.22  $\mu\text{m}$  Millipore Millex-VV, PVDF), the samples were stored in closed containers under vacuum in the glove box until analysis. The alkalinity, pH, and redox potential (pE) of the solutions were determined and the concentrations of the major elements (Mg, Si) were quantified by inductively coupled plasma atomic emission spectrometry (ICP/AES). The composition of the synthetic solutions is given in Table 1.

The natural talc sample, used as a reference material, is from Luzenac deposit in the French Pyrenees. According to Martin et al. [23], its structural formula is  $[\text{Mg}_{0.978}\text{Fe}_{0.019}^{2+}\text{Mn}_{0.001}^{2+}\text{Fe}_{0.005}^{3+}\text{Al}_{0.007}]_{\Sigma 3} \cdot [\text{Si}_{3.984}\text{Fe}_{0.004}^{3+}\text{Al}_{0.007}]_{\Sigma 4}\text{O}_{10}(\text{OH})_{1.952}\text{F}_{0.048}$ .

### 2.2. Characterization of the solids

X-ray diffraction (XRD) analysis was done on randomly-oriented powders. The XRD patterns were recorded on a Bruker D8 Advance diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). XRD patterns were acquired in the 5 to 80  $^{\circ}2\theta$  range with a counting time of 10 s per step of 0.02  $^{\circ}2\theta$ . Calculated patterns were obtained using a software from Plançon [24], which is based on the numerical formalism developed by Drits and Tchoubar [22]. This modeling approach has been successfully applied to the study of various lamellar structures having a variety of layer defects (e.g., isomorphous substitutions, layer vacancies) and stacking faults (including well-defined and random stacking faults),

**Table 1**  
Chemical composition of solution in equilibrium with M-S-H samples.

	pH	Mg		Si
		mol · L <sup>-1</sup>		
M-S-H 0.6	9.1	$3 \cdot 10^{-4}$		$3.5 \cdot 10^{-3}$
M-S-H 1.2	10.6	$2.1 \cdot 10^{-4}$		$1.8 \cdot 10^{-5}$

including phyllosilicates [25], nanocrystalline phyllosilicates [26–28], nanocrystalline calcium silicate hydrates [29,30] and nanocrystalline layered double hydroxides [31]. 00l calculations were realized with the MLM2C software, developed by Plançon and Drits [32].

TEM 8-bit gray scale images (4008 × 2672 pixels) were acquired on a Philips CM20 microscope, operated at 200 kV which has a line resolution of 0.14 nm. Low magnification bright field images were recorded.

Thermo-gravimetric analyses were performed with a SDT Q600 TA Instruments using 20 mg of sample. The heating rate was 10 °C min<sup>-1</sup> and the temperature range was 25–1000 °C. The analyses were done using a 100 mL · min<sup>-1</sup> air flow. The deconvolution was realized using the Fityk on dTG spectra, in two individuals asymmetric Gaussians at 55 °C and 450 °C.

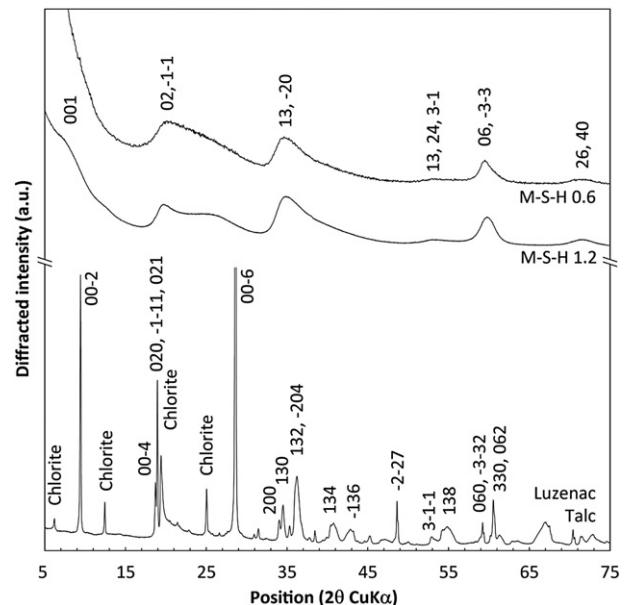
The <sup>29</sup>Si MAS NMR spectra were acquired using a Bruker Advance 400 MHz ( $B_0 = 7.0 \text{ T}$ ) at 79.4 MHz and were recorded at 12 kHz. <sup>29</sup>Si chemical shifts are given relative to tetramethylsilane (TMS) at 0 ppm. All data were acquired using a rotor-synchronized spin echo ( $\theta$ -s- $2\theta$ ) experiment, where the  $\theta$  and  $2\theta$  pulse durations of 4.5 and 9.0  $\mu\text{s}$ , respectively, were employed, and where the rotor-synchronized s delay was 281  $\mu\text{s}$ . The recycle delay was typically 5 s. All the spectra were deconvoluted using the Dmfit program [33], in individual Gaussian-Lorentzian peaks, whose integration corresponded to the relative amount of the differently coordinated species. This deconvolution was performed using the minimum possible number of component peaks to describe the spectrum accurately, based on information available in the literature for cements [34].

Quantitative electron probe micro-analyzer (EPMA) analyses were made with a CAMECA SX FIVE electron microprobe using a 15 kV acceleration voltage, a 30 nA beam current, and a 1–2  $\mu\text{m}$  wide beam. Mg and Si elements were analyzed simultaneously. Counting times were 40 s.

## 3. Results and discussion

### 3.1. XRD analyses

The XRD patterns of the two M-S-H samples are reported on Fig. 1. They display the same number of diffraction maxima having similar position and relative intensity. The difference between these two XRD patterns arises essentially from the intensity of the  $\sim 7$  and  $\sim 20$   $^{\circ}2\theta$  maxima. In both patterns, only a few broad maxima of low diffracted intensity are visible. This characteristic pattern suggests that M-S-H



**Fig. 1.** Powder X-ray diffraction patterns of talc and synthetic M-S-H samples.

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