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Phase relations in the $CaO–SiO_2–H_2O$ system to 200 °C at saturated steam pressure

S.-Y. Hong, F.P. Glasser*

Chemistry Department, University of Aberdeen, Meston Building, Meston Walk, Aberdeen, AB24 3UE, UK

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Abstract

Phase relations in the title system were studied using crystalline and amorphous precursors. These were treated in sealed steel alloy autoclaves for periods ranging up to 12 months. Many of the synthetic precursors crystallised to give high purity, single-phase preparations.

Although the $CaO–SiO_2–H_2O$ system is marked by metastable phase formation, it is demonstrated that a number of reactions important to establish the low-temperature phase relationships can be shown to occur reversibly and therefore define the phase equilibrium. New stability data are presented for hillebrandite, afwillite, xonotlite, tobermorite and jennite. Synthetic jennite is shown to have a Ca/Si atomic ratio ~ 1.45, rather less than the reported 1.5 ratio. A phase diagram revised in light of new knowledge is presented.

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Keywords: System $CaO–SiO_2–H_2O$; Calcium silicate hydrates; Phase equilibria; Hydrothermal reactions

1. Introduction

Hydration of Portland cement at or near ambient temperature produces more than 50% of a calcium silicate hydrate, shorthand C–S–H. This nearly amorphous product can have a variable Ca/Si ratio, ranging from 0.8 to 2.0, approximately. However, commercial Portland cement paste is characterised by the occurrence of crystalline $Ca(OH)_2$ together with high ratio C–S–H and thus consists of a mixture of ordered and disordered phases. In blended cements containing a siliceous additive such as fly ash or silica fume, $Ca(OH)_2$ may be consumed and the Ca/Si ratio of the C–S–H may decrease. Compositions intended for autoclaving may be formulated with quartz flour so as to produce low bulk Ca/Si ratios in the range 0.8–1.5, depending on the mineralogical nature of the desired product. Thus, a broad understanding of the $CaO–SiO_2–H_2O$ system, including stable and persistent metastable phase relations, is essential to interpreting the mineralogy and properties of the solid products.

C–S–H “gel” is thermodynamically unstable at all temperatures. Nevertheless, it is persistent, having been found in uncarbonated form in Roman mortars and concretes as well as in natural occurrences. In its natural occurrences, it may be in intimate association with crystalline phases. Taylor [1] lists the known crystalline $CaO–SiO_2–H_2O$ phases relevant to cement and reviews phase relations. The crystal structures of most of these phases have been determined, and two phases (tobermorite and jennite) have been suggested as structural models for short-range order in C–S–H. In this type of model, the gel-like phase is considered to be a highly disordered version of the crystalline phase or phases. X-ray diffraction discloses a certain similarity in terms of the appearance of the relevant patterns, although the similarity could be fortuitous. NMR discloses only the local order of the silicons and neither confirms nor conflicts with the postulated structural similarities [2]. A weakness of this approach is that the crystal structure of one of the model minerals, jennite, is not known, while the one known structure, that of tobermorite having Ca/Si ~ 0.83, differs greatly in composition from the gel in unmodified Portland cement, which has Ca/Si ratios in the range 1.7–2.0.

Under hydrothermal conditions, C–S–H gels of appropriate compositions can convert rapidly to crystalline phases. For example, commercial autoclaved cements based on $Ca(OH)_2$ and quartz frequently develop high yields, >50%, of minerals such as tobermorite and xonotlite in 12–18 h at 160–190 °C. On the other hand, minerals frequently crystallise metastably such that the high yields of particular phases obtained in short autoclaving times, for example, tobermorite, may diminish as the duration of autoclaving is

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* Corresponding author. Tel.: +44-1224272906; fax: +44-1224272908. *E-mail address:* f.p.glasser@abdn.ac.uk (F.P. Glasser).

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extended, leading to the conclusion that rapid crystallisation does not necessarily occur under equilibrium conditions.

Phase relations in the $CaO-SiO_2-H_2O$ are thus not well-established, although conditions for synthesis of many of the constituent phases are well-known [3–10]. Flint, McMurdie and Wells [2] report the preparation of gyrolite, xonotlite, tobermorite and hydrates of di- and tricalcium silicate. They were, however, unable to obtain afwillite and hillebrandite. Taylor found that tobermorite became unstable above 150 °C, transforming in part to xonotlite [3]. He encountered 14 Å tobermorite amongst preparations made at 60 °C but 11 Å tobermorite at 100 °C [3,4] leading to the supposition that higher temperatures favour the lower water 11 Å phase [5]. Peppler [6] reported xonotlite to be stable at temperatures less than 180 °C although noting that xonotlite apparently contained more water than demanded by the formula $Ca_6Si_6O_{17}(OH)_2$ [7,8]. This observation has not been confirmed in subsequent studies. Foshagite has been reported to occur in the range 300–500 °C and afwillite to form from C–S–H compositions in the range 98–160 °C [4], thus essentially confirming a previous report that afwillite was stable in the range 110–140 °C [9]. The upper limit of stability of afwillite is apparently determined by its dissociation to xonotlite and hillebrandite in saturated steam [4,5]. Although dicalcium silicate hydrate is frequently encountered in hydrothermal preparations, its stability is uncertain; it is reported to be unstable below 140 °C with respect to hillebrandite [10]. Reports of the stability of hillebrandite differ; its stability range is variously claimed to be between 150 and 250 °C [4,5] or between 140 and 180 °C [7,9].

Thus current versions of the $CaO-SiO_2-H_2O$ phase diagram at saturated steam pressures and at temperatures between 85 and 200 °C are based on data of variable quality. They utilise in part data that fit experimental criteria for a phase equilibrium but in part include data reflecting the mode-of-occurrence of crystalline phases. Moreover, at least one phase, jennite, that is almost certainly stable at low pressure, ~ 1 bar, is not accorded a place on the phase diagram. In the course of a thesis [11], it was discovered that calcium silicate hydrates could be interconverted more readily and reversibly than hitherto supposed. The discovery that many formation and decomposition reactions amongst $CaO-SiO_2-H_2O$ minerals occur reversibly, coupled with new data on the composition and stability of jennite, has enabled the phase diagram to be determined with greater accuracy than hitherto possible. These data and the resulting revised phase diagram are presented. In view of the many contributions made by H.F.W. Taylor to studies of this system, it seemed appropriate that they appear in this special issue commemorating his life and work.

2. Experimental

Crystalline calcium silicate hydrates were made in a two-stage process. Amorphous C–S–H was first prepared by slurrying an aerosil (Degussa, Aerosil 300) with fresh, high purity (>99.9%) $Ca(OH)_2$. Preparations were made under N_2 to avoid CO_2 contamination and the resulting slurries were stored, with occasional agitation for 24 months at 20 °C; 6–12 months were required to homogenise the samples. The slurries, made at w/s ~ 10, did not carbonate in the course of reaction. The target Ca/Si ratios for the slurries were 2.0, 1.8, 1.6, 1.5, 1.4, 1.2, 1.0 and 0.85. Determination of the Ca/Si ratio of the homogenised product by atomic absorption disclosed that the target ratios were achieved to an accuracy of ± 0.025. The sample with Ca/Si ratio 2.0 contained 5–10 wt.% of $Ca(OH)_2$, the content of which was estimated independently by both thermal analysis and a Franke extraction. With this exception, the gels appeared to be homogeneous, although the presence of small amounts, ca. 1%, of $Ca(OH)_2$ in the gel with bulk ratio 1.8 is not excluded.

Crystallisations were done in "Teflon"-lined stainless steel autoclaves. A Teflon-coated magnetic follower was placed in the autoclave, the closure made and the autoclave wrapped in glass wool insulation and covered with aluminium foil. The assembly was placed on a powerful magnetic hotplate that provided stirring and heating. Temperatures were monitored by an internal copper–constantin thermocouple. Initially temperatures were recorded on a strip chart recorder, but this proved unnecessary: once heat flows stabilised, experience disclosed that temperatures remained at the set point within ± 1.5 °C. A few samples were reacted in autoclaves at < 110°; for this purpose, the entire autoclave assembly was placed in a commercial thermostatted electric oven. While not strictly necessary to contain pressure, the autoclave excluded CO_2.

At the completion of an experiment, mineralogical characterisation was performed by X-ray powder diffraction and, as appropriate, by petrographic examination, electron microscopy (scanning and transmission) with analysis by an energy-dispersive system; also, by electron diffraction, thermal analysis and Fourier transform infrared spectroscopy (FTIR). Occasional autoclaved samples were subjected to total chemical analysis: autoclaving did not affect the Ca/Si ratio within limits of error, ± 0.01.

Phase pure preparations of jennite were analysed by transmission electron microscopy, using an energy-dispersive system: calibration of the analytical system was done using synthetic xonotlite with an estimate purity of ≥ 95%.

3. Results

3.1. Single-phase preparations

A necessary preliminary step for the phase equilibrium studies was the preparation of crystalline $CaO-SiO_2-H_2O$ minerals preferably in phase pure form. A number of experiments were made to optimise synthesis conditions using as criteria product crystallinity and purity. There are no infallible criteria with which to judge phase purity; main reliance was placed on X-ray diffraction, FTIR spectroscopy and thermogravimetry. The latter was particularly useful where a sharp, well-defined step occurs in the weight loss vs. temperature curve. Xonotlite is an example: the dehydroxylation weight loss of preparations judged to be phase pure by X-ray diffraction and microscopy corresponded almost exactly to the theoretical loss. The synthesis reported in Ref. [8] was probably impure: both gel and other impurity phases contain more water than xonotlite and are probably the source of excess water.

We were unsuccessful in obtaining pure α dicalcium silicate hydrate and tricalcium silicate hydrate, which always gave broad X-ray reflections and contained minor portlandite. However, the remaining phases were obtained in essentially phase pure form: Table 1 records the optimised preparative conditions.

3.2. Compositions of jennite and afwillite

Both jennite and afwillite are reported to have the same Ca/Si ratio, 1.5 [1]. However, they cannot be polymorphs because of differences in water content. The Ca/Si ratio of afwillite, as well as its water content, is known beyond doubt from its crystal structure [12]. Thermograms of the afwillite product obtained in the course of the present study give a sharp step in the water loss curve, the size of which matches closely (± 1%) to the theoretical water content. Preparations at the stoichiometric Ca/Si ratio, 1.50, gave the best yields of afwillite, so theory and experiment agree. This contrasts with jennite, which was obtained in traces but never in phase pure form at ratio 1.5. However, it was found that mixing silica gel with either crystalline afwillite or a C–S–H gel, both of Ca/Si ratio 1.5, in sufficient quantity to lower the mean Ca/Si ratio to within the range 1.4–1.46 resulted in apparently complete conversion of both sets of the reactants to jennite in the course of a subsequent autoclaving, suggesting that the characteristic Ca/Si ratio of synthetic jennite is less than 1.5. A fresh series of C–S–H gels were prepared having closely spaced Ca/Si ratios in the range 1.4–1.5. Prolonged hydrothermal annealing of these gels in the appropriate temperature range gave the best yields of jennite in the range Ca/Si 1.45–1.46, both these Ca/Si ratios giving essentially phase pure jennite. However, all compositions in the range 1.40–1.50 gave at least some jennite, albeit with decreasing yields as these limiting Ca/Si ratios were approached.

Table 1

Preferred conditions for synthesis of crystalline C–S–H phases from $Ca(OH)_2$ and amorphous silica

Phase/formula[a]	Ca/Si ratio	Temperature (°C)	Curing time (days)	Pressure
11 Å Tobermorite, $Ca_5(Si_6O_{16})(OH)_2 \cdot 4H_2O$	~ 0.83	140	90	saturated steam
Xonotlite, $Ca_6(Si_6O_{17})(OH)_2$	1.0	200	90	saturated steam
Foshagite, $Ca_4(Si_3O_9)(OH)_2$	1.33	180	56	saturated steam
Jennite,[b] $Ca_9H_2Si_6O_{18}(OH)_8 \cdot 6H_2O$	1.45	85	540	–
Afwillite, $Ca_3(SiO_3)_2(OH)_2 \cdot 2H_2O$	1.5	85	240	–
Hillebrandite, $Ca_2SiO_3(OH)_2$	2.0	180	56	saturated steam
α-C_2S hydrate, $Ca_2(HSiO_4)OH$	2.0	170	35	saturated steam
Tricalcium silicate hydrate, $Ca_6Si_2O_7(OH)_6$	3.0	200	28	saturated steam

[a] Among these phases, three were impossible to obtain as high quality crystalline phases: α C_2S hydrate and tricalcium silicate hydrate.

[b] The chemical constitution of jennite is discussed in the text; the formula given in the literature, with Ca/Si = 1.5, is believed to be incorrect for the synthetic, actual Ca/Si ratios for which lie in the range 1.45–1.46. See Table 2 for abbreviations.

Crystals of jennite were isolated and identified by means of their electron diffraction patterns. Subsequent analysis of isolated crystals, obtained from preparations whose Ca/Si bulk ratio varied between 1.40 and 1.50, always gave selective, single crystal jennite analyses with Ca/Si ratio in the range 1.45 ± 0.02. However, the weight loss of phase pure jennite preparations gives a water content that, within limits of error, agrees with that in the literature. We therefore conclude that (i) the Ca/Si ratio of synthetic jennite is close to 1.45, (ii) jennite and afwillite differ significantly in Ca/Si ratio and can therefore coexist over a range of temperatures without violation of the phase rule and (iii) jennite has a range of thermodynamic stability in the $CaO-SiO_2-H_2O$ system at saturated steam pressure. As will be shown, these conclusions enable a mass of apparently conflicting evidence about phase compatibility between jennite and afwillite, as well as with other phases, to be resolved.

3.3. Hydrothermal reactions

Approximately 200 experiments were made, mostly using single-phase C–S–H phase(s) as reactants. Table 2 records experiments that were used to fix the temperatures of phase boundaries. Tobermorite, while apparently stable indefinitely at 120 °C, begins to break down at temperatures ≥ 130 °C, mainly to xonotlite. Xonotlite appears to be stable at all temperatures in the range studied, 85–200 °C. Jennite, readily synthesised in phase pure form at 85 °C, becomes unstable at elevated hydrothermal temperatures, decomposing at 150 °C to xonotlite and presumably also afwillite, although the latter was not detected by XRD at 150 °C. At higher temperatures, ≥ 160 °C, jennite decomposes to mixtures of foshagite and afwillite. Afwillite is stable to 160 + 10 °C; at higher temperatures, it decomposes to mixtures of foshagite and hillebrandite. Hillebrandite is stable only over a short range of temperatures: literature studies show that its upper limit of stability is ~ 210 °C; above which, it decomposes to α C_2SH. The present study does not define the lower limit of stability of hillebrandite accurately: it is persistent at and above 150 °C, but at

Table 2
Interconversion reactions of crystalline calcium silicate hydrates

Sample	Ca/Si	Temperature (°C)	Phase change	Time (days)	Products	Apparent phase transition range (°C)
11 Å TOB	0.83	>130	yes	90	11 Å TOB + XON	>130
XON	1.0	85	no	100	XON	stable up to 180 °C
		130	no	100	XON	
FOS	1.33	85	yes	270	FOS	stable above ~ 130 °C
		110	yes	270	FOS	
		130	no	100	FOS	
		130	no	100	FOS	
JEN	1.5	130	no	180	JEN	>150
		150	no	63	XON	
		170	yes	39	FOS + AFW	
AFW	1.5	85	no	360	AFW	>170
		130	no	150	AFW	
		150	no	150	AFW	
		170	yes	43	HIL + FOS	
JEN + AFW	1.5	55	no	350	JEN + AFW	>85
		85	no	350	JEN + AFW	
		150	no	150	JEN + AFW	
HIL	2.0	130	no	100	HIL, AFW and POR	stable between 210 and 160 °C
		150	no	100	HIL	
		170	no	90	HIL	
TRI (+ HIL + POR)	3.0	160	yes	10	HIL + POR	>160

TOB, tobermorite; JEN, jennite; FOS, foshagite; AFW, afwillite; HIL, hillebrandite; POR, $Ca(OH)_2$ (portlandite).

130 °C, it undergoes appreciable decomposition to mixtures of afwillite and portlandite in 100 days. Tricalcium silicate hydrate was not obtained in phase pure form, but from formation and decomposition experiments, it appears to be stable over a narrow range of temperatures between 160 and 210 °C, approximately. These data, together with others in the literature, have been used to construct Fig. 1, showing phase relations in the lime-rich [>50% $Ca(OH)_2$] portion of the $CaO-SiO_2-H_2O$ system.

The identity of the tobermorite phase is of interest. In general, 14 Å tobermorite was obtained at low temperatures while 11 Å tobermorite was obtained in increasingly large amounts at 85 °C and above. At 85 °C, 14 Å tobermorite in contact with a saturated solution slowly dehydrates to 11 Å, although mixtures of the two solids persisted for >100 days. However, both composition and temperature determine whether 11 or 14 Å will be the preferred phase. For example, at 85 °C, 130 days, Ca/Si ratios ≤ 1.1 gave the 14 Å phase,

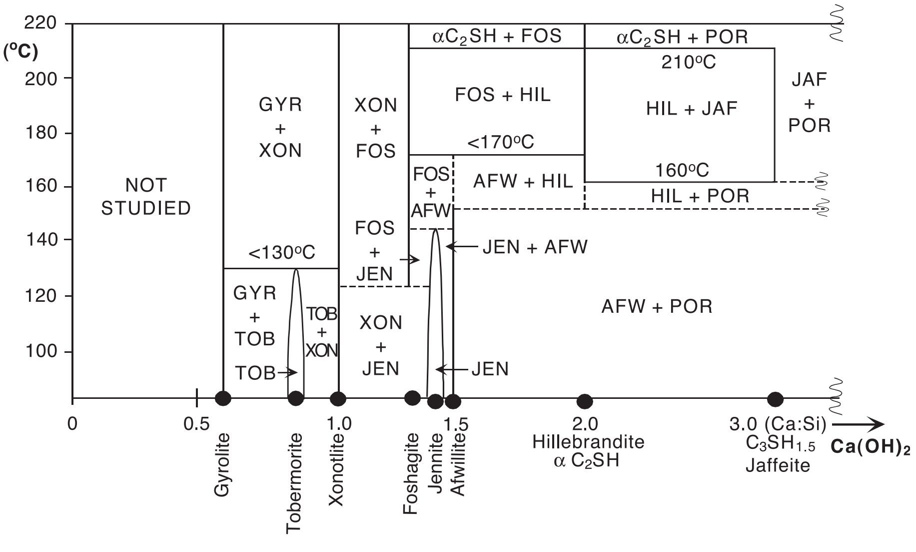

Fig. 1. Phase relations in the lime-rich (>50% $Ca(OH)_2$) portion of the $CaO-SiO_2-H_2O$ system at saturated steam pressures. Molar CaO/SiO_2 ratios are shown. The extent of solid solution in tobermorite and jennite is conjectural. Dashed lines indicate uncertainties.

whereas in higher Ca/Si ratios, such that the product contained mixtures of tobermorite and afwillite, 11 Å tobermorite predominated, sometimes mixed with minor 14 Å tobermorite. At higher temperature, 130 °C for 150 days, 11 Å tobermorite was the sole phase encountered at Ca/Si ratios ≥ 1.1, where it occurred together with jennite. However, 14 Å tobermorite occurred together with the 11 Å phase at Ca/Si = 0.91 and 1.01 cured for 150 days at 130 °C. These observations do not present a systematic pattern but it is suspected that "tobermorite" varies in Ca/Si ratio. It is further hypothesised that an excess of Ca over the normal Ca/Si ratio for tobermorite, 0.83, enables the 14 Å phase to persist to higher temperatures. The temperature dependence of the range of tobermorite phase compositions is a factor that, although not determined in the course of present studies, needs to be assessed in future investigations.

Jennite, like tobermorite, has a highly disordered structure and may on that account also have variable Ca/Si stoichiometry. However, no definite evidence of non-stoichiometry has been adduced in the course of the present study, although Fig. 1 indicates this possibility.

4. Additional discussion

The revised phase diagram (Fig. 1) resolves a number of long-standing problems concerning phase relations in this system such as the composition of synthetic jennite, its stability and coexistence with other C–S–H phases. However, a number of problems remain unresolved. Many C–S–H phases occur in nature or have been reported in the literature that do not appear in experimental studies. This is either because they are not included in the temperature–composition range studied or because they may be stabilised by pressure, or both. Examples include the "phase Z" of Assarasson and Rydberg [10] and Assarsson [11,12], the Ca/Si ratio of which may be as low as 0.4. Assarsson suggests a range of Ca/Si ratios, 0.4–0.6, but this range lies totally outside that of the present study. Moreover, its nonoccurrence in nature suggests that it may be metastable. Calciochrondrodite is another example: it is probably stable only at temperatures in excess of the maximum used here, 200 °C. Other phases, such as rustumite, $Ca_4[OH]Si_2O_7$, are probably stable at < 200 °C but only at high pressures. While it is possible that additional stable phases remain to be discovered in this range of compositions and temperatures, the present study has failed to disclose their formation.

Both tobermorite and jennite are readily synthesised at temperatures well in excess of their stability limit. For example, commercial processes for tobermorite production often operate at 160 °C and occasionally at temperatures as high as 180 °C. It is well known that in this thermal regime, optimum tobermorite yields are attained in short, 12–24 h, autoclaving cycles. However, if tobermorite preparations are held isothermally at high temperatures, yields decline as tobermorite is replaced by other phases. This observation is explained by the ease with which tobermorite forms metastably but, being metastable, subsequently degrades in crystallinity and/or recrystallises to other and more stable phases, especially at 160 °C and above. Jennite behaves similarly: it is readily formed from precursor gels at temperatures as high as 160 °C but is not believed to be stable above ~ 140 °C.

Formation conditions for 11 and 14 Å tobermorite are conditioned by temperature, as expected, but are also influenced by small changes in Ca/Si ratio, excess calcium favouring stabilisation of the 14 Å variety to higher temperatures. It is likely, but not proven, that Ca/Si ratio of tobermorite is variable and that the two varieties also differ significantly in Ca/Si ratio. However, it is unlikely that composition is the sole factor that controls the appearance of 14 Å tobermorite. All the synthetic tobermorites encountered in the present study and, in all probability, in other studies, have a complex order–disorder structure. It is speculated that interactions between stoichiometry and the order–disorder structure are responsible for the strength of interaction between "water" and calcium silicate portions; these interactions affect the ability of the water-rich 14 Å phase to form and persist to high temperatures. Much more detailed characterisation work is required before the mechanisms controlling the 11–14 Å phase boundary can be elucidated. "Real" tobermorites of the type occurring in nature as well as in autoclaved Portland cement-based compositions also contain structural $A\ell$, the role of which requires further study.

Jennite and tobermorite have both been proposed as structural models for C–S–H gel. In this view, the structure of C–S–H is a disordered version of either jennite or tobermorite, or perhaps both. A weakness of this theory is that until now structure of jennite is not actually known, although a structure has been postulated from its supposed composition and known cell dimension [13,14]: This issue presents a complete determination of the structure of jennite, thus removing one uncertainty. However, the present study casts doubt on the composition assigned to synthetic jennite, the Ca/Si ratio of which is shown to be significantly less than 1.5 over the range of temperatures and pressures studied. The possible similarities between tobermorite, jennite and C–S–H are therefore supported. However on purely chemical grounds, one might question the structural analogy between tobermorite (Ca/Si ~ 0.83) and the C–S–H gel of cement (Ca/Si ~ 1.8 or above): the differences in composition are arguably too great to be bridged by minor substitution of $Ca(OH)_2$-like units. Moreover, if the tobermorite and jennite structures were similar, extensive or perhaps complete solid solution between end-member phases—tobermorite and jennite—might be expected. Synthesis discloses that solid solution between tobermorite and jennite, if any, must be relatively minor: other phase fields, notably those with xonotlite, occupy the intermediate composition–temperature space (Fig. 1).

The application of NMR to determining the local environment of Si in C–S–H gel does not depend on assumptions, that is, that the gel has a tobermorite-like structure, but because NMR is relatively insensitive to longer-range order, it has not as yet contributed significantly to the debate about the crystallochemical relationships between gels and those of $CaO-SiO_2-H_2O$ minerals, although clearly NMR has potential in this respect. The present study has yielded crystallites of jennite, but these were too small for a structure determination. Like tobermorite, it is possible that natural jennite may differ from the synthetic in composition and defect content so it would be desirable to determine both structures.

The crystalline calcium silicates obtained in the course of the present study have been obtained mainly by dissolution of a precursor solid or solids and nucleation with subsequent growth of the more stable product. This is evident from product morphology: crystals show characteristic faceting, which are considered to occur as a result of free and unconstrained growth from aqueous solution. This is also consistent with the high water content typical of our hydrothermal preparations. However, in the presence of restricted water, other but slower crystallisation mechanisms may occur. We describe some of these phenomena in a related study, in which experiments were done at fixed 1 bar water vapor pressure [16].

The system $CaO-SiO_2-H_2O$ is noteworthy for at least three reasons: the presence of a very persistent gel that crystallises often with great difficulty; the presence of one, possibly two, crystalline compound(s) that do not have fixed stoichiometry in terms of Ca/Si ratio; and finally, the large number of entropy-stabilised compounds.

The crystalline phases of variable composition are tobermorite and, possibly, jennite. On account of the commercial and technical importance of this system, the mechanisms whereby ions retain their fixed normal valency but compensate for variable stoichiometry deserve further study; this behaviour is unusual in hydrous systems containing a high content of an electropositive ion such as calcium. The presence of a number of crystalline compounds stable only at moderately elevated temperatures—foshagite, hillebrandite, dicalcium silicate hydrate and jaffeite—is remarkable. In the thermodynamic sense, these compounds behave like Ca_3SiO_5 in the anhydrous $CaO-SiO_2$ system: Ca_3SiO_5, it will be recalled, has a minimum temperature of thermodynamic stability at ~ 1275 °C, below which it decomposes at equilibrium to CaO and Ca_2SiO_4. The reason for the increased stability of Ca_3SiO_5 at elevated temperatures is attributed to its unusual crystal structure; one in five oxygens is bonded only to calcium, and the structure as a whole has very nonideal electrostatic bond valence sums. It is thus stabilised at high temperature by additional thermal entropy contributions. The high-lime hydrates of the $CaO-SiO_2-H_2O$ system exhibit analogous behaviour: they are stabilised by rising temperatures. It would be useful to review the structural data for the entropy-stabilised hydrates, possibly in light of new and more accurate structure determinations, to relate crystal structure to phase stability using thermodynamics to characterise the extent to which they are entropy stabilised and determine other thermodynamic quantities. The application of ab initio quantum mechanical calculations, now possible with access to fast computers, may assist this task. It is also noteworthy that many of the high-lime phases in this system that are believed to be thermodynamically unstable at < 100 °C also have anomalously high solubilities measured at 25–85 °C, relative to the solubility trends of the stable phases [15].

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