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Comments on "The chemistry of dicalcium silicate mineral"

I read with great interest the review article on C_2S* [1], and I wish to raise a few points.

We studied the polymorphic transformation scheme of pure γ-C_2S (stoichiometric value of Ca:Si = 2.85) using a Guinier–Lenné high-temperature X-ray camera [2]. From our observations we presented a revised stability diagram of C_2S polymorphic forms. The transformation scheme in Fig. 1 is somewhat different to those suggested by Niesel [3] and Midgley [4].

From our investigations it was found that, on heating, γ-C_2S transforms to an orthorhombic phase (named the "transient phase") at 816° C. At 910° C, α'_L-C_2S appears. A slow rate of heating (40° C h^{-1}) yields α'_H-C_2S at 1165° C, whereas with rapid heating (100° C h^{-1}) α'_H-C_2S fails to appear even at 1250° C (the limit of the apparatus). During cooling, α'_H-C_2S inverts to α'_L-C_2S at 1165° C and then to the β_H phase at 670° C. With further cooling β-C_2S appears at 560° C and finally, at ambient temperatures, a mixture of β- and γ-C_2S is obtained. Samples air-quenched from 1250° C also produce a mixture of β- and γ-phases at room temperatures. The crystallite particle size is seen to affect the transformation temperatures by only 10° C [3]. No evidence of superstructuring between the α'_H- and α'_L-C_2S was found [5]. The cell parameters of all these forms have been calculated from the X-ray powder patterns using a set of standard computer programs (COMPUTE, DECAL and modified CELL) (Table I). Our β_H-phase is seen to resemble Midgley's α'_m-C_2S [4].

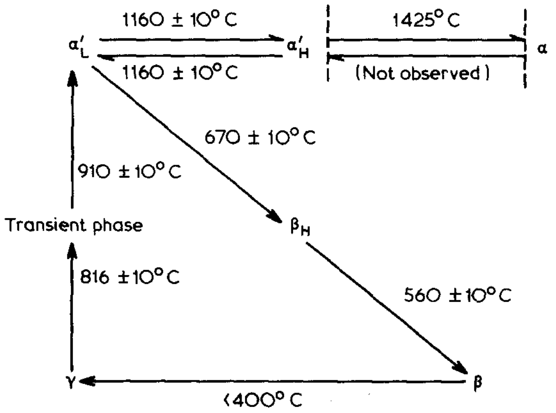

Figure 1 Stability diagram of C_2S polymorphs.

TABLE I Lattice parameters of C_2S polymorphs

Form	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	Crystal system	Space group
γ-C_2S	5.086	11.213	6.773	–	Ortho	P*bnm*
β-C_2S	5.427 ± 0.004	6.629 ± 0.004	9.148 ± 0.006	94.57	Mono	$P2_1/n$
β_H-C_2S	5.364 ± 0.009	6.709 ± 0.012	9.299 ± 0.016	91.51	Mono	$P2_1$
Trans. phase	10.978 ± 0.015	18.567 ± 0.026	6.740 ± 0.010	–	Ortho	$Cmc2_1$
α'_L-C_2S	11.020 ± 0.030	18.696 ± 0.050	6.758 ± 0.020	–	Ortho	P*mcn*
α'_H-C_2S	10.734 ± 0.009	19.072 ± 0.016	6.656 ± 0.006	–	Ortho	P*nmm*

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*Cement chemists' standard notation: C = CaO, S = SiO_2, N = Na_2O, P = PO_3.

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From crystallochemical evidence we suggested that the $\gamma \rightarrow$ transient phase transformation involves no change in symmetry. The transition is monotropic and of distortional nature. The transient phase $\rightarrow \alpha'_L$-C_2S conversion takes place with a small adjustment in the axes of the two forms. A displacive transformation is plausible in the case of $\alpha'_L \leftrightarrow \alpha'_H$-$C_2S$ transition. $\beta_H \rightarrow \beta$-$C_2S$ transformation is again displacive involving small changes in axial dimensions of the two forms. The $\beta \rightarrow \gamma$-C_2S change, however, is monotropic, and large structural changes take place at a fairly low temperature.

Some 200 belite (C_2S) grains from 21 different commercial clinkers were analysed under the scanning electron microscope fitted with an energy dispersive spectrometer [6]. The minor elements detected in the grains were Na, Mg, Al, P, S, K, Ti, V, Cr, Mn and Fe, although not all are necessarily present in every grain except for Al. As would be expected, Ti, V, Cr and Mn, if present in a belite grain, occur only in trace amounts (< 0.05% by weight).

Based on microprobe analyses, we proposed molar compositions of $Ca_{2-x}Mg_xSiO_4$ ($x = 0.22$) and $Ca_2Si_{1-y}AlO_{4-y/2}$ for natural bredigite and larnite, respectively [6].

X-ray patterns of a number of laboratory-synthesized samples of C_2S polymorphs were studied and their lattice parameters calculated [2].

β-C_2S: samples were stabilized using the following additives:

(i) $MgO + Al_2O_3 + Na_2O$
(ii) $MgO + Al_2O_3$
(iii) $MgO + K_2O + Na_2O$
(iv) H_3BO_3
(v) Mn_2O_3
(vi) V_2O_5

An interesting feature observed in the X-ray patterns was the minor displacement of diffraction lines between 32 and 33°2θ, containing the reflections $\bar{1}$0 3, $\bar{1}$2 1, 2 0 0, 0 2 2 and 1 2 1. Variation in cell dimensions and in intensity of diffraction lines was evident.

α'-C_2S: a sample of $MgO + K_2O$-stabilized α'-C_2S [8] was seen to have the following lattice dimensions: $a = 5.533 \pm 0.037$, $b = 9.151 \pm 0.062$, $c = 6.846 \pm 0.046$ Å, space group *Pmcn*, whereas a 0.25% C_2NP-stabilized sample yielded an orthorhombic unit cell with lattice parameters $a = 5.671 \pm 0.055$, $b = 9.311 \pm 0.091$, $c = 6.866 \pm 0.068$ Å, space group *Pmcn*. Midgley [4] claims this to be α'_m-C_2S.

α-C_2S: an $Fe_2O_3 + Na_2O + Al_2O_3$-stabilized sample [8] gave a hexagonal cell with $a = b = 5.499 \pm 0.035$, $c = 7.727 \pm 0.050$ Å, $\gamma = 120°$.

The cell parameters obtained for β- and α-C_2S closely resemble those of other workers, but the X-ray patterns of the room-temperature stabilized forms of α'-C_2S vary between themselves and also show significant differences from the high-temperature X-ray patterns of the pure α'_H- and α'_L-phases.

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