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DISCUSSION

REPLY TO THE DISCUSSION OF THE PAPER “NEUTRON POWDER DIFFRACTION INVESTIGATION OF MODEL CEMENT COMPOUNDS”[1]

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The authors wish to express their thanks to Dr. Simon for pointing out the errors in our recent paper (1). We have reexamined the original refinement computer files and are pleased to report that the refinements described in our paper were performed using the appropriate atomic and crystallographic models. Nevertheless, our description in a table footnote of one of the atomic models employed is incorrect, and we have reported the wrong space group for another as has been noted by Dr. Simon. The following is a corrected description of those atomic models.

Problem 1: The Space Group for Triclinic $(CaO)_3SiO_2$

Dr. Simon correctly points out that the space group for triclinic C_3S is $P\bar{1}$, not the space group P21/n that is listed in our Table 2a. In the refinements of our neutron data, the space group $P\bar{1}$ was used. It appears that the incorrect space group was inserted into Table 2a when the format for Table 3 (for β-C_2S, which has space group P21/n) was used as the model for the final formatting of the manuscript.

Problem 2: The Atom Occupancies for Monoclinic $(CaO)_3SiO_2$

The atomic model used by Nishi et al. (2) for monoclinic tricalcium silicate (C_3S) is very complicated—too complicated, as we stated in our paper, to be directly used in GSAS (3) for profile refinement. In a misguided attempt to reduce the volume of our Table 1, we removed the columns that listed the occupancy and multiplicity of the atomic sites that describe the monoclinic structure. The description in the footnote text that was to replace the table entries was inappropriately shortened to the single sentence, “The occupancy of all of the sites has been taken as one,” which referred only to the 36 Ca-atom positions. These two errors create a serious misrepresentation of the complexity of the monoclinic structure that we have employed for the refinement of the neutron powder diffraction, although the description of

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[1] Cem. Concr. Res. 27, 551–575 (1997).
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the model on pages 555 and 556 of the text is accurate. We correct that misrepresentation and elaborate our description in the material below.

First, Nishi et al. describe the positions of the 36 Ca-atoms in the unit cell in terms of 72 “split” (closely paired) sites with 0.5 occupancy. There are also 36 “split” O-atom sites with 0.5 occupancy that are associated with the “split” Ca-atom sites. Second, they describe the disorder of the 18 SiO_4-tetrahedra in the unit cell by assigning each tetrahedron to a statistical distribution of orientations: those with their apex along the c-axis of the pseudorhombohedral unit cell (U); oppositely directed (D); or tilted off the pseudo threefold axis (G). Some of the tetrahedra are oriented 100% U (tetrahedra 1 and 3) and some of the tetrahedra are oriented 100% D (tetrahedra 2, 4, 5, and 6), whereas the others are distributed among two or three of the possibilities (U, D, and G). It is interesting to note that there are two G orientations prescribed for tetrahedra 17. This information is summarized by Nishi et al. in their Table 3.

To avoid unnecessary further complications, we retained the atomic designations used by Nishi et al. The atomic model used for the refinement of the neutron powder diffraction data approximated their model by averaging the atomic position of the 72 (0.5 occupancy) split Ca-atom sites and representing them as 36 Ca-atom sites, each with unit occupancy. We retained the description of the 36 split O-atom sites each with 0.5 occupancy that are designated O(1A), O(1B), . . . , O(18A), O(18B) in Table 1b in our paper. We have used the same model for the statistical disorder of the SiO_4-tetrahedra as that of Nishi and Takeuchi so that the atom occupancies are those specified by their Table 1b.

The O-atoms belonging to the silicate tetrahedra are designated as O(Anm) where A is either U, D, or G, n is the tetrahedra number (1–18), and m is the atom designator. There are three unique sites for the O-atoms belonging to the U or D tetrahedra and four for the G tetrahedra.

The atom occupancy and site multiplicity data for our approximation to the Nishi et al. atomic model for monoclinic C_3S is listed here in Table 1.

Combining the multiplicity and occupancy data, one can calculate that there are 108 Ca-atoms, 36 Si-atoms, and 180 O-atoms, which is appropriate for $Z = 36$ and the formula $(CaO)_3SiO_2$. In addition, the GSAS output reports the density as 3.102 g/cm^3.

Additional Errata

- In the process of preparing this reply, the authors have discovered that the O-atoms labeled O(D104), O(D105), and O(D106) are U, not D, and should be labeled O(U104), O(U105), and O(U106). Their cell coordinates are unchanged.
- Dr. Simon has also pointed out to the authors in a private communication that there are some additional errors in four atomic positions for the triclinic C3S structure, which was taken from Golovastikov et al. (4). The atomic positions used for the refinement are as tabulated in Table 2b of reference 1 and repeated here in the first column of Table 2. These previously undiscovered transcription errors of the values obtained from reference 4 are not expected to make a significant impact on the conclusions of the neutron powder data refinement.
- On page 567, in the paragraph under Figure 4, the text refers to neutron diffraction data for C_3A being shown in Figure 6. This is incorrect; it should refer to Figure 5.
- At the bottom of page 570, carrying over to page 572, a line of text was omitted in publication. The sentence should read:

TABLE 1
Site occupancies and multiplicities for the approximation to the monoclinic C_3S atomic model used for Rietveld refinement.

Atom	Site occupancy	Multiplicity
Ca(1)–Ca(18)	1.0	2
Ca(19)–Ca(36)	1.0	4
Si(1)–Si(18)	1.0	2
O(1A)–O(18A)	0.5	2
O(1B)–O(18B)	0.5	2
O(D11)–O(D13)	1.0	2,2,4
O(U24)–O(U26)	1.0	2,2,4
O(D31)–O(D33)	1.0	2,2,4
O(U44)–O(U46)	1.0	2,2,4
O(U54)–O(U56)	1.0	2,2,4
O(U64)–O(U66)	1.0	2,2,4
O(D71)–O(D73)	0.68	2,2,4
O(U74)–O(U76)	0.32	2,2,4
O(G81)–O(G84)	0.5	4,4,4,4
O(D91)–O(D93)	0.59	2,2,4
O(U94)–O(U96)	0.32	2,2,4
O(G91)–O(G94)	0.045	4,4,4,4
O(D101)–O(D103)	0.59	2,2,4
O(U104)–O(U106)	0.41	2,2,4
O(D111)–O(D113)	0.57	2,2,4
O(U114)–O(U116)	0.43	2,2,4
O(U124)–O(U126)	0.43	2,2,4
O(G121)–O(G124)	0.28	4,4,4,4
O(D131)–O(D133)	0.37	2,2,4
O(G131)–O(G134)	0.315	4,4,4,4
O(D141)–O(D143)	0.37	2,2,4
O(U144)–O(U146)	0.63	2,2,4
O(D151)–O(D153)	0.22	2,2,4
O(U154)–O(U156)	0.78	2,2,4
O(D161)–O(D163)	0.93	2,2,4
O(U164)–O(U166)	0.07	2,2,4
O(U174)–O(U176)	0.07	2,2,4
O(G171)–O(G174)	0.233	4,4,4,4
O(G175)–O(G178)	0.233	4,4,4,4
O(U184)–O(U186)	0.78	2,2,4
O(G181)–O(G184)	0.11	4,4,4,4

There are a few small peaks in the diffraction diagram which we believe are unrelated to the specimen and are probably the result of parasitic scattering from an improperly centered sample holder. For this reason, the refinements of C_4AF utilize a 6-term Chebyshev background to accommodate the increase in background level observed at low scattering angles.

TABLE 2
Corrections to atomic coordinates for triclinic C_3S.

Atom	Berliner et al.	Golovastikov et al.
O(4)	0.1548 0.0685 0.1427	0.1584 0.0685 0.1427
O(5)	0.2204 0.2685 0.6425	0.2204 0.2685 0.6427
O(19)	0.2778 0.0582 0.7617	0.2777 0.0582 0.7617
O(20)	0.9492 0.4028 0.1070	0.9492 0.4026 0.1070

The authors again thank Dr. Simon for his interest in this work and his efforts at correcting these errors in our presentation.

References

1. R. Berliner, C. Ball and P.B. West, Cem. Concr. Res. 27, 551 (1997).
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4. N.I. Golovastikov, R.G. Matveeva and N.V. Belov, Sov. Phys. Crystallogr. 20, 441 (1975).