Influence of Fe and Mg-doped Silicate on Garnet Phase Formation on Thermal Barrier Coatings

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Introduction

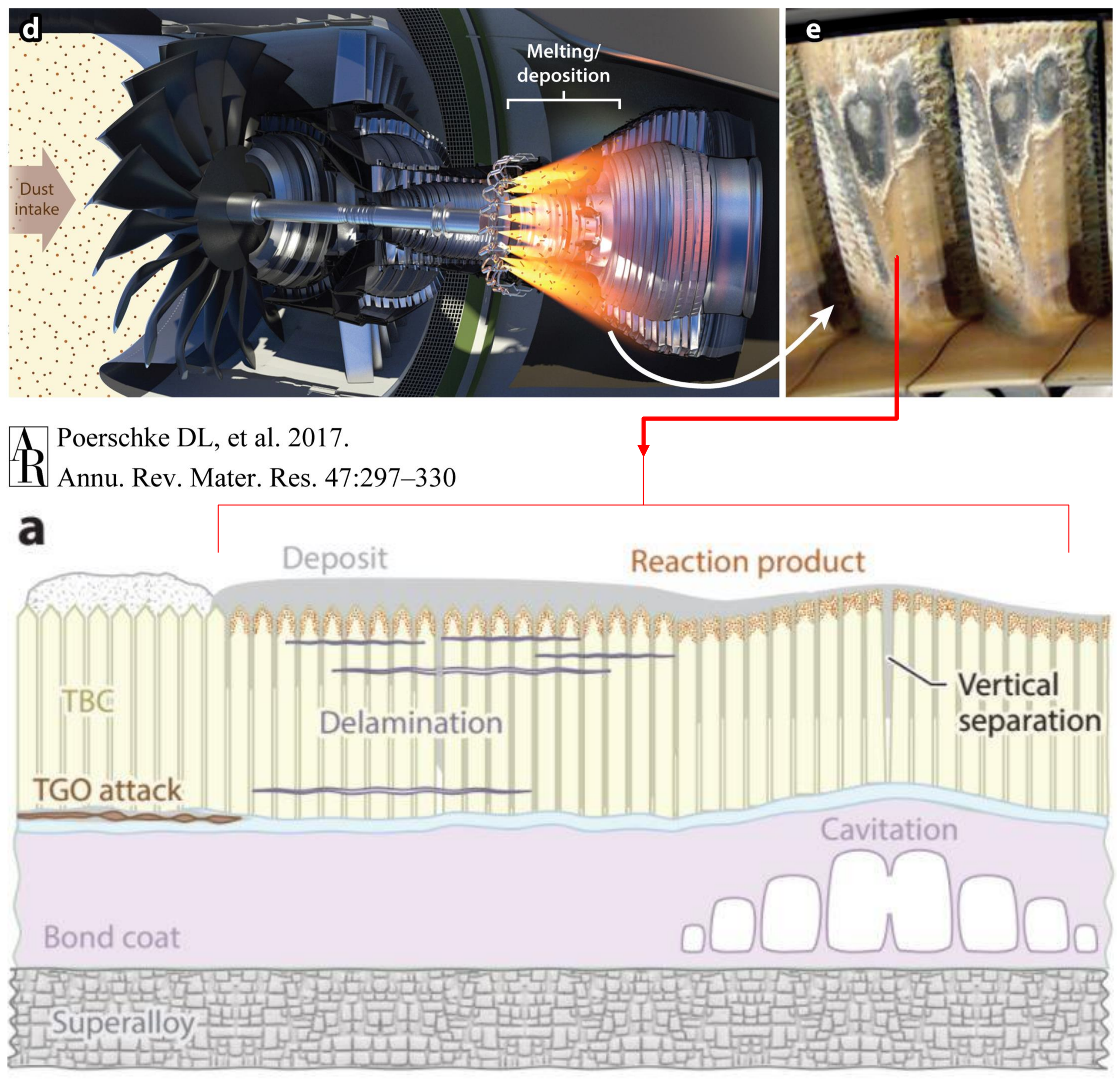


Figure 1: : The effect of silicate attack on the TBC. Deposits react with and penetrate the TBC, causing delamination and cavitation. An apatite crystal structure in the reaction product can protect from addition molten silicate attack.[1]

Thermal barrier coatings (TBCs) are oxide ceramic coatings applied to the hot metal surfaces of gas-turbine engines. Coating the engine superalloys increases the efficiency and performance of the engines by allowing for higher temperature operation.

During service calcium-magnesium-aluminum-silicon (CMAS) deposits melt and wet the TBC (Fig 1). The purpose of this study is to identify the effect of $FeO_{1.5}$ and MgO on the competing formation of the garnet phase and the apatite phase in the recrystallized silicate deposit.

Repeated garnet formation will cause greater penetration by the reaction product, further degrading the coating and lowering performance

Silicate Reaction Model

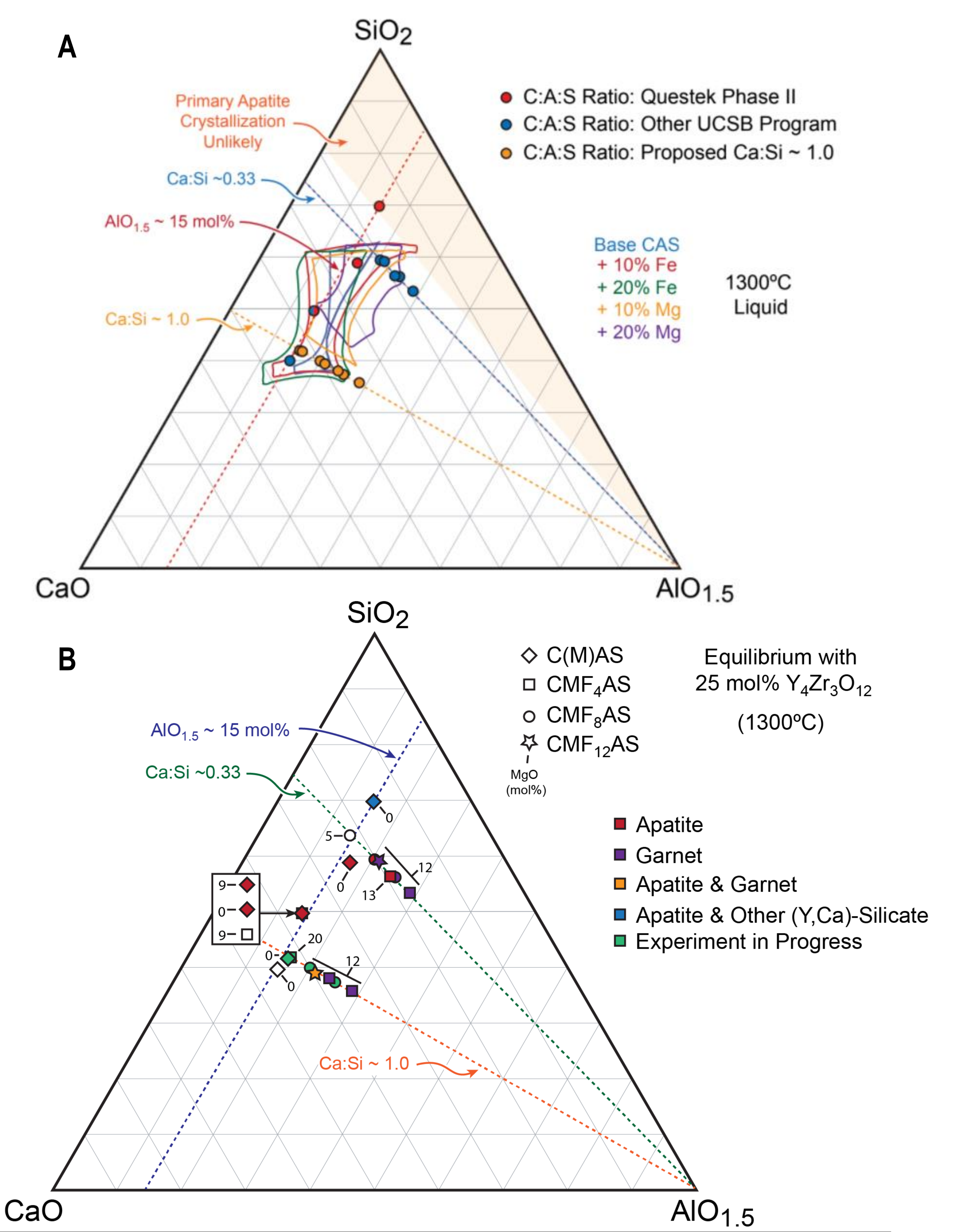


Figure 2: (a) Liquid phase fields were generated for the silicate composition CAS with fixed mole % of 10% $FeO_{1.5}$, 20% $FeO_{1.5}$, 10% MgO, and 20% MgO at 1300℃. A set of compositions was selected (C:A:S Ratio: Proposed Ca:Si ~1.0). **(b)** Precise silicate compositions from previous study (reference), as well as the results from reaction, and the silicates studied in this project.

Apatite and Garnet Formation

The motivation for studying $FeO_{1.5}$ and MgO doping is the competitive formation of garnet and apatite based on the ionic substitutions in the unit cell.
Garnet formation would dominate for increasing amounts of Fe^{3+} and Mg^{2+}.

<u>Composition Formula</u>

Apatite: $A_2B_8(TO_4)_6O_2$

Garnet: $A_3B_2T_3O_{12}$

	A	B	T
Apatite	Ca, Y	Y	Si
Garnet	Ca, Y, Mg, Fe	Mg, Al, Fe	Si, Al, Fe

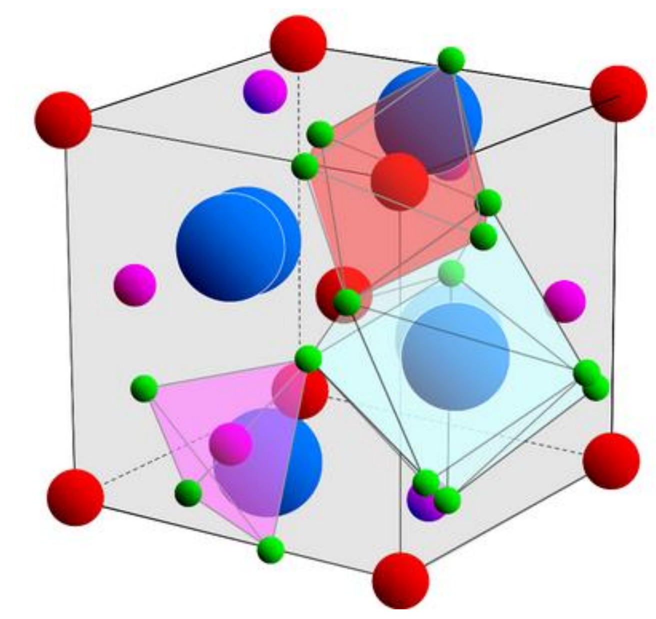


Figure 3: Crystal structure of the garnet phase (A→Blue, B→Red, T→Pink) [2]

CM(F)AS Pre-Reaction

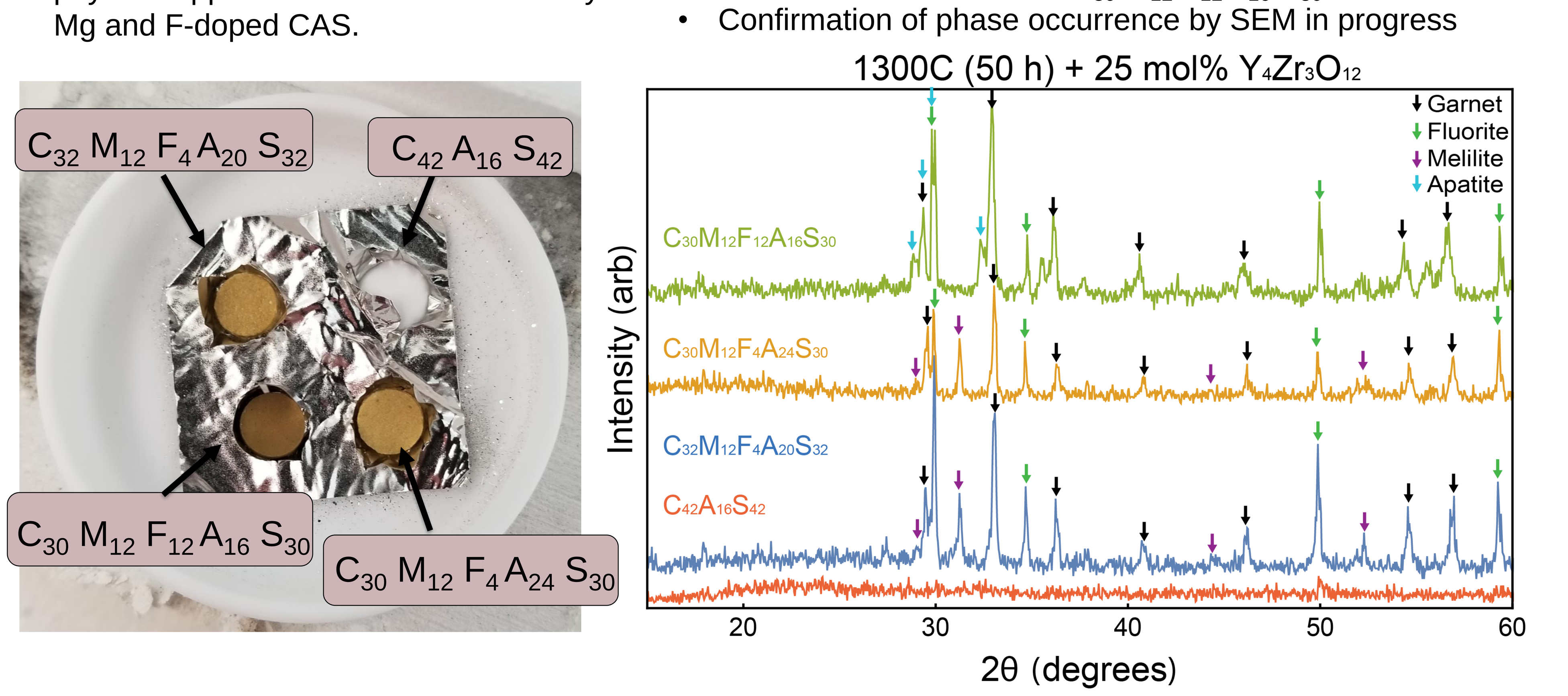
- Previously calcined silicates undergo mixing and a pre-reaction at 1150ºC (24 h)
- Improves homogeneity and limits carbonation

Fig 4: Calcined powder mixture to homogenous pre-reacted silicate (left). Effects of incipient melting during pre-reaction (right).

CM(F)AS Attack on RE-Zirconate

Fig 5:
(a) 0.10 g pellets annealed at 1300℃ (50 h)
- Only $C_{42}A_{16}S_{42}$ shows evidence of melting during annealing. Original physical appearance was maintained by Mg and F-doped CAS.

(b) X-Ray diffraction ((10,70) 2θ range, 0.04 step, 1.2 sec dwell)
- Garnet and Y-doped fluorite appeared in each doped CMFAS.
- A melilite end member appeared in the lower F doped silicate.
- Probable apatite peak for $C_{30}M_{12}F_{12}A_{16}S_{30}$
- Confirmation of phase occurrence by SEM in progress



Conclusion

❖Early results conform to previously seen phenomena: garnet appearing with increasing $FeO_{1.5}$.
❖A change in Ca:Si ratio (0.33 → 1.0) yields apatite in addition to garnet.
❖$C_{42}A_{16}S_{42}$ XRD analysis was inconclusive; awaits SEM to confirm phases present.

Acknowledgements

[1] Poerschke, D. L.; Jackson, R. W.; Levi, C. G. *Annual Review of Materials Research* **2017**.
[2] Poerschke, D. L. Garnet Phase Crystal Chemistry and Experimental Phase Equilibrium Assessment [PowerPoint]. University of Minnesota: Questek STTR Sequential Phase II Project; **2017**.

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