FORMATION OF SILICATE GLASS VERSUS CRYSTALLINE INCLUSIONS THROUGH CONTRASTING PHOSPHORUS-IRON REACTIONS IN THE MILES IIE IRON METEORITE. Rachel S. Kirby[1], Penelope L. King[1] and Fiona Nguyen[1], [1]Research School of Earth Sciences, the Australian National University, Acton ACT 2601, Australia.

Introduction: Phosphorus impacts geochemical systems, modifying both the physical and chemical properties of silicate melts [e.g., 1]. The behavior of P in silicate melts is highly sensitive to redox conditions [2] and the presence/absence and relative abundances of other ions such as Na^+, Al^{3+}, Ca^{2+} and Si^{4+} [2, 3]. Phosphorus is also a critical element in the development and evolution of life [e.g., 4], and meteoritic schreibersite ($(Fe,Ni)_3P$) is speculated to be an important source of P on the early Earth [5].

The IIE iron meteorites likely formed in an impact event on the H chondrite parent body [6] with the silicate inclusions formed through partial melting [7]. Whilst the vast majority of silicate inclusions in IIE irons are crystalline, glassy inclusions have been found in Miles, Colomera and Weekeroo Station [8-10]. To understand why glasses co-exist alongside well-crystallized inclusions with no evidence of differential temperature quenching, we studied a glassy inclusion in the Miles meteorite. Miles is a IIE iron meteorite with 20 vol.% silicate inclusions that encompass a range of compositions from phosphatic-ultramafic to felsic with the majority of inclusions well-crystallized [7].

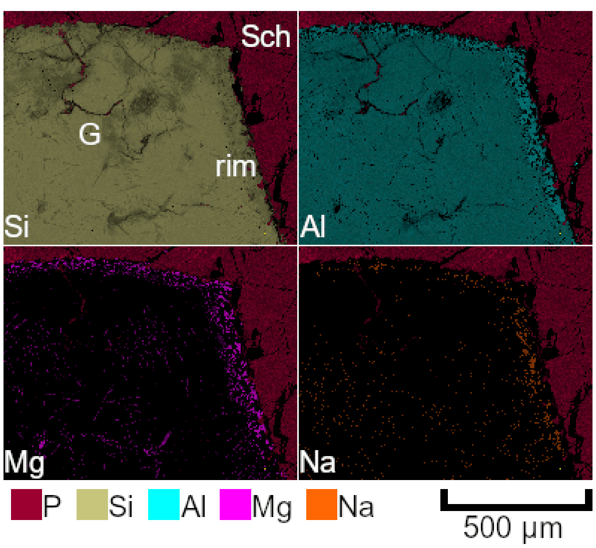

Figure 1: *Element maps of i43 generated from a QEMSCAN. Si is depleted and Al, Mg and Na are enriched in the rim where the glass (G) is in contact with schreibersite (Sch).*

Results: Inclusion i43 is glassy, rounded and approximately 2mm in diameter (Figs. 1, 2). Approximately 60% of its margin is in direct contact with schreibersite, with the remaining margin primarily in contact with Fe,Ni metal and a small (~200 µm) troilite (FeS) grain. Inclusion i43 is intermediate in composition (66.6 wt% SiO_2, 19.0 wt% Al_2O_3, 8.1 wt% Na_2O, 4.1 wt% K_2O, 0.1 wt% FeO, 1.1 wt% MgO, 0.3 wt% CaO), and a normative mineralogy of ~69% albite, 24 % orthoclase, 4% hypersthene, 1% anorthite and 1% quartz (calculated through CIPW norms adapted from [11] for typical meteoritic mineralogy). A QEMSCAN (quantitative evaluation of minerals by scanning electron microscopy) map shows a rim with Na_2O, Al_2O_3 and MgO concentrated in the outer 50 microns of the glass, and SiO_2 depleted (Fig. 1). This rim is present where the inclusion contacts schreibersite, however it is not always present where the inclusion is in contact with Fe,Ni metal.

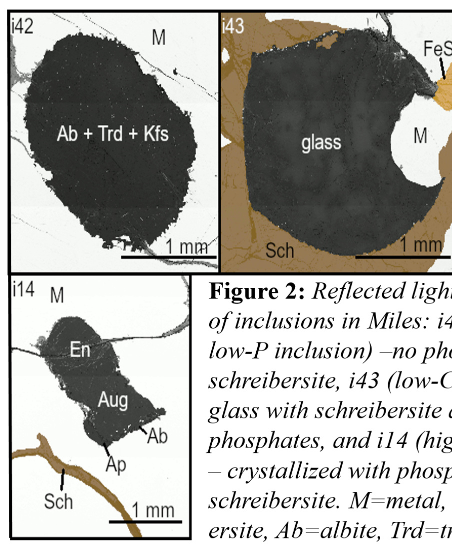

Figure 2: *Reflected light micrographs of inclusions in Miles: i42 (low-Ca, low-P inclusion) –no phosphates or schreibersite, i43 (low-Ca, high-P) – glass with schreibersite and no phosphates, and i14 (high-Ca, high-P) – crystallized with phosphates and no schreibersite. M=metal, Sch=schreibersite, Ab=albite, Trd=tridymite, Kfs=K-feldspar, En=enstatite, Aug=augite, Ap=apatite.*

Discussion: To form a glass, a melt must undercool below the glass transition temperature, T_g, the temperature at which an amorphous viscous fluid becomes a brittle glass. Undercooling is commonly achieved through temperature quenching; rapidly cooling a silicate melt prior to crystallization. In Miles, however, there is no evidence of quenching because most other inclusions including those nearby of a similar composition are well-crystallized [7].

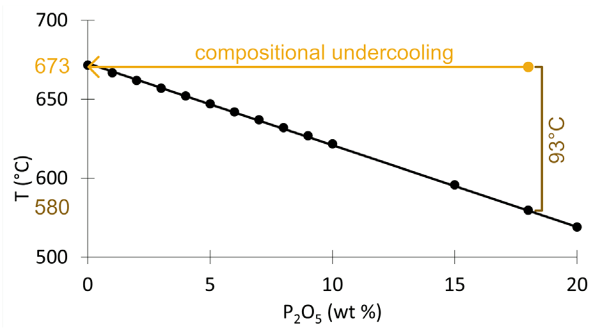

Figure 3: *Modelled T_g for i43 and inclusions of a theoretical composition of i43 + increasing P_2O_5 content. A pathway for compositional undercooling from 18 wt% P_2O_5 (highest P content of an inclusion observed in [7] is shown, equivalent to 93°C quenching with no compositional change. T_g calculated following [12].*

It is possible to undercool through compositional change instead of temperature change. Figure 3 shows the calculated T_g [12] for i43 (with 0 wt% P_2O_5), and the same composition modelled with increasing P_2O_5 content. As P_2O_5 increases, T_g decreases. Thus removal of P from the silicate liquid could undercool the melt without any associated temperature change.

Removal of P from the silicate melt occurs through the reduction of phosphate, oxidation of iron, and the formation of schreibersite [7]. In the Na + Al-rich i43 inclusion, the following equation describes this process:

$$11Fe^{0}{}_{(metal)} + Si\text{-}O\text{-}Si_{(Si\text{-}melt)} + 2AlP^{5+}O_{4\,(Si\text{-}melt)} \rightarrow 2Fe^{2+}{}_{3}P^{6-}{}_{(sch)} + 2SiAlO_{2\,(Si\text{-}melt)} + 5Fe^{2+}O_{(Si\text{-}melt)} \quad (1)$$

In a melt with relatively high SiO_2, Al_2O_3 and Na_2O and low in CaO (such as i43) the activity of P_2O_5 in the melt is relatively high, promoting reaction 1.

In contrast, inclusions with high-Ca and high-P result in the formation of Ca-phosphates [13] following:

$$2Fe_3P_{(sch)} + 5FeO_{(Si\text{-}melt)} + 3CaO_{(Si\text{-}melt)} \rightarrow 11Fe_{(metal)} + Ca_3(PO_4)_{2\,(Si\text{-}melt)} \quad (2)$$

The role of P and Ca on inclusion petrography: In inclusions initially low in Ca and high in P (e.g. i43, Figs. 1,2), the activity of P is high and dephosphorisation of the silicate melt undercools the melt prior to crystallization, forming a glass and schreibersite (Fig. 3 and Eqn. 1). Dephosphorisation cannot occur in a melt without P, therefore those with both low-Ca *and* low-P (e.g. i42, Fig. 2) crystallize before crossing the T_g. In inclusions with both high-Ca and high-P (e.g. i14, Fig. 2), Ca-phosphates form (Eqn. 2).

Equation 1 shows that removal of P from the silicate melt results in depolymerisation of the silicate network and formation of $SiAlO_2$. Al^{3+} in tetrahedral coordination supports more positively charged network modifiers such as Na^{+} and Mg^{2+} than a highly polymerized silicate network [14]. Therefore, these cations would move towards the reaction interface forming a rim high in Al_2O_3, Na_2O and MgO along the glass-schreibersite interface, with SiO_2 depleted over the same region. Furthermore, this effect is mostly absent along the glass-Fe,Ni-metal interface, supporting the hypothesis that quenching is associated with the formation of schreibersite.

Conclusions: Glassy inclusions are able to form alongside crystallized inclusions in IIE iron meteorites through P_2O_5-loss resulting in undercooling without associated temperature quenching. Melts high in P and low in Ca can undergo dephosphorisation through Fe and P redox reactions, forming a glass and schreibersite. Melts with low-Ca and low-P or high-Ca and high-P will not undergo significant compositional change and form crystallized inclusions.

Understanding the behavior of P in high T, low fO_2 conditions such as impact events and core formation is important because it affects the behavior of residual silicate melts (e.g. the formation of glasses), P speciation and ultimately the availability of P to life in the early solar system.

References:

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