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Primary Feldspar in the Semarkona LL3.00 Chondrite:
Constraints on Chondrule Formation and Secondary Alteration
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Abstract

Feldspar in ordinary chondrites (OCs) is often associated with thermal metamorphism, as a secondary mineral that forms from the crystallization of matrix and chondrule mesostasis. However, studies of feldspar in equilibrated OCs show that there is a range of plagioclase compositions within chondrules, some of which may be primary products of chondrule crystallization. It is important to recognize primary feldspar within chondrules because it can be used to help understand the secondary effects of thermal metamorphism and aqueous alteration. The presence of primary feldspar also provides important petrologic constraints on chondrule formation timescales. We undertook a careful study of Semarkona (LL3.00) and observed feldspar in 18% of chondrules. The feldspar is plagioclase covering a wide range of compositions (An_2 - An_{99}) with little K-feldspar component ($<Or_3$). We show that plagioclase is a primary igneous phase, based on grain morphology and compositions consistent with growth from a melt having the bulk compositions of the host chondrules. Based on experimental studies, the presence of plagioclase suggests chondrules cooled slowly at temperatures close to the solidus. We also observed several secondary features consistent with the aqueous alteration. These features include zoning of Na and Ca in plagioclase, heterogeneity in plagioclase compositions in altered chondrules, development of porosity from the dissolution of chondrule glass, and alteration of glass to phyllosilicates. Alteration of major Al-bearing phases, like plagioclase and glass, has important implications for interpretations of ages derived from Al-Mg dating of chondrules, if they have been affected by secondary processes.

Introduction

Feldspar in ordinary chondrites (OCs) is commonly considered to be a secondary phase that forms during thermal metamorphism. As chondrule mesostasis glass, often feldspathic in composition, and chondrite matrix recrystallize, plagioclase and other phases develop in what has historically been treated as a solid-state, temperature-dependent process (Huss et al. 2006). The classification scheme of Van Schmus and Wood (1967), used to differentiate degrees of thermal metamorphism, describes the crystallization of chondrule mesostasis into albite as an important feature of the effect of thermal metamorphism. According to this classification scheme, fine-grained albite crystallizes by petrologic type 4 and then undergoes textural equilibration through types 5 and 6, ultimately resulting in grains of albite $>50\text{ }\mu\text{m}$ in size (Huss et al. 2006; Van Schmus and Wood 1967).

However, recent studies of feldspar in equilibrated OCs (Kovach and Jones 2010; Lewis and Jones 2016) show that the general model of Van Schmus and Wood (1967) does not fully define the feldspar equilibration process or the range in compositions and textures found in OC feldspar. Plagioclase is not solely albitic in composition and a wide range of plagioclase compositions (An_2 - An_{88}) is present in relict chondrules in type 4 L and LL chondrites (Kovach and Jones 2010; Lewis and Jones 2016). Only in type 6 chondrites is feldspar equilibrated chemically, as well as texturally, to an albitic composition of $\sim An_{11}$.

The wide range of feldspar compositions within chondrules in type 4 L and LL chondrites is plausibly derived from variable initial mesostasis compositions. However, chondrules may also contain primary igneous plagioclase, with a range of compositions that could reflect the compositions of plagioclase observed in type 4 OCs. Primary, igneous anorthitic feldspar has been described in Type I chondrules in OCs (Huss et al. 2001; Russell et al. 2000) but it is not well characterized, unlike similar occurrences in carbonaceous chondrites (CCs) (Brearley and Jones 1998; Wick and Jones 2012). Al-rich chondrules in OCs also contain primary anorthite that is useful for age dating using Al-Mg systematics

(e.g., Huss et al. 2001). Although Type II chondrules in OCs are relatively rich in Na and K, albitic plagioclase or alkali feldspar is not generally observed (Jones 1990). Grossman and Brearley (2005) noted that crystalline albite is present within some Semarkona chondrules, but did not indicate whether it is primary or secondary in origin.

To understand how secondary plagioclase develops during metamorphism, it is essential to know the abundance and composition of primary plagioclase. The mineralogical and chemical changes that affect chondrule mesostasis during thermal metamorphism depend on the composition and initial crystallinity of the mesostasis, in addition to temperature and available fluids. The presence of primary feldspar can influence the subsequent crystallization of the mesostasis glass by providing surfaces on which secondary plagioclase can nucleate. Plagioclase is also affected by alkali metasomatism, so secondary effects recorded in primary plagioclase can provide an indicator of the presence of fluids in type 3 chondrites. Plagioclase alteration can affect Al-Mg systematics resulting in low precision isochrons or ages that are difficult to interpret. In addition to its importance in terms of interpreting metamorphism, understanding the origin and development of primary feldspar can help constrain chondrule cooling rates, an important parameter in chondrule formation models (Connolly and Jones 2016).

We have investigated the presence and characteristics of primary igneous plagioclase within chondrules of the LL3.00 chondrite Semarkona. Semarkona is the least thermally metamorphosed OC fall with a maximum metamorphic temperature estimated to be less than 260°C (Alexander et al. 1989). It is the ideal sample in which to investigate primary chondrule minerals because chondrule mesostasis glass has not undergone crystallization (Huss et al. 2006). The mineralogy and petrology of Semarkona chondrules were studied extensively by Jones and Scott (1989) and Jones (1990, 1994, 1996), but primary igneous plagioclase was not recognized in those studies. Marked improvements in SEM technology has enabled higher resolution investigations into chondrule mineralogy and allowed for studies on phases too small to be fully characterized in earlier studies. We show that primary igneous plagioclase is abundant in Semarkona chondrules and that careful observations of plagioclase are important for interpreting the effects of metamorphism, alteration, and the results of Al-Mg isotope systematics.

Samples & Analytical Methods

For this study, we examined a single thin section of Semarkona from the Institute of Meteoritics Collection at the University of New Mexico, UNM 549. Feldspar was identified using backscattered electron (BSE) imaging and energy-dispersive spectroscopic (EDS) analysis on an FEI Quanta 3D Field Emission Gun Scanning Electron Microscope (FEG-SEM) at the University of New Mexico. High contrast BSE images were captured at 10 kV and 16 nA. Cathodoluminescence (CL) images were acquired at the Williamson Research Centre, University of Manchester using a CITL Cold Cathode CL 8200 MK3 with optical stage operated at 15-20 kV and 300-400 μ A.

Quantitative wavelength-dispersive spectroscopic (WDS) analysis was performed on a JEOL 8200 Electron Probe Microanalyzer (EPMA) at the University of New Mexico operated at 10-15 kV and 10 nA with a focused beam. The low accelerating voltage was used to minimize the interaction volume when analyzing small feldspar grains. We used the following standards: Taylor olivine (Mg, Fe), Taylor albite (Na, K), Taylor orthoclase (K, Al, Si), and a doped diopside (Ca, Cr, Mn). We used time dependent intensity corrections on Na using the Probe for EPMA software to compensate for the effects of Na migration in Na-bearing plagioclase during focused-beam analysis.

We determined bulk silicate compositions for four chondrules, based on quantitative WDS maps obtained using the EPMA. 300x300 pixel maps were acquired in two passes using an 80 ms/px dwell time and a 1-3 μ m spot size. This provided coverage of between 300x300 μ m and 900x900 μ m, depending on the size of the chondrule. The resulting intensity maps were processed using mean atomic number (MAN) background corrections to produce quantitative oxide maps. MAN curves were generated using the following Taylor standards: olivine, albite, orthoclase, chromite, spessartine, MgO, hematite, and nickel and additional standards: doped diopside, labradorite, and sodalite. Chondrules were masked in Adobe Photoshop and the bulk silicate compositions of the chondrules were calculated. We used a custom MATLAB script to identify the chondrule pixels in which analytical sums lie between 90% and 110%. In

addition, pixels with SiO₂ content less than 20% were omitted to eliminate Fe-Ni metal and sulfides. Densities were determined for each pixel based on the assigned mineral phase and the bulk silicate composition of each chondrule was calculated as the mean density-weighted composition of accepted pixels.

A section from Ch 28 was prepared using a focused ion beam (FIB) on the FEI Quanta 3D Dual-beam FEG-SEM/FIB with a final polish conducted at 5 kV to reduce surface amorphization. The section was imaged at the University of New Mexico using a JEOL 2010F Scanning Transmission Electron Microscope (STEM) operated at 200 kV in scanning mode using a high-angle annular dark-field (HAADF) detector. A qualitative EDS map was acquired over a 2.4 μm x 1.8 μm region.

Results

Figure 1 shows a BSE map of thin section UNM 549 in which feldspar-bearing chondrules are outlined in white. Chondrules referred to in the text, figures, and tables are labeled in Fig. 1 by chondrule number. Eighteen percent of chondrules were found to contain primary igneous feldspar and consist of a range of sizes and textures described below.

Petrography

Examples of chondrules that contain near-endmember albite and anorthite (Ch3 and Ch36, respectively) are illustrated in Fig. 2. Ch3 (Fig. 2a) is a Type II (FeO-rich) porphyritic olivine-pyroxene (POP) chondrule. It is dominated by a single large (450 μm) olivine grain in addition to smaller grains of olivine (up to 150 μm) and low-Ca pyroxene (up to 75 μm). The olivine grains show normal igneous zoning and the low-Ca pyroxene grains have oscillatory zoning (Fig. 2b). Calcium-rich pyroxene is present around the perimeter of the low-Ca pyroxene grains. The albite has a composition of An₂ and is present predominantly along the chondrule perimeter in bunches of thin, 1-8 μm wide, laths (Fig. 2b) up to 60 μm in length within the chondrule glass. Some of these laths are curved and have convex terminations indicating rapid growth. Albite luminesces bright blue in the CL image (Fig. 2b, inset), but the glass does not luminesce significantly making albite easy to recognize via CL in this, and other, albite-bearing chondrules. Along the chondrule edge, in contact with the matrix, mesostasis glass is partially altered to phyllosilicates and the albite laths are zoned subparallel to the regions of alteration (Fig. 2c).

Ch36 (Fig. 2d) is an FeO-poor barred olivine (BO) chondrule that has 10-30 μm wide bars of forsteritic olivine. The chondrule has extensive fracturing, particularly in the central region, and appears to have been crushed. Between the olivine bars are abundant 1-6 μm wide laths of anorthite (An₉₉, Fig. 2e). Interstitial to the anorthite laths are small (~1 μm) clinopyroxene quench crystallites and minor remnant glass. The glass is largely intact but is replaced by voids in a few places throughout the chondrule. A CL image of Ch36 (Fig. 2f) shows that plagioclase luminesces light blue. Olivine bars luminesce red and are zoned, with the brightest parts toward the exterior of the grains. The mesostasis glass luminesces bright yellow along the chondrule rim and pale yellow toward the interior.

Representative BSE images of chondrules that contain plagioclase with intermediate compositions are shown in Fig. 3. Ch28 (Fig. 3a) is a Type II POP chondrule with olivine grains up to 150 μm long and low-Ca pyroxene grains up to 250 μm long. Similar to Ch3, the olivine and low-Ca pyroxene grains in Ch28 are zoned and Ca-rich pyroxene is found along the perimeter of the olivine and low-Ca pyroxene grains. Several large voids (up to 370 μm in diameter) are present in the chondrule interior. Albitic plagioclase (Fig. 3b) is present as 1-6 μm wide laths that are interstitial to the olivine and pyroxene grains throughout the chondrule and is zoned with a range of compositions from An₃ to An₁₉. Pores and porous phyllosilicates are present within, and between, the plagioclase laths.

A FIB section (Fig. 4a) was extracted from Ch28 (white line in Fig. 3b) to further investigate the plagioclase zoning seen in the BSE image (Fig. 3b). Plagioclase laths in the HAADF STEM image (Fig. 4b) show zoning parallel to the grain boundaries. This zoning is visible in the Ca EDS map (Fig. 4c), which shows that Ca is moderately enriched in the core but heterogeneously distributed from core to rim within individual laths. Between the plagioclase laths, adjacent to the low-Ca zones, are porous

phyllosilicates. Vertical lineations in Fig. 4a, also seen in Fig. 4b inclined to the right, are a curtaining artefact produced during sample preparation.

Ch23 (Fig. 3c) is a Type I (FeO-poor) POP chondrule containing large low-Ca pyroxene grains up to 250 μm long and smaller (up to 150 μm long), zoned olivine grains. Interstitial to the major grains are 1-2 μm wide laths of intermediate plagioclase (An_{37} , Fig. 3d), up to 30 μm long. The plagioclase laths are zoned like those in Ch28 and much of the mesostasis interstitial to the plagioclase laths appears to have been dissolved away as it is now void space. Calcium-rich pyroxene is found along the perimeter of the low-Ca pyroxene grains with plagioclase largely interstitial to it. However, the terminations of the plagioclase laths slightly embay into the Ca-rich pyroxene.

Ch20 (Fig. 3e) is also a Type I POP chondrule with 30-70 μm olivine grains clustered near the interior and pyroxene grains up to 120 μm long near the chondrule exterior. Plagioclase is located at the center of the chondrule and occurs as 1-3 μm wide laths, up to 60 μm long, with a composition of An_{66} (Fig. 3f). Calcium-rich pyroxene is present both interstitial to the plagioclase laths and along the low-Ca pyroxene perimeters. Like Ch23, some of the mesostasis glass appears to have been dissolved away, leaving voids interstitial to the plagioclase and Ca-rich pyroxene grains.

Feldspar compositions

EPMA data for feldspar measured in 14 chondrules are presented in Fig. 5, average compositions for individual chondrules are given in Table 1, and individual analyses are tabulated in Table S1. Feldspar compositions span the full range along the Ab-An plagioclase join, from An_2 to An_{100} . The K_2O contents are minor, but increase slightly with decreasing An content to a maximum of Or_2 in Ch3 (An_2). No K-feldspar was observed in any of the chondrules. The compositional range of plagioclase within each chondrule varies considerably from chondrule to chondrule. In the truncated ternary diagram in Fig. 5, each spot represents an individual analysis. On the scale to the left of Fig. 5, we illustrate the range in anorthite contents by plotting the average plagioclase composition for each chondrule with error bars representing one standard deviation of the mean.

Greater compositional ranges are correlated with secondary features such as dissolved mesostasis glass and the presence of phyllosilicates (e.g., Ch28: Figs. 3b and 4 and Ch23: Fig. 3d). Ch3 also has phyllosilicates and dissolved mesostasis glass (Fig. 2c) but a low standard deviation in its An content because only a few of the plagioclase grains in contact with the matrix have undergone alteration and the majority appear to be unaltered. Ch10 has the greatest standard deviation because only 3 points are included in the calculation and there is a 15 mol. % spread between the highest and lowest values (An_{21} - An_{36}). The lowest An value measured in Ch10 is associated with the region of greatest alteration.

Tenner (2017) and Tenner et al. (2014) have shown that plagioclase in chondrules from several highly unequilibrated chondrites can have an appreciable excess silica component, indicating an anhydrous, high-temperature origin. Based on our EPMA analyses, we see some evidence for this, but the data show a lot of scatter. The presence of a silica excess in chondrule plagioclase does not impact the results of this study, but it is an interesting feature with implications for chondrule alteration.

The Cr_2O_3 and MnO contents of plagioclase in all chondrules are low, typically less than 0.1 wt.% each, and there is no correlation with anorthite content. The minor elements FeO and MgO vary greatly from chondrule to chondrule as well as within each chondrule but can be of significant abundance (up to 4.5 wt.% total in individual analyses). It is not clear whether these elements are incorporated into plagioclase or not, and if they are incorporated, how they are substituting into the crystal structure. The high abundances of these elements do not correlate significantly with An content as would be expected if they were directly substituting for Ca, and the system is too reducing for Fe to be trivalent and substitute for Al. However, the $\text{Mg\#}$ ($\text{Mg}/(\text{Mg}+\text{Fe})$) of the plagioclase does correlate with An content, for example atomic $\text{Mg\#} = 24$ and 95 for An_2 and An_{99} , respectively, suggesting that the composition is controlled during crystallization. FeO and MgO (up to 3 and 1.2 wt.%, respectively) are commonly reported in meteoritic plagioclase over a range of compositions, summarized by Smith and Brown (1988), so the presence of these cations in our measurements is not unusual. The crystallization conditions may be such

that the incorporation of FeO and MgO into plagioclase represent a disequilibrium feature of rapid plagioclase growth.

However, Smith and Brown (1988) caution about the over interpretation of feldspar EPMA data without careful consideration of the analytical conditions. Secondary fluorescence can be a major issue, particularly in Fe-rich samples. It is also possible that some of the FeO and MgO content comes from analytical overlap of adjacent phases such as Ca-rich pyroxene, metals, and sulfides. Despite using low accelerating voltages (10-15 kV) during EPMA analysis to reduce the analytical interaction volume, the small sizes of the plagioclase laths (~1-5 μm wide) means some overlap with other mesostasis phases is difficult to avoid. Hence, we cannot be sure that the analyses are not influenced by analytical artefacts. However, TEM EDS estimated up to 0.5 wt.% FeO and 0.2 wt.% MgO in Ch28 zoned plagioclase (Fig. 4), values in the range of those measured by EPMA for Ch28. This suggests that at least some of the FeO and MgO measured by EMPA resides in plagioclase.

Bulk chondrule composition and modal mineralogy

Bulk silicate compositions of selected chondrules measured using quantitative EPMA maps are tabulated in Table 2. The oxide maps used to determine the bulk compositions are illustrated in Fig. S1. The data show a clear trend of increasing An content in plagioclase with increasing bulk Mg#. The bulk Na/Al ratio decreases with increasing An content (1.1-0.1) in the plagioclase, but the Ca/Al ratio remains constant across the four chondrules (1.4-1.5). K₂O is enriched in the type II chondrule Ch3 (0.13 wt.%) relative to the other three chondrules that have relatively constant, and low, K₂O abundances (0.07-0.08 wt.%). Bulk Cr₂O₃ is depleted in the BO chondrule Ch36 (0.25 wt.%) relative to the other three chondrules that are similar in Cr₂O₃ content (0.63-0.71 wt.%).

The modal silicate mineralogies of the chondrules (Table 2) were estimated from the EPMA maps and are illustrated as mineral maps in Fig. S1. Ch3 is a POP chondrule dominated by olivine (63 vol.%) and containing approximately equal amounts of low-Ca pyroxene and Ca-rich pyroxene (13 vol.% and 14 vol.%, respectively), and 10 vol.% mesostasis. The measured mesostasis abundance includes plagioclase, glass, and small amounts of Ca-rich pyroxene. Ch23 and Ch20 are similar with 27 vol.% and 19 vol.% olivine, 57 vol.% and 66 vol.% low-Ca pyroxene, similar amounts of Ca-rich pyroxene (7 vol.%), and 9 vol.% and 8 vol.% mesostasis, respectively. The BO chondrule Ch36 consists of 66 vol.% olivine and 32 vol.% mesostasis. The 2 vol.% that was measured as Ca-rich pyroxene represents large grains while most of the Ca-rich pyroxene is ~1 μm in size (Fig. 2e) and is included in the reported mesostasis abundance.

Discussion

Primary chondrule minerals contain important information about the physical and chemical conditions during chondrule formation. They can provide information about the timing of the chondrule forming events through relative radiogenic chronometers (e.g., Al-Mg dating), and about cooling rates through petrologic studies. Characterizing primary minerals is also important for revealing the effects of secondary processes. Because these processes alter the chemistry and mineralogy of chondrules, well characterized primary minerals are important for interpreting the effects of thermal metamorphism and metasomatism.

While the presence of primary plagioclase has been noted in OC chondrules before (e.g., Grossman and Brearley 2005; Huss et al. 2001; Russell et al. 2000), its petrography and relationship to bulk chondrule composition have not been studied in detail. In the discussion that follows, we will show that primary plagioclase nucleated and grew as an igneous phase during chondrule cooling, discuss the conditions under which it formed, and consider the implications for chondrule formation including cooling rates and nebular environment. We will also show how secondary features in plagioclase indicate parent body alteration and discuss why an accurate chondrule chronology depends on detailed investigations of chondrule mineralogy.

Primary igneous plagioclase

Although plagioclase is not thought of as a common primary mineral in OC chondrules, we have shown that it is relatively abundant. Brearley and Jones (1998) did not mention plagioclase in their review of chondrules in type 3 OC. However, anorthite has been noted in Al-rich OC chondrules (Huss et al. 2001; Russell et al. 2000), used largely for Al-Mg chronology, and crystalline albite was seen in a Semarkona chondrule (Grossman and Brearley 2005). It is important first to show that the plagioclase within these chondrules is a primary igneous phase, so that we can use it to understand chondrule formation and the environment in which chondrules were formed.

Feldspar as an igneous phase

Mineral textures can be used to illustrate the igneous nature of plagioclase in Semarkona chondrules. The plagioclase grains we observe are smooth laths, regardless of their composition (Figs. 2b,c,e, 3b,d,f), consistent with an igneous origin. In contrast, plagioclase that crystallizes from devitrified mesostasis glass is extremely fine grained in the lower petrologic types and does not display a lath-like morphology (Huss et al. 2006). The morphology of plagioclase in Ch3 (Fig. 2b) is similar to fan spherulites, indicating rapid growth with high degrees of undercooling (Corrigan 1982; Lofgren 1974). Albitic laths such as these are common in the outer portions of albite-bearing chondrules. An external nucleation agent, such as nebular dust impinging on the outside of the chondrule, could have helped the plagioclase to nucleate and, combined with undercooling, grow rapidly as the textures indicate. In a similar manner, Connolly and Hewins (1995) were able to experimentally reproduce a variety of chondrule textures by puffing dust onto the surface of molten chondrule droplets to induce nucleation. Although these experiments did not produce plagioclase, it is a reasonable mechanism for producing the albite textures we observe here.

Another way to assess whether the plagioclase in Semarkona chondrules is a primary phase is to look at the bulk compositions of the chondrules in which it is found. A relationship between plagioclase composition and bulk chondrule composition is expected for growth of plagioclase from the melt. As discussed above, the anorthite content in chondrule plagioclase is directly related to the bulk composition of the chondrule: increasing atomic Mg# from 78 to 98 in the bulk chondrule corresponds to average plagioclase compositions varying from An₂ to An₉₉, an increase in bulk chondrule abundances of refractory elements Al and Ca, and a decrease in the volatile element Na (Table 2). Because the Ca/Al ratio is constant across the four measured chondrules, the composition of the plagioclase seems tied to the bulk Na abundance and Na/Al ratio, which in turn is inversely correlated with Mg#, as has been shown previously Grossman and Wasson (1983).

We can use bulk chondrule and plagioclase compositions to provide upper limits on the temperatures at which the plagioclase formed. However, as we discuss further below, plagioclase and mesostasis glass in some of these chondrules have been affected by aqueous alteration, although the major phases (olivine and pyroxene) appear unaffected. Because plagioclase and mesostasis glass are rich in Na, Ca, Al, and Si, these elements are likely to differ slightly in the bulk silicate composition we measured when compared to the fresh, unaltered chondrule. For this discussion, we assume that the measured bulk silicate compositions are the original igneous compositions.

We used the thermodynamic model rhyolite-MELTS (Ghiorso and Gualda 2015; Gualda et al. 2012) to model the equilibrium crystallization of the bulk compositions listed in Table 2. We used rhyolite-MELTS instead of the classic MELTS package because of the increased computational stability added to rhyolite-MELTS. The calibration for low-SiO₂ compositions, relevant to the bulk composition of Semarkona chondrules, is the same for the two programs. Chondrule compositions were cooled from the calculated liquidus temperature (Table 2), in 1 °C increments, at a constant 1 bar pressure, and kept at a constant *f*O₂ along the IW buffer.

The results are illustrated in Fig. 6. Lines show the equilibrium plagioclase composition predicted to crystallize for each bulk chondrule composition. Crosses indicate the measured plagioclase composition and corresponding equilibrium crystallization temperature. For Ch36, the cross is not on the line because the measured anorthite composition (An₉₉) was not produced during the modeled plagioclase crystallization: this will be discussed below. Circles indicate the point at which Ca-rich pyroxene

becomes stable. For each chondrule, the range of plagioclase compositions predicted to crystallize from the bulk composition is close to the measured plagioclase composition from those chondrules: more anorthitic chondrules (Ch36 and Ch20) have plagioclase compositions closer to the first compositions to crystallize, whereas the more albitic chondrules (Ch23 and Ch3) are closer to the final compositions to crystallize.

Rhyolite-MELTS simulates batch crystallization under equilibrium conditions, but the rapid cooling experienced by chondrules means that equilibrium conditions were unlikely during crystallization. In fact, due to the extremely slow rate of Si-Al interdiffusion, it is unlikely that any feldspar truly grows under equilibrium conditions (Brown and Parsons 1994). However, using rhyolite-MELTS to look at the equilibrium plagioclase compositions is instructive to understand the expected plagioclase compositions and to provide upper limits for formation temperatures. These temperatures are 1197 °C, 1098 °C, and 792 °C for Ch20, Ch23, and Ch3, respectively.

The measured plagioclase composition in Ch36 has a greater anorthite content (An_{99}) than the most anorthitic composition predicted by the rhyolite-MELTS model (An_{93}). This puts an upper limit for the crystallization temperature for this composition of >1260 °C, the temperature at which rhyolite-MELTS nucleated plagioclase. We can also consider this chondrule within the ternary Fo-Di-An system in order to provide a better constraint on the upper limit of the plagioclase crystallization temperature. Forsterite, diopside, and anorthite are the three major phases present within this chondrule and their compositions are close to the Mg-free and Na-free endmembers of the system. We projected the bulk composition measured for Ch36 onto the Fo-Di-An ternary resulting in a relative composition of 70, 8, and 22 wt.% Fo, Di, and An, respectively, and close to the measured modal mineral abundances (Table 2). Under equilibrium crystallization conditions, the melt composition, which begins in the Fo primary field, intersects the Fo-An join around 1317 °C (Osborn and Tait 1952), consistent with the rhyolite-MELTS estimate of >1260 °C. Hence, 1317 °C is the temperature used to indicate the plagioclase crystallization temperature for Ch36 on Fig. 6.

Figure 6 also shows the expected relative timing of plagioclase and Ca-rich pyroxene during equilibrium crystallization. Textures showing the relative timing of plagioclase and Ca-rich pyroxene crystallization are a further indicator that plagioclase is primary. Ca-rich pyroxene is often one of the last silicate phases to crystallize in chondrules and it nucleates off the existing phenocrysts of olivine and low-Ca pyroxene (e.g., red in the phase maps in Fig. S1). The temperature at which Ca-rich pyroxene becomes stable is relatively insensitive to bulk composition (1055-1225 °C, Fig. 6). Because the crystallization temperature of plagioclase is strongly dependent on its composition, we would expect albitic plagioclase to crystallize after Ca-rich pyroxene and anorthitic plagioclase to crystallize before Ca-rich pyroxene but after low-Ca pyroxene. Ch3, Ch28, and Ch23 have albitic plagioclase compositions and the plagioclase is interstitial to the Ca-rich pyroxene growth (Figs. 2b,c, 3b,d). Ch20, with an intermediate plagioclase composition (An_{66}), has plagioclase intergrown with Ca-rich pyroxene (Fig. 3f): Ca-rich pyroxene appears to have nucleated first but continued to grow during plagioclase crystallization. Ch36 has an anorthitic plagioclase composition (An_{99}) and Ca-rich pyroxene is present between plagioclase laths (Fig. 2e). Hence, despite the undercooling discussed above, our observations are broadly consistent with the equilibrium model.

Overall, the plagioclase textures, the dependence of plagioclase composition on bulk chondrule composition, the similarities between measured and modeled plagioclase compositions, and the relative timing of crystallization of the plagioclase and Ca-rich pyroxene provide evidence that the plagioclase in these chondrules are primary igneous phases. Rhyolite-MELTS predicts a wide range in the equilibrium crystallization temperatures, 792-1317 °C. These are considered upper limits because of the effects of undercooling. The presence of primary plagioclase in chondrules has implications for chondrule formation that will be explored in the following section.

Implications for chondrule formation and chondrule forming conditions in the solar nebula

Chondrules are the most abundant constituent of the most common type of meteorite in our collections. Understanding chondrule formation is vital for understanding of what appears to have been a

ubiquitous process (or set of processes) in the solar nebula (Connolly and Jones 2016). However, the myriad petrologic and experimental constraints provided by chondrule chemistry and mineralogy have not yet stemmed the proliferation of chondrule formation models (Connolly and Desch 2004; Connolly and Jones 2016). Most of these constraints are based on the high-temperature primary minerals olivine and low-Ca pyroxene. Because plagioclase crystallizes at a lower temperature, it can put further constraints on the physical conditions and environment in which chondrules formed.

We observe a wide range of plagioclase compositions (An_{37} - An_{100}) in FeO-poor chondrules. Plagioclase has not previously been recognized in Type I porphyritic chondrules in OCs (Brearley and Jones 1998), but it has been noted as a common phase in Al-rich OC chondrules (Huss et al. 2001; Russell et al. 2000). Plagioclase in Al-rich chondrules has a range of compositions (An_{70} - An_{100}) and is commonly $\geq An_{90}$ (Huss et al. 2001). Aluminum-rich chondrules have a close affinity to Ca-Al-rich inclusions that are anorthite-bearing. Anorthite has also been described in Type I chondrules in various CCs (Brearley and Jones 1998). Approximately 10% of Type I chondrules in CO chondrites contain anorthite (Jones 1997; Wick and Jones 2012). Type I chondrules are the dominant chondrule type in CO chondrites, comprising ~85% of all chondrules compared to only ~20% of OC chondrules (Jones 2012). The implications of anorthite-bearing Type I chondrules in CO chondrites were explored experimentally by Wick and Jones (2012). They melted a Type I chondrule-like composition at 1500-1600 °C and cooled the chondrules in stages at rates between 1 °C and 25 °C per hour. They found that only the slowest cooling rate (1 °C/hour in the final cooling stage from 1000-800 °C) could nucleate anorthitic plagioclase. All experiments with faster cooling rates produced glass instead of crystalline plagioclase.

We observed Na-rich plagioclase (An_2 - An_{32}) in FeO-rich chondrules in Semarkona, which has not been widely recognized before (Brearley and Jones 1998; Jones 1990, 1996). This is not surprising due to the fine scale of the plagioclase laths observed in the chondrules of this study (e.g., Fig. 2b). Grossman and Brearley (2005) identified crystalline albite in Semarkona chondrules through TEM analysis. The recent availability of high resolution FEG-SEMs has allowed for more detailed petrologic studies of chondrules, revealing mineral phases and textures overlooked in previous studies.

The presence of plagioclase in Type II chondrules can also provide constraints on their cooling rates. Rocha and Jones (2012) used the inferred absence of plagioclase in Type IIA OC chondrules to experimentally constrain cooling rates in these chondrules. Using a relatively rapid constant cooling rate, 30 °C/hour, they reproduced plagioclase-free Type IIA textures. However, by reducing the final cooling rate to 1 °C/hour (950-900 °C) they crystallized plagioclase, but only when a Type IIAB-like texture developed. This plagioclase had a composition of An_{97} , closer to the composition expected in the Type I chondrules, which was the result of Na loss during the experiment. Because of the low Na content, these experiments are not perfectly analogous to the albite-bearing Type II chondrules we observe in Semarkona. Nucleation of alkali feldspar in anhydrous crystallization experiments is known to be extremely difficult (Smith and Brown 1988), and this is supported by the absence of plagioclase in typical chondrule analogue experiments that are cooled at rapid rates. However, the presence of albite growing from the chondrule exterior suggests that it might have been nucleated by dust impinging on the chondrule exterior after the melt was supercooled well below the equilibrium crystallization temperature (Connolly and Hewins 1995).

Baecker et al. (2017) uses zoning in low-Ca pyroxene from FeO-rich chondrules, like the albite-bearing Ch3 (Fig. 2b), to argue for multiple heating events and rapid cooling. In their model, each heating event re-melted the chondrule mesostasis glass, formed successive overgrowth layers on the low-Ca pyroxene grains, and then cooled rapidly. However, Jones (1996) describes the same zoning in low-Ca pyroxene as oscillatory zoning and attributes it to formation through disequilibrium kinetic effects at the mineral/melt boundary. Allègre et al. (1981) argues that oscillatory zoning in plagioclase only occurs during slow cooling to account for a near absence of such zoning in lab-grown plagioclase. The presence of albite in FeO-rich chondrules, the nucleation of which requires slow cooling rates, favors the interpretation of Jones (1996) that zoning in low-Ca pyroxene is oscillatory and not an overgrowth texture. Furthermore, Ohnensetter and Brown (1992) estimated the cooling rates inferred for oscillatory-zoned pyroxenes in a terrestrial boninite dyke to be 1-5 °C/hour, in agreement with the cooling rates that

nucleated plagioclase in the chondrule analog experiments (Rocha and Jones 2012; Wick and Jones 2012).

The presence of volatile elements, such as Na and K, in chondrules is a conundrum for chondrule forming scenarios. These elements should have rapidly diffused out of molten chondrules at the high temperatures and low ambient nebular pressure thought to be present during their formation (Yu and Hewins 1998; Yu et al. 2003) and then they could have recondensed back onto the chondrule during cooling (Lewis et al. 1993). Models show that the Na and K lost at liquidus temperatures can condense on the molten chondrule near the end of crystallization if the chondrule forming region had a dust to gas ratio much greater than solar (Ebel and Grossman 2000), resulting in high partial pressures of Na and K (Hewins et al. 2005). However, measurements of Na zoning in olivine are consistent with constant bulk Na during olivine crystallization (Alexander et al. 2008) suggesting high solid densities and Na retention even during the relatively slow cooling rates necessary to nucleate plagioclase. The presence of albite in chondrules supports the model of a Na-enriched atmosphere in the chondrule forming region(s) allowing for Na to be retained within the chondrules.

Secondary alteration of chondrule glass and feldspar

Semarkona has undergone a limited degree of aqueous alteration. Evidence for this includes the presence of phyllosilicates (Alexander et al. 1989; Grossman and Brearley 2005; Hutchison et al. 1987), carbonates (Alexander et al. 2015; Hutchison et al. 1987), carbide-magnetite assemblages (Krot et al. 1997), sulfide-magnetite assemblages (Huss 1979), altered chondrules (Hutchison et al. 1987; Rubin 2013), bleached chondrules (Grossman et al. 2000), and zoned chondrules (Grossman et al. 2002). Our observations of the dissolution of mesostasis glass, the presence of phyllosilicates in chondrules, and the alteration of primary igneous feldspar add to these arguments for fluid activity. Understanding whether feldspar grains are pristine or altered has important implications for early solar system chronology as determined by Al-Mg systematics.

Evidence for the presence of fluids in chondrule glass

Nearly all the plagioclase-bearing chondrules we examined show at least some porosity between plagioclase laths that we interpret as the dissolution of chondrule mesostasis glass by an aqueous fluid. The chondrules in Fig. 3 (Ch28, Ch23, and Ch20) show extensive dissolution of glass, while Ch3 and Ch36 in Fig. 2 have smaller patches of dissolved glass, typically along the chondrule perimeter (e.g., Fig. 2e). Large pores (>50 μm in diameter) are also present in several chondrules (e.g., Ch28) and are easily visible as black spots within chondrules on the thin section BSE map (Fig. 1). Ch28 has very large pores (up to 370 μm in diameter, Fig. 3a) although it is not clear if the large pores are inherent to the sample or a product of the sample preparation process (i.e., plucked metal grains). The FIB section of the zoned albite in Ch28 (Fig. 4a) shows pores between plagioclase laths as small as 20 nm.

Grossman et al. (2000) conducted a detailed study of bleached chondrules in Semarkona: these are fine-grained, cryptocrystalline and radiating pyroxene chondrules that have zones of dissolved mesostasis along their outer edges. They showed that these chondrules were affected by a parent body alteration process that preferentially dissolved the mesostasis without affecting the adjacent pyroxene. They noted that the mesostasis in porphyritic chondrules did not appear to be affected by the alteration process in the same way as the fine-grained chondrules and attributed this to either differences in mesostasis compositions or grain sizes between the various chondrule types.

The glass in cryptocrystalline and radiating pyroxene chondrules contains a high percentage of normative albite, whereas the glass in Type I chondrules is anorthitic and in Type II chondrules is rich in normative quartz (Grossman et al. 2000). However, we have shown that all the porphyritic chondrules we studied have varying amounts of dissolved mesostasis glass, some quite extensive (e.g., Ch23, Fig. 3d). This implies that mesostasis composition cannot be the determining factor for glass dissolution. Grossman et al. (2000) also pointed out that uniformly fine-grained chondrules contain more grain boundaries than the relatively coarse-grained porphyritic chondrules and thus more avenues for fluid to flow into and out of the chondrules from the matrix. In porphyritic chondrules, radial bleaching zones,

like those seen in uniformly fine-grained chondrules, are less likely to occur due to heterogeneous distributions of grain sizes and regions of mesostasis.

Phyllosilicates have been identified in Semarkona matrix and, like the bleached chondrules, imply alteration of primary phases by an aqueous fluid (Alexander et al. 1989; Hutchison et al. 1987). Hutchison et al. (1987) noted hydrous alteration of chondrule glass and Rubin (2013) illustrated an alteration front in the glass of a BO chondrule. Grossman et al. (2000) showed that bleached chondrules contain phyllosilicates that are compositionally distinct from those found in the matrix, and argued that they formed by the alteration of chondrule glass in the same event that dissolved some of the mesostasis glass. We observe phyllosilicates in place of mesostasis glass in Ch28 (Figs. 3b,4a) and Ch26 and in very minor amounts in Ch3 (Fig. 2c) that likely formed in a similar way. In these chondrules, the mesostasis glass between feldspar laths has both been dissolved, resulting in pores, and replaced by phyllosilicates (Fig. 4a).

Dobrică and Brearley (2016) investigated a fine-grained matrix inclusion in a Semarkona POP chondrule. They showed porosity associated with glass altered to phyllosilicates, like what we describe above. Clearly this mode of fluid alteration was widespread in Semarkona and resulted in the alteration of a range of chondrule types (and matrix), not just fine-grained, bleached chondrules. Grossman et al. (2000) noted that bleached chondrules were present in nearly all petrologic types and suggested that all OCs underwent fluid alteration of this sort before the onset of thermal metamorphism. It would be reasonable to extend this model to porphyritic chondrules as well.

Secondary alteration of primary plagioclase

Feldspar is nearly homogeneous in chondrules that either do not show the mesostasis alteration described above, or are minimally altered (e.g., Ch3 and Ch36, Table 1, Fig. 5). However, chondrules with extensively dissolved mesostasis glass or the presence of phyllosilicates show much more variation in their feldspar compositions. This variation in chondrule-wide plagioclase compositions is illustrated in Fig. 5. The vertical error bars represent one standard deviation about the mean An content measured for each chondrule and can be over 5 mol. % An. Variation is also seen within individual plagioclase laths that are present adjacent to regions of alteration. Plagioclase in Ch28 (Fig. 3b,4) and Ch23 (Fig. 3d) is irregularly zoned subparallel to the regions of dissolved chondrule mesostasis glass and, in the case of Ch28, glass alteration to phyllosilicates.

A FIB section (Fig. 4a) was prepared of a zoned plagioclase region in Ch28 (white line in Fig. 3b) to explore the zoning in more detail. A HAADF image of a representative area is shown in Fig. 4b and the corresponding EDS Ca K α map is shown in Fig. 5c. Zoning is observed in Al, Na, and Ca, but Ca shows the most heterogeneity and is likely responsible for the zoned appearance of the plagioclase grains in the BSE image (Fig. 3b). Calcium is variably zoned and predominantly absent from the outer 100-150 nm of the ~650 nm wide laths. There also appear to be enrichments of Ca on the border of the low-Ca outer zone as well as in the phyllosilicates themselves.

A similar zoning profile (Ca-rich core, Na-rich rim) is expected from normal igneous zoning, but several features are inconsistent with an igneous origin for the zoning in these grains. First, the Ca zoning shows considerable variation along the long axis of the grain and is not symmetric about the core (Fig. 5b). Second, the degree of Ca zoning appears to reflect proximity to areas of dissolved mesostasis glass or phyllosilicate growth. Third, plagioclase in chondrules from which the glass has not been dissolved does not show similar compositional zoning or widespread heterogeneity. Fourth, Ch3 has dominantly homogeneous albite (Fig. 2b) but zoned albite is only seen in regions of alteration (Fig. 2c). Clearly, plagioclase zoning in these chondrules is due to secondary processes and is not attributable to primary igneous growth.

Closely related to our observations of Ca-zoning in altered primary plagioclase, calcic plagioclase is replaced by more sodic compositions as the result of Na-metasomatism during metamorphism in higher petrologic type chondrites. In petrologic types 4 and 5, anorthitic plagioclase is affected by albitization, creating rims of nearly pure albite (Kovach and Jones 2010; Lewis and Jones 2016). Progressive metamorphism equilibrates plagioclase compositions to a uniform ~An₁₁ by petrologic type 6 (Kovach

and Jones 2010; Van Schmus and Wood 1967). The presence of alteration in Semarkona plagioclase grains possibly represents the first step in the feldspar equilibration process that was experienced in varying amounts by all ordinary chondrites.

Characteristics of the fluid environment

The alteration of mesostasis glass and primary plagioclase in Semarkona chondrules strongly argues for open system behavior between chondrules and the matrix and the transport of material into and out of chondrules by an aqueous fluid. The characteristics of this process are described at length by Grossman et al. (2000, 2002) in their studies of bleached and zoned chondrules and our observations generally agree with their conclusions. The bleaching process, removal of chondrule glass, results in depletions of Na, K, Sr, Si, and Al from the outer regions of the affected chondrules. The hydration and alteration of the remaining glass to phyllosilicates is associated with the introduction of Fe, Ni, halogens, and water (Grossman et al. 2000).

Complementary to the bleached chondrules, chondrule mesostases in many low-FeO chondrules display concentric chemical zoning with enrichments in Na, K, other moderately volatile elements, and water and depletions in Ca, Cr, and Ti (Grossman et al. 2002). We observe a similar pattern in the homogeneous anorthite-bearing BO chondrule Ch36 in which the CL image shows zoning of mesostasis glass from pale yellow in the center to bright yellow along the rim (Fig. 2f), a signature of Na enrichment in the rim noted by Grossman et al. (2002). The transfer of these elements by an aqueous fluid did not result in the devitrification of the chondrule glass nor the extensive leaching seen in bleached chondrules (Grossman et al. 2002).

Water in chondrites is commonly assumed to be derived from ices present during accretion. The ices melt and water flows through the permeable matrix and along grain boundaries in order to redistribute a variety of water soluble elements. However, the conditions of glass and plagioclase alteration were not severe enough to affect olivine or pyroxene. Grossman et al. (2000) argued that the alteration temperature may have been less than 100°C based on similarities to CC alteration assemblages. This is less than the maximum temperature of 260°C estimated by Alexander et al. (1989) based on the stability of the phyllosilicates found in the matrix. The dissolution of Si from the mesostasis glass implies a high pH (Alexander et al. 1954) and is consistent with the presence of calcite in Semarkona (Alexander et al. 2015). Incomplete and inconsistent alteration between chondrules, even of similar chemical compositions, implies a low water-rock ratio, the effects of which may be exaggerated by limited chondrule permeability.

Overall, the degree of aqueous alteration observed in Semarkona chondrules is not consistent between chondrules, from grain to grain within a chondrule, or within individual mineral grains. Limited fluid availability, variation in fluid permeability of the matrix and chondrules, and the wide variety of chondrule mesostasis compositions, some of which were more easily altered than others, likely gave rise to the complex pattern of alteration we now see.

Implication for Al-Mg dating of Semarkona chondrules and solar system chronology

High resolution chronology using short-lived radioactive isotopes is a powerful tool for understanding the relative order of events during a very important time in the history of the early solar system. The Al-Mg system is used for dating chondrules because they contain significant amounts of Al. Bulk chondrule compositions typically contain 1-5 wt.% Al_2O_3 , but can be >10 wt.% Al_2O_3 in Al-rich chondrules (Brearley and Jones 1998). Mesostasis glass and plagioclase are major hosts of Al in chondrules, although minor amounts are also present in Ca-rich pyroxene and spinel. As shown above, chondrule mesostasis glass in a significant number of Semarkona chondrules shows evidence of being dissolved and/or altered to phyllosilicates. Plagioclase also shows evidence for alteration through Na-Ca and Al-Si exchange. Therefore, it is important to evaluate what effects alteration may have had on measured Al-Mg ages.

Chondrules within Semarkona have been dated using Al-Mg systematics by a number of workers (Hutcheon and Hutchison 1989; Kita et al. 2000; Mishra and Goswami 2014; Mishra et al. 2010;

Mostefaoui et al. 2002; Rudraswami et al. 2008; Russell et al. 1997; Villeneuve et al. 2009). These studies report ages that range between 0.76 Ma and 3.07 Ma after CAI formation, a span of 2.3 million years. The wide range of ages has been explained as the period during which chondrules were formed (e.g., Villeneuve et al. 2009). However, the reported errors in many of the Semarkona measurements are broad (0.5-1 Ma) implying that the isochrons were defined through considerable scatter. Alexander and Ebel (2012) showed that the errors associated with Al-Mg systematics are consistent with a single formation age and that additional scatter is due to disturbance during parent body processing. Kita and Ushikubo (2012) also conclude that chondrules in each chondrite group formed over a short period of time, including those in Semarkona, based on their review of existing Al-Mg data.

Since we observe ubiquitous aqueous alteration of Al-bearing phases in Semarkona, we concur that it is likely that the Al-Mg systematics have been inconsistently disturbed by secondary processes on Semarkona's parent asteroid. This disturbance would generate large errors in the measured isochrons or may have reset the Al-Mg system in some chondrules altogether, yielding younger ages. Thus, the reported chondrule formation ages in Semarkona may record a combination of secondary aqueous alteration and primary chondrule formation. Furthermore, thermal modeling of OC asteroids, based on internal heating from the decay of ^{26}Al , is consistent with accretion 2.05-2.25 Ma after CAI formation (Blackburn et al. 2017), suggesting that chondrule ages younger than this were disturbed or reset.

In additional support of this argument, aqueous alteration in carbonaceous chondrites, measured by Mn-Cr dating of carbonates (Fujiya et al. 2012, 2013; Hoppe et al. 2007; Jilly et al. 2014; Lee et al. 2012; de Leuw et al. 2009; Petit et al. 2011), overlaps the formation period for Semarkona chondrules (between 0.4 Ma and 6.2 Ma after CAIs). However, it is important to note that the history of low temperature secondary processes on the ordinary and carbonaceous chondrite parent bodies are not necessarily identical.

These conclusions reinforce the need for high-resolution petrographic studies of chondritic materials prior to utilizing high precision analytical techniques on what is only assumed to be unaltered nebular material. Careful consideration needs to be made of the state of the major, and possibly minor, phases relevant to the technique. For Al-Mg, dissolution of chondrule mesostasis glass, alteration of primary plagioclase, formation of secondary minerals, like phyllosilicates, and zoning of volatile elements like Na within the chondrule glass would be reason to suspect a compromised system. For example, Mostefaoui et al. (2002) found a correlation between younger Al-Mg age and increasing bulk Na, Mn, and Cr abundances relative to Mg. These are elements shown by Grossman et al. (2002) to be zoned in Semarkona chondrules, the result of aqueous alteration.

Summary & Conclusions

We conducted a detailed study of plagioclase in Semarkona chondrules to characterize this mineral as a primary igneous phase and to understand how it might be affected by secondary processes such as aqueous alteration and thermal metamorphism. We found plagioclase with a wide range of compositions (An_{2-99}) was present within 18% of the chondrules in the thin section we studied. The plagioclase grains have lath-like morphologies consistent with growth from a melt. Plagioclase compositions are also directly related to the bulk composition of the chondrule: plagioclase in FeO-poor chondrules is more Ca-rich, and plagioclase in FeO-rich chondrules is more Na-rich. Experimental investigations into plagioclase growth in chondrules suggest plagioclase-bearing chondrules cooled extremely slowly as they approach the solidus (1 °C/hour for anorthitic plagioclase), so these slow cooling rates apparently apply to a high proportion of OC chondrules.

The aqueous alteration that is known to affect Semarkona mineralogy has also altered the texture and composition of primary plagioclase in many chondrules. This has led to zoning of Na and Ca in plagioclase grains and a general spread in the plagioclase compositions within altered chondrules. These effects are seen in association with the development of porosity from the dissolution of chondrule mesostasis glass and the alteration of glass to phyllosilicates. These features have been observed previously in bleached and zoned chondrules in Semarkona and imply a low temperature, high pH fluid at a low water-rock ratio (Alexander et al. 1954; Grossman et al. 2000, 2002). The pervasive nature of

alteration calls into question the reliability of Al-Mg systematics for understanding the chronology of chondrule formation, in cases where chondrules have undergone alteration of mesostasis glass and plagioclase.

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Figure Captions

Fig. 1. BSE mosaic of Semarkona thin section UNM 549. Plagioclase-bearing chondrules are circled in white. Numbered chondrules are referenced in the text, figures, and tables.

Fig. 2. Examples of albite- and anorthite-bearing chondrules with end-member plagioclase compositions. (a,b) BSE images of Ch3, a Type I POP chondrule with laths of albite (ab, An_2) in mesostasis glass (gl) between grains of olivine (ol), low-Ca pyroxene (px), and Ca-rich pyroxene (cpx). Inset in (b) shows CL image of the same region illustrating the bright blue luminescence of albite laths. (c) Region of Ch3 along the rim in which the albite laths are zoned and some of the glass is replaced by phyllosilicates (phy). (d,e) BSE images of Ch36, an FeO-poor BO chondrule with light grey mesostasis (ms) and laths of anorthite (an, An_{99}) between the olivine bars. Ca-rich pyroxene and glass occur interstitial to the anorthite. (f) CL image of the entire chondrule in which the anorthite luminesces light blue and the glass luminesces pale yellow in the center and bright yellow along the rim.

Fig. 3. Examples of chondrules with plagioclase of intermediate composition. Ch28 (a,b) is a Type II POP chondrule with large voids. Plagioclase (plg, An_{10}) in this chondrule is present as laths that are interstitial to grains olivine (ol), Ca-rich pyroxene (cpx), and minor sulfides (sul). The plagioclase is zoned and pores and phyllosilicates are present between the plagioclase laths. The white line shows the region from which a FIB section was made (see Fig. 4). Ch23 (c,d) is a Type I POP chondrule with plagioclase (An_{37}) interstitial to olivine, low-Ca pyroxene (px), and Ca-rich pyroxene. The mesostasis glass has been completely leached out leaving voids. Ch20 (e,f) is a Type I POP chondrule with plagioclase (An_{66}) interstitial to low-Ca pyroxene and some Ca-rich pyroxene. Smaller grains of Ca-rich pyroxene and glass are present in between the plagioclase laths as well as some areas of leached mesostasis glass that are replaced with void space.

Fig. 4. FIB section from Ch28 (see Fig. 3b). (a) HAADF image showing plagioclase (plg), Ca-rich pyroxene (cpx), and porous phyllosilicates (phy) interstitial to the plagioclase laths. Vertical banding is curtaining, a sample preparation artefact. (b) Close-up of the selected area in (a) illustrating zoning in the plagioclase laths and the relationship of zoning to grain boundaries, pores, and phyllosilicates. (c) Ca K α EDS image of the same region as (b) which illustrates the loss, and heterogeneous zoning, of Ca in the altered plagioclase.

Fig. 5. Compositions of plagioclase measured by EPMA. The range of measured plagioclase compositions in Semarkona chondrules is illustrated on the left. Each point represents the mean plagioclase composition in each chondrule. Error bars represent 1 standard deviation of the mean and the points are offset horizontally for ease of viewing. Individual analyses are plotted on a feldspar ternary on the right. The ternary is truncated at Or_{10} and the colors in the ternary correspond to those for the chondrule means on the left-hand side of the diagram.

Fig. 6. Results of equilibrium crystallization of chondrule bulk compositions in rhyolite-MELTS. Lines illustrate equilibrium plagioclase compositions with decreasing temperature (increasing crystallization). The average plagioclase composition measured in each chondrule is marked with a cross at the corresponding temperature. The plagioclase composition for Ch36 (An_{99}) is not on the plagioclase crystallization line, so the crystallization temperature of anorthite in the Fo-Di-An system (1317 °C) is plotted instead. Circles mark the temperatures at which Ca-rich pyroxene becomes stable. See text for details.

Supporting Information

Fig. S1. Data from EPMA maps of Ch3, Ch23, Ch20, and Ch36, used to determine bulk chondrule compositions. The anorthite content of primary plagioclase in these chondrules increases from left (An₂) to right (An₉₉). The first row shows BSE images for each chondrule. The second row shows phase maps highlighting the dominant phases of olivine (blue), low-Ca pyroxene (green), Ca-rich pyroxene (red), and mesostasis (white). Here, mesostasis consists of glass, plagioclase, and minor Ca-rich pyroxene. The third row shows atomic Mg# maps illustrating the increase in Mg# from left to right. Rows 4, 5, and 6 show quantitative wt. % oxide maps of Al₂O₃, CaO, and Na₂O, respectively.

Table S1. Individual EPMA analyses of feldspar in Semarkona chondrules.

Table 1. Average feldspar compositions, ordered by increasing An content.

	Chondrule 3		Chondrule 28		Chondrule 10		Chondrule 33		Chondrule 23		Chondrule 47		Chondrule 20	
	wt. %	1σ	wt. %	1σ	wt. %	1σ	wt. %	1σ	wt. %	1σ	wt. %	1σ	wt. %	1σ
SiO ₂	69.4	0.9	65.8	2.1	62.2	2.5	60.4	0.7	61.7	1.2	57.2	1.1	53.1	0.9
Al ₂ O ₃	18.3	0.6	20.4	0.8	20.4	1.8	23.0	1.1	22.4	0.6	26.2	1.1	27.6	1.0
Cr ₂ O ₃	0.01	0.01	0.02	0.01	0.04	0.02	0.02	0.01	0.08	0.05	0.04	0.04	0.05	0.03
FeO	1.29	0.55	1.33	0.74	2.13	0.15	1.92	1.08	1.34	0.20	0.58	0.24	0.50	0.27
MnO	0.04	0.02	0.04	0.02	0.03	0.01	0.06	0.04	0.18	0.07	0.07	0.06	0.14	0.04
MgO	0.23	0.06	0.31	0.40	1.07	0.06	0.33	0.32	1.42	0.71	0.51	0.13	1.31	0.49
CaO	0.41	0.17	2.15	1.15	5.71	1.59	6.61	0.35	7.03	0.82	9.50	0.82	13.2	0.7
Na ₂ O	11.3	0.6	10.3	0.7	8.50	1.20	7.50	0.29	6.48	0.40	6.09	0.36	3.73	0.24
K ₂ O	0.43	0.10	0.34	0.11	0.19	0.03	0.26	0.06	0.33	0.04	0.15	0.04	0.08	0.03
Total	101.4	1.5	100.8	0.9	100.2	1.1	100.2	0.7	101.0	0.7	100.3	0.8	99.7	1.0
<i>formula based on 8 oxygens</i>														
Si	3.01	0.01	2.89	0.06	2.79	0.09	2.71	0.02	2.73	0.05	2.57	0.05	2.42	0.04
Al	0.94	0.02	1.06	0.05	1.08	0.10	1.22	0.05	1.17	0.03	1.38	0.05	1.48	0.05
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.05	0.02	0.05	0.03	0.08	0.01	0.07	0.04	0.05	0.01	0.02	0.01	0.02	0.01
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
Mg	0.01	0.00	0.02	0.03	0.07	0.01	0.02	0.02	0.09	0.05	0.03	0.01	0.09	0.03
Ca	0.02	0.01	0.10	0.05	0.27	0.08	0.32	0.02	0.33	0.04	0.46	0.04	0.64	0.03
Na	0.95	0.03	0.88	0.05	0.74	0.11	0.65	0.02	0.56	0.04	0.53	0.03	0.33	0.02
K	0.02	0.01	0.02	0.01	0.01	0.00	0.01	0.00	0.02	0.00	0.01	0.00	0.00	0.00
Total	5.01	0.02	5.03	0.02	5.05	0.03	5.01	0.02	4.97	0.04	5.01	0.01	5.00	0.01
An	1.9	0.8	10.1	5.4	26.9	8.3	32.3	1.6	36.7	3.2	45.9	3.5	65.8	2.1
Ab	95.7	0.7	88.0	5.1	72.0	8.2	66.2	1.6	61.2	3.1	53.3	3.3	33.7	2.0
Or	2.4	0.6	1.9	0.6	1.0	0.1	1.5	0.4	2.1	0.4	0.9	0.3	0.5	0.2
n ¹	4		11		3		8		3		8		5	

¹ n = number of analyses

Table 1. (Continued). Average feldspar compositions, ordered by increasing An content.

	Chondrule 41		Chondrule 26		Chondrule 30		Chondrule 1		Chondrule 68		Chondrule 36		Chondrule 22	
	wt. %	1 σ	wt. %	1 σ	wt. %	1 σ	wt. %	1 σ	wt. %	1 σ	wt. %	1 σ	wt. %	1 σ
SiO ₂	52.6	1.3	46.2	1.1	48.8	0.8	49.9	0.6	44.3	1.1	48.3	0.7	44.8	0.6
Al ₂ O ₃	28.5	1.0	32.6	2.2	30.4	1.5	30.9	0.8	34.0	1.9	30.0	1.3	35.5	0.6
Cr ₂ O ₃	0.04	0.02	0.03	0.02	0.06	0.03	0.03	0.03	0.05	0.06	0.02	0.02	0.02	0.02
FeO	1.03	0.59	0.90	0.92	0.49	0.25	0.43	0.20	0.17	0.14	0.20	0.15	1.03	0.19
MnO	0.10	0.06	0.06	0.04	0.05	0.05	0.02	0.02	0.03	0.03	0.01	0.01	0.03	0.02
MgO	0.99	0.37	1.64	1.17	1.83	1.08	1.82	0.68	1.20	1.26	2.19	0.37	0.73	0.20
CaO	13.3	1.0	17.8	1.3	17.6	0.5	18.3	0.3	19.5	0.4	19.4	0.3	19.8	0.2
Na ₂ O	3.61	0.36	0.84	0.42	0.60	0.17	0.22	0.09	0.22	0.07	0.10	0.07	0.04	0.03
K ₂ O	0.09	0.03	0.07	0.04	0.07	0.06	0.03	0.01	0.04	0.02	0.03	0.02	0.04	0.01
Total	100.2	0.9	100.2	1.3	99.9	0.8	101.7	0.7	99.4	0.6	100.3	0.7	102.1	0.3
<i>formula based on 8 oxygens</i>														
Si	2.39	0.05	2.13	0.05	2.24	0.04	2.25	0.02	2.06	0.05	2.22	0.04	2.04	0.03
Al	1.53	0.05	1.77	0.10	1.65	0.07	1.64	0.04	1.87	0.11	1.62	0.06	1.91	0.03
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.04	0.02	0.03	0.04	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.04	0.01
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.07	0.03	0.11	0.08	0.13	0.07	0.12	0.05	0.08	0.09	0.15	0.03	0.05	0.01
Ca	0.65	0.05	0.88	0.05	0.86	0.02	0.89	0.01	0.97	0.02	0.96	0.01	0.97	0.01
Na	0.32	0.03	0.08	0.04	0.05	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.00	0.00
K	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	5.00	0.02	5.02	0.02	4.96	0.03	4.94	0.02	5.02	0.02	4.97	0.01	5.01	0.01
An	66.6	4.0	91.7	4.3	93.8	1.7	97.7	0.8	97.8	0.8	98.9	0.7	99.5	0.2
Ab	32.8	3.8	7.9	4.1	5.7	1.5	2.1	0.8	2.0	0.7	1.0	0.6	0.3	0.3
Or	0.6	0.2	0.4	0.3	0.4	0.4	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.0
n ¹	3		5		6		16		7		15		4	

¹ n = number of analyses

Table 2. Bulk silicate compositions of selected chondrules.

	Ch3	Ch23	Ch20	Ch36
	Type II	Type I	Type I	BO
SiO ₂	45.4	52.1	53.9	43.4
Al ₂ O ₃	2.08	2.44	2.50	6.93
Cr ₂ O ₃	0.63	0.78	0.71	0.25
FeO	16.3	5.31	3.43	1.76
MgO	32.7	36.7	37.1	41.7
CaO	1.58	1.99	1.91	5.65
Na ₂ O	1.21	0.59	0.40	0.28
K ₂ O	0.13	0.08	0.07	0.07
Total	100.0	100.0	100.0	100.0
Mg# ¹	66.8	87.4	91.5	95.9
Mg# ²	78.2	92.5	95.1	97.7
Na/Al ³	1.1	0.5	0.3	0.1
Ca/Al ³	1.4	1.5	1.4	1.5
An ⁴	1.9	36.7	65.8	98.9
Liquidus ⁵	1672°C	1688°C	1685°C	1744°C
Modal mineral abundances ⁶				
Olivine	63%	27%	19%	66%
Low-Ca pyx	13%	57%	66%	0%
Ca-rich pyx	14%	7%	7%	2%
Mesostasis ⁷	10%	9%	8%	32%

¹ Mg# = Mg/(Mg+Fe)x100, wt. % oxide² Mg# = Mg/(Mg+Fe)x100, atomic³ atomic⁴ average plagioclase compositions, from Table 1⁵ estimated using Rhyolite-MELTS⁶ estimated from EPMA maps (see Fig. S1)⁷ includes glass, plagioclase, and minor Ca-rich pyroxene

Chondrule 3

Chondrule 36

Chondrule 28

Chondrule 23

Chondrule 20