Pyroxene-selective impact smelting in ureilites

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Abstract

A characteristic feature of ureilite meteorites is reduction of FeO. But the reduction is usually confined to the rims of olivine. In the LAR 04315, LAP 03587 and Almahata Sitta ureilites, pyroxene was extensively reduced by impact smelting. In LAR 04315, the impact caused nearly all of the original pigeonite to melt or otherwise become sufficiently structurally compromised to allow smelting, and yet a minor proportion of the pyroxene escaped smelting and survived with its original composition (En74.1Wo10.2). Olivine mosaicism confirms that LAR 04315 experienced a major shock event. The smelted pyroxenes also show a distinctive patchiness in their interference colors (although each grain’s basic optical continuity, often including twinning, is still discernible). They also have reduced compositions, are ubiquitously porous (~15%), and contain sprinklings of Fe-metal and felsic glass. For the most part the olivine underwent only very slight reduction. Much of the (small) pyroxene component of LAP 03587 shows the same oddly porous texture. LAR 04315 also contains large traces of silica and felsic glass (with a typical composition of, in wt%, 61 SiO₂, 23 Al₂O₃, 11 CaO, 3.7 Na₂O) glass; these two phases together form selvages that line the walls of many of the largest voids in the rock. Silica is a by-product of pyroxene smelting. The felsic glass probably derives largely from interstitial basaltic melt that predated the impact. However, the comparatively stiff surrounding/included silica may have promoted unusually high melt retention within LAR 04315 through the smelting episode (one aspect of which was a major stream-out, through the same large voids, of CO₂ gas). The impact-smelted pyroxene of LAP 03587 is enigmatic because this ureilite also features little-shocked euhedral graphite laths and no olivine mosaicism. The fine-grained ureiliteic component of Almahata Sitta appears to have likewise formed by impact smelting, but with more extensive melting of pyroxene (especially a Ca-rich pyroxene component), more pulverization and melting of olivine, and more displacement of both. However, in places the original coarse-equant ureilite texture is still discernible in relict form. Ordinarily, an impact shock melts olivine before, or at least no later than, pyroxene. But in the case of LAR 04315 and LAP 03587, the great shock event evidently occurred when the material was already anatectic or very nearly so; and thus the difference in melting temperature between pyroxene and olivine, ~300 degrees lower for pyroxene, was decisive. If literature inferences of extremely fast cooling rates, implying shallow burial depths, are accurate, the proportion of CO₂ gas generated by ureilite smelting exceeded by a very large factor (of order 10³ but possibly much greater) the volume represented as porosity in the final ureilites. The outflow of so much gas may have, by near-surface explosive expansion and jetting, enhanced the thoroughness of the impact-triggered catastrophic impact disruption of the parent asteroid.

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1. INTRODUCTION

Ureilites are extremely depleted asteroidal-mantle petrologicites, typically containing about 2/3 olivine, 25% pyroxene (mainly pigeonite), and generally no observable feldspar. As reviewed by Goodrich et al. (2004), the number of ureilites has reached well over 100, qualifying this distinctive group as the second most numerous variety of achondrite (only HEDs are more common). Ureilites show considerable diversity in terms of their modal proportions of olivine, pigeonite, orthopyroxene and augite, and in the compositions of these silicates (e.g., olivine ranges from Fo75 to Fo90); and yet they are remarkably consistent in...
several important respects. Almost every ureilite contains an important proportion (average 3 wt%) of carbon, mostly as either amorphous “C-matrix” or, in some of the lowest-shock ureilites, graphite. The rims of ureilite olivines show distinctive indications of FeO reduction: tiny inclusions of Fe-metal scattered amidst olivine that is reversely zoned toward pure Mg-olivine. In contrast, the mafic-silicate cores in any individual monomict ureilite are remarkably uniform in composition. Nearly all ureilites exhibit a remarkably step-wise cooling history: slow at first, but very rapid later (Miyamoto et al., 1985).

Takeda (1987) was the first to propose that ureilites formed as asteroidal mantle residues, contrary to the once-popular view (e.g., Berkley et al., 1980; Goodrich et al., 1987) that they originated as igneous cumulates. Today, largely in consideration of the great oxygen-isotopic diversity among ureilites (Clayton and Mayeda, 1988), there is a general consensus (e.g., Warren and Kalleneyn, 1992; Scott et al., 1993; Singletary and Grove, 2003; Goodrich et al., 2004; Kita et al., 2004; Warren and Huber, 2006b) that most ureilites formed as mantle residues. Still, the role of smelting (“the chemical reduction of a metal from its ore by a process usually involving fusion” — Thrush, 1968) in ureilite petrogenesis remains controversial. Many authors argue that smelting affected ureilites from an early stage of their igneous evolution, and engendered the wide range of ureilite mafic-silicate core compositions (e.g., Singletary and Grove, 2003; Goodrich et al., 2004; Wilson et al., 2008). A contrasting interpretation holds that smelting occurred almost exclusively as a short-lived disequilibrium process which left the silicate-grain cores essentially unaltered. The presumed trigger for both the abortive smelting and the rapid cooling that limited it to the olivine rims was a large impact that disrupted the preheated, anatectic parent asteroid(s), with the ordinary mechanical-disruptive effect of impact greatly amplified by rapid production, within the hot, fractured mantle, of copious CO₂ gas as a by-product of smelting (Warren and Kalleneyn, 1992; Warren and Huber, 2006b; cf. Scott et al., 1993; Goodrich et al., 2004, and more elaborately Downes et al., 2008, have argued for derivation from a single asteroid). As noted by Warren and Huber (2006b), this process was not in a strict sense “smelting,” because the materials were cooling, not melting, as the reduction of the olivine rims took place.

The Larkman Nunatak (LAR) 04315 ureilite described in this paper (and preliminarily by Warren and Rubin, 2006) represents an exceptional case of extensive smelting (sensu stricto) as the result of intense shock, including pigeonite-localized shock melting, of an otherwise normal ureilite. One of this meteorite’s most distinctive features is unusual porosity within the altered pyroxenes, presumably produced by smelting (yielding CO₂ gas). However, in contrast to the limited reduction of olivine rims in other ureilites, reduction in LAR 04315 primarily affected shock-melted pyroxene. Although impact smelting is exemplified by LAR 04315, we also describe similar manifestations within a relatively low-shock ureilite, LaPaz Icefield (LAP) 03587; and in the Almahata Sitta ureilite, which was tracked, as asteroid TC₃, on its approach to Earth (Jenniskens et al., 2009). Pyroxene-selective impact smelting probably accounts for the reported characteristics of several other Antarctic ureilites (Saito and Takeda, 1990) and may have also occurred in the very recently discovered porous ureilite, Jiddat al Harasis 422 (Janots et al., 2009). Impact-smelted ureilites afford new insight into the evolution, and especially the probable catastrophic disruption, of the ureilite asteroid(s).

2. METHODS

Backscattered electron (BSE) and secondary-electron images were acquired on a LEO 1430 SEM and a JEOL JXA-8200 electron probe. Mineral compositions were determined using wavelength-dispersive detectors on the JXA-8200. In general, analyses were run at an accelerating voltage of 15 KV, with focused beam and count durations of 15–20 s. However, for volatilization-prone phases (alkali feldspars and glasses) currents as low as 3 nA, beam diameters as wide as 3 μm, along with ~0.5 times shorter count times, were employed. Semiquantitative analyses, a few of which were never superseded by quantitative electron-probe analyses, were obtained using an EDAX system on the SEM. In addition, bulk compositional data for three splits derived from a single 1.27-g chip of LAR 04315 were obtained using the INAA technique of Warren et al. (2006).

3. EVIDENCE FOR IMPACT SMELTING OF PYROXENE

3.1. Exemplary LAR 04315

LAR 04315 is a 1.165 kg ureilite that was recognized as texturally anomalous by McCoy (2005). We have studied two thin sections, LAR 04315.20 and LAR 04315.21, each ~1.1 cm². Modal analysis (1700 points from LAR 04315.20 and 2700 from LAR 04315.21) indicates that, discounting porosity, the meteorite consists of 47 vol% olivine, 40 vol% pyroxene, 9.4 vol% Fe-oxides (weathering products such as limonite derived, judging from their consistently interstitial context in relation to the silicates, from a combination of Fe-metal, Fe-sulfide and possibly a carbon phase), 2.2 vol% Fe-metal, 0.95 vol% sulfoxides, 0.26 vol% of low-reflectance silicate phases, probably mostly felsic-silicic glass and silica (see below), plus a trace of Cr-spinel. The coarsest Fe-metals and Fe-sulfides occur as grains (Fe-metal up to 0.25 mm long: McCoy, 2005) at interstices and along boundaries between apparent individual silicate grains of the pre-shock peridotite.

It is difficult to reconstruct the unweathered Fe-metal and sulfide abundances, but they were surely considerably higher than the present abundances. Contextual relationships (adjacent grains) allow us to estimate that for ~30% of the Fe-oxides the parent phase was probably Fe-metal, while for 13% it was probably sulfide. For the other 57%, contextual relationships provide little or no hint as to the oxide’s parent phase. But probably roughly half of the total Fe-oxide (i.e., 4.7 vol% of the rock) is weathered Fe-metal; the rest is weathered sulfide. To complete the modal reconstruction, we need to convert from vol% Fe-oxide back to
vol% of Fe-metal (or Fe-dominated sulfide). If we assume that the Fe-oxides are OH-rich and somewhat porous, and thus average roughly $3000 \text{ kg m}^{-3}$, then production of these oxides would inflate the original volumes by a factor of $2.6 \times$ starting from Fe-metal, or $1.6 \times$ starting from FeS. Our reconstruction thus implies that $\sim 1.8 \text{ vol}\%$ Fe-metal and $\sim 3 \text{ vol}\%$ Fe-sulfide need to be added to the mode, while $9.4 \text{ vol}\%$ Fe-oxide needs to be deleted. After renormalization of all values to yield a sum of 100%, the reconstructed mode becomes 50% olivine, 42 vol% pyroxene, $\sim 4 \text{ vol}\%$ Fe-metal, $\sim 4 \text{ vol}\%$ sulfide, roughly 0.28 vol% low-reflectance silicate phases, and a trace of Cr-spinel. Although the preterrestrial Fe-metal abundance (which figures prominently in our discussion below) is uncertain, 3 vol% seems a very safe lower limit.

The preterrestrial porosity, a distinctive feature of this ureilite (Figs. 1–5), is mainly concentrated within expanses of pyroxene (i.e., former individual pyroxene grains, in the pre-shock ureilite). Including this porosity and minor included (porosity-associated) opaques, these relict pyroxene grains constitute $\sim 50 \text{ vol}\%$ of the sample. Within them, average porosity is variable but averages $\sim 15 \text{ vol}\%$; i.e., 8% of the overall section area. In the meteorite’s present state an additional 5 vol% consists of elongate voids located along boundaries between the silicates (i.e., associated with the coarsest Fe-metal and Fe-sulfide, and Fe-oxide weathering products). Some of this grain-boundary porosity probably formed by a combination of weathering and (less importantly) plucking during section preparation. However, for the most part these large, interstitial-elongate pores appear to be preterrestrial dilated/flushed spaces, based on the common occurrence of delicate selvages of felsic glass that appear to have once lined the walls of the pores (Figs. 4 and 5 show some examples). Overall, the preterrestrial porosity was probably between 9% and 12%.

The original, pre-shock configuration of the silicate grains is easily discernible, and it was the typical equigranular texture of ureilites, with olivines and pyroxenes both up to 3 mm in length, but more typically 1–2 mm across (see Fig. EA-1 in the Electronic Annex to this paper). Shock...
metamorphism altered the olivines and pyroxenes in very different ways. The olivines now consist of mosaics of small (usually \(<0.5\) mm, typically of order 0.1 mm, across) often angular pieces (Fig. 6; cf. the initial description of LAR 04315: McCoy, 2005), indicating that they were strongly shocked, shattered, and subsequently welded together by an annealing process. Mosaicized olivine is typical of highly shocked ureilites such as Goalpara and ALH 81101 (Berkley et al., 1980; Berkley, 1986; cf. Rubin, 2006; and Mittlefehldt et al., 1998, who cite 5 additional examples).

In terms of porosity and general texture, two distinct types of pyroxene are readily observable. A few widely scattered patches, constituting less than 1% of the total pyroxene, have sharp optical features (birefringence, also rare cleavages) and are free of all pores greater than about 2 \(\mu\)m across (Fig. 2). By far the largest such patch is a near-conterminous zone of \(\sim0.9\times0.7\) mm (Fig. 2, top). Although, for simplicity, we refer to these isolated remnants as intact, even within them the submicrometer porosity is generally 2–3% (Fig. 3). Patches completely free (\(<1\)% of submicrometer porosity are only a minor subvolume of what we call “intact” pyroxene. In shape, the submicrometer pores of the “intact” pyroxenes tend to be nearly round.

Compositionally (Fig. 7), the intact pyroxenes form a tight cluster in the usual fashion of ureilite pigeonites (e.g., Goodrich et al., 1987) at \(\sim\text{En}_{74.1}\text{Wo}_{10.2}\) (Table 1); it is an analytical challenge to resolve any significant variation. The boundaries of the intact patches tend to be wavy, and vary (even from side to side of the same intact patch) between sharp and gradational.

The other, far more prevalent type of LAR 04315 pyroxene features the aforementioned \(\sim15\) vol% porosity in a distinctive vermiculate form (Fig. 2). The vermicular pores are generally \(\sim10\) \(\mu\)m in diameter, and thus when sliced for a thin section are typically about 1/4 as deep as the thickness of the thin section. They often appear light in secondary-electron SEM images, but always appear dark in backscattered electron images and generally also in optical-light images. From 2-dimensional slices the total lengths of these tubular pores are difficult to assess, but most appear curvylongate, with apparent maximum dimension of 30–40 \(\mu\)m. Compositionally, this porous variety of pyroxene is diverse...
but consistently higher-mg than the intact type (Fig. 7), presumably as a result of smelting (kinetics and local chemical gradients apparently caused the second-generation, FeO-depleted pyroxenes to nucleate with diverse Ca contents). The vermicular pores may not be completely empty. In X-ray maps, they show locally higher Ca, Mg and O than the larger, interstitial voids. However, this may merely be an artifact related to the vermicular pores’ frequently shallow depth. The common, porous type of LAR 04315 pyroxene also contains a smattering of Fe-metals, usually <10 μm across (e.g., Figs. 2 and 5), and similar-sized patches of Si-rich glass.

This prevalent, 15%-porous (smelted) type of LAR 04315 pyroxene was not completely disordered by shock melting. After the impact, the grains consisted recovered into birefringent and optically near-continuous crystals (Figs. 1b, and 2a and c). The recovery was not complete (optical continuity is far from perfect), but it is nonetheless obvious within each and every former pigeonite crystal. In the rare areas where isolated patches of intact pigeonite survived, the surrounding smelted portion of the same grain consistently shows interference color close to that of the intact remnant. Twin boundaries manifest as sharp, distinct planes (Fig. 1b). These coarse twins probably developed during rapid cooling, as the initial post-shock crystals transformed from protoenstatite to pigeonite.

The most obvious effect of shock on the olivines was mosaicism. Olivine mosaic tiles show a loose tendency to overlap being smaller near rims (of the original large olivine grains) and larger near cores. As usual with ureilite olivines, the (original) rim areas are exceptionally magnesian as a result of reduction (e.g., darkening of the olivine near the lower left corner of Fig. 6). In some areas of the approximate (original) rims, clusters of small, reduced and often rounded olivine remnants are set amidst interstitial pyroxene, mostly of relatively high-Ca, magnesian (subcalcic diopside) composition, and/or glass of that approximate composition (Figs. 8 and 9). Our informal term for this phenomenon is “olivine microporphyrity” texture. Larger, interior mosaic tiles are commonly surrounded by a “necklace” of minute (of order 1 μm) opaques, probably mostly Fe-metal with lesser Fe-sulfide (Fig. 6). At least some of these Fe-metals (those distributed in long quasi-circular arcs unlikely to represent injections) probably formed by reduction of olivine FeO; ultra-high-contrast BSE imagery suggests subtle compositional variation between adjacent large interior tiles (Fig. 6).

In LAR 04315, most of the olivine appears to have undergone only limited reduction. Ureilites in general feature an excellent correlation between core (unreduced) olivine mg and low-Ca pyroxene mg (Fig. 10). The tight compositional clustering for the structurally “intact” type of LAR 04315 pigeonite (from four separate original grains) suggests this composition is unaltered pigeonite.

Based on the general ureilite correlation (Fig. 10) the olivine that coexisted with this pigeonite was originally very close to (most likely within 1 mol% of) Fo81. The observed compositions for (original) core-portion olivines cluster tightly at Fo81; so the extent of reduction, apart from (original) rim materials, appears to have raised the core olivine mg by only ~1 mol%, and certainly less than 4 mol%.

The pyroxene Fe/Mg vs. Fe/Mg trend (Fig. 12) is to first approximation consistent with simple loss (reduction) of FeO with negligible reduction of MnO; i.e., the data distribute close to a line between the intact pigeonite composition and the origin. There is a slight tendency for high-Ca varieties of reduced pyroxene to have lower Fe/Mn than their lower-Ca counterparts. Curiously, the trend of the reduced compositions extrapolates slightly to the high-Fe/Mn side of the intact composition. The pyroxene Fe/Mg vs. Cr/Mg trend (Fig. 13) indicates that Cr was also lost by reduction. On this diagram, pure Fe loss would drive the compositions, as they diverged from the intact pigeonite, horizontally toward the left. The actual data instead trend downward in Cr/Mg, although the trend is complicated by a strong tendency for high-Ca varieties of reduced pyroxene to have higher Cr/Mg than their lower-Ca counterparts.

As shown on the pyroxene quadrilateral (Fig. 7), apart from the very minor intact and near-intact patches, the final pyroxenes have mg consistently >87 mol%. In the data set shown in our figures (e.g., Fig. 7), extreme high-mg and Ca-rich compositions are, along with intact patches, surely overrepresented, as we have sought to characterize the full compositional diversity engendered by the smelting process. McCoy (2005) found that the pyroxene is “dominantly” Fs7–9Wo7–9; i.e., pigeonitic with mg ~90. Assuming (a) that the pre-shock peridotite had negligible high-Ca pyroxene, (b) that the average composition for the final, mostly smelted pyroxene is near to a line from the Fs apex (Fig. 7), and (c) that its mg is ~89 mol%, we infer the average final composition to be En0.05Fs10.56Wo1. Thus, the pyroxene FeO content has been reduced from an original 10.2 to
Translated from pyroxene into whole-rock composition, this FeO reduction is ~1.6 wt% of the whole rock. At the same time, FeO was also undergoing reduction within the LAR 04315 olivine. Reduction was minor (leading to ~1 mol% increase in Fo) in regions of the original-grain cores, but extensive (locally all the way to Fo90) in the original-grain rims. Assuming that 80–90% of the olivine is core material little-modified by reduction (if mg increased from Fo81 to Fo82, the implied FeO reduction amounted to ~0.9 wt% of this olivine, i.e., from ~17.9 to 17.0 wt%), and that on average the rim olivine (10–20% of the total) was reduced to ~Fo91, we estimate as a rough average for the total LAR 04315 complement of olivine an extent of FeO reduction that amounts to ~2.0 wt% of the olivine (from ~17.9 to 15.8 wt%), or ~1.1 wt% of the whole rock.

Probably there was also finite reduction of FeO from Cr-spinel (cf. Warren, 2004). In total, the textural and mineral compositional observations suggest that FeO constituting roughly 3 wt%, or as a fairly conservative lower limit 2.5 wt%, of the original rock was reduced to Fe-metal. Indeed, this ureilite is uncommonly rich in Fe-metal. The modal abundance of ~4 vol% translates into 9 wt%, 1.5 times the highest known precedent among ureilites (5.9 wt% in Goalpara: Wiik, 1972).

The most common occurrence of glass in LAR 04315, apart from minute patches within smelted pyroxene, is as a thin selvage, often interstitial to a silica phase, on the rim of coarse olivine or pyroxene grains. As suggested by Figs. 4 and 5, and EA-2, these selvages usually occur where the outward (in relation to the coarse mafic silicate) side of the selvage is a large elongate pore; possibly a former narrow space between grains that has been dilated by gas expansion during smelting. In these selvages the innermost grains of the silica phase, where silica more or less continuously coats the complexly altered rim of a coarse mafic silicate, typically have an elongate, vermicular appearance, with apparent dimensions of order 100 μm, or even longer (Figs. 4 and 5, and EA-2). Further out, where the silica phase tends to be embedded in a comparable volume of felsic glass, the silica grains appear (at least in 2-dimensional thin section views) as shorter, more equidimensional ovoids (Fig. 4). The silica phase generally contains <2 wt% Al2O3 (Table 1).

The felsic glasses of LAR 04315 are remarkably diverse in composition (Fig. 11), probably because a complex mix
Fig. 5. BSE image of LAR 04315,20, showing selvages developed along the interfaces between large, tubular pores and large grains of both olivine (bottom and right edges of the view) and impact-smelted pigeonite (upper left). The field of view is \( \sim 480 \times 360 \) µm. For most of their length, the selvages here are dominated by silica (darkest grey). In lower left (10–80 µm to the left of the large white opaque), the silica is intergrown with felsic (\( \sim 21\text{ wt}\% \text{ Al}_2\text{O}_3 \)) glass, which is a lighter grey. Glass of similar composition (18 wt% Al2O3) is also present within the impact-smelted pigeonite. Farther from the central void channel, the extended selvages consist of a complex variety of high-mg pyroxenes and glasses (cf. Fig. 4). Note toward lower right corner that a thin septum of selvage-silica separates the long, sausage-shaped, vertically aligned void from the similarly broad, near-round void to its left.

Fig. 6. Typical olivine mosaicism in LAR 04315,21. The larger, cross-polarized light view is 800 \( \times \) 600 µm. The BSE image (left; likewise 600 µm from top to bottom) shows that some individual mosaic tiles in the interior of the olivine have undergone perceptible reduction (manifested by the relatively darker grey of the central mosaic tile). However, the difference is so slight it cannot be detected by electron-probe analysis (with normal count duration, beam current, etc., settings).
of disequilibrium processes led to their origin. Al₂O₃ is as high as 25 wt%, and shows a strong inverse correlation with Na₂O (Fig. 11). Three of our analyses represent a round (d = 8 μm) blister-like feature (Fig. EA-3) within the rim of an olivine (the blister is surrounded to a distance of ~20 μm by pure, albeit reduced, olivine, and is 40–50 μm from the typically complex selvage at the rim of the olivine). Possibly as an original characteristic, or perhaps due to late reaction with the enclosing olivine, this glass has a distinctively Al-poor and yet CaO-rich composition (Fig. 11). Glasses deep within grains of smelted pyroxene have moderate Al₂O₃ but high SiO₂ and Na₂O (Fig. EA-4).

The glass-rich region shown in Fig. 8 is unique in that the glass + silica texture, usually found as a selvage between a large mafic silicate grain and a comparably large pore, is here found spanning the space between the rims (albeit highly modified) of two olivine grains. This locale appears to represent an exceptional clotting of the terminal-stage melt (i.e., the melt was not blown out through the dilated space between grains). Compositionally, the glasses here tend to be unusually Na-poor compared to other selvage glasses (Fig. 11).

The metals of LAR 04315 are also compositionally diverse (Table 3, and Figs. 14 and EA-5). The diversity in Si is especially interesting, because the partitioning of Si into Fe-metal (i.e., the reduction of SiO₂ into metallic Si) is a strong function of /O₂ (Ziegler et al., 2009). Thus, in the extremely reduced enstatite (E) chondritic meteorites, Si contents in metals are typically 0.2–2.0 wt% in EL and 2–4 wt% in EH (Zhang et al., 1995; these authors also noted that Si content tended to increase as the E chondritic metals were altered by thermal and impact metamorphism). Most ureilite metals contain <0.4 wt% Si (Goodrich et al., 2009), but several metals in ALH 78019 have 2.8–2.9 wt% (Berkley and Jones, 1982). Paradoxically, in LAR 04315 the lowest Si contents are found for the metals most obviously affected by smelting; i.e., metals that are deeply embedded within pyroxene (and thus probably formed primarily by smelting of pyroxene FeO). The large, elongate metal grains sited in the interstitial gaps between the original coarse mafic silicates have the highest Si, at 2.1–2.6 wt%, comparable to the metals of extremely reduced EH chondrites (Fig. 14). A small ovoid (d ~ 20 μm) of metal within one of the felsic–silicic selvages yielded two analyses with ~2.0 wt% Si. Four small (roughly 5 μm) metal grains in one of the largest regions of “olivine microphorphy” texture (i.e., where shattered remnants from the rim of an original-coarse olivine have been rounded and reduced to near-pure forsterite by reaction with interstitial, compositionally near-pyroxyene melt) have relatively low Si levels of order 0.2–0.4 wt%, comparable to metals of the least metamorphosed EL chondrites (Zhang et al., 1995).

In the felsic–silicic selvages Fe-sulfide is far more abundant than Fe-metal. High levels of Cr in some of the Fe-sulfides (Table 3; also numerous semiquantitative analyses) provide additional evidence for smelting having occurred at extremely low /O₂. The large sulfide shown in Fig. EA-6 contains 6.3 wt% Cr. The lowest Cr (1.2 wt%) was found in a sulfide within an olivine microphorphy area.

3.2. Enigmatic LAP 03587

LAP 03587 is a 0.26 kg ureilite, when paired samples LAP 03721, 03722 and 031109 are included (LAP 03587, per se, is 0.13 kg). LAP 03587 is an extraordinarily ferroan ureilite. Our 24 analyses of core portions of olivines (6 different grains) average F₀₉₅₋₇. There are two precedents, or near precedents, for F₀₉₅ olivine among ureilites, LEW 88774 (Goodrich and Harlow, 2001; Warren and Huber, 2006a) and Y-791839 (Yanai et al., 1987), but no true ureilite has olivine significantly more ferroan than LAP 03587 (NWA 1500 is more ferroan, but Mittlefehldt and Hudon, 2004, and later Goodrich et al., 2006, concluded that is not a ureilite). LAP 03587 is enigmatic inasmuch as its pyroxene, like that of LAR 04315, is porous and reduced; and yet its overall texture, as described below, suggests a mild shock history, quite unlike the heavy shock inferred for LAR 04315.

We have studied thin section LAP 03587,7 (~1.0 cm²). It contains only ~5 vol% pyroxene. The rest is nearly all olivine, except for typical ureilite abundances of carbon (mostly graphite, in this case) and other opaque phases. The texture (Fig. 15; see also Figs. EA-7–EA-9) is typically ureilite inasmuch as the mafic silicates are granular and mostly 1–2 mm across. In their initial description Corrigan and McCoy (2005) noted that the pyroxenes “exhibit mosaicism.” We note that the portions of the pyroxenes that exhibit mosaicism also show porosity, with the pores strikingly similar in abundance, size and shape (Fig. 15) to the pores in a typically smelted LAR 04315 pyroxene. In this case, a larger proportion (roughly 1/3) of the pyroxene survived with approximately “intact” structural and compositional characteristics. Compositionally, the intact pigeonite is tightly clustered at En₉₀Wo₁₀, whereas the reduced, porous pyroxenes span a compositional range similar to that observed in LAR 04315 (Fig. 7). Pyroxene minor-element variation trends (Figs. 12 and 13) are also similar to those observed in LAP 04315. One small
Table 1
Representative electron microprobe analyses (oxides in wt%) of phases in the LAR 04315 ureilite.

<table>
<thead>
<tr>
<th>Olivine</th>
<th>Pyroxene “intact”</th>
<th>Pyroxene reduced in olivine micro porphyry</th>
<th>Set of similar glasses in olivine micro porphyry</th>
<th>Glass within pyroxene “reduced in olivine micro porphyry”</th>
<th>Glass within olivine micro porphyry</th>
<th>Set of similar glasses in olivine micro porphyry</th>
<th>Set of similar glasses in olivine micro porphyry</th>
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| Stoichiometry: Total cations based on relevant number of oxygens / ideal pyroxene = 4 cations per 6 oxygens; olivine and spinel = 3 per 4 oxygens; silica = 2 per 4 oxygens | 3.00 | 4.00 | 4.00 | 3.99 | 4.00 | 4.00 | 2.03 | 2.04 | 2.04 | 2.02 | 2.01 | 2.03 | 3.01
| En        | 74.1               | 86.7                                        | 62.1                                               | 78.7                                                         | 61.8                             | 40.4                                            | 2.03                                               | 2.04                                              | 2.04                                              | 2.02                                              | 2.01                                              | 2.03                                              | 3.01
| Fs        | 15.8               | 5.5                                         | 2.1                                               | 9.9                                                          | 8.2                              | 2.0                                             | 0.02                                               | 0.08                                              | 0.08                                              | 0.08                                              | 0.08                                              | 0.08                                              | 0.08
| Wo        | 10.2               | 7.8                                         | 35.8                                              | 11.4                                                         | 30.0                             | 65.6                                            | 65.1                                               | 61.2                                              | 91.2                                              | 47.9                                              | 96.0                                              | 95.0                                              | 48.5 |
| mg        | 81.65              | 82.46                                       | 94.0                                              | 96.8                                                         | 88.8                             | 88.2                                            | 65.1                                               | 61.2                                              | 91.2                                              | 47.9                                              | 96.0                                              | 95.0                                              | 68.4 |
| Abbreviations: px, pyroxene, ol, olivine. | | | | | | | | | | | | | | |
| a “px/gl” designates fine-grained materials that could be either crystalline pyroxene or glass that is very near to pyroxene in composition. | | | | | | | | | | | | | | |
olivine-rim area was noted that is similar to the “olivine microporphyry” zone of LAR 04315 (Fig. EA-9). Apart from its porous-reduced pyroxenes, the texture of LAP 03587 does not indicate particularly intense shock metamorphism. Roughly half of its olivines show wavy extinction, but none shows clear mosaicism (one grain does show a vague, coarse mosaicism). Its graphite is almost exclusively in the form of long, euhedral laths, often with pyramidal terminations (Fig. 15; see also Figs. EA-8 and EA-9). The longest such euhedron in LAP 03587,7 is 2.5 mm long and nowhere wider than 0.10 mm. Olivine near-contact with graphite is typically reduced and clouded by abundant tiny opaques (mostly Fe-metal) to a depth of roughly 100 μm. Euhedral ureilitic graphite is generally interpreted as evidence of an uncommonly mild shock history, as in the cases of ALH 78019 (Berkley and Jones, 1982), ALH 83014 (Bischoff et al., 1999) and Nullarbor 010 (Treiman and Berkley, 1994).

However, Steele et al. (2009) have detected submicrometer diamond aggregates within a shock-metamorphosed graphitic phase in LAP 03587. These diamonds must have formed by at least moderately intense shock. According to Matsuda et al. (1995) a minimum shock P of roughly 25 GPa is required (cf. Bischoff et al., 1999; Nakamuta and Aoki, 2000). Another curious and possibly shock-related feature of LAP 03587: some of its olivines contain a sprinkling (\(\approx 1\) vol%) of tiny, submicrometer Fe-rich opaques, uniformly scattered even within the grain cores. We have not been able to identify the opaque phase(s), but it seems likely that they are dominated by Fe-metal that formed when the host olivines underwent a dispersed albeit exceedingly mild degree of smelting in the immediate aftermath of a fairly intense shock event. Mainly based on the state of its pyroxenes and the presence of diamond, we infer that despite its euhedral graphite, LAP 03587 probably experienced a typically ureilitic intensity of shock.

Fig. 8. This BSE image of LAR 04315.21 is centered on an unusual clot-like mass of selvage-like glass + silica matter. The surrounding coarse grains were originally olivine (upper right), pigeonite (lower right corner; now a typical mass of impact smelting products) and olivine, which in this area (lower left) is largely broken up into an “olivine microporphyry” zone (cf. Fig. 9). The darkest grey phase in the selvage is silica (however, an area of extremely reduced olivine near the upper left corner of the image is equally dark). The silicas are set amidst two different phases that are difficult to distinguish here. Above and to the left of the (discontinuous) yellow line, the interstitial phase is highly felsic (~24 wt% Al₂O₃) glass. To the right of the yellow line, the interstitial phase is a pyroxene, or glass with almost perfect pyroxene stoichiometry, the composition of which clusters near En₉₀Wo₂₀ (this pyroxene manifests as a slightly darker grey than the felsic glass). In the olivine microporphyry zone, the dark grey is reduced (Fo₉₀) olivine; the light grey interstitial phase is a high-CaO (17–19 wt%) glass, whose composition is reduced (Fo₉₀ = 90 mol%) and slightly Sr-poor relative to pyroxene stoichiometry. The extension of the selvage into the more intact olivine (upper right) consists of a complex variety of high-mg (and mostly high-Ca) pyroxenes and glasses (cf. Fig. 4). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

olivine-rim area was noted that is similar to the “olivine microporphyry” rim areas of LAR 04315 (Fig. EA-9).

Apart from its porous-reduced pyroxenes, the texture of LAP 03587 does not indicate particularly intense shock metamorphism. Roughly half of its olivines show wavy extinction, but none shows clear mosaicism (one grain does show a vague, coarse mosaicism). Its graphite is almost exclusively in the form of long, euhedral laths, often with pyramidal terminations (Fig. 15; see also Figs. EA-8 and EA-9). The longest such euhedron in LAP 03587,7 is 2.5 mm long and nowhere wider than 0.10 mm. Olivine near-contact with graphite is typically reduced and clouded by abundant tiny opaques (mostly Fe-metal) to a depth of roughly 100 μm. Euhedral ureilitic graphite is generally interpreted as evidence of an uncommonly mild shock history, as in the cases of ALH 78019 (Berkley and Jones, 1982), ALH 83014 (Bischoff et al., 1999) and Nullarbor 010 (Treiman and Berkley, 1994).
The Almahata Sitta meteorite fell as a shower of many tens of stones in 2008 (Jenniskens et al., 2009). It is a ureilite-dominated but extraordinarily complex and porous polymict breccia with a wide variety of ureilitic materials, including some that are unusually fine-grained, plus clasts of various kinds of chondrites (Bischoff et al., 2010). We have studied thin sections from five distinct Almahata Sitta stones: three acquired direct from Jenniskens and two loaned from John Kashuba, who in turn acquired them from Siegfried Haberer.

One of these (Jenniskens’ stone number 25) is an H5 chondrite containing olivine (Fa18.1±0.4), low-Ca pyroxene (Fs16.2±0.4Wo1.8±1.0), 6–10-μm-size plagioclase grains (Ab82.9±3.6Or3.9±1.3), and minor chromite. Opaque phases include polycrystalline kamacite averaging 0.49 wt% Co, martensite with 14.1 ± 5.0 wt% Ni, and thin veins of troilite with variable Ni (<0.04 – 0.39 wt%). Shock-stage S3 is inferred from polysynthetically twinned low-Ca pyroxene grains as well as undulose extinction and planar fractures in many olivine grains. Haberer’s stone number 32 is an EL6 chondrite, containing enstatite (Fs0.21Wo1.6), relatively coarse (10–80 μm across) plagioclase (Ab2.0Or3.5), kamagate (0.75 wt% Si), and sulfides including oldhamite, troilite and ferromagnesian alabandite. Almahata Sitta chondrite components reported by Bischoff et al. (2010) include EH3, EH4/5, EH5, EL3/4 and EL6.

Another of the studied Almahata Sitta stones (Jenniskens’ number 27) is an essentially unbrecciated common ureilite with Fo85.3 olivine cores and En82.1Wo4.7 pigeonite.

Fig. 9. Areas of “olivine microporphyry” material in LAR 04315,20 (top) and LAR 04315,21 (bottom). Scale bars are 25 μm. The dark grey rounded grains are reduced (Fo99.9) olivines. The light grey interstitial matter is either pyroxene or, more likely, a glass, typically CaO-rich (~10–15 wt%), reduced (mg ~89 mol%), and very close to pyroxene stoichiometry. The opaques (white) are mostly Fe-metal. Typically porous products of impact melting of pigeonite are seen in the lower left and upper right of the top image.

Fig. 10. When compositions of “intact” pigeonite are used, the olivine (core) and pigeonite mg ratios of LAR 04315 and LAP 03587 conform to a strong correlation among ureilites in general (using data compilation of Mittlefehldt et al., 1998).

Fig. 11. Concentrations of four oxides (the balance is almost entirely SiO2) in various glasses from LAR 04315. Most of these glasses are found in selvages at boundaries between the original coarse mafic silicates. However, as indicated by Fig. EA-3, the “blister” is uniquely situated within the intact interior of an olivine crystal. For Na2O, open symbols designate glasses within the “clot” area shown in Fig. 8; these glasses are unusually Na-poor.
The original texture was probably poikilitic, with equant olivines 1–2 mm across and pigeonites in optical continuity up to 6 mm, but the optical continuity issue has been obscured somewhat by shock (the pigeonites show abundant and complex twinning; olivines show undulose extinction). Olivine reduction affected to a mildly unusual extent the deep interiors of some grains, as the reducing fluid apparently coursed through in-grain cracks (Fig. EA-10). The olivine cores average 0.70 wt% Cr₂O₃, but the reduction trend shows depletion of Cr along with Fe, so that the most extreme composition measured is Fo₉₇.₂ with 0.31 wt% Cr₂O₃. One of the largest pigeonites contains within 300 µm (mostly within 100 µm) of its rim numerous blebs, mostly 20–40 µm across, that appear to have been altered by reduction; they are seldom more reduced than En₈₄.₀–₈₆.₃Wo₅.₀–₅.₈, but one position, <4 µm from the grain’s rim, is En₉₄.₈Wo₁.₁. In general, however, this piece of Almahata Sitta is a rather ordinary ureilite.

The other two Almahata Sitta stones that we studied are samples of the unusually fine-grained ureilitic lithologies unique (as major components of a meteorite) to Almahata Sitta. One of these, Haberer’s number 109 (hereafter AS-H109), consists of a porous mix that is largely (roughly half) two distinctive sublithologies (Figs. 16 and 17 and EA-11); the other half consists of similar but more chaotic arrangements of the same minerals (possibly derived by mixing-brecciation of the same ingredients that were precursors to the two sublithologies). Both sublithologies occur in the form of domains typically ~0.5 mm across. The more abundant (~30 vol%) of the two sublithologies we call AS-H109-OP (for olivine + pyroxene). It consists of Fo₈₅–₉₈ (average Fo₉₁) olivine as the dominant (~80 vol%) phase, in the form of equant and typically roundish grains of order 10 µm across; along with, as anhedral masses interstitial to the olivine, a phase (~20 vol%) that is either subcalcic pyroxene or glass with near-pyroxene composition (average En₆₃Wo₃₀; the stoichiometry shows a slight excess of Si). In Fig. 18, all of the “Haberer 109” pyroxenes with Wo > 9 mol% (except for a few analyses from undocumented random positions) are from the OP sublithology. Even the least reduced (Fo₈₅–₈₈) 109OP olivines have moderate “Cr₂O₃”, 0.31–0.60 wt%.

The less abundant (~20 vol%) sublithology we call AS-H109-LPS (for low-Ca pyroxene + silica). It consists
mainly (~95 vol%) of low-Ca pyroxene grains of order 10 μm across; along with, as scattered anhedral masses interstitial to the pyroxene, a phase (~5 vol%) that is either silica or glass with near-silica composition. The largest pores and opaques tend to occur at OP/LPS boundaries. The pyroxenes that dominate 109LPS range from En₉₃Wo₄ to En₉₀Wo₃. They tend to be more angular than the rounded olivines that dominate 109OP. The 109LPS pyroxenes typically show effects of reduction, in the form of FeO-depleted (BSE-dark) rims; in some areas their interiors are richly sprinkled with minute (~1 μm) opaques that are probably Fe-metals. Otherwise, however, Fe-metal tends to be coarser and also slightly more abundant in LPS than in OP. In transmitted light, the LPS sublithology appears nearly opaque; and elsewhere in the thin section it assumes long, narrow schlieren-like forms (Fig. EA-11), suggesting that it was once, locally, mobilized in a near-fluid state.

A third, extremely minor sublithology in AS-H109 consists of ~10 μm olivine (Fo₉₄₋₉₆) grains with interstitial feldspathic glass (wt% concentrations: 3.3 Na₂O, 7.2 MgO, 18.5 Al₂O₃, 65 SiO₂, 0.4 K₂O, 3.3 CaO, 0.4 TiO₂, 0.8 FeO). The olivines in this sublithology are angular and euhedral (Fig. 17) compared to typical olivines in OP domains. Probably each ~0.5-mm OP or LPS domain represents most of the volume of a former relatively coarse (normal ureilitic) grain that underwent granulation followed by pervasive impact smelting.

The other fine-grained sample, Jenniskens’ stone number 1, is similar to the chaotic 1/2 of AS-H109, inasmuch as the dominant texture features rounded ~10 μm olivines intergrown with pyroxene (or pyroxenitic glass) amidst extraordinary porosity. However, in this case there is little if any OP material (i.e., material in which olivine is preponderant and pyroxene only a minor interstitial phase) or LPS material. Domains of striking modal consistency are seldom ~100 μm across. The pyroxenes intergrown with olivine are mostly low-Ca but have Wo ranging, even among moderate (~92 mol%) mg compositions, from 0.7 to 33 mol% (Fig. 18). The most extremely reduced pyroxene is En₉₀₋₉₁Wo₁₋₂. The least reduced (Fo₈₃₋₈₅) stone 1 olivines have diverse “Cr₂O₃”, 0.32–0.81 (average 0.47) wt%.

In texture and mineralogy, the AS-H109-OP sublithology is similar to the minor “olivine microporphry” components of LAR 04315 (Fig. 9) and LAP 03587 (Fig. EA-9). The extent of the lithology is vastly greater in Almahata Sitta, but as will be discussed below, a similar basic scenario of impact smelting probably determined the late evolutions of all three meteorites.

4. DISCUSSION

4.1. Other possible instances of ureilite pyroxene smelting

According to a preliminary description (Janots et al., 2009), Jiddat al Harasis 422 is an impact-melt breccia with 8.4 vol% vesicles. The role of impact in engendering the reported diversity of pyroxene composition (En₈₆₋₈₉Wo₀₋₅ orthopyroxene and En₉₆₋₇₁Wo₂₀₋₃₁ augite) is not yet clear, but amidst so much impact melting and porosity, the pyroxene may have undergone some degree of smelting.

Saito and Takeda (1990) described five ureilites (LEW 85328, LEW 86216, Y-75154, Y-791839 and Y-8448) with diverse pyroxene compositions that were interpreted as “shock effects . . . produced during the break-up of their parent body.” In general, the pyroxene compositional diversity in these ureilites resembles what we have observed in LAR 04315 and LAP 0587 (Fig. 7; cf. Fig. EA-12). In the interpretation of Saito and Takeda (1990), for most of the ureilites of this group (Y-75154, Y-791839 and Y-8448) the compositional diversity and “cloudy” appearance of pyroxene was simply attributed to some type of shock effect, without explicit reference to reduction. In general, the interpretation was that “the chemical variations of pyroxenes . . . can be explained by partial melting and vaporization mainly at grain boundaries and rims.” However, in the case of the “moderately shocked” LEW 85328, “portions of a pigeonite were partially melted” and Si-rich glasses found within cloudy pigeonite “may have been produced by reduction.” In the highly shocked...
(mosaicized olivine) ureilite LEW 86216, its pyroxene diversity “may be one of characteristics of shock reduction, but ... it is difficult to deduce its origin.”

Reviewer C. A. Goodrich reports seeing in ALH 81101, a ureilite with mosaicized olivine and compositionally diverse pigeonite (Takeda et al., 1985), “all the features (including abundant pores)” of the LAR 04315 pyroxene texture. The Y-790981 ureilite was described by Ogata et al. (1991) as having compositionally diverse “cloudy pigeonite in which many phases [such as augite, chromite, metal and glass] were produced by shock partial melting.” Finally, the NWA 2634 ureilite has been described in the Meteoritical Bulletin (89) as “highly shocked with pyroxenes completely converted to mosaic texture, olivine less so.” Except for Jiddat al Harasis 422, none of these ureilites has been previously described (in print) as especially porous. However, from the perspective of LAR 04315 and LAP 03587, diverse pigeonite compositions in a monomict ureilite might be viewed as prima facie evidence of pyroxene-focused impact smelting.

4.2. Extreme shock metamorphism, ureilite-style

In LAR 04315, the terminal-igneous smelting process characteristic of all ureilites took an unusual course, with smelting more extensive, and overall more destructive of FeO, in pyroxene than in olivine. LAP 03587 is similar, except it has much less modal pyroxene. The smelting obviously occurred as a disequilibrium, uncompleted process, in a rapidly cooling environment. In an asteroidal context, the trigger for such a cascade of rapid change was presumably a large impact. Apart from stochastic factors including possible proximity to the impact and heterogeneous shock-wave propagation, it is unclear why LAR 04315 and LAP 03587 happened to undergo unusually extensive impact smelting. However, we can suggest a reason why impact smelting in ureilites tended to be pyroxene-selective.

Heating by impact shock is a function of the target material’s volume response during shock compression and release, i.e., the area between the loading and unloading paths on a plot of volume $V$ vs. $P$. We have used the formalism of Sharp and DeCarli (2006; especially their Appendix A) and equation of state constants based primarily on Ahrens and Johnson (1995) to obtain rough estimates for post-shock temperature $T_S$ in orthopyroxenite and dunite (“bronzitite, Stillwater” and “dunite, low density”), as near-approximations of the pigeonites and olivines in ureilites. Key material-specific variables in the calculation of $T_S$ include the initial density $\rho_0$, the bulk compressional velocity $C$, and the dimensionless slope constant $S$. The product
\( q_0 \) defines the "shock impedance" (He et al., 1996). To convert from the \( q_0 \) listed by Ahrens and Johnson (1995) to one appropriate for an anatectic or near-anatectic ureilite at roughly 1100 °C, we modeled thermal expansion after Fei (1995); i.e., the values of \( q_0 \) shift from 3262 to 3164 kg/m\(^3\) for the dunite and from 3277 to 3172 kg/m\(^3\) for the orthopyroxenite. We assume (conventionally) that for both materials the specific heat is 1 kJ kg\(^{-1}\) K\(^{-1}\) and the Grüneisen parameter \( \gamma \approx 1 \). The thin curves in Fig. 19 show results using values of \( C \) and \( S \) from Ahrens and Johnson (1995).

Fig. 19 also shows a set of results (thick curves) designed to account for the effects on \( C \) of a pre-shock \( T \) of order 1100 °C, along with relatively higher Fe in the olivine, as well as higher Fe and Ca in the pyroxene (caveat: parallel effects on \( S \) are admittedly unknown). For simplicity, we assume that for both pyroxene and olivine the overall effect (the \( \Delta T \) effect dominates) is a reduction in \( C \) by a factor of 0.86. Compositional and thermal effects on \( C \) for mafic silicates were reviewed by Hood and Jones (1987), but we base \( dC/dT \) for olivine on the more recent data and review of Speziale et al. (2005). Although the modeling behind Fig. 19 is crude, and neglects possible complexities such as pre-existing porosity or unusually strong shock reverberations, it is probably safe to infer that the shock pressure that engenders mosaicism in olivine (roughly 20–50 GPa: Stöffler et al., 1955) could lead to a \( T_S \) of anywhere from a few tens to roughly 500 degrees above the pre-shock \( T \); and that under such conditions the post-shock temperature rise will not differ greatly between pigeonite and olivine. The latter conclusion in turn implies that proximity of the pre-shock temperature \( T_0 \) to the melting temperature of the pigeonite was probably crucial. Raman studies indicate that when magnesian orthopyroxene (bronzite) is shocked at room temperature, it retains its crystalline structure in almost unaltered form up to shock \( P \) of 62.5 GPa (Johnson et al., 2002) and undergoes only limited structural change even at 100 GPa (Estep et al., 1972). But if \( T_0 \) was close to 1100 °C, and the shock \( P \) was a few tens of GPa (as implied for LAR 04315 by the olivine mosaicism), \( T_S \) within
pigeonite was likely high enough to induce scattered melting, and widespread degradation of whatever crystalline structure survived, to a point at which diffusive communication between grain interiors and rims was vastly faster than in a normally crystalline silicate. However, the survival and/or recovery of the LAR 04315 pigeonites in a state of near optical continuity (Figs. 1 and 2, and EA-1) indicates that they were never completely melted. In general, the crystalline structure of the pigeonite was degraded, but not erased.

We envisage transformation of most of the LAR 04315 pigeonite (in the immediate lead-up to its subsequent melting) into a state comparable to that of the plagioclase-derived glassy phase “maskelynite.” The detailed nature and origin of maskelynite are controversial. Although maskelynite has been customarily regarded as a diaplectic glass, Chen and El Goresy (2000) argued from flow features in shocked meteorites that it must actually be a quenched dense melt. However, Yamaguchi and Sekine (2000) produced analogous flow features experimentally, and inferred that maskelynite “may be a mixture of plagioclase crystals and fused glass.” A similar and probably still mainstream view is that of Fritz et al. (2005; cf. Sazanova et al., 2007), who consider maskelynite to be a diaplectic glass “intermediate between a truly glassy state and the crystalline state.” From the evidence of LAR 04315, we infer that once a ureilitic pigeonite was transformed into such a state, under \( P-T/\text{O}_2 \) conditions that favored melting (rapidly declining \( T \) probably became the limiting factor), this material was vulnerable to thorough-going melting.

Shock-degradation of crystalline structure is presumably related to the melting temperature \( T_m \) of the pure mineral. In LAR 04315, the localization of penetrative, thorough melting within pigeonite probably reflects this mineral’s low \( T_m \) in comparison to olivine (Fig. 20). For \( \text{Fo}_{70}, \text{Fo}_{90}, \text{and Fo}_{90} \), olivine, \( T_m \) is \( \sim 1580, 1670 \) and \( 1770 \) \( ^\circ \text{C} \), respectively (Presnall, 1995). In contrast, by interpolation from data for Fe-free pigeonites and other pyroxenes, we estimate that \( T_m \) for LAR 04315-like (\( \text{En}_{24}\text{Wo}_{16} \) /\( \text{mg} \sim 82 \text{ mol} \% \)) pigeonite is probably roughly 1350 \( ^\circ \text{C} \). Thus, for the original LAR 04315 silicates, \( T_m \) was about 300 K higher for olivine than for pigeonite. From the concentration of melting into pigeonite, we can infer that the pre-shock temperature was probably such that \( T_m = T \), \( T_m \) was still stewing at a \( T \) not far below 1200 \( ^\circ \text{C} \) when the impact that catastrophically altered its evolution, and probably that of the entire parent asteroid, struck.

The size-frequency distribution of pores formed within LAR 04315 pigeonite is decidedly bimodal, with modes at roughly 1 \( \mu \text{m} \) (Fig. 3) and 20 \( \mu \text{m} \) (as an equivalent diameter for pores that, in 2-dimensional exposures, are typically \( \sim 40 \times 10 \mu \text{m} \)). We speculate that this bimodality developed because at a scale of order 10 \( \mu \text{m} \) the bubbles reached coalescence, at which point access to reducing fluid was greatly enhanced, and thus the melting rate was enhanced. Further widening may have been limited by a combination of increasingly easy gas outflow as the local volume became rich in closely spaced and interconnected pores, and diminution of gas production as cooling led to slower and slower melting.

Even a small amount of porosity, by rendering a material more compressible, leads to higher \( T_g \) (Sharp and DeCarli, 2006). Conceivably the pre-shock pyroxene was porous while the olivine was not, perhaps because an episode of annealing erased olivine porosity while leaving some pyroxene porosity. But such a complex pre-history is difficult to reconcile with most of the textural evidence. The near optical continuity of the pyroxene, even after the melting process, suggests it was in a coherent condition before the major melting-trigger shock. The only textural features that arguably point toward previous brecciation are a few instances where shock-injected opaque veins appear (but the evidence is ambiguous) to cross “intact” zones of pigeonite without extending into the surrounding groundmass of smelted pyroxenitic matter. Olivine-pyroxene boundaries are consistently smooth, as if unaltered from a normal ureilitic texture, except at scales below \( \sim 10 \mu \text{m} \), where in places granulation left the rims somewhat jagged.

In the LAR 04315 olivine, individual mosaic tiles do not show shock effects, such as undulose extinction or planar fractures. We infer that a single major shock event was followed by an episode of reheating, or slow cooling, which caused sufficient annealing to erase the shock effects. Even if the mosaicing of the olivine involved only minor displacement, the interiors of the olivine domains (i.e., of the original-coarse olivines) were rendered somewhat porous. Without an intervening period of annealing-compaction, reduction would have operated almost as effectively in the interiors as on the edges. We assume that this thermal-com-
paction process, and also the shock twinning of the pyroxene (Fig. 1), both could have happened soon after the initial shock, before shock heating triggered the impact smelting. Admittedly, however, these aspects of the history of LAR 04315 are enigmatic.

The smelting of pigeonite more than olivine is especially noteworthy in the case of LAP 03587. Typically, in ureilites, olivines have prominent reduction rims but pyroxenes do not (e.g., Berkley, 1986). The lack of mosaicism in olivine and the preservation of euhedral graphite both suggest that in LAP 03587 the shock pressure of the smelt-triggering event was not much greater than the minimum \( P \) for production of its diamonds (\( \geq 25 \) GPa; Matsuda et al., 1995), and thus the increment from the pre-shock \( T_0 \) to \( T_S \) was probably not \( >100 \) K. We can only speculate that in this instance \( T_0 \) was even nearer to the \( T_M \) of this ureilite’s pigeonite than was the case with LAR 04315; and/or some circumstance caused this sample to undergo an unusual thermal evolution (e.g., an unusual pre-shock porosity; or perhaps after the smelt-triggering event the cooling rate was unusually moderate). It may not be pure coincidence that LAP 03587 is the most ferroan ureilite (Fig. 10), which implies an especially low \( T_{M,\text{pigeonite}} \) (although probably only by a few degrees relative to the \( mg \sim 82 \) mol% pigeonite of LAR 04315). But the impact process is highly stochastic, so it should not surprise that other almost equally ferroan ureilites show little evidence for pyroxene smelting (Goodrich et al., 2001; Warren and Huber, 2006a).

4.3. LAR 04315 as a post-depressurization ureilite

The impact smelting of LAR 04315 appears to represent an extreme example of the complex, disequilibrium processing that altered all ureilites at the terminal stage of their igneous evolution, when rapid depressurization occurred in association with impact disruption of the parent asteroid (Warren and Kallemeyn, 1992; Weber et al., 2003; Goodrich et al., 2004). Depressurization-triggered anatexis is the dominant process that produces mantle melts on Earth.

With ureilites, the depressurization involved only a few tens of bars; and instead of triggering anatexis, the overall process modified the end and very short-term aftermath of anatexis. In typical ureilites, with redox effects mainly evident only in the rims of the olivines, the disruption caused the thermal regime to abruptly transition from one of mantle anatexis (or cooling shortly after anatexis) into one of rapid, small-body cooling. But in the case of LAR 04315, the same impact that led to rapid cooling also initially caused pyroxene-localized impact melting, which in the changed pressure conditions immediately took on the character of impact smelting.

In all ureilites, the key consequence of hot excavation-depressurization was oxidation of solid carbon into CO gas; in most cases with the oxygen derived almost exclusively from reduction of olivine rims (Warren and Huber, 2006b). The olivine reduction reaction, the form of “smelting” observed in virtually all ureilites, is approximately

\[
2C + 2(\text{Mg}_3\text{Fe}_2\text{Si}_2\text{O}_8) = 2(\text{Mg}_2\text{SiO}_4) + 2(\text{MgSiO}_3) + 2\text{Fe} + 2\text{CO (gas)} \quad (1a)
\]

where \( 2(\text{Mg}_3\text{Fe}_2\text{Si}_2\text{O}_8) \) is an atomistic way of denoting 4 moles of Fo 75 olivine. This assumes that the SiO\(_2\) liberated by Fe-olivine reduction manages to efficiently react with surviving Mg-olivine to form pyroxene. Under disequilibrium conditions, the reaction might go more like

\[
3C + 3(\text{Mg}_3\text{Fe}_2\text{Si}_2\text{O}_8) = 4(\text{Mg}_2\text{SiO}_4) + 3\text{Fe} + 3\text{CO (gas)} + \text{MgSiO}_3 + \text{SiO}_2 \quad (1b)
\]

or even

\[
2C + 2(\text{Mg}_3\text{Fe}_2\text{Si}_2\text{O}_8) = 3(\text{Mg}_2\text{SiO}_4) + 2\text{Fe} + 2\text{CO (gas)} + \text{SiO}_2 \quad (1c)
\]

which yields silica instead of Mg-pyroxene among the final products.
The pyroxene reduction process exemplified by LAR 04315 is approximately
\[
C + MgFeSi_2O_6 = MgSiO_3 + Fe + CO \text{(gas)} + SiO_2
\]
where we use a simplified chemical formula, sans CaO, for the pigeonite. In both Eqs. (1) and (2), the presence of CO gas only on the products side implies that the reaction must be extremely pressure-sensitive. Note that the yield ratio of SiO_2 per mole of FeO that is reduced (or per mole of Fe-metal formed) is two times higher in the pyroxene reduction process (2) than in even the (1c) version of olivine-reduction.

In both cases, the detailed fate of this SiO_2 is unclear. It may, in principle, manage to recombine with olivine to form new pyroxene; it may enter into an interstitial silicate melt; and/or it may remain as isolated new grains of silica. Probably it partitions to some degree into all three of these end states. But presumably the yield of silica, and/or silica-rich interstitial melt, was relatively high in the case of LAR 04315. The silicate melt was probably (as discussed in detail below) fugitive, and may also have entrained some solid silica. But even at \(-0.26\ \text{vol\%}\), the modal abundance of silica + felsic–silicic glass is indeed uncommonly high for a ureilite (Figs. 4, 5 and 11, and EA-2).

Before the advent of porous impact-smelted ureilites such as LAR 04315, the most striking examples of depressurization effects were found in a few extraordinarily ferroan ureilites such as Asuka-881391 (Ikeda, 1999), NWA 766 and LEW 88774 (Warren and Huber, 2006a). Having equilibrated (i.e., undergone anatexis) at relatively high \(\text{H}_2\text{O}\) (e.g., Warren and Kallemeyn, 1992), ferroan ureilites are more prone to contain Cr-spinel. They also started with more FeO to “burn”. As, upon depressurization, the creation of CO gas out of solid C sucked free oxygen out of the system, Cr tended to be reduced into a divalent state (valency of Cr CO gas out of solid C sucked free oxygen out of the system, gas only on the products side implies that the reaction must be extremely pressure-sensitive. Note that the yield ratio of SiO_2 per mole of FeO that is reduced (or per mole of Fe-metal formed) is two times higher in the pyroxene reduction process (2) than in even the (1c) version of olivine-reduction.

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In LAR 04315 and LAP 03587, as indicated by the examples of Figs. 4, 5 and 8, and EA-2, -3 and -9, the felsic glass + silica association tends to occur as a rimming selvage where coarse silicates of the pre-impact lithology were separated by large voids. These assemblages appear to have formed by crystallization/quenching of felsic melts that clung as linings of the large voids. However, it would be a mistake to assume that the original melt can be modeled as a recombination of the observed subequal proportions of glasses and silicas. Even as the glasses were crystallizing (or anyway, reacting with) the silicas, other processes were occurring, including melting, which potentially, per (1c) and/or (2), added SiO_2. Ureilites such as Asuka-881391, NWA 766 and LEW 88774 show that major smelting of pyroxene was not necessary to form a tiny proportion of silica in association with relatively larger amount of felsic glass.

As suggested for Asuka-881391 by Ikeda (1999), all of these glasses probably derived in part from minor proportions of interstitial anatectic melts that were present before the impact disruption of the ureilite mantle. However, the high relative amount of silica in LAR 04315 (in several areas, the rimming selvages consist preponderantly of silica: e.g., Figs. 5 and EA-3) is presumably related to the extraordinary importance of pyroxene melting (2) in this rock. Compared to most of its counterparts in Asuka-881391, LEW 88774 and NWA 766 (Table 2), the typical LAR 04315 selvage-area felsic glass composition is lower in SiO_2, and richer in CaO and especially Al_2O_3. We speculate that the LAR 04315 felsic glass became (or stayed) relatively Si-poor because it was consistently in near-contact with a silica phase, whereas in other ureilites the felsic glass was generally more isolated from silica, and became (or stayed) supersaturated in SiO_2 as a consequence of nucleation kinetics.

Although none of the LAR 04315 glasses have Na_2O \(>4.5\ \text{wt\%}\), an anticorrelation between Al_2O_3 and Na_2O (Fig. 11, excepting the olivine-blister glass) may in part reflect volatilization of Na. However, Na volatilization is probably not the sole reason for the diversity of Al_2O_3 in the LAR 04315 glasses, because loss of \(-4\ \text{wt\%} Na_2O (K_2O is \(<0.1\ \text{wt\%}\) even in the most Na-rich glasses) cannot account for increase in Al_2O_3 from \(-18\ \text{to}\ 25\ \text{wt\%}. Also, if another refractory element, Ti, is substituted for Al, the anticorrelation disappears into a cloud of random scatter.

SiO_2-rich clasts occur in some enstatite and ordinary chondrites (Rubin, 1983; Hezel et al., 2006). However, these clasts do not seem very relevant. The SiO_2-rich clasts in the ordinary chondrites apparently represent survival of extreme products of solar-nebular (e.g., fractional condensation) processing (Hezel et al., 2006).

High-SiO_2 glasses that occur as minor components of some peridotites derived from the mantle of the Earth (Hirschmann et al., 1998) may be more useful analogs. Some are even associated with a “spongy” texture within incipiently melted pyroxene that superficially resembles the LAR 04315 melted pyroxenes (Carpenter et al., 2002; Zhu, 2008). These terrestrial glasses are believed to represent quenched anatectic melts, and factors that lead to high-SiO_2 are believed to include low melt fraction, low \(P\), and high alkali-oxide activities (Hirschmann et al., 1998). Alkali ions tend to reduce Si–O–Si linkages in the melt, which translates into negative deviations from ideality for mixing between alkalis and silica, which in turn requires high alkali to be accompanied by high silica for liquids in equilibrium with peridotite. The importance of low \(P\) may stem from a tendency for alkali-carbonate complexes to form at high \(P\) (Schiano et al., 1998). Experiments at \(P \sim 1\ \text{GPa}\) (still off-scale high by asteroidal standards) indicate that incipient peridotite melts begin to acquire unusually high-SiO_2 as the melt Na_2O + K_2O surpasses \(-9\ \text{wt\%}\) (Hirschmann et al., 1998).
Table 2
Representative electron microprobe analyses (oxides in wt%) of phases in LAP03587, Almahata Sitta and other ureilites.

<table>
<thead>
<tr>
<th></th>
<th>LAP 03587</th>
<th>Almahata Sitta, AS-H109</th>
<th>Almahata Sitta, PJ-27</th>
<th>Asuka-881391&lt;sup&gt;b&lt;/sup&gt;</th>
<th>LEW 88774&lt;sup&gt;b&lt;/sup&gt;</th>
<th>NWA 766&lt;sup&gt;b&lt;/sup&gt;</th>
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<tbody>
<tr>
<td></td>
<td>cores</td>
<td>“intact”</td>
<td>reduced</td>
<td>interstitial</td>
<td>interstitial</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>24</td>
<td>13</td>
<td>4</td>
<td>16</td>
<td>1</td>
<td>4</td>
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<tr>
<td>SiO₂</td>
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<td>53.83</td>
<td>56.52</td>
<td>49.89</td>
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<td>0.06</td>
<td>0.22</td>
<td>0.03</td>
<td>0.78</td>
<td>0.35</td>
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<tr>
<td>Al₂O₃</td>
<td>0.03</td>
<td>0.95</td>
<td>1.83</td>
<td>0.23</td>
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<tr>
<td>Cr₂O₃</td>
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<td>1.20</td>
<td>1.06</td>
<td>1.00</td>
<td>2.23</td>
<td>0.03</td>
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<td>MgO</td>
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<td>22.70</td>
<td>30.60</td>
<td>18.34</td>
<td>0.98</td>
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<tr>
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<tr>
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<td>0.40</td>
<td>0.51</td>
<td>0.45</td>
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<td>0.10</td>
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<tr>
<td>FeO</td>
<td>22.93</td>
<td>13.11</td>
<td>6.24</td>
<td>6.97</td>
<td>3.54</td>
<td>1.01</td>
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<tr>
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<td>0.11</td>
<td>0.02</td>
<td>0.15</td>
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<td>K₂O</td>
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<tr>
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<td>99.93</td>
<td>99.11</td>
<td>99.43</td>
<td>100.56</td>
<td>98.83</td>
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</table>

Stoichiometry: Total cations based on relevant number of oxygens (ideal pyroxene = 4 cations per 6 oxygens; olivine and spinel = 3 per 4 oxygens; silica = 2 per 4 oxygens)

<table>
<thead>
<tr>
<th></th>
<th>3.99</th>
<th>3.99</th>
<th>3.99</th>
<th>2.01</th>
<th>3.02</th>
<th>4.02</th>
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<tr>
<td>En</td>
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<td>64.4</td>
<td>82.5</td>
<td>55.3</td>
<td>62.7</td>
<td>84.0</td>
<td>91.9</td>
<td>82.1</td>
<td></td>
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<tr>
<td>Fs</td>
<td>20.6</td>
<td>9.9</td>
<td>10.5</td>
<td>6.0</td>
<td>7.1</td>
<td>10.7</td>
<td>2.5</td>
<td>13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wo</td>
<td>10.0</td>
<td>25.7</td>
<td>7.0</td>
<td>38.7</td>
<td>30.2</td>
<td>5.3</td>
<td>5.5</td>
<td>4.7</td>
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<tr>
<td>mg</td>
<td>74.66</td>
<td>77.07</td>
<td>86.6</td>
<td>88.7</td>
<td>90.2</td>
<td>63.4</td>
<td>10.9</td>
<td>90.7</td>
<td>89.9</td>
<td>88.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> "px/gl" designates fine-grained materials that could be either crystalline pyroxene or glass that is very near to pyroxene in composition.

<sup>b</sup> Data for Asuka-881391 from Ikeda (1999); LEW 88774 and NWA 766 from unpublished UCLA/Warren analyses.
To a zeroth approximation, the LAR 04315 glass diversity can be modeled as a mixing of three components: the high-Si, high-Na glass that formed within pyroxene (i.e., formed more or less directly by smelting), the olivine-blister glass, and an Al-basaltic melt, perhaps representing a minor melt component that was present interstitially to the coarse mafic silicates as this material was stowing in the ureilite asteroid mantle prior to the impact smelting episode. By analogy with the low-\(P\) anatectic melts discussed by Hirschmann et al. (1998), the initial interstitial melt may have already been SiO\(_2\)-rich even before the smelting process added SiO\(_2\). The interstitial melt may also have been modified by abortive equilibration to the extreme low FeO activity associated with the rock’s pervasive smelting. LAR 04315 glasses typically have \(mg > 90\) mol\% (Table 1).

Both Eqs. (1) and (2) imply that the molar proportionality of CO\(_2\) gas to Fe-metal in the products, i.e., to FeO in the reactants, is close to 1. By thermodynamical calculation, at magmatic temperature \(T\) and low \(P\) near the graphite–CO\(_2\) buffer, the gas is preponderantly CO (Warren and Kallemeyn, 1992). Thus (factoring in the molecular weights of CO, SiO\(_2\) and Fe), for each 1 wt\% of FeO that is reduced, “smelting” will form \(\sim 0.39\) wt\% of CO along with 0.78 wt\% of Fe-metal and roughly 0.3 (olivine reduction) to 0.8 (pigeonite reduction) wt\% of SiO\(_2\). In other words, for each \(cm^3\) of pre-smelt rock (with density of roughly 3 g \(cm^3\)), reduction of 1 wt\% of FeO yields 0.012 g, i.e., 0.00042 moles, of CO. By the gas law, the volume of 0.00042 moles of gas at \(1200°C\) is 0.50 \(cm^3\) at 100 bar; and for other pressures the volume is simply \(50P\) (for \(P\) in bar). For the putative scenario of reduction with no escape of CO gas, the implied volume fraction \(\Gamma\) of CO (i.e., the porosity) that forms as a result of reduction is

\[
\Gamma = (50\psi/P)/(1 + 50\psi/P)
\]

(3)

where \(\psi\) is the proportion (as wt\% of the bulk rock) of FeO that undergoes reduction. Relationships among \(\psi\), \(P\) and (indirectly) \(\Gamma\) are illustrated in Fig. 21. As discussed above, in LAR 04315 it appears that \(\psi\) was \(\sim 2.7\) wt\% (1.6 wt\% from pigeonite reduction, 1.1 wt\% from olivine reduction). C–CO driven redox processing will not reduce olivine past \(mg > 92\) mol\% (at magmatic \(T\) unless \(P\) is less than about 100 bar (Warren and Kallemeyn, 1992). It follows that the final porosity of 9–12\% (see above) must represent only a small fraction, at most \(\sim 1/10\), of the total CO\(_2\) gas volume produced by the C–CO driven redox processing of LAR 04315. If the cooling was at the typical end-stage ureilite rate of \(>1\) degree/hour (Miyamoto et al., 1985; cf. Goodrich et al., 2001; and Tribaudino, 2006; suggesting roughly 7–20 degree/hour), then the burial depth was probably no more than a few meters, \(P\) was of order 0.01 bar, and the final porosity of 9–12\% represents only \(\sim 0.001\)\% of the total CO\(_2\) gas volume produced. In short, almost all of the gas escaped, by outward flow that probably ended with explosive expansion (Warren and Kallemeyn, 1992; Scott et al., 1993) into the vacuum of space.

This conclusion is almost equally strong for ureilites in general. Typical ureilites have olivines roughly 1 \(x 0.7 \times 0.5\) mm in size (e.g., Berkley et al., 1980) with reduced rims whose average thickness is roughly 20–40 \(µm\) (Wittke et al., 2007); i.e., the perceptibly reduced rims are in general roughly 9–17\% of the olivines. By stoichiometry, the amount of FeO reduced within any given rim is \(\sim 0.95\) wt\% for each mol\% of Fo reduction. Assuming that on average the reduced rims have lower Fo than the cores by 5–10 mol\% (5 mol\% is probably a conservative lower limit), the rims have 4.8–9.5 wt\% lower average FeO. Thus, a typical ureilite is implied to have had 0.4–1.6 wt\%, and mostly likely close to 1 wt\%, of its olivine FeO reduced. In an average ureilite most of the FeO is in olivine (Mittlefehldt et al., 1998), so we can conclude that for ureilites in general, \(\psi\) was also not \(< 1\) wt\%. This result, per (3), implies a gas yield (Fig. 21) that is for any plausible \(P\) larger than the typical preterrestrial ureilite porosity, i.e., so low that it is hard to measure and seldom reported (Britt et al., 2010, found for \(\sim 14\) samples an average porosity...
Warren et al., 2006). Surface tension and high viscosity as the CO gas streamed outward through the void channels. The melt to cling as selvages to the walls of the larger voids, may have been important factors in allowing a fraction of granulation of the olivine, and it engendered an even higher post-shock temperature, which led to a more intense impact smelting of the pyroxene. There was also much more displacement of materials, including in some areas a stretching of pyroxenes into schlieren-like structures (Fig. EA-11), and elsewhere complete distortion to the point where no vestiges of the original grain shapes are discernible.

The detailed mineralogy of AS-H109 prior to the major impact and consequent impact smelting is unknown. There are no fully “intact” grains of either pyroxene or olivine. Conceivably the pre-impact lithology was a polymict breccia. Provided it was either monomict or unbrecciated, the mg ratios of the most ferroan pyroxene (84.5 mol%; Fig. 18) and olivine (84.9 mol%) represent upper limits on the mg of the pre-smelting pyroxene and olivine. One interesting feature is the differentiation of its pyroxenes between the two sublithologies. The pyroxene that is the dominant (~95%) phase within the 109LPS sublithology is almost exclusively low-Ca (Wo <9 mol%); the sole exception, Wo13, is within ~30 μm of (or put another way, separated by 2–3 LPS pyroxene grains from) a large, ragged pore that separates its LPS domain from an OP domain. In the AS-H109-OP sublithology, which as discussed above resembles the olivine microphosphorites of LAR 04315 and LAP 03587, the interstitial pyroxene (or pyroxene-like glass) is consistently Ca-rich (Wo >23 mol%). Thus, it appears that shock melting and mobilization of AS-H109 pyroxene was compositionally selective. Without knowing the detailed pre-impact mineralogy, it is hard to constrain the mechanism of this selectivity. Very possibly, in addition to the low-Ca grains that survive in relict form as the LPS domains, the pre-impact meteorite contained a considerable proportion of high-Ca pyroxene. A sizeable minority of ureilites have both augite and low-Ca pyroxene (Mittlefehldt et al., 1998; Goodrich et al., 2004). Conceivably, the selective melting of Ca-pyroxene arose during the complex impact smelting of an original pigeonite; and presumably a finite proportion of CaO was added from reduced Mg-olivine. In LAR 04315 and LAP 03587, where the interstitial pyroxenes or pyroxene-like glasses of the olivine microphosphorites also mostly have Wo >25 mol%, there is no evidence of any pre-impact high-Ca pyroxene. However, olivine microphosphorite is only a trace component of LAR 04315, and even rarer in LAP 03587, while the OP sublithology constitutes ~60% of the non-chaotic half of AS-H109.

As in LAR 04315, the smelting of low-Ca pyroxene in the AS-H109-LPS sublithology engendered, per (2), both silica and Fe-metal. In detail, however, the smelted low-Ca pyroxene of 109LPS is different. The material is broken into discrete, angular ~10–20 μm grains, each of which typically features a distinctly reduced rim (dark in BSE images, such as Fig. 17). In many cases, as in Fig. 17, the interior of the grain appears to have undergone a later stage of smelting that formed a sprinkling of tiny (~1 μm) Fe-metals. Our electron-probe analyses of the interiors of these grains do not detect such tiny inclusions, except as “FeO” ingredients in pyroxene (the analysis is effectively a defocused-beam analysis, except the Fe-metals are so tiny that their high density probably has minimal effect on electron and X-ray transmission). In reality the final state of the 109LPS low-Ca pyroxene is probably more reduced than reflected by Fig. 18. (This “later
The mosaicized state of the olivine in LAR 04315 confirms that it experienced a severe impact shock. However, LAP 03587, which contains some pyroxene derived primarily from smelting of pyroxene. We infer that during a brief interval after smelting had formed these metals but before the pyroxenes resolidified, and before much Si had reduction had occurred, these metals managed to equilibrate with the large elongate metal grains (interstitial to the coarse pre-shock mafic silicates) that were the rock’s main repository of Ni. The Ni data thus tend to confirm that during the smelting of LAR 04315 even the pyroxene cores were opened to rapid exchange with their rims as a consequence of pervasive CO₂-fluid porosity.

5. CONCLUSIONS

1. As exemplified by the meteorites LAP 03587 and especially LAR 04315, the terminal, impact-triggered redox processing of the ureilites was in some cases more effective at reducing FeO from pyroxene than in the usual manner from the rims of olivines.

2. Unlike the olivine-rim reduction phenomenon that has often been termed smelting, the process that reduced the pyroxene of LAR 04315 probably was true smelting; i.e., reduction occurring along with and facilitated by melting. The LAR 04315 pyroxenes were reduced (impact-smelted) almost as efficiently in their centers as in their rims; they are now almost uniformly porous (~15%) and sprinkled with small Fe-metals and pockets of glass. However, these pyroxenes also managed to retain to an enigmatically large extent their former optical continuity. Overall, the perterrestrial porosity of LAR 04315 was probably between 9% and 12%.

3. Fortunately, in a few minor areas LAP 03587 pyroxene happened to avoid smelting, so we know that the pre-impact pyroxene was, in typical ureilite fashion, a pigeonite with a very tight compositional range near En₂₄Wo₇₆.

4. The mosaicized state of the olivine in LAR 04315 confirms that it experienced a severe impact shock. However, LAP 03587, which contains some pyroxene

---

Table 3

<table>
<thead>
<tr>
<th>Fe-metals in LAR 04315</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
<th>Co</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>N</th>
<th>NG</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average, large elongate grains in original interstices</td>
<td>93.42</td>
<td>4.56</td>
<td>2.30</td>
<td>0.32</td>
<td>0.14</td>
<td>0.01</td>
<td>0.03</td>
<td>15</td>
<td>5</td>
<td>100.79</td>
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<tr>
<td>Average, tiny grains within smelted pigeonites</td>
<td>93.95</td>
<td>5.23</td>
<td>0.01</td>
<td>0.30</td>
<td>0.09</td>
<td>0.02</td>
<td>0.08</td>
<td>5</td>
<td>5</td>
<td>99.68</td>
</tr>
<tr>
<td>Average, tiny grains in olivine ovoids areas</td>
<td>97.63</td>
<td>1.14</td>
<td>0.26</td>
<td>0.14</td>
<td>0.19</td>
<td>0.05</td>
<td>0.09</td>
<td>5</td>
<td>4</td>
<td>99.49</td>
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<tr>
<td>Grain in felsic glass + silica area</td>
<td>91.46</td>
<td>6.58</td>
<td>2.04</td>
<td>0.30</td>
<td>0.10</td>
<td>0.05</td>
<td>0.01</td>
<td>2</td>
<td>1</td>
<td>100.53</td>
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<table>
<thead>
<tr>
<th>Fe-metals in Almahata Sitta, AS-H109</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
<th>Co</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>N</th>
<th>NG</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grains (mostly large) not interior to either LPS or OP</td>
<td>92.44</td>
<td>3.69</td>
<td>3.52</td>
<td>0.29</td>
<td>0.10</td>
<td>0.01</td>
<td>nd</td>
<td>19</td>
<td>10</td>
<td>100.06</td>
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<tr>
<td>Interior LPS sublithology grains, Si-rich</td>
<td>91.55</td>
<td>4.08</td>
<td>3.61</td>
<td>0.29</td>
<td>0.09</td>
<td>0.02</td>
<td>nd</td>
<td>4</td>
<td>4</td>
<td>99.89</td>
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<tr>
<td>Interior LPS sublithology grains, Si-poor</td>
<td>94.95</td>
<td>4.39</td>
<td>0.13</td>
<td>0.34</td>
<td>0.10</td>
<td>0.02</td>
<td>nd</td>
<td>7</td>
<td>7</td>
<td>99.94</td>
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<tr>
<td>Interior OP sublithology grains</td>
<td>97.03</td>
<td>1.65</td>
<td>0.09</td>
<td>0.14</td>
<td>0.16</td>
<td>0.02</td>
<td>nd</td>
<td>8</td>
<td>7</td>
<td>99.09</td>
</tr>
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<table>
<thead>
<tr>
<th>Sulfides in LAR 04315</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
<th>Co</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>N</th>
<th>NG</th>
<th>Total</th>
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<tbody>
<tr>
<td>Round 100 μm grain in felsic glass + silica area</td>
<td>59.21</td>
<td>0.10</td>
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<td>0.00</td>
<td>0.02</td>
<td>35.07</td>
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<td>2</td>
<td>2</td>
<td>97.27</td>
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<tr>
<td>Large elongate grain in original interstice</td>
<td>60.62</td>
<td>0.14</td>
<td>0.00</td>
<td>0.03</td>
<td>0.00</td>
<td>34.50</td>
<td>1.75</td>
<td>2</td>
<td>1</td>
<td>97.05</td>
</tr>
<tr>
<td>Large elongate grain in original interstice</td>
<td>61.07</td>
<td>0.14</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>34.71</td>
<td>2.03</td>
<td>2</td>
<td>1</td>
<td>97.95</td>
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<td>Large elongate grain in original interstice</td>
<td>55.16</td>
<td>0.11</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>35.16</td>
<td>6.30</td>
<td>2</td>
<td>1</td>
<td>96.74</td>
</tr>
</tbody>
</table>

Abbreviations: N, number of similar analyses averaged; NG, number of separate grains involved in the average; nd, not determined.
almost as impact-smelted and porous as that of LAR 04315, features little-shocked euhedral graphites and no olivine mosaicism.

5. By-products of impact smelting in LAR 04315 include diverse felsic glasses, mostly with 58–66 wt% SiO2 and 19–25 wt% Al2O3. Together with a similar proportion of silica, these glasses typically occur as selvages that line the walls of some of the largest voids in the meteorite.

6. The fine-grained ureilite lithology of Almahata Sitta probably also formed by a kind of impact smelting. In places, this lithology retains the relict structure of a typical ureilite, although the former coarse-equant olivines have been granulated and infiltrated by a melt close to Ca-rich pyroxene in composition, and the former pyroxenes (consistently low-Ca) have been granulated and reduced to yield minor interstitial silica and Fe-metal.

7. The concentration of smelting into pigeonite in LAR 04315 and LAP 03587 probably arose because the materials were already very hot (anatectic) before the impact. Although the impact heating was only moderate, the melting temperature of the pigeonite was about 300 degrees lower than that of the accompanying olivine.

8. The unusual aspects of LAR 04315 and LAP 03587 thus confirm previous indications that the terminal episode of smelting and rapid cooling was triggered when the parent ureilite asteroid underwent a catastrophically disruptive impact while its mantle was in a hot, anatectic condition.

9. The proportion of CO2 gas generated by ureilite smelting exceeded by at least a small factor the volume represented as porosity in the final ureilites; by a very large factor (of order 103 or greater), if literature inferences of extremely fast cooling rates, implying slight burial depths, are accurate. The outflow of so much gas may have significantly enhanced the purging of the ureilite melt component; and explosive expansion and jetting of the gas may have enhanced the thoroughness of the catastrophic impact disruption of the parent asteroid.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2010.05.026.

REFERENCES


Pyroxene-selective impact smelting in ureilites


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