Incremental melting in the ureilite parent body: Initial composition, melting temperatures, and melt compositions

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Abstract–Ureilites are carbon-rich ultramafic achondrites that have been heated above the silicate solidus, do not contain plagioclase, and represent the melting residues of an unknown planetesimal (i.e., the ureilite parent body, UPB). Melting residues identical to pigeonite-olivine ureilites (representing 80% of ureilites) have been produced in batch melting experiments of chondritic materials not depleted in alkali elements relative to the Sun’s photosphere (e.g., CI, H, LL chondrites), but only in a relatively narrow range of temperature (1120 °C–1180 °C). However, many ureilites are thought to have formed at higher temperature (1200 °C–1280 °C). New experiments, described in this study, show that pigeonite can persist at higher temperature (up to 1280 °C) when CI and LL chondrites are melted incrementally and while partial melts are progressively extracted. The melt productivity decreases dramatically after the exhaustion of plagioclase with only 5–9 wt% melt being generated between 1120 °C and 1280 °C. The relative proportion of pyroxene and olivine in experiments is compared to 12 ureilites, analyzed for this study, together with ureilites described in the literature to constrain the initial Mg/Si ratio of the UPB (0.98–1.05). Experiments are also used to develop a new thermometer based on the partitioning of Cr between olivine and low-Ca pyroxene that is applicable to all ureilites. The equilibration temperature of ureilites increases with decreasing Al2O3 and Wo contents of pyroxene and decreasing bulk REE concentrations. The UPB melted incrementally, at different fO2, and did not cool significantly (0 °C–30 °C) prior to its disruption. It remained isotopically heterogenous, but the initial concentration of major elements (SiO2, MgO, CaO, Al2O3, alkali elements) was similar in the different mantle reservoirs.

INTRODUCTION

Ureilites are the largest group of ultramafic achondrites (550 samples at the time of writing) and the second largest group of achondrites after howardites-eucrites-diogenites. Most ureilites are composed of olivine and pigeonite with a significant fraction of metal (<5 wt%), graphite (~3 wt%), and traces of sulfide concentrated along silicate grain boundaries. Fewer samples contain orthopyroxene and augite instead of or in addition to pigeonite (e.g., Takeda et al. 1989; Goodrich et al. 2001). With the exception of brecciated ureilites (i.e., polymict ureilites) and a single monomict ureilite (Goodrich et al. 2016), they are completely devoid of plagioclase. Their bulk composition is depleted in incompatible lithophile elements and chalcophile elements relative to all chondrites.

While they were once described as ultramafic igneous cumulates (Berkley et al. 1980; Goodrich et al. 1987), most ureilites are now recognized as residues of partial melting representing the mantle of a planetesimal that lost abundant FeNi-sulfide eutectic melts (e.g., Warren et al. 2006; Goodrich et al. 2013a; Barrat et al. 2015) and silicate melts (Warren and Kallemeyn 1992; Scott et al. 1993; Kita et al. 2004; Goodrich et al. 2007; Warren 2012; Barrat et al. 2016). The ureilite parent body (UPB) was violently disrupted while its internal temperature was still high (1150°C–1300 °C; e.g.,
Batch melting experiments of H, LL, and CI chondrites produce pigeonite-olivine residues in a relatively narrow temperature interval, between 1120 °C and 1180 °C, while many ureilites are thought to have formed at 1200 °C–1270 °C (e.g., Takeda et al. 1989; Sinha et al. 1997). Here, we investigate whether pigeonite can persist at higher temperature when CI and LL chondrites are melted incrementally and while partial melts are progressively extracted. Experimental results are compared to 12 ureilites that were analyzed for this study and ureilites described in the literature to constrain the initial composition of the UPB and its Mg/Si ratio in particular. Then, we develop a new thermometer based on the partitioning of Cr between olivine and low-calcium pyroxene (LCP; orthopyroxene or pigeonite) that can be used to constrain the temperature of equilibration of all ureilites. The $D_{\text{Cr}^{2+}}^{\text{olivine-LCP}}$ thermometer is used to distinguish between ureilites representing simple melting residues and ureilites representing cumulates or the products of more complex igneous processes. We compare the former (most pigeonite-olivine ureilites) to our experiments to constrain melting processes and estimate the composition of the last silicate melts that were in equilibrium with ureilites. We also use the new temperature of equilibration of ureilites to discuss the thermal history of the UPB and the nature of the heterogeneity in $f_{\text{O}_2}$ and oxygen isotopes of the UPB.

**METHODS**

**Experimental Approach**

All experiments were performed in the MIT Experimental Petrology Laboratory in a molybdenum hafnium carbide pressure vessel (MHC-PV) placed in a Deltech vertical furnace following the same overall approach described in Walker and Grove (1993) and Singletary and Grove (2006). One key difference is that several starting compositions (~10 mg each) were equilibrated simultaneously in individual graphite capsules positioned vertically in a single Pt outer capsule. The temperature gradient is small at the base of the MHC-PV (<3 °C over the length of the Pt capsule) and all experimental charges were equilibrated under the same P-T-$f_{\text{O}_2}$ conditions. The outer Pt capsule was loosely crimped but not sealed to allow for equilibration with the CO pressure medium and set the $f_{\text{O}_2}$ to the CCO buffer (French and Eugster 1965). In all but two experiments, the temperature was fixed for the duration of the experiments. In the other two experiments (CHS 46 and 71), the temperature was first raised 20 °C–50 °C above the final temperature for 2 hours. After 7 hours to 5 days, experiments were...
purity oxides, silicates (CaSiO3), carbonates (Na2CO3), and Fe metal (Grove and Bence 1977). Additional compositions, RCa and RCa2, represent arbitrary “near-chondritic” compositions depleted in alkali elements relative to the Sun’s photosphere (NaK# = 50). Yet, they are characterized by contrasting Mg/Si (0.92 and 1.03, respectively) and Ca/Si ratios (0.052 and 0.06). In addition, CI and LL compositions are relatively close in Mg# (68.5 – 70) to the most FeO-rich ureilites (74), after removal of sulfur as FeS. Two additional compositions, RCa and RCa2, represent arbitrary “near-chondritic” compositions depleted in Al2O3, Na2O, and K2O but enriched in CaO. They were included to produce two-pyroxene assemblages that could be compared to orthopyroxene-augite ureilites.

EPMA Analyses

The JEOL-JXA-8200 SuperProbe electron probe micro analyzer (EPMA) of the MIT Electron Microprobe Facility was used to acquire quantitative analyses of experimental run products as well as olivine and pyroxene in 12 ureilites. Silicates were analyzed with a focused beam, a voltage of 15 kV, and a current intensity of 10 nA. All elements were measured for 40 s

| Exp. # | P (CO) MPa | T int °C | \( \log fO_2 \) (CCO) | \( \Delta IW \) | t (h) | \( \Delta T^* \) °C | Starting compositions per experiment |
|--------|------------|---------|----------------|-------------|------|----------------|-----------------------------------|
| CHS 46 | 6.2        | 1191    | −13.7          | −1.61       | 72   | 20             | LLR1                             |
| CHS 47 | 6.6        | 1200    | −13.6          | −1.63       | 72   | 0              | CIR1, LLR1, LLR2                  |
| CHS 48 | 4.1        | 1194    | −14.0          | −1.98       | 72   | 0              | CIR1, LLR1, H                     |
| CHS 49 | 10.0       | 1248    | −13.0          | −1.62       | 24   | 0              | CIR1, CIR3, LLR1, LLR2            |
| CHS 50 | 7.2        | 1248    | −13.3          | −1.89       | 27   | 0              | CIR1, CIR2a, CIR3                 |
| CHS 51 | 8.1        | 1217    | −13.3          | −1.58       | 68   | 0              | CIR2a, CIR1, CIR3, LLR1, LLR2     |
| CHS 53 | 12.1       | 1248    | −12.8          | −1.47       | 46   | 0              | CIR2a, CIR1, CIR3                 |
| CHS 63 | 9.1        | 1202    | −13.3          | −1.38       | 72   | 0              | CIR2b, CI, H                      |
| CHS 65 | 3.1        | 1201    | −14.2          | −2.27       | 52   | 0              | CIR2b, CIR1, RCa, CI, H           |
| CHS 66 | 3.4        | 1250    | −13.9          | −2.53       | 42   | 0              | CIR1, CIR2b, RCa, CI              |
| CHS 67 | 13.3       | 1274    | −12.6          | −1.59       | 20   | 0              | CIR2b, CIR1, CI                   |
| CHS 68 | 5.2        | 1159    | −12.5          | −1.53       | 100  | 0              | CIR2b, RCa2, RCa, CI              |
| CHS 69 | 5.9        | 1301    | −13.2          | −2.44       | 9    | 0              | RCa, RCa2, CIR2b, H, CI           |
| CHS 70 | 3.8        | 1205    | −14.2          | −1.84       | 96   | 0              | RCa2, RCa, CI                     |
| CHS 71 | 7.9        | 1216    | −13.3          | −1.59       | 90   | 58             | LLR1, CIR1, CIR2b, CI             |

\( fO_2 \) calculated based on the CCO buffer (extended formulation, French and Eugster, 1965) and expressed relative to the IW buffer (Huebner 1971).

Experimental charges with starting chondritic compositions (italic) are described in Collinet and Grove (2020a). *T (°C) of initial 2 h step—final T (°C); 0 = isothermal.

terminated by pulling the MHC-PV out of the furnace, inverting it, and hitting it with a wrench to ensure that the capsule dropped into the water-cooled head of the pressure vessel and quench. Experiment conditions are summarized in Table 1.

This study is a complement to a larger series of melting experiments of chondritic materials (Collinet and Grove 2020a, 2020b). In previous manuscripts, we reported on experimental charges that contain strictly chondritic bulk compositions (H, LL, CI, CM, and CV) and simulate the batch melting of planetesimals. In this study, we describe distinct experimental configurations and simulate the batch melting of planetesimals. In this study, we describe distinct experimental configurations and simulate the batch melting of planetesimals. In this study, we describe distinct experimental configurations and simulate the batch melting of planetesimals. In this study, we describe distinct experimental configurations and simulate the batch melting of planetesimals.
Table 2. Experimental starting compositions and bulk ureilite compositions.

|                | CI* | CIR1 | CIR2a | CIR2b | CIR3 | PCA | North | LLR1 | LLR2 | DPD | RCa1 | RCa2 |
|----------------|-----|------|-------|-------|------|-----|-------|------|------|-----|------|------|
|                | 1/1 | 15.5 | 15.5  | 19.5  |      | 82506 | mmict | pmict |      |      |      |      |
| SiO2           | 40.8| 39.7 | 37.1  | 38.1  | 38.3 | 42.0 | 40.3  | 37.6 | 36.0 | 41.6| 40.3 | 41.8 |
| TiO2           | 0.13| 0.09 | 0.07  | 0.05  | 0.04 | 0.09 | 0.12  | 0.12 | 0.19 | 0.05| 0.05 | 0.09 |
| Al2O3          | 2.86| 1.15 | 0.65  | 0.37  | 0.38 | 0.10 | 0.20  | 0.22 | 0.44 | 0.39| 0.37 | 0.85 |
| Cr2O3          | 0.69| 0.60 | 0.79  | 0.66  | 0.82 | 0.73 | 0.51  | 0.59 | 0.63 | 0.81| 0.65 | 0.88 |
| FeO            | 21.8| 22.4 | 24.6  | 22.7  | 23.3 | 23.8 | 23.8  | 30.8 | 21.9 | 23.5| 24.5 | 21.3 |
| MnO            | 0.44| 0.36 | 0.36  | 0.36  | 0.37 | 0.41 | 0.44  | 0.31 | 0.38 | 0.39| 0.36 | 0.30 |
| MgO            | 28.2| 32.1 | 32.4  | 34.2  | 34.1 | 36.3 | 37.9  | 23.8 | 26.8 | 28.8| 30.7 | 33.2 |
| CaO            | 2.30| 1.87 | 1.99  | 2.00  | 1.34 | 1.00 | 1.38  | 1.78 | 2.11 | 1.96| 1.41 | 1.54 |
| Na2O           | 1.20| 0.54 | 0.24  | 0.26  | 0.25 | 0.03 | 0.09  | 0.89 | 0.99 | 0.56| 0.26 | 0.07 |
| K2O            | 0.12| 0.03 | 0.00  | 0.01  | 0.01 | 0.01 | 0.03  | 0.10 | 0.10 | 0.03| 0.01 | 0.05 |
| P2O5           | 0.39| 0.20 | 0.32  | 0.19  | 0.19 | 0.19 | 0.23  | 0.26 | 0.22 | 0.21| 0.21 | 0.18 |
| NiO            | 1.13| 1.04 | 1.11  | 1.10  | 1.12 | 0.10 | 0.15  | 1.48 | 1.01 | 1.09| 1.18 | 1.32 |
| Mg/Si           | 1.03| 1.21 | 1.30  | 1.34  | 1.33 | 1.29 | 1.40  | 0.94 | 0.92 | 1.03| 1.14 | 1.18 |
| (Ca/Mg)Cl      | 1.01| 0.72 | 0.76  | 0.73  | 0.49 | 0.34 | 0.45  | 0.93 | 0.98 | 0.57| 0.58 | 1.31 |
| (Al/Mg)Cl      | 1.00| 0.35 | 0.20  | 0.11  | 0.11 | 0.05 | 0.05  | 0.92 | 0.90 | 0.41| 0.13 | 0.25 |
| Mg#            | 69.7| 71.9 | 70.1  | 72.9  | 72.3 | 77.1 | 78.6  | 57.9 | 68.6 | 68.7| 69.1 | 73.6 |

F = estimated melt fraction extracted from residues relative to chondritic composition CI and LL, respectively; mmict and pmict = bulk composition of monomict and polymict ureilites from Jarosewich (2006), DPD: Dingo Pup Donga.

*Average chondritic starting compositions of Lodders and Fegley (1998), renormalized without FeS or volatile elements; starting compositions of batch melting experiments (Collinet and Grove 2020a).

Incremental melting in the ureilite parent body

(20 s for backgrounds) except Na, which was counted first for 8 s (4 s for backgrounds). In many experiments, the small quantity of melt (<5 wt%) wetting grain boundaries, but rarely pooling, precluded reliable measurement of its composition (quench-modified glass). When attempted, the analysis of experimental glasses was done with a 5 nA current intensity, a spot size of 2–4 µm, and a counting time of 4 s for Na.

Elemental X-ray maps of Si, Mg, Fe, Ca, and Al were acquired for 10 of the 12 ureilites. The maps were performed with a beam size of 5–10 µm, a step size of 15–25 µm, a voltage of 15 kV, a current intensity of 30 nA, and a counting time of 40 ms. Elemental intensities were acquired simultaneously with five wavelength dispersive spectrometers.

Calculation of the Mode of Ureilites and Experiments

Elemental X-ray maps were compiled with MultiSpec© and used to create automatically 50 clusters of pixels in five dimensions with the algorithm ISODATA. Pixel clusters were then manually grouped into classes representing the different phases (1) Fe-metal, sulfide, and oxides; (2) olivine; (3) low-Ca pyroxene; and, if present, (4) augite. Graphite, the residual porosity, and all ambiguous clusters were grouped as background. The number of pixels in each class, representing the modal composition of ureilites in vol%, was counted with ImageJ. This treatment was applied to the 10 ureilite thin sections mapped for this study and to eight additional ureilites studied by Singletary and Grove (2003) using their original X-ray maps.

The phase proportions in experiments were estimated by mass balancing the composition of the different phases against the bulk composition of the starting material with the function fitlm in Matlab©. However, because the chemical composition of most melts could not be analyzed, we first had to estimate their composition by altering the composition of experimental batch melts at the same temperature and fO2 conditions (Collinet and Grove 2020a). The concentrations of SiO2, Al2O3, and alkali elements were progressively lowered while the concentrations of CaO and, to a lesser extent, FeO and MgO, were slightly increased. Five to ten multiple linear regressions were performed and the one with the lowest sum of squared residuals was selected. In practice, we find that as long as a melt is included in mass balance calculations, the relative proportions of olivine and pyroxene are not very sensitive to small variations in the estimated melt composition. However, when no melt is included, mass balances tend to overestimate the proportion of pyroxene relative to olivine by ~5 wt% (or 5 py units; where py is the ratio px/[px + oliv]*100 in wt%) even in experiments that apparently contain only a few percent of liquid (e.g., LLR2 in CHS 47, 51). Finally, to confirm that this method provides reasonable estimates of py, we calculated phase proportions in vol% by image analysis of 10 backscattered electron (BSE)
images for two experimental charges: LLR2 in CHS 47 and CIR2b in CHS 63. Modal compositions in vol% were converted into wt% by multiplying the phase proportions by the densities of olivine and pyroxene of appropriate composition. The py calculated by image analysis is consistent (within ~3 py units) with the ones calculated by mass balance: 23.1 (versus 21.2) and 42 (versus 44.6) for CHS 47 and CHS 63, respectively.

RESULTS

Experiments on Chondritic Residues

Most experimental charges performed using the LLR1-2 and CIR1-3 bulk compositions (chondritic residues) contain olivine, pigeonite (or orthopyroxene), glass, and metal (Fig. 1). Only one charge, CIR2 in CHS 65 (1201 °C, IW −2.3), has minor augite in addition to pigeonite. All crystalline phases are homogenous in composition. Experimental runs using CIR1 and LLR1, the least depleted residues, contain more melt than CIR2-3 and LLR2 runs at a given temperature. We calculate the aggregate melt fraction (i.e., the total amount of melt produced from the initial chondritic composition), by adding the melt fraction in CIR1-3 or LLR1-2 experiments to the melt fractions associated with the different starting compositions (Table 2). At a given temperature, aggregate melt fractions are significantly smaller (15–22 wt%) in remelted residues than in batch melting experiments (up to 35 wt%; Fig. 2). The main effect of removing partial melts as melting progresses is to considerably lower the melt productivity at higher temperature.

Because melt removal slows down the melting process considerably, the pigeonite (i.e., LCP with Wo content greater than 5, when defined based on composition) can persist in experimental residues up to ~1280 °C, 80 °C higher than in batch melting experiments (Fig. 3). The bulk CIR2 composition corresponds to the residue immediately following the disappearance of plagioclase (F = 15.5 wt %; Collinet and Grove 2020a) and produces pigeonite with a high wollastonite content (Wo) at the highest temperature (1280 °C). LLR1-2 charges contain a pigeonite with lower Wo content and pigeonite disappears at ~1220 °C (as opposed to 1170 °C in batch melting experiments of H and LL compositions).

The pigeonite in LLR1-2 charges has a lower Wo content because py is significantly larger than in CIR1-3 charges (Fig. 4). The larger proportion of pyroxene
relative to olivine in experimental charges with LLR1-2 compositions results from their lower bulk Mg/Si ratios (Table 2). In other words, in LLR1-2 charges, similar bulk CaO concentrations are “diluted” into a larger volume of pyroxene than in CIR1-3 charges. As melting progresses, pyroxene is consumed and py decreases along with the Wo content in the remaining pyroxene. However, at a given total extent of melting, there is ~20 wt % less pyroxene in CI residues, with a higher Wo content, than in LL residues. The Mg# of olivine and pyroxene increases with decreasing fO2 conditions from 75 at IW/C0 1.3 to 95 at IW/C0 2.5. In parallel, the fraction of Fe metal increases by 12 wt% (Fig. S1 in supporting information).

Experimental charges with CaO-rich bulk compositions that do not correspond to known chondritic residues (DCA1 and DCA2) contain olivine, pigeonite, augite, glass, and metal. No attempt was made to estimate the melt fractions in those experiments. They are used, together with other experimental charges, to constrain the temperature of equilibration of ureilites and the thermal history of the UPB. The detailed composition of experimental run products is reported in the supporting information (Tables S1–S5).

**Mineral Composition and Petrographic Description of Ureilites**

Among the 12 ureilites analyzed for this study, eight are US Antarctic samples provided by the Meteorite Working Group. Several of them have been described to various extents in the literature: ALHA82106 (Takeda et al. 1989), EET 96293 (Singletary and Grove 2003), LAP 03721 (paired to LAP 03587; Warren and Rubin 2010), EET 90019 (Warren 2012). Four additional samples from Northwest Africa were acquired from private collectors and have not been previously described in detail. The phase compositions and the phase proportions are reported in Table 3 and the BSE images of six samples are shown in Fig. 5.

Three of the nine ureilites that we studied are orthopyroxene-augite-olivine ureilites (EET 96293, NWA 11754, and ALHA82106), one is an orthopyroxene-pigeonite-olivine ureilite (NWA 5555), and the remaining eight are pigeonite-olivine ureilites. EET 90019 and NWA 4852 are some of the most FeO-poor pigeonite-olivine ureilites (Fo89.4 and Fo 87.7, respectively). We observed a single 80 µm pigeonite in section 15 (0.6 cm2) of DOM 08012. Chromite was only found in MIL 07447 as two 50 µm spherical crystals: one zoned and enclosed in olivine and the other relatively homogenous and enclosed in pigeonite (Fig. S2 in supporting information). In addition to the grain boundary metal and sulfide, spherules of variable size (1–20 µm), made of C-rich metal (possibly cohenite), C-poor metal, sulfides, and frequently all three, occur as inclusions in pigeonite and olivine (Fig. S2). Most samples also display the typical 10–50 µm rims of MgO-rich olivine containing sub-µm metal blebs and produced by reduction during the disruption of the UPB (i.e., “secondary smelting”).

In four of the eight pigeonite-olivine ureilites (NWA 11755, LAP 03721, MIL 090076, and EET 96042), the pyroxene has been extensively smelted (Fig. 5e–f), probably due to a brief episode of shock heating that followed the impact (Warren and Rubin 2010). In those
samples, but not in the other four, olivines contain sub-μm metal inclusions in their cores (Fig. S4 in supporting information). Unlike the metal-sulfide spherules mentioned in the previous paragraph, they are homogenously distributed and exclusively sub-μm.

NWA 11755 (Fig. 5e) displays particularly clear evidence of this reduction process, including the same bimodal porosity affecting “relic” pigeonite cores and reduced FeO-poor pyroxene as in LAR 04315 (Warren and Rubin 2010). Because the pyroxene was almost completely smelted and is porous, we did not attempt to estimate the pre-impact phase proportions of NWA 11755. Unlike smelted rims, the core of olivine and pyroxenes are homogeneous in composition.

NWA 11754 has a large fraction of pyroxene, including abundant augite, and a large fraction of metal that fills fractures and silicate grain boundaries (Fig. 5d). NWA 11754 is in every way identical to Hughes 009 and other members of the “Hughes cluster”, a group of ureilites interpreted as igneous cumulates rather than melting residues (Goodrich et al. 2001, 2009, 2016). EET 96293 has the same Fo content in olivine as Hughes 009 and, while it contains less augite than Hughes 009/NWA 11754, it contains a similar fraction of total pyroxene (Fig. 6).

ALHA 82106 is a unique orthopyroxene-augite-olivine ureilite that contains wavy exsolution lamellae of augite in orthopyroxene (Fig. 5c). Because ALHA 82106 also contains coarse-grained augite, its silicate phase assemblage at peak temperature is believed to have been augite-pigeonite-olivine (Takeda et al. 1989). The element maps used to calculate the modal composition of 10 of the 12 ureilites and eight of the ureilites analyzed by Singletary and Grove (2003) are available in the supporting information. All but three ureilites form an overall trend of increasing py with Fo in olivine (Fig. 6; $R^2 = 0.74$), similar to the py-Fo trends previously documented by Singletary and Grove (2003) and Goodrich et al. (2007). Only the two anomalous “Hughes cluster” samples and MET 01083, which displays a poikilitic texture (Fig. S11 in supporting information), were excluded. The trend formed by ureilites in Fig. 6 has the same slope as residues with constant Mg/Si ratios, having lost the same aggregate melt fraction at various $fO_2$. It is also parallel to similar trends formed by ordinary chondrites.
DISCUSSION

The Initial Composition of the UPB

Ureilites have long been thought to be related to carbonaceous chondrites due to their high graphite content. In support of this view, Clayton et al. (1976) and Clayton and Mayeda (1988) showed that ureilites form a trend of mass-independent fractionation in three-isotope plots and are coarsely aligned with CV chondrites (Greenwood et al. 2017). However, the discovery of nucleosynthetic anomalies in Cr, Ni, and Ti isotopes in bulk ureilites has raised questions about the connection between ureilites and carbonaceous chondrites (Qin et al. 2010; Warren 2011). On a $\Delta^{17}$O–$\varepsilon^{54}$Cr diagram, ureilites, which have higher concentrations of neutron-rich isotopes (e.g., $^{54}$Cr and $^{50}$Ti) relative to carbonaceous chondrites, are part of the “NC” group along with enstatite and ordinary chondrites (Qin et al. 2010; Warren 2011). On a $\Delta^{17}$O–$\varepsilon^{54}$Cr diagram, ureilites, which have higher concentrations of neutron-rich isotopes (e.g., $^{54}$Cr and $^{50}$Ti) relative to carbonaceous chondrites, are part of the “NC” group along with enstatite and ordinary chondrites. Goodrich et al. (2015) inferred that ureilites still formed in the same region of the nebula as carbonaceous chondrites (greater heliocentric distance) but at a time when nucleosynthetic anomalies were distinct (~0.5 Ma after CAIs). However, the NC and CC reservoirs are thought to have been present and isolated from each other very early (~1 Ma after CAIs), presumably by a proto-Jupiter, based on the Mo isotopes of NC and CC iron meteorites (Kruijer et al. 2017). If this is true, and if the UPB accreted relatively late (1.4–1.7 Ma after CAIs) as suggested by Budde et al. (2015), then the UPB would have accreted within the orbit of proto-Jupiter together with the other NC parent bodies. However, the accretion time of the UPB is still debated and Van Kooten et al. (2017) and Zhu et al. (2020) argued that the UPB was partly differentiated earlier than 1 Ma after CAIs (and as early as 0.6 Ma ΔCAIs), an older age compatible with the thermal evolution models of Wilson et al. (2008) and Goodrich et al. (2015). Based on a presumed relationship between Si isotopes and the Mg/Si ratio of parent bodies, Dauphas et al. (2015) calculated a value of 1.00/0.08 for the UPB, but the uncertainty overlaps with both carbonaceous and ordinary chondrites. In summary, at present, isotopic systematics do not provide strong constraints on the initial major element composition of the UPB.

Using MAGPOX (Longhi 1991), Goodrich (1999) and Goodrich et al. (2007) showed that superchondritic CaO/Al$_2$O$_3$ ratios were required to stabilize pigeonite in ureilites. They extensively discussed whether this could represent a primary feature of the UPB. Other workers have commented on this issue and the consensus that has emerged is that the superchondritic CaO/Al$_2$O$_3$ ratios resulted from parent body processes rather than nebula processes (Kita et al. 2004; Warren 2012; Goodrich et al. 2013c). In a recent experimental study (Collinet and Grove 2020b), we show that the UPB was initially characterized by a chondritic CaO/Al$_2$O$_3$ and only became depleted in Al$_2$O$_3$ following the extraction of low-degree silicate melts. We also show that the initial composition of the UPB was not depleted in alkali elements relative to the Sun’s photosphere (NaK# = 50). All high NaK# chondritic compositions (H, LL,
CI) produce pigeonite-olivine residues upon melting, contrary to CM (33) and CV (25) compositions. Therefore, the assumption that the precursor material of FeO-poor ureilites contained more CAIs than the one of FeO-rich ureilites (Singletary and Grove 2006; Goodrich et al. 2013a) appears to be no longer justified. Any significant addition of CAIs to FeO-poor ureilites would drive down the NaK# toward the value of CM (33) and CV chondrites (25), which do not form pigeonite-olivine residues by partial melting.

The new incremental melting experiments and additional analyses of ureilites performed for this study can be used to constrain the initial Mg/Si ratio of the UPB in more detail. Warren (2011) argued that, despite being carbon-rich, ureilites could derive from “NC” chondritic materials with Mg/Si ratios resembling ordinary chondrites (0.92–0.95) but lower Fe/Si ratios. Goodrich (1999) also concluded that the initial Mg/Si ratio was close to the one of ordinary chondrites and Goodrich and Wilson (2013) proposed that it was even

Fig. 5. Backscattered images of a subset of the ureilites analyzed for this study. See text for description of samples (a), (b), and (c). All samples display reduction rims in olivine. Pyroxene is almost completely “smelted” in NWA 11755 (e). It displays a coarse porosity in the FeO-poor area and a fine porosity in the FeO-rich area. MIL 090076 displays a similar texture, but the pyroxene cores are homogeneous and free of porosity (f). NWA 11754 is characteristic of the “Hughes cluster” (d). See text for description of samples (a), (b) and (c).
lower, close to the Mg/Si ratio of enstatite chondrites (0.74–0.88).

The olivine and pigeonite of CIR2 experimental charges are identical, both in terms of chemical composition and relative proportions (py), to the olivine and pigeonite in ureilites (compare Fig. 4 to Fig. 6). LLR1-2 experimental charges contain an overabundance of low-Ca pyroxene, with relatively lower Wo contents (4–6.5) compared to ureilites (up to Wo12). Therefore, the Mg/Si ratio of the LL starting composition (0.92) places a firm lower limit on the initial Mg/Si ratio of the UPB. Any composition with a lower ratio would contain no pigeonite at all (Wo <5). The Mg/Si ratio of the CI composition (1.03) is likely much closer to the average initial ratio of the UPB. The positive correlation between the Fo content in olivine and the py of ureilites displays some scatter that allows for a certain degree of heterogeneity in the initial Mg/Si ratio (i.e., 0.98–1.05). However, the slope of the Fo-py trend, which is identical to experimental trends of constant aggregate melt fraction, suggests that, if present, slight variations in the Mg/Si ratio were independent of the Fo content in olivine.

If the initial Fe/Mg of the UPB had been homogenous, high-Fo ureilites that formed under more reducing conditions (IW −2/−2.5) should also contain more metal, unless some of the metal was extracted from the residues along with FeS (Barrat et al. 2015), in which case highly siderophile element concentrations would be expected to be lower (Warren and Huber 2006; Warren et al. 2006). Ureilites with Fo95 olivine should contain 6 wt% and 12 wt% more Fe0 than ureilites with Fo75 olivine (Fig. S1). Because neither metal fractions nor siderophile element concentrations correlate with Fo content in olivine, the UPB is often thought of as initially heterogeneous in Fe/Mg. However, the siderophile element concentrations of ureilites are still not well understood despite extensive studies. It remains possible that the UPB was heterogeneous in siderophile elements or that a fraction or exogenous metal overprinted siderophile element concentrations (Goodrich et al. 2013a; Goodrich and Desch 2019).

Literature Estimates of Ureilite Equilibration Temperatures

Estimating the temperature of equilibration (T_E) of individual ureilite samples has been a central issue in interpreting their petrogenesis. As most ureilites only contain pigeonite and olivine, two-pyroxene (Lindsley 1983; Lindsley and Andersen 1983; Sack and Ghiors 1994) and olivine-chromite thermometry (Evans and Frost 1975; Wlotzka 2005) can only be applied to relatively small subgroups of ureilites. Most two-pyroxene temperatures that have been calculated for augite-orthopyroxene or pigeonite-orthopyroxene ureilites are in the range 1200 °C–1270 °C (Takeda 1989; Takeda et al. 1989; Sinha et al. 1997; Chikami et al. 1997; Weber et al. 2003) while olivine-chromite
temperatures are much lower 1040 °C–1060 °C (Goodrich et al. 2014).

Singletary and Grove (2003) made the first attempt at estimating the temperature of pigeonite-olivine ureilites by calibrating an empirical thermometer based on the MgO and CaO concentrations of pigeonite. Our batch and incremental melting experiments of chondritic compositions can be used to evaluate its utility. Of 22 experimental charges containing olivine, pigeonite, metal, and melt, only five have a calculated temperature within ±20 °C of the experimental temperature. Five experiments have a calculated temperature within ±50 °C and the last 10 experiments are within ±100 °C. The pigeonite thermometer of Singletary and Grove (2003) overestimates the actual temperatures of most of our experiments (Fig. S8 in supporting information). Pyroxene phase diagrams (Lindsley and Andersen 1983; Sack and Ghiorso 1994), previous experiments on basaltic compositions (Grove and Juster 1989), and the experiments of this study show that the minimum temperature at which pigeonite is stable increases with the Mg#. The maximum temperature of pigeonite stability (i.e., melting temperature in simple systems) is also a function of the Mg#: 1409 °C for a pigeonite En90Wo10 but probably ~1350 °C for the pigeonite of FeO-rich ureilites (En74Wo10; Presnall 1995; Warren and Rubin 2010). Therefore, if permitted by the bulk composition of the system, pigeonite with given MgO and CaO concentrations (or En and Wo contents) can be stable over a temperature interval of 150 °C–250 °C.

The apparent temperature dependence of MgO and CaO concentrations in pigeonite used by Singletary and Grove (2003) reflected the restricted temperature and compositional range of the melts produced in earlier experiments. The UPB was initially rich in alkalis (Kita et al. 2004; Bischoff et al. 2014; Collinet and Grove 2020b), but the absence of Na2O in ureilite pyroxenes did not allow Singletary and Grove (2003) to include this important element in the calibration of their single-pyroxene thermometer. Therefore, the thermometer of Singletary and Grove (2003) should be replaced by the thermometer described in the next section.

New Thermometer Based on the Partitioning of Cr Between Olivine and Low-Ca Pyroxene

The compatibility of Cr in olivine and LCP strongly decreases with increasing temperature in batch melting experiments of chondrites (Figs. 7a–b). At 1100 °C, the Cr2O3 content of olivine is less than half of the Cr2O3 content of coexisting LCP. However, the Δ\text{Cr}_{\text{oliv-LCP}} (Cr2O3_{\text{LCP}}/Cr2O3_{\text{liq}} in wt%) decreases faster with increasing temperature than the Δ\text{Cr}_{\text{oliv-liq}} and the Cr2O3 content of olivine becomes nearly identical to that of the coexisting LCP at 1300 °C. Therefore, with increasing temperature, the ratio of Δ\text{Cr}_{\text{oliv-liq}} and Δ\text{Cr}_{\text{LCP-liq}} (i.e., Δ\text{Cr}_{\text{oliv-LCP}}) increases with increasing

![Fig. 7. Calibration of the Δ\text{Cr}_{\text{oliv-LCP}} thermometer. a–b) Different temperature dependence of the Cr partition coefficients between olivine (a) or low Ca pyroxene (b) and silicate melt in batch melting experiments of a CI composition (fO2: IW –1.3/–2.2; Collinet and Grove 2020a). c–d) Linear relationship between the Δ\text{Cr}_{\text{oliv-LCP}} and the experimental temperature of 60 charges with various bulk compositions (supporting information and see text for detail). The linear relationship is used as a simple mineral thermometer that is independent of the fO2 (within the experimental range) and the Wo content. (Color figure can be viewed at wileyonlinelibrary.com.)](image-url)
temperature and follows a linear relationship (Fig. 7c–d). The $D_{\text{Cr}}^{\text{oliv}}$, $D_{\text{LCP}}^{\text{liq}}$, and $D_{\text{Cr}}^{\text{oliv-LCP}}$ do not seem to be influenced by the $f_{\text{O}_2}$ over the range of IW -1.3 and IW -2.5 (Fig. 7c).

Because the melt does not have to be analyzed to calculate the $D_{\text{Cr}}^{\text{oliv-LCP}}$, we can use all of our experimental charges, including residues with only a few percent of melt, to calibrate a $D_{\text{Cr}}^{\text{oliv-LCP}}$ thermometer. In practice, we use a subset of 60 charges for which $\text{Cr}_2\text{O}_3$ contents were the most accurately determined (Table S6 in supporting information). The 60 experimental charges include all 10 starting compositions (Table 1): H, LL, and CI (31); LLR1-2 and CIR1-3 (23); and RCa1-2 (6).

All experimental charges, whether they contain one LCP (orthopyroxene or pigeonite) or one LCP and augite, visible traces of chromite, and regardless of the experimental $f_{\text{O}_2}$, fall on the same linear trend with an accuracy of $\pm 15 \, ^\circ\text{C}$ (Fig. 7c–d). The $D_{\text{Cr}}^{\text{oliv-LCP}}$ also appears to be largely independent of the wollastonite content in LCP (Fig. 7d). Nonetheless, a few experiments with very low Wo content in pyroxene (<3), not observed in ureilites, could be characterized by slightly higher $D_{\text{Cr}}^{\text{oliv-LCP}}$ and were not included in the linear regression.

The independence of the $D_{\text{Cr}}^{\text{oliv-LCP}}$ to $f_{\text{O}_2}$ is not intuitive because the average valence state of Cr decreases with decreasing $f_{\text{O}_2}$. Most Cr is present as $\text{Cr}^{3+}$ at QFM +1 (-IW +4.5), but $\text{Cr}^{2+}$ predominates at conditions more reducing than IW -1 (Hanson and Jones 1998; Papike et al. 2005) and $\text{Cr}^0$ becomes the dominant oxidation state under IW -5/~6 (Holzheid and O’Neill 1995). Cations with contrasting charge and size such as $\text{Cr}^{2+}$ and $\text{Cr}^{3+}$ would be expected to partition differently in the M1 and M2 octahedral sites of the olivine and pyroxene crystal structures. Presumably, this is not the case in olivine, for which the partition coefficients $D_{\text{Cr}}^{\text{3+}}$ and $D_{\text{Cr}}^{\text{2+}}$ appear to be identical and largely independent of the $f_{\text{O}_2}$ (Papike et al. 2005), as suggested by our experimental results. In pyroxene, $\text{Cr}^{3+}$ should fit easily in the smaller M1 site and can be charged balanced by $\text{Al}^{3+}$ in the tetrahedral site (Tschemak substitution) while $\text{Cr}^{2+}$ would only fit in the larger M2 site. Therefore, $D_{\text{Cr}}^{\text{oliv-LCP}}$ could be expected to decrease with $f_{\text{O}_2}$, a behavior that has been shown experimentally between IW +1 and IW -1 (Karnem et al. 2007), but that should become negligible under IW -1 as most Cr is already in the $\text{Cr}^{2+}$ state, as suggested by our experiments (Fig. S6 in supporting information). The predominance of $\text{Cr}^{2+}$ in ureilites is also indicated by XANES analyses (calculated valence of 2.0–2.2; Goodrich et al., 2013b; Sutton et al. 2017). In summary, the $D_{\text{Cr}}^{\text{oliv-LCP}}$ thermometer can be used at conditions more reducing than IW -1 without any $f_{\text{O}_2}$-dependent term, as the influence of $f_{\text{O}_2}$ is undetectable.

The $D_{\text{Cr}}^{\text{oliv-LCP}}$ thermometer is specifically designed for ureilites and is likely not directly applicable to more oxidizing systems in its current form.

The $D_{\text{Cr}}^{\text{oliv-LCP}}$ thermometer can be used to calculate the temperature of equilibration ($T_E$) of all ureilites, regardless of their mineral assemblage, as long as they contain olivine and at least one LCP. It can be directly applied to 76 samples with detailed EPMA analyses of both olivine and LCP (Table S8 in supporting information). Their $T_E$ covers a large range of temperature, 1054 °C–1276 °C, which is identical to the range of previous $T_E$ estimates. However, the $D_{\text{Cr}}^{\text{oliv-LCP}}$ $T_E$ offers a new highly reliably representation of the temperature distribution in the UPB and provide important new constraints on the petrogenesis of ureilites.

Ureilites with low Fo content in olivine ($\text{Fo}_{75-80}$) have the most contrasting $T_E$ (1054 °C–1276 °C) while ureilites with high Fo content in olivine ($\text{Fo}_{90-95}$) have more restricted and higher $T_E$ of 1180–1250 °C (Fig. 8). Histograms of the $T_E$ of ureilites with either Fo74-85 or Fo97-96 olivine display overlapping modes at 1180 °C–1220 °C. In other words, FeO-poor and FeO-rich ureilites are characterized by identical average $T_E$ and eight of the nine samples with $T_E$ higher than 1240 °C are FeO-rich. This result is in stark contrast with the positive correlation between $T_E$ and olivine Fo contents (i.e., Mg#) that was predicted by the pigeonite thermometer of Singletary and Grove (2003). Because the new $T_E$ no longer correlates with the Mg# of ureilite samples, a strict separation between FeO-poor and FeO-rich ureilites appears arbitrary. In the remainder of the discussion, these two groups should be thought of as the endmembers of a continuum.

All ureilites with two pyroxenes show a $D_{\text{Cr}}^{\text{oliv-LCP}}$ equilibration temperature that is lower than the minimum temperature of pigeonite stability of Sack and Ghiorso (1994). The few ureilite samples containing euhedral chromite, such as NWA 766, LEW 88774, and NWA 3109, display low olivine-chromite temperatures (1037 °C, 1042 °C, and 1058 °C; Goodrich et al. 2014) and low $D_{\text{Cr}}^{\text{oliv-LCP}}$ temperatures (1054 °C, 1085 °C, and 1141 °C) that correlate with the Cr# (i.e., Cr/[Cr + Al] in mole%) of chromites: 0.65, 0.71, and 0.76, respectively.

Anomalous Low-Temperature Ureilites

Ureilites containing orthopyroxene and augite, characterized by low $T_E$ (open symbols in Fig. 8), display poikilitic textures with large (up to 15 mm) orthopyroxene oikocrysts enclosing rounded olivine and augite crystals: LEW 88774 (Chikami et al. 1997), MET 78008 and Y 74130 (Takeda et al. 1989), RaS 517
Many such samples contain unusually large fractions of pyroxene (e.g., LEW 88774, the “Hughes cluster” samples, RaS 517) or, more rarely, unusually little pyroxene (MET 01083). Those anomalous low-temperature ureilites are the only ones that do not plot on the trend of increasing pyroxene content in olivine (Fig. 6b). In addition, the Al2O3 concentrations of their LCP are significantly higher (1.3–2.2 wt%) than in other ureilites (0.3–1.0 wt%; Fig. 9a). The “Hughes cluster” samples traditionally contain a large fraction of augite (>30 vol%) and their bulk Ca/Mg ratios are super-chondritic (Goodrich et al. 2001, 2009).

Due to their large pyroxene fractions and poikilitic textures, some anomalous ureilites have been interpreted as cumulates or older residues that reacted with silicate melts (Downes et al. 2008; Goodrich et al. 2009). All of the aforementioned samples are characterized by lower T_E than the temperature of plagioclase disappearance in chondritic materials (Fig. 8). If they represented simple melting residues quenched at peak temperature following the destruction of the UPB, they would be expected to contain plagioclase. Yet, only one sample contains plagioclase (Goodrich et al. 2016). This sample, equilibrated at 1144 °C, is part of the Hughes cluster. It contains a plagioclase much more calcic (An68.4) than the plagioclase of the melting residues of high NaK# chondrites (An20-40; Collinet and Grove 2020a).

Collectively, those observations are consistent with the idea that all anomalous low-temperature samples do not represent melting residues but cumulates or products of melt-rock reactions during melt migration. RaS 517 was recently described as containing primary melts and recording the ureilite anatexis (Rosén et al. 2019). Due to its very low T_E (1072 °C) and high augite fraction, this scenario does not seem viable. Instead, the silicate melt could represent a residual liquid crystallizing in a superficial intrusion or magma conduit. Some brachinite-like meteorites display similar coarse poikilitic textures and are inferred to form by...
partial crystallization of the melt during melt migration (Goodrich et al. 2017a).

**Temperatures and Extents of Melting Recorded by Pigeonite-Olivine Ureilites**

The anomalous samples described in the previous section are in part responsible for the once popular view that ureilites were igneous cumulates (Berkley et al. 1980; Goodrich et al. 1987). However, since the 1990s, pigeonite-olivine ureilites have largely been regarded as melting residues (Warren and Kallemeyn 1992; Scott et al. 1993). If FeO-rich pigeonite-olivine ureilites (Fo 76-82), which represent 70–80% of all ureilites, are melting residues from a relatively homogeneous chondritic material, the samples that equilibrated at high temperature should have experienced larger extents of melting than the samples that equilibrated at lower temperature. The chemical composition and petrologic features of pigeonite-olivine ureilites should correlate with $T_E$. Several such correlations are indeed observed. In ureilites with Fo 76-82 olivine, the Al$_2$O$_3$ content of LCP decreases linearly with increasing $T_E$ from 1 wt% at 1150°C to 0.35 wt% at 1276°C (Fig. 9b). The Wo content in LCP decreases in parallel, albeit with more scatter, from Wo$_{10.5-12}$ to Wo$_{4.5-5}$ (Fig. 9c). The variability of Wo contents at a given temperature could result from the interaction of migrating CaO-rich “late stage melts” with melting residues (see next section). Finally, Barrat et al. (2016) have recently analyzed the rare earth element (REE) concentrations of a large number of ureilites. They identified two main patterns (1) “group B” with steeper LREE profiles and high HREE concentrations, representing MgO-rich ureilites (Fo$_{89-95}$), and (2) “group A” with less steep LREE profiles and more variable bulk REE depletions, representing FeO-rich ureilites. The REE concentrations as well as the Zr concentrations of the ureilites of “group A” (bulk leachates) correlate negatively with $T_E$ (Fig. 10).

The ureilites of “group B” (Fo$_{89-95}$ olivine) could represent the melting residues, produced under more reducing conditions, of a chondritic material with initial NaK# and Mg/Si ratios similar to the chondritic material that produced FeO-rich ureilites. In addition, FeO-poor ureilites were equilibrated over the same range of temperature as FeO-rich ureilites (1180–1220 °C; Fig. 8). Because the melting temperature of ferro-magnesian silicates increases with the Mg#, FeO-poor ureilites should represent residues that melted to a lower extent than the FeO-rich ureilites equilibrated at the same temperature. A lower bulk degree of melting could explain in part the higher REE concentrations of group B ureilites (Fig. 10).

**Incremental Melting and Composition of “Late-Stage” Silicate Melts**

As described at the beginning of the discussion, a chondritic composition with a high NaK# (50) and a relatively homogenous Mg/Si ratio (0.98–1.05) can produce ureilite-like residues by partial melting (F = 15–
24 wt%) under variable $f_\text{O}_2$ conditions. In batch melting experiments, pigeonite melts out at 1170°C–1200°C while it persists up to 1280°C in incremental melting experiments. The ureilite samples with the highest $T_\text{E}$ (Goalpara, 1276°C, and Dingo Pup Donga, 1267°C) have an LCP with low Wo content (4.6/4.7, i.e., orthopyroxene). However, many FeO-rich samples with $T_\text{E}$ between 1240°C and 1260°C contain Wo$_{6.5-10}$ pigeonite: RC 027, Y 74123, NWA 11755, Y 82100, and GRO 95575 (Table S8). Residues containing pigeonite (Wo$_{6.5-10}$) at 1250°C cannot form by batch melting of any chondritic material (Fig. 3) and, instead, suggest that silicate melts were extracted in several steps (i.e., incremental melting).

The composition of the first silicate melts produced in ureilites has been constrained by batch melting experiments of high NaK# chondritic materials (Collinet and Grove 2020a). Low-degree partial melts (<15 wt%), rich in alkali elements Al$_2$O$_3$ and SiO$_2$ were likely extracted from their source and formed the ALM-A trachyandesite (Bischoff et al. 2014) and the albite/oligoclase-rich clasts of polymic ureilites (Ikeda and Prinz 2001; Cohen et al. 2004; Kita et al. 2004). If pigeonite-ureilites melted incrementally, the melts that were produced in later melting stages would have been radically different in composition from the melts of batch melting experiments. Because the melt productivity drops significantly following the extraction
of alkali-rich melts (\~5 wt\% between 1120/1260°C and 1250/1280°C; Fig. 2), ureilites would have contained very little melt at the time of the destruction of the parent body. Similarly, LLR2 and CIR2-3 experimental charges contain very little melt (2–5 wt\%) that could not be analyzed successfully. These “late-stage” melts are expected to be depleted in alkali elements relative to batch melts. Following the disappearance of plagioclase, Na2O concentrations decrease rapidly with successive increments of melting (see pMELTS simulations in supporting information).

Pigeonite-olivine ureilites with Fo 75-82 olivine and high T_E (1200°C–1260°C) have the highest concentrations of CaO in olivine (0.36–0.44; Fig. 11b). The partition coefficient of CaO between olivine and liquid \( (D_{\text{Ca\ oliv-liq}} = \text{CaO}_{\text{oliv}}/\text{CaO}_{\text{liq}}) \) decreases with increasing temperature (Fig. 11a), and can be parameterized to calculate the CaO content of the late-stage melts that were in equilibrium with specific samples (Fig. 11c). At low temperature (<1170 °C), the CaO content of the melts in equilibrium with ureilites was identical to batch melts of high NaK\# chondrites (H, LL, and CI). However, at higher temperature, the late-stage melts were increasingly CaO-rich (8–12 wt\%; Fig. 11d) while the CaO content of batch melts plateaus at 7–8 wt\% and then decreases from 1220 °C. The high CaO content of late-stage melts cannot result from batch melting and supports an origin of ureilites as residues of incremental melting.

The Al2O3 content of late-stage melts could be estimated based on the \( D_{\text{Al\ LCP-liq}} \). In practice, due to the low Al2O3 content of pyroxene in experiments, the
$D^{\text{LCP-\text{liq}}}_{\text{Al}}$ is difficult to calculate precisely. In the batch melting experiments of Collinet and Grove (2020a), and the experiments of Singley and Grove (2006), the $D^{\text{LCP-\text{liq}}}_{\text{Al}}$ varies between 0.04 and 0.07 at 2–13 MPa for a pigeonite with Wo$_{10}$–10, but we could not identify systematic variations. In Collinet et al. (2015), the $D^{\text{LCP-\text{liq}}}_{\text{Al}}$ and $D^{\text{opx-\text{liq}}}_{\text{Al}}$ strongly increases with pressure but are constant over a 150 °C temperature interval (i.e., 0.11 at 0.5 GPa, 0.2 at 1.0 GPa, and 0.3 at 2.0 GPa). Therefore, we estimate the Al$_2$O$_3$ concentrations of late-stage melts with a constant $D^{\text{LCP-\text{liq}}}_{\text{Al}}$ of 0.055 and find that, within the ±20 wt% relative uncertainty, they are indistinguishable from the Al$_2$O$_3$ concentrations of batch melts. Our best estimate of the composition of a late-stage melt, produced at 1240 °C by incremental melting and in equilibrium with olivine Fo$_{79}$, is reported in Table 4. The MgO content is estimated as a function of the temperature and is used to constrain the FeO content, assuming a $K_{\text{Mg}}^{\text{Fe-\text{liq}}}$ of 0.31, from batch melting experiments.

The Na$_2$O content of late-stage melts is more difficult to constrain. Following the disappearance of plagioclase, Na behaves as an incompatible element and is rapidly exhausted from the residue. Therefore, the Na$_2$O content of the melts produced at this stage was likely variable and decreased rapidly (from ~2 to 0 wt% Na$_2$O). Late-stage melts such as the one reported in Table 4 could easily have crystallized the labradorite-rich clasts observed in polymict ureilites (Cohen et al. 2004; Kita et al. 2004; Goodrich et al. 2017b). With the algorithm MELTS (Ghiorso and Sack 1995), equilibrium and fractional crystallization of a late-stage melt containing 1 wt% Na$_2$O produce ~20–30 wt% labradorite plagioclase (An$_{20}$–70). This is also consistent with the composition of plagioclase (An$_{80}$) in one Hughes cluster sample and with the idea that this sample represents an olivine-rich residue in which a silicate melt migrated and partly recrystallized (Goodrich et al. 2016). Cumulate–residue hybrids have occasionally been advocated to explain the origin of ureilites under the term “paracumulates” (Warren and Kallemeyn 1989; Goodrich et al. 2004). The Hughes cluster samples and other anomalous low-T ureilites rich in augite could represent such lithologies and derive from the crystallization of CaO-rich and alkali-poor late-stage melts.

The behavior of melting of the UPB has been disputed based on differing interpretations of REE patterns (Warren and Kallemeyn 1992; Warren and Huber 2006; Goodrich et al. 2007, 2013c; Warren 2012). Most recently, Barrat et al. (2016) used REE melting models to argue that ureilites formed by continuous/dynamic melting, a specific case of incremental melting during which a fixed melt fraction, the critical melt fraction, is retained in the residue. We reproduced their calculations using the modal proportions and melting coefficients of Collinet and Grove (2020a) and find that the REE patterns of FeO-rich ureilites can be explained by 15–24 wt% of continuous melting with a 2 wt% critical melt fraction (Fig. 12a), a range that is identical to the aggregate melt fractions of experimental charges containing ureilite-like residues (Fig. 4). In agreement with their more restricted TE, FeO-poor ureilites can be explained by 16–18 wt% of continuous melting. In detail, REE melting models are non-unique and the REE patterns can be reproduced by different incremental melting processes, such as the complete removal of larger melt increments (e.g., 5–10 wt%; Fig. S10 in supporting information). Near-fractional melting would produce stronger depletions in LREE (Fig. 11c), unless melting was faster than LREE diffusion in pyroxene (Goodrich et al. 2007). Because all ureilites represent melting residues that melted enough to exhaust plagioclase (F >15.5 wt%), and because REE melting models produce model-dependent results (Fig. S10), it is impossible to constrain uniquely the size of the melt increments. We infer that they were in the range 2–5 wt%.

### Table 4. Average composition of melt extracted.

|          | 1104 °C | 1240 °C |
|----------|---------|---------|
| SiO$_2$  | 62.44   | 55.7    | by diff |
| TiO$_2$  | 0.52    | 0.3     | ±0.1   |
| Al$_2$O$_3$ | 15.99  | 10      | ±2     |
| Cr$_2$O$_3$ | 0.09   | 0.65    | ±0.15  |
| FeO      | 5.05    | 12.1    | ±1.5   |
| MnO      | 0.17    | 0.55    | ±0.10  |
| MgO      | 3.09    | 8       | ±1     |
| CaO      | 4.13    | 11.5    | ±1.0   |
| Na$_2$O  | 6.78    | 1       | ±1     |
| K$_2$O   | 0.82    | 0.05    | ±0.05  |
| P$_2$O$_5$ | 0.86   | 0.1     | ±0.1   |

1—Aggregate melt extracted immediately prior to plagioclase exhaustion (Collinet and Grove 2020a).
2—Average composition of “late-stage” melt. SiO$_2$ calculated by difference; see text for detail.

**Peak Temperatures of Ureilites and Thermal History of the UPB**

Ureilites are sometimes described as having a two-stage cooling history: an initial episode of slow cooling followed by an episode of rapid cooling simultaneously with the destruction of the UPB (e.g., Goodrich 1992). It could be argued that the T$_E$ of ureilites, estimated with the $D^{\text{opx-LCP}}_{\text{Cr}}$ thermometer, does not represent the peak temperature. Cr diffuses relatively fast in olivine and in orthopyroxene. Diffusion coefficients are only one order of magnitude slower than the ones of Fe-Mg interdiffusion (Ito and Ganguly 2006; Dohmen et al.
2007; Ganguly et al. 2007). If main group ureilites had stopped melting and started cooling following the extinction of $^{26}$Al, the $D_{Cr}^{ody-LCP}$ thermometer would have recorded a lower final temperature rather than the peak melting temperature. However, the cores of olivine and pyroxene display homogeneous Cr$_2$O$_3$ contents. Either slow cooling did not occur or ureilites systematically and completely re-equilibrated at an intermediate temperature. Because olivine and pyroxene cores are also homogeneous in Fe, Mg, and Ca, two-pyroxene thermometers should record the same final temperature of equilibration. Only a handful of samples have actually been suggested to record two distinct temperatures of equilibration and, therefore, a slow-cooling event. In the next paragraphs, we use our experiments, the new $D_{Cr}^{ody-LCP}$ thermometer, and the phase diagrams and two-pyroxene temperatures of Sack and Ghiorso (1994) to re-evaluate whether some ureilites, and more generally the UPB, went through a stage of slow cooling.

As long as pigeonite-olivine ureilites remained in the field of pigeonite stability, a stage of slow cooling could be undetectable. However, many pigeonite-olivine ureilites with Wo$_{6.5-10}$ were last equilibrated at 1240–1260 °C, a temperature which is close to the highest temperature at which we observe pigeonite (Wo 5.5-7) in incremental melting experiments (1274 °C). At higher temperature (1300 °C), melting residues become extremely CaO-poor and pigeonite is replaced by orthopyroxene. If ureilites had cooled slowly over a significant interval of temperature (from 1300 °C to 1240 °C), they would have contained less CaO and orthopyroxene would have replaced pigeonite. In addition, if the final $T_E$ had been significantly lower than the peak temperatures, the correlation of $T_E$ with bulk REE concentrations and Al$_2$O$_3$ contents in pyroxene might have been erased. This is not the case.

Only one ureilite displays inverted pigeonite with augite lamellae in an orthopyroxene host: ALH 82106 (Takeda et al. 1989; Fig. 5c). This unique sample has a high $T_E$ of 1245 °C, just under the minimum temperature of pigeonite stability (see symbol 22 in Fig. 8). One of our experiments (CHS 66; RCa1) performed at 1250 °C contains olivine (Fo$_{95.3}$ versus Fo$_{95.5}$ in ALH 82106), augite, and a pigeonite that is almost identical to the bulk unmixed pyroxene of ALH 82106 (opx + augite lamellae; Wo$_{10.5}$). Table S7 in supporting information). This experiment suggests that ALH 82106 reached its peak temperature at 1250 °C and only had to cool by a few to 20 °C to form inverted pigeonite. The large majority of ureilites that equilibrated below the minimum temperature of pigeonite stability contain distinct,
randomly orientated, orthopyroxene and augite crystals. We posit that if those ureilites had cooled slowly by more than 0 °C–20 °C below their peak temperatures, many more samples should instead contain inverted pigeonite.

To our knowledge, only one other ureilite displays clear signs of slow cooling: the highly anomalous sample LEW 88774 (Chikami et al. 1997), which contains coarse ~50 μm intergrown lamellae of orthopyroxene and augite. Based on the bulk composition of the pyroxene (Wo15-20; sub-calcic augite), Chikami et al. (1997) argued that the pyroxene progressively recrystallized during slow cooling, starting at 1280 °C. The model of Sack and Ghiorso (1994), which agrees closely with our experimental results (Fig. S5 in supporting information), suggests that a bulk pyroxene with a composition of En66Wo15 is stable at 1180 °C–1200 °C as opposed to 1280 °C (Chikami et al. 1997). LEW 88774 might have cooled slowly from 1200 °C to 1100 °C, the D_{C_In-LCP} temperature. Because LEW 88774 is a highly unusual pyroxenite (py = 76), it could represent a cumulate formed within an outer layer of the UPB and its thermal history is likely not representative of the conditions recorded by most ureilites in the deeper interior of the UPB.

Several other “anomalous low-temperature ureilites” are thought to have equilibrated at two distinct temperatures. For example, Goodrich et al. (2001) suggest that Hughes 009, containing orthopyroxene and augite (Mg# of 88–89), cooled from 1250 °C to 1050 °C. One of our experiments places an upper limit to the peak temperature of Hughes 009. CIR1-CHS 48 contains pigeonite (Mg# 88) at 1194 °C, which is close to the minimum temperature of pigeonite stability at that Mg# (1190 °C; Sack and Ghiorso 1994). Because Hughes 009 contains no exsolution lamellae but “standard” anhedral crystals of orthopyroxene and augite, it probably reached a peak temperature lower than the temperature of pigeonite stability (1190 °C), while the final temperature recorded by the D_{C_In-LCP} thermometer is 1167 °C ± 15 °C. Those two temperatures suggest that Hughes 009 cooled, at most, over 30 °C instead of 200 °C. Using a similar reasoning, and comparing the ureilite HaH 064 to experiment CI-CHS 54 performed at 1129 °C (Collinet and Grove 2020a), we infer that its peak temperature was in the range 1125 °C (Sack and Ghiorso 1994)–1089 °C (D_{C_In-LCP} Te) rather than 1200 °C (Weber et al. 2003) and that, therefore, it did not cool significantly.

In summary, ALH 82106 is the only sample that has recorded an episode of slow cooling at high temperature and in the region of the UPB representing the residual mantle. It cooled by only ~20 °C. The bulk of evidence suggests that the ureilites that represent melting residues were maintained very close to their peak temperature, and might have been actively melting, at the time of the disruption of the UPB.

**Variable fO2 During Melting and Mantle Heterogeneity of the UPB**

The metal and carbon polymorphs present along silicate grain boundaries have occasionally been interpreted as being added by the impactor that disrupted the UPB (Boynton et al. 1976; Wasson et al. 1976; Day et al. 2017). However, the weakly shocked ureilite ALHA 78019 (Berkley and Jones 1982) contains euhedral crystals of graphite intergrown with metal and sulfide. In addition, mixed cohenite-metal-sulfide inclusions occur in the silicates of many ureilites (Goodrich et al. 2013a; Fig. S2) and strongly suggest that graphite and metal were in equilibrium with silicates during partial melting. The presence of metal in equilibrium with olivine places strict constraints on the fO2 of the system (OSI equilibrium; Nitsan 1974). A composition of Fo75.95 in olivine and Fe90.95Ni10.5 in the metal at 1100 °C–1300 °C corresponds to ΔIW −1.3 to −2.5, which is identical to our experimental range of fO2. In experiments, the fO2 relevant to the formation of ureilites is imposed by the C-CO buffer. Its position relative to the IW buffer is strongly dependent on both the temperature and the pressure. If the temperature is increased or the pressure is decreased, Fe2+ is progressively reduced to Fe0.

Because ureilites contain abundant graphite, it has long been assumed that the C-CO buffer imposed the fO2 of equilibration of ureilites, like in our experiments, and was responsible for the variable Fo content of olivine cores (Fo75.95) between samples (e.g., Berkley et al. 1980; Berkley and Jones 1982). In metallurgy, the process by which Fe metal is produced by heating FeO ores in the presence of C is called “smelting”. By analogy, a primary control of the C-CO buffer on the composition of silicate cores (i.e., Mg#) in ureilites has been called smelting by Walker and Grove (1993). It is now called “primary smelting” or “equilibrium smelting” in the recent ureilite literature, by opposition to “secondary smelting” or “disequilibrium smelting”, which refers to the reduction event associated with the disruption of the parent body. Despite minor semantic disagreement (Warren and Huber 2006), disequilibrium smelting has not been a source of contention. It is widely recognized as having produced the ubiquitous 10–50 μm wide rims of olivine that are increasingly FeO-poor outward and contain small metal blebs and free SiO2 (Fig. 5a), following the pressure drop and rapid cooling at 2 °C h⁻¹–20 °C h⁻¹ caused by the destruction of the UPB (Miyamoto 1985; Takeda et al.
In most cases, the pyroxene is less affected by this process, probably due to the slower rate of Fe-Mg interdiffusion. However, a few samples display pyroxene smelted to different extents (Figs. 5e–5f and Fig. S3 in supporting information) associated with olivine crystals containing homogenously distributed sub-µm metal inclusions (Fig. S4). Such samples are interpreted as briefly shock-heated by the impact before being rapidly cooled (Warren and Rubin 2010).

Equilibrium smelting, which would control the composition of olivine cores, has been more controversial. It has been invoked in the context of cumulate and residue models alike and encompasses different processes (Goodrich et al. 1987, 2007; Walker and Grove 1993; Sinha et al. 1997; Singletery and Grove 2006). In Goodrich et al. (1987), equilibrium smelting is envisioned as affecting the parental melts of ureilites as they migrate upward and decompress before pooling at various depths. In the model of Singletery and Grove (2006), smelting affects partly molten diapirs heated more rapidly than the surrounding mantle due to their higher CAIs contents, and higher $^{26}$Al concentrations. In the model of Goodrich et al. (2007), primary smelting is driven by an increase in temperature at constant pressure and happens simultaneously with partial melting.

In detail, those simple primary smelting models appear to be inconsistent with the new $D_{Cr}^{LCP}$ thermometer. For example, the model of Goodrich et al. (2007) assumed that ureilites, regardless of their Mg#, reached peak temperatures of 1250 °C–1275 °C and that FeO-rich ureilites (Fo75,80) melted deeper in the parent body than FeO-poor ureilites, as a consequence of the pressure sensitivity of the C-CO buffer (Warren 2012; Goodrich et al. 2013c). However, it is now clear that the equilibration temperatures of FeO-rich pigeonite-olivine ureilites span a 150 °C interval (1130 °C–1280 °C). The Fo content of olivine in our experiments, which is a function of the temperature and of the CO pressure, is used to calculate the pressure of equilibration of ureilites, assuming that the $f$O$_2$ is primarily controlled by the C-CO buffer (Fig. 13a and Fig. S9 in supporting information).

Because FeO-rich ureilites formed over a large range of temperature, they would also have melted over a large range of pressure (4–14 MPa), which would overlap with the pressure of equilibration of FeO-poor ureilites (2–8 MPa; Fig. 13a).

If melting occurred at higher pressure (>15 MPa), where graphite can be stable with olivine of various compositions (Fo74–95) over the same temperature (1130 °C–1280 °C), the pressure of equilibration of FeO-poor ureilites is fixed by the Fo content of olivine of the C-CO buffer. Graphite is stable and there are no precise constraints on the pressure of equilibration ($P_E$). The various $T_E$ of ureilites can still be interpreted as representing a “geotherm” (a temperature profile). Although the slope of the geotherm is unconstrained, ureilites with different Fo content in olivine but identical $T_E$ could be assumed to have equilibrated at the same pressure. (Color figure can be viewed at wileyonlinelibrary.com.)

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**Fig. 13.** a) Pressure of equilibration of ureilites assuming that the $f$O$_2$ is primarily controlled by the C-CO buffer. The pressure of equilibration ($P_{C-CO}$) is fixed by the Fo content of olivine of individual samples and their $D_{Cr}^{LCP}$ temperature of equilibration ($T_E$; Fig. S9). b) If the actual pressure of equilibration of all ureilites is larger than 15 MPa, the $P_{C-CO}$ of (a) is no longer relevant and the $f$O$_2$ is not controlled by the C-CO buffer. The intrinsic $f$O$_2$ of ureilites is variable (IW $–1.3/–2.5$) and is higher than the $f$O$_2$ of the C-CO buffer. Graphite is stable and there are no precise constraints on the pressure of equilibration ($P_E$). The various $T_E$ of ureilites can still be interpreted as representing a “geotherm” (a temperature profile). Although the slope of the geotherm is unconstrained, ureilites with different Fo content in olivine but identical $T_E$ could be assumed to have equilibrated at the same pressure. (Color figure can be viewed at wileyonlinelibrary.com.)
interval (1130 °C–1280 °C), the Fo content in olivine and the $T_E$ based on the $D_{Cr}^{Me-LCP}$ would not be sufficient to constrain the pressure of ureilite equilibration (Warren and Kallemeyn 1992; Walker and Grove 1993; Warren and Huber 2006). Nevertheless, the temperature interval over which pigeonite-olivine ureilites equilibrated (1130 °C–1280 °C) could represent a radial temperature gradient within the UPB. The slope of such a temperature profile is unconstrained as it would be influenced by many parameters (e.g., Neumann et al. 2012). In any case, the identical equilibration temperatures of FeO-poor and FeO-rich ureilites could indicate that they melted at the same depth (Fig. 13b).

There is little doubt that the UPB accreted from isotopically heterogeneous materials. The fact that C (Barrat et al. 2017), Cr (Zhu et al. 2020), and O isotopes (Clayton and Mayeda 1988) all correlate with the Mg# of silicates suggests that the intrinsic $f_O_2$ of ureilites was at least partly inherited from the precursor chondritic materials. The origin of the intrinsic $f_O_2$ of meteorite parent bodies is an active area of research. The formation of FeO in the nebula setting is nontrivial and could require high dust-to-gas ratios and dust rich in H$_2$O (e.g., Fedkin and Grossman 2016). Similar correlations between the Mg# of silicates (i.e., the intrinsic $f_O_2$) and the $\Delta^{17}O$ are observed in various meteorite groups other than ureilites. Such trends could be connected to the distribution of ice and/or water vapor, either in the accretion disk or within parent bodies (e.g., Tenner et al. 2015; Sanders et al. 2017).

Regardless of their origin, the initial heterogeneities in intrinsic $f_O_2$ of ureilites do not preclude that reduction processes involving C and various gas species occurred during melting and melt migration. Such “equilibrium smelting” reactions could have partly overprinted the initial heterogeneities in intrinsic $f_O_2$. The presence of a gas phase could explain the incremental nature of the melting process (Wilson et al. 2008), but it is no longer seen as a requirement to drive rapid melt extraction from the residues (Goodrich et al. 2015). New models for the origin of ureilites should evaluate which primary/equilibrium smelting processes are compatible with the presence of initial heterogeneities in $f_O_2$ and the T-P conditions of equilibration of ureilites (Fig. 13a). The large span in $T_E$ and extent of melting recorded in ureilites suggests a UPB that was heterogeneous in intrinsic $f_O_2$, Mg#, and isotopic compositions, resulting in a residual mantle where both FeO-rich and FeO-poor ureilites were generated over a range of depths (Fig. 14).

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**SUPPORTING INFORMATION**

Additional supporting information may be found in the online version of this article.

**Figure S1.** Metal fraction in experiments as a function of the forsterite content in olivine.

**Figure S2.** (a) Backscattered electron images of chromite, metal and sulfide inclusions in ureilites.

**Figure S3.** Additional BSE images of disequilibrium pyroxene melting.

**Figure S4.** Sub-μm metal inclusions in the olivine cores of ureilites that suffered pyroxene melting.

**Figure S5.** Composition of pyroxene in experiments and ureilites compared to the phase diagram of (Sack and Ghiorso 1994).

**Figure S6.** Oxygen fugacity dependence of the partitioning coefficients of Cr between pyroxene and...
silicate melt extrapolated from Karner et al. (2007) experiments at 1170 °C.

Figure S7. Equilibration temperature of 75 ureilites as a function of the Mg# in low-Ca pyroxene.

Figure S8. Offset between the thermometer of Singletary and Grove (2003) and the experimental temperature of experiments.

Figure S9. Relationship between experimental pressure and temperature and the forsterite content in olivine of experiments.

Figure S10. Additional rare-earth elements melting models and comparison with the REE ureilite patterns of Barrat et al. (2016).

Figure S11. RGB (FeMgCa) image of anomalous (poikilitic) sample MET 01083.

| Table S1. Modal composition of experiments. |
| Table S2. Olivine composition in experiments. |
| Table S3. Low Ca pyroxene composition in experiments. |
| Table S4. Augite composition in experiments. |
| Table S5. Melt composition in experiments. |
| Table S6. Experiments used for the calibration of the DCr oliv-LCP thermometer. |
| Table S7. Olivine, pigeonite, orthopyroxene and augite composition of ureilites analyzed for this study. |
| Table S8. Phase compositions of ureilites from the literature. |