Ureilite petrogenesis: A limited role for smelting during anatexis and catastrophic disruption

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Abstract—A popular model for ureilites assumes that during anatexis in an asteroidal mantle, pressure-buffered equilibrium smelting (partial reduction coincident with partial melting) engendered their conspicuous mafic-silicate-core mg diversity (75–96 mol%). Several mass-balance problems arise from this hypothesis. Smelting inevitably consumes a large proportion of any plausible initial carbon while generating significant proportions of Fe metal and copious proportions of CO gas. The most serious problem concerns the yield of CO gas. If equilibrium smelting produced the ureilites’ entire 21 mol% range in olivine-core mg, the proportion of gas within the asteroidal mantle (assuming plausibly low pressure <\sim80 bar) should have reached \geq85 vol%. Based on the remarkably stepwise cooling history inferred from ureilite texture and mineralogy, a runaway, CO-leaky process that can loosely be termed smelting appears to have occurred, probably triggered by a major impact. The runaway scenario appears likely because, by Le Châtelier’s principle, CO leakage would tend to accelerate the smelting process. Also, the copious volumes of gas produced by smelting would have led to explosive, mass-leaky eruptions into the vacuum surrounding the asteroid. Loss of mass would mean diminution of interior pressure, which would induce further smelting, leading to further loss of mass (basalt), and so on. Such a disruptive runaway process may have engendered the ureilites’ distinctive reduced olivine rims. But the only smelting, according to this scenario, was a short-lived disequilibrium process that reduced only the olivine rims, not the cores; and the ureilites were cooling, not melting, during the abortive “smelting” episode.

INTRODUCTION

Ureilites are a very common and distinctive type of achondrite. As reviewed by Mittlefehldt et al. (1998), they are, in essence, extremely depleted peridotites, typically with about two-thirds olivine, 30% pyroxene (mostly pigeonite), and no observable feldspar. In nearly all cases, they are strangely endowed with carbon (average 3 wt%), usually as intergranular “veins” of semiamorphous “C-matrix” (often with traces of diamond). In a few of the least shocked samples, the intergranular C phase is euhedral graphite (e.g., Berkley and Jones 1982). Takeda (1987) was the first to propose that ureilites formed as mantle restites, contrary to the once-popular view that they originated as igneous cumulates (e.g., Berkley et al. 1980; Goodrich et al. 1987). Today, largely in consideration of the great oxygen-isotopic diversity among ureilites (Clayton and Mayeda 1988), most authors assume that most ureilites formed as asteroidal mantle restites (e.g., Warren and Kallemeyn 1992; Scott et al. 1993; Singletary and Grove 2003; Goodrich et al. 2004; Kita et al. 2004).

The term smelting, related to the German verb schmelz, meaning “to melt or fuse,” refers to a simultaneous reduction and partial melting of rock: “the chemical reduction of a metal from its ore by a process usually involving fusion” (Thrush 1968). Most ureilites show obvious vestiges of what was, at least in a loose sense, an iron-smelting process. Their mafic silicates, especially their olivines, feature distinctive reduced (FeO-depleted, Fe-metal-sprinkled) rims (e.g., Berkley et al. 1980; Singletary and Grove 2003). However, these rims are discrete subvolumes of the grains (e.g., Singletary and Grove 2003). The larger olivines invariably retain cores that are, within any given ureilite, quite uniform in mg (\equiv\text{MgO}/(\text{MgO} + \text{FeO}) in mol%). The first-order classification of ureilites is typically based on their olivine-core mg. Many authors (e.g., Goodrich 1992; Sinha et al. 1997; Lee et al. 2003; Goodrich et al. 2004; Singletary and Grove 2003, 2004) have argued or assumed that the great diversity (Fo_{75–96}) of the ureilite mafic-silicate core compositions was engendered mainly by varied degrees of smelting of an initial proto-ureilitic material with uniform, or near-uniform, olivine-core mg. In these models,
the range of olivine-core mg developed as a result of systematic smelting, buffered by the modest range of pressure within the mantle, or upper mantle, of a moderately large asteroid. However, Walker and Grove (1993), and more explicitly and emphatically Warren (1996), have argued that it is more plausible to simply assume that pre-igneous (nebular) processes produced an originally diverse suite of materials, and the only major smelting was that which produced the discrete metal-rich, FeO-poor rims. Strong evidence for the diversity of starting material comes from oxygen isotopes (Clayton and Mayeda 1988; cf. Warren and Kallemeyn 1992 and Scott et al. 1993). Recently, Hudon and Mittlefehldt (2004) and Mittlefehldt et al. (2005) have also stated a preference for limited smelting.

All recently published models assume that smelting, at least as loosely defined, was important in engendering the final ureilite mineralogy. The area of controversy concerns the degree to which smelting affected the mafic-silicate cores. To distinguish the thoroughgoing (Singletary and Grove 2003; Goodrich et al. 2004) type of smelting model from Warren’s (1996) limited smelting model, we will refer to the former as the smelted-cores model.

The redox component of smelting in the ureilite context is basically the following chemical reaction:

$$C + MgFeSiO_4 = MgSiO_3 + Fe + CO$$ (1)

in which MgFeSiO_4 (olivine), C (solid, either graphite or “amorphous”), MgSiO_3 (enstatite component of pyroxene), and Fe (metal) all are solids, but CO is a gas. The reaction may have sometimes been more like:

$$2C + 2(MgFeSiO_4) = Mg_2SiO_4 + 2Fe + 2CO + SiO_2$$ (2)

where the SiO_2 might be a component of an interstitial melt and there is no direct yield of pyroxene. Again, CO is the only gas involved. Equation 2 might account for the extremely Si-rich glasses, commonly 75–85 wt% SiO_2, that are observed in interstitial areas of Yamato (Y-) 74123 and Y-79081 (Ogata et al. 1991) as well as Northwest Africa (NWA) 766 (Warren et al. 2006). Yet another variant of the smelting reaction (Singletary and Grove 2003) assumes that a melt is involved in the reactants. Melt could potentially contribute CaO to produce typical (pigeonitic) ureilite pyroxene instead of the pure enstatite implied by Equation 1. However, CaO might also, or instead, have come from preexisting pyroxene that was more Ca-rich than the final, observed pyroxenes. In any event, adding melt to the reactants only slightly exacerbates the problematical aspects of core-smelting to be discussed at length below, namely the low proportionality of moles of olivine reduced in relation to moles of C consumed, moles of Fe (metal) produced, and worst of all, moles of CO (gas) produced.

The approximate temperature at which this occurred in the ureilites is well constrained. One of the most characteristic features of ureilites is that detailed aspects of their mineralogy indicate a remarkably stepwise cooling history (Miyamoto et al. 1985; Takeda et al. 1989). After initial equilibration in a slow-cooling, if not slow-warming, environment (inferred from their coarse, equant-granular textures, their environment was suddenly transformed into one in which cooling was so rapid that the equilibration temperatures from the earlier environment are “frozen in” (e.g., pigeonite is scarcely exsolved). Presumably, therefore, smelting occurred at or near the temperature of the first environment. Probably the best constraints on these equilibration temperatures are from Singletary and Grove (2003), who used olivine-pyroxene compositional relationships to derive a range of 1213–1301 °C, with a strong tendency for high mg mafic silicates to correlate with high T.

Ureilites generally have major pyroxene, so accounting for the MgSiO_3 in this mass balance is not especially problematic; it would have diffused into, and arguably equilibrated even with the cores of, preexisting, relatively ferroan pyroxenes. The mass balances for C and Fe metal are discussed below. The most potentially egregious problem with the mass balance involves the CO gas. Some of the CO gas produced might have soon undergone further oxidation into CO_2 (Warren and Kallemeyn 1992), but this is a detail of no great moment for the present discussion.

One observation often cited in support of the smelted-cores model (e.g., Singletary and Grove 2003) is a loose correlation between mafic-silicate core mg and py (≡pyroxene/[pyroxene + olivine] in mol%) among ureilites (Fig. 1). Equation 1 predicts such a relationship. However, the very same correlation is expected and indeed well manifested among chondritic meteorites (Fig. 1) as a consequence of fO_2-related nebular fractionations. Enstatite chondrites are named for the combination of extremely high values of both (silicate) mg and py (e.g., Jarosewich 1990), produced in them by nebular processing.

** MASS BALANCE CONSTRAINTS ON SMELTING **

**Mass and Volume Balance for CO Gas**

Equation 1 indicates the proportions of materials in units of moles, but these can translated into units of mass or, for any assumed pressure, volume, by application of the gas law, $PV = nRT$. The smelted-cores model (Singletary and Grove 2003; Goodrich et al. 2004) assumes that the olivine-core mgs reflect equilibria governed by the modest pressures of the asteroidal interior. The equilibrium (or rather, maximum permissible) pressures implied by the observed range of olivine-core mgs (75–96 mol%) have been constrained by thermodynamics as well as experiments to range from roughly 20 to 80 bars (Warren and Kallemeyn 1992) or perhaps 100 bars (Walker and Grove 1993). The volume of 1 mole of CO gas at ~1200 °C and 20–80 bars is 6.0–1.5 liters. For comparison, 1 mole of MgFeSiO_4 (at ~3700 kg m^-3) is 0.047 liters. Stoichiometry implies precisely
how much FeO must be reduced to yield a given olivine mg shift, and the relationship can be approximated as linear, with a slope of \(-0.91\) wt% FeO/mol% mg. To shift mg from 75 to 96 mol% (the range of ureilite olivine-core mg) in an assemblage of (originally) \(\sim 75\) wt% olivine implies reduction of \(14\) wt% FeO (i.e., \(19\) wt% of the olivine), which in turn implies formation of \(5.5\) wt% CO gas. At 100 bars, a 0.945:0.055 mixture of solids (\(\sim 3200\) kg m\(^{-3}\)) with CO gas (35.7 moles/kg) is 89 vol% gas, 11 vol% solid. Modifications for different pressures involve trivial application of the gas law to change the density of the CO gas. For example, keeping all other assumptions the same except \(P = 20\) bars, the relative gas volume increases to 97% of the product mixture.

Figures 2 and 3 illustrate the relationship between olivine-core mg shift and implied CO gas in the final product mixture. Note that while the relationship between olivine-core mg shift and gas yield in terms of rock volumes (Fig. 2) is approximately linear, the relationship between olivine-core mg shift and gas vol% (Fig. 3) is far from linear—gas vol% is a “closed” variable, so the curves gradually flatten and only asymptotically approach 100%.

In the most detailed version to date of the smelted-cores model, the olivine FeO reduction is explicitly assumed to occur as an equilibrium process. Singletary and Grove (2003) write that “We are also assuming CO is confined by lithostatic pressure and our discussion is based on CO being in equilibrium at each pressure.” Figure 3 indicates that this assumption is highly implausible. The ureilite petrogenetic environment was at low gravity, but buoyancy forces were sufficient to allow small proportions (\(<50\)% of silicate melt (\(\sim 2800\) kg m\(^{-3}\)) to separate from the residual solids (\(\sim 3200\) kg m\(^{-3}\)). The density of the CO gas would have been, for example at \(P = 80\) bars, 25 kg m\(^{-3}\); i.e., 100 times less than that of silicate melt. Yet mass balance to account for the full range of ureilite olivine-core mg as a smelting effect implies formation of at least (at \(P \leq 100\) bars) 87 vol% gas (Fig. 3). An olivine-core mg shift of 7 mol% (one-third of the full ureilite range) would imply at least (at \(P \leq 100\) bars) 75 vol% gas. Even a modest olivine-core mg shift of 3 mol% would imply at least (at \(P \leq 100\) bars) 50 vol% gas. Obviously, the volume proportion of roughly 30 kg m\(^{-3}\) gas that could be sustained in the asteroidal interior would have been far less than volume proportion of \(\sim 2800\) kg m\(^{-3}\) silicate melt.

It might be argued that the smelted-cores model is basically correct and that it merely needs fine-tuning into a variant where smelting was not an equilibrium process (Singletary and Grove 2003), but rather the reduction proceeded with continual leakage of the CO gas. The problem with such a CO-leaky scenario is that the reduction, once started, would almost inevitably become a runaway process. Two factors would combine to render a system undergoing CO-leaky anatexis unstable. First and most important, the principle of Le Châtelier (1888) would take effect. “Every system in chemical equilibrium undergoes, as a result of a change in one of the factors of the equilibrium, a transformation in the direction that, if it occurred alone, would lead to a change in the opposite sign of the factor considered.” In the context of ureilite smelting, Le Châtelier’s principle implies that smelting in a CO-leaky environment would, once started, proceed until one of the reactants in
Equation 1 became exhausted, or until an insufficiency of heat (the overall reaction is mildly endothermic) stalled the process—but in that case, anatexis of the silicates would presumably have stalled as well.

A secondary factor promoting runaway would be the diminution of pressure resulting from escape of a significant proportion of the original material as CO gas rising to the surface of the asteroid, where it would explode into the vacuum of space. As mentioned above, the proportion of CO formed in shifting the olivine-core mg from 75 to 96 mol% would be ~5.5 wt%. Realistically, the explosively escaping CO would entrain a comparable volume, i.e., many times greater mass, of silicate melt (cf. Keil and Wilson 1993). The gases would probably escape in spurts, triggered by build-up to “excess” pressure in the interior. Each major spurt-out of gas (plus entrained melt) would have promoted smelting, not only by Le Châtelier’s principle, but also because the lithostatic pressure would have been subtly but surely
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diminished by sheer loss of mass from the asteroid. For a material already, as a premise of the smelted-cores model, at a pressure at least marginally conducive to smelting, even a small (say, a few tenths of a percent) diminution in lithostatic pressure would be significant because, as a reaction with not only condensed reactants but a gaseous phase among the products, the $\text{C} \rightarrow \text{CO}$-based smelting process is extremely pressure-sensitive (French and Eugster 1965; Warren and Kallemeyn 1992).

Neither of these “runaway” arguments rules out all possible forms of CO-leaky smelting. They only suggest that CO-leaky smelting probably would not have occurred in a steady, extensive way, having major effects on the olivine cores. The topic of runaway CO-leaky smelting will be revisited later in this paper. For now, suffice it to say that the abortive smelting episode that produced the olivine reduction rims so characteristic of ureilites was almost certainly a CO-leaky variety of smelting. Had it been a closed-system smelting, ureilites, especially those with extensive rims, would be extremely porous.

Mass Balance for Carbon

Equation 1, with conversion from moles to weights, implies that for every gram of original FeO (in olivine) reduced to Fe metal, 0.18 g of solid C is oxidized to form CO gas. By stoichiometry, to shift mg from 75 to 96 mol% (the range of ureilite olivine-core mg) in an assemblage of originally ~75 wt% olivine implies oxidation of ~2.5 wt% C. Thus, an end-member form of the smelted-cores model, i.e., one that assumes the ureilites’ mafic-core mg diversity resulted from smelting of an originally uniform starting material, would predict that a plot of bulk C (wt%) versus olivine-core mg (mol%) should show a trend starting near the high-C and low-Fo corner of ureilite composition space and having slope of about $-9$. A slight adjustment for the likely production of minor CO$_2$ along with CO (Warren and Kallemeyn 1992) modifies the slope prediction to $-10$ (Fig. 4).

The actual bulk C versus olivine-core mg distribution (Fig. 4) shows no hint of the predicted anticorrelation. Instead, the data evince random scatter. Presumably some of this scatter stems from inadequate sampling, and also from disparate extents of solid C oxidation in the abortive smelting episode that produced the olivine reduction rims without noticeably affecting the cores. However, several of the ureilites with low Fo and low C combinations, Goalpara and Haverö, have no more than typical extents of rim development (Marvin and Wood 1972; Berkley et al. 1980) and have been analyzed for C multiple times (Mueller 1969; Wiik 1972; Grady et al. 1982, 1985; Bogard et al. 1973), and yet they consistently show low C concentrations—in clear contradiction of the end-member smelted-cores model, at least for application to all ureilites.

Fig. 4. Bulk-rock C versus olivine-core mg for ureilites (literature data). Data for mg are mostly from review by Mittlefehldt et al. (1998); for C, mostly from the Open University group (Grady et al. 1982, 1985; Grady and Pillinger 1993; Smith et al. 2001). Other sources include: Mueller (1969), Wiik (1972), Bogard et al. (1973), Jarosewich (1990), and Yamamoto et al. (1998). Error bars (1σ) are shown where the plotted C value is an average of multiple analyses. The fractionation curve is calculated from mass balance implied by Equation 1, assuming, for purposes of illustration, an initial composition close to the low-mg, high-C corner of ureilite composition-space (see text).
Singlelery and Grove (2003), who advocated formation of all olivine-pigeonite ureilites (i.e., most ureilites) by core-smelting of a near-uniform (at least in terms of mafic silicate mineralogy) initial material, admitted that the initial materials might have been diverse in terms of C content. But if a highly non-uniform initial C can be invoked, the assumption of near-uniform initial mafic silicate mineralogy appears commensurately open to doubt.

Nakamuta (2005) interpreted a plot of olivine-core mg versus modal C-phase abundance (i.e., a plot strongly analogous to Fig. 4) for 15 ureilites as supportive of a multiple-source variant of the smelted-cores model. Again, the smelted-cores model predicts a negative correlation. Actually, Nakamuta’s Fig. 1a shows random scatter. By arbitrarily assigning the four highest mg (86–92 mol%) samples to a putatively cogenetic “group,” Nakamuta was able to claim that this one small subset of his data set forms a negative correlation. But even this claimed anticorrelation appears dubious. The two highest-mg ureilites in Nakamuta’s data set have Δ17O ratios of ~1.9 to ~2.3, whereas the two Fo86–87 ureilites that constitute the balance of the supposed anticorrelation have Δ17O of ~0.81 to ~0.09 (Clayton and Mayeda 1988; cf. Franchi et al. 1998; also Fig. 39 of Mittlefehldt et al. 1998), so it seems highly unlikely that these four ureilites all descended from a single, uniform starting material.

To make matters worse for the smelted-cores model, Franchi et al. (1998) have shown that among ureilites bulk δ13C is strongly correlated with bulk Δ17O. Since bulk Δ17O also shows a strong anticorrelation with olivine-core mg (Franchi et al. 1998), this implies an anticorrelation between δ13C and olivine-core mg. More recently, a loose anticorrelation has been directly reported, by Hudon et al. (2004). In other words, the ureilites that the smelted-cores model implies experienced the most extensive burn-away of their carbon tend to have lighter C than the ureilites less affected by smelting. The observed δ13C/olivine-core mg relationship is the reverse of what the smelted-cores model implies it should be (Hudon et al. 2004).

Mass Balance for Fe Metal and Siderophile Elements

Equation 1 implies that for every gram of original FeO (in olivine) reduced, 0.78 grams of Fe metal must form. By stoichiometry, to shift mg from 75 to 96 mol% (the range of ureilite olivine-core mg) in an assemblage of originally ~75 wt% olivine implies production of ~11 wt% Fe metal. Even more total metal should have formed, because there was also a later, abortive stage of smelting that produced the reduced rims without strongly affecting (extending as far inward as) the cores of the olivine grains. Apart from the late rim-reduction smelting, the smelted-cores model implies a correlation between olivine-core mg and wt% metal, with a positive slope of ~1.9 (Fig. 5). Removal of silicate, roughly picritic, partial melt at some stage(s) of the smelting process would likely raise the restite’s mg by a few mol%, so the overall predicted slope is more realistically ~2.5, but this still implies production of ~8 wt% Fe metal (Fig. 5), not including the Fe metal formed in the later rim-reduction stage of smelting.

No ureilite has been reported to contain as much as 8 wt% metal. The highest reported metal abundances are 5–6 wt%, in two relatively ferroan (Fo76) samples, Goalpara and Havero (Wilk 1972). The ureilite with the highest olivine-core mg, Allan Hills (ALH) 82106/4136, has only 0.5 wt% FeNi metal (Jarosewich 1990). If anything, the relationship between ureilite Fe metal abundance and olivine-core mg resembles an anticorrelation rather than a correlation (Fig. 5).

In principle, the predicted correlation between Fe metal and olivine-core mg (Fig. 5) might have been offset because the nascent-anatectic ureilites lost S-rich metallic melt, and this S-rich metallic melt loss was more extensive in the thoroughly smelted high-mg ureilites than in the low-mg ureilites (Goodrich et al. 2004). In fact, the total Fe (Fe in FeO plus Fe metal plus Fe in FeS) contents of ureilites are strongly anticorrelated with their olivine-core mg (Fig. 6). Hughes 009 appears to represent an exception, but it has augite instead of pigeonite as its pyroxene, contains no petrographically recognizable carbon phases and is severely weathered, so it is a highly atypical ureilite (Goodrich et al. 2001). The Fig. 6 trend is obviously inconsistent with any model in which smelting occurs without accompanying or subsequent loss of Fe. Of course, some Fe would have been removed as FeO in the basaltic melts that undoubtedly separated from the ureilites. However, melt/peridotite partitioning is not prone to engender major depletion in the FeO concentration of a restite (e.g., Singletary and Grove 2003 or Appendix 3 of Kita et al. 2004).

Any such metal-loss variant of the smelted-cores model should have engendered strong depletions of siderophile elements, particularly in the ureilites that were most extensively smelted, and thus should have produced the most Fe metal, i.e., the high-olivine-core mg ureilites. If the Fe metal was removed mainly as S-rich metallic melt, the depletions should be strongest for chalcophile elements, i.e., S itself and elements with high distribution coefficient for S-rich metallic liquid over FeNi solid metal, Dmol/sm (Chabot and Jones 2003). Warren et al. (2006) reviewed the data for S and chalcophile elements in ureilites. Sulfur itself shows no correlation with olivine-core mg. The chalcophile elements Zn, Ag, and In show essentially no correlation with olivine-core mg, and Cd shows only a marginally significant (r = 0.48 for 18 data pairs) (Warren et al. 2006) anticorrelation. On balance, the available data seem permissive of considerable loss of S-rich metallic melt; and perhaps of the high-mg ureilites having lost generally more than low-mg ureilites, but not by large and systematic factors.

If the Fe metal was removed mainly as an S-poor metallic phase (either metal or molten metal), there should be major depletions of highly siderophile elements. In the case of Ir, the
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Fig. 5. Fe metal abundances in ureilites plotted versus olivine-core mg (literature data from Jarosewich 1990; Wiik 1972). Shown for comparison is a fractionation curve implied by Equation 1, assuming an initial composition with approximately three-fourths olivine (mg 75 = mol%, near the extreme low end of the ureilite range) and no Fe metal. A second, more curved path shows schematically the effect of possible basaltic melt removal during smelting (see text).

Fig. 6. Olivine-core mg versus bulk-rock total Fe for ureilites, after a similar figure in Mittlefehldt et al. (2005) (literature data; little-weathered samples only, except Hughes 009). Data for mg mostly from review by Mittlefehldt et al. (1998); for total Fe, from sources cited by Warren et al. (2006). Arrow shows the approximately flat trend expected from closed-system, or basalt-leaky but metal-retentive, smelting (see text).
highest-mg ureilites do tend to have below-average concentrations, but only by a small factor (Fig. 7). Average Ir in 25 ureilites (database of Warren et al. 2006) with olivine-core mg < 82 mol% is 282 ± 153 ng/g; in 15 ureilites with mg ≥ 82 mol% the average is 162 ± 54 ng/g, and the trend at high mg shows signs of converging near the Ir concentration of the highest-mg ureilite, ALH 82106/4136, 157 ng/g (three analyses from two distinct pair-stones range from 149 to 163 ng/g: Warren and Kallemeyn 1992; Spitz and Boynton 1991). For several other very strongly siderophile elements, the difference between ferroan-core and magnesian-core ureilites is undetectable. For Ni, the average in 27 ureilites with olivine-core mg < 82 mol% is 1190 ± 440 µg/g; in 16 ureilites with mg ≥ 82 mol% average Ni is 1160 ± 610 µg/g, and in ALH 82106/4136 it is 1390 µg/g—above the overall average. Average Au in 26 ureilites with olivine-core mg < 82 mol% is 25 ± 12 ng/g; in 15 ureilites with mg ≥ 82 mol% it is 22 ± 10 ng/g, and in ALH 82106/4136 it is 36 ng/g—1.5× the overall average. These relationships suggest that metal loss was not extraordinarily extensive during petrogenesis of the high-mg ureilites. Metal loss is not a plausible explanation for the failure of high-mg ureilites to contain abundant Fe metal as implied by the smelted-cores model.

Implication: The Smelted-Cores Model is Implausible

Any one of the three mass-balance problems discussed above seems severe enough to decisively discredit the smelted-cores model, at least in its full-blown form, which assumes that all ureilites formed on a single asteroid, out of a single, petrologically uniform initial material. Yet, except for stemming from Equation 1, the three problems are quite independent. For example, even if the CO gas problem might be alleviated by appeal to CO leakage (a very different scenario, but arguably still a variant of the smelted-cores model), the solid carbon and Fe metal/siderophile problems would remain as severe contradictions of the smelted-cores model.

DISCUSSION

Implications of Inferred Catastrophic Breakup vis-à-vis Smelting

Despite recent discoveries of many tens of “new” ureilites, without exception their coarse-equant textures and detailed mineralogy (e.g., lack of pigeonite exsolution) indicate the distinctive, extremely step-wise cooling history first noted by Miyamoto et al. (1985). The mechanism for sudden and ubiquitous transition to rapid cooling is inferred to have been late-stage disruption of the ureilite-parent asteroid(s); and the disruption is plausibly assumed to have been a major impact (Takeda et al. 1989; Warren and Kallemeyn 1992; Scott et al. 1993; Goodrich et al. 2004). In the remainder of this section, it will be assumed that this impact-disruption inference is correct, and also that at least
several wt% of interstitial basaltic melt was present before the disruptive impact. Justification for the several wt% melt assumption is beyond the scope of this paper. It is hardly a novel concept (e.g., Walker and Grove 1993) and Warren et al. (2006) justify it in detail, based on data for trace incompatible elements, trace siderophile elements, and physical modeling of time-limited, low-g melt percolation.

A point that should be emphasized, and may seem counterintuitive, is that impact may have only supplied the initial impetus for the overall disruption. Once the parent asteroid(s), primed with ~3 wt% of mantle carbon, became so hot that several percent of melt (~5–10%) was stewing in much of its mantle, it was ripe for an episode of “runaway” smelting. If, in this delicate state, a major portion (say, one-quarter) of the partly molten body was spalled away, the interior pressure would have immediately dropped, simply due to the loss of mass; and probably would soon have dropped slightly further due to a loss of melt from the environment of the impact (and, probably, its antipode), as conduits suddenly opened for melt to flow up and out to the surface, where the Wilson and Keil (1991) explosive basalt-loss mechanism probably operated. As these authors noted, eruption of basalt at the surface of a low-gravity, atmosphereless body leads to explosive expansion of any gas bubbles; depending upon assumed volatile content of the erupting magma—and ureilites obviously formed in an environment with abundant potential CO—the explosive force could suffice to propel silicate melt clear away from the feebly gravitational bond to the asteroid.

Interior pressures scale with mass$^{2/3}$ (Turcotte and Schubert 1982), so in the short-term aftermath of the hypothetical impact event, average pressure inside the remnant asteroid would have dropped to ~0.8× the pre-impact pressure. As a result of the displacement effects of the impact, locally the new $P$ would be only a small fraction of the pre-impact $P$. In parts of the mantle brought to low $P$, the pressure-sensitive smelting process would suddenly have acquired great impetus. Very rapid CO gas outflow literally would have blown apart the affected region of the remnant asteroid; and would also have engendered rapid, efficient removal of melt to the surface (by gross fissuring of the mantle, and by actively, directly propelling the melt). Upon arrival at the surface, the CO-charged magma would have tended to explode permanently off the asteroid, by the Wilson and Keil (1991) mechanism. Thus (cf. Warren and Kallemeyn 1992; Scott et al. 1993), the overall asteroid would enter into a runaway smelting mode: pressure loss causing mass loss causing pressure loss, etc.; which would continue through a stage of temporary gross inflation into a gas-filled rubble pile, until the remaining materials (fast-cooling because less compact and suddenly purged of whatever $^{26}$Al had remained in the melt) became so cool and melt-purged that the endothermic reaction (Equation 1) could not continue. The steep thermal gradients implied for the mantle remnants during the fast-cooling loose rubble pile stage would have presented an almost ideal scenario for the “thermal migration” mechanism advocated by Walker and Agee (1988) for purging of melt from the interior of the ureilite parent asteroid(s). Remarkably efficient purging of melt has been inferred based on the dearth of feldspar (i.e., basaltic matter) among ureilites, especially monomict ureilites (Warren and Kallemeyn 1992; Scott et al. 1993).

As an aside, it is not even certain that an impact would be required to trigger this scenario. Assuming the mantle melt fraction grew by gradual heating of the interior, its inherent “excess pressure” (Keil and Wilson 1993) would sporadically generate cracks through which the buoyant melt would rise to the surface; upon encountering the surface vacuum it would, assuming a high enough gas content, erupt explosively and mostly be permanently lost from the asteroid (Wilson and Keil 1991). Provided this crack-venting process waited to occur until a large proportion of melt had formed in the mantle, a significant mass loss would be associated with the eruptive spurt, and the sudden interior pressure drop associated with the mass loss conceivably might have triggered essentially the same runaway smelting scenario described in the previous paragraph.

As soon as their declining temperatures braked runaway smelting, the scattered solid materials mostly would reaccrete, or recompact, into a few (or possibly just one) altered, partially reduced and thoroughly melt-purged, smaller versions of the original parent asteroid. The principal nucleus for the reaccretion would probably be the primary asteroid’s S-rich metallic core (inferred from siderophile element systematics) (Warren et al. 2006), which although mostly molten at the time of the impact would be more cohesive (more ductile, less prone to react to the post-impact pressure drop as a runaway gas-maker, and also well-shielded from the impact, per se) in comparison to the silicate portion. The reaccretion process must have been selective, in that basaltic melt droplets exploded out by the Wilson-Keil process generally had traveled too far off to be recaptured.

An interesting corollary of this hypothesis is that the extent of reduced-rim development should be almost random in relation to other geochemical or petrological traits of the samples. The extent of rim-reduction depends largely upon vagaries of the physical aspects of runaway smelting. The blow-apart process presumably caused considerable jumbling of the pre-impact materials. Parcels of the original mantle(s) that happened to be at shallow depth during most of the blow-apart process would tend, for any given mg, to be at pressures highly conducive to smelting, but also would tend to cool especially rapidly. Parcels that remained relatively deep during the blow-apart would (in general) not be at pressures conducive to smelting until the asteroid was thoroughly blown apart, but would also tend to cool more slowly, allowing the smelting process to continue after shallower materials had already become too cool for smelting. (Of
course, many other factors might contribute to diversity in the extent of reduced-rim development; e.g., multiple primary ureilite-parent asteroids of varying size and average composition.)

We searched for, but could not find, any systematic relationship between the proportion of olivine rim reduction and other petrologic traits. Singletary and Grove (2003) claimed that proportion of olivine-rim reduction shows an inverse correlation with modal pigeonite. However, using the same data set used in their Fig. 2, except averaging the paired Queen Alexandra Range (QUE) 93336/41 samples, the statistical $r = 0.16$. For a set of 20 data pairs, this $r$ is far below statistical significance. Singletary and Grove (2003) argued that the worst “outlier” sample, Dingo Pup Donga, “might not be representative” because it is brecciated. However, Dingo is a monomict breccia that has only undergone moderate shock (Berkley et al. 1980; Mittlefehldt et al. 1998), and moderate shock can hardly be expected to increase modal pigeonite or induce major rim-reduction of the olivines. Also, one of the samples of Warren et al. (2006), Hammadah al Hamra (HaH) 126, has rim development to the extent of at least 80% of the olivine and yet near-average (~30%) modal pigeonite. With HaH 126 added (Fig. 8), the relationship between proportion of olivine rim reduction and modal pigeonite appears thoroughly random ($r = 0.13$, 21 data-pairs).

Singletary and Grove (2003) cited another petrographic feature as evidence for the core-smelting model. These authors reported that pigeonites, but not olivines, in ureilites are “riddled” with “metal inclusions,” from which they inferred “coformation” of the pigeonite and metal by the core-smelting scenario. Citing absence of reduction haloes around the “metallic inclusions,” Singletary and Grove (2003) inferred origin by core-smelting well before the late-stage reduction process that was essentially confined to the olivine rims. Using backscattered electron images, Singletary and Grove (2003) determined modal data for “percent of pigeonite grains as metal” for 21 olivine-pigeonite ureilites.

Rubin (2005), who also studied a large number of ureilites, noted that, contrary to the assertion of Singletary and Grove (2003), “trails” of metal inclusions are also present in olivine. Rubin (2005) further argued that at least some of these metal-in-olivine inclusions did not form by reduction, because the metallic “trails” also contain small grains of Fe sulfide, a phase that cannot form from olivine by reduction. This same argument can now be applied to the pigeonites, because in the sample for which Singletary and Grove (2003) reported the highest “percent of pigeonite grains as metal” (2.6%), Graves Nunataks (GRA) 95205, we find that slightly more than half (by volume) of the opaque inclusions within pigeonite are Fe sulfides (Fig. 9). Similarly in ALH 78262, a sample described by Singletary and Grove (2003) as having pigeonites with 1.3% “metal inclusions,” we find that most of the opaque inclusions within pigeonite are actually Fe sulfides (including one grain with molar Fe:S far less than 1). The opaque-in-pigeonite inclusions in these two ureilites, and by extrapolation in the pigeonite-bearing ureilites in general,
are too sulfide-rich to plausibly be products of mafic silicate reduction. According to Rubin (2005), the trails of mixed metals and Fe sulfides in ureilite olivines, and we can now extend his reasoning to the pigeonites, are “exactly analogous to silicate darkening in shocked ordinary chondrites,” i.e., they formed by shock-melting of metals and sulfides above the Fe-FeS eutectic temperature (990 °C), and displacement of the melts into fractures (since healed) within adjacent silicate grains.

The literature contains many confident assertions that ureilites are products of smelting. For the sake of simplicity and continuity with past literature, even we, in this paper, continue to apply the term “smelting” to the process that produced the ureilites’ reduced silicate rims. But “smelting,” inasmuch as this term tends to imply simultaneous reduction and partial melting, is probably a misnomer. At the time the reduced rims formed, melting was probably virtually over. Although melt-crystal-gas reactions may proceed for a while, new melting is hardly likely within a set of materials that are suddenly, at disparate rates but nonetheless all, cooling.

A limited degree of true smelting (simultaneous reduction and partial melting) conceivably occurred, in portions of the predisruption asteroid(s) that were both hot enough and at low enough pressure to sustain smelting. The temperature criterion must be at least the Fe-FeS eutectic, ~990 °C (Usselman 1975—if production of metallic melt is assumed to satisfy the “melting” aspect of smelting); or arguably the chondritic silicate solidus, ~1150 °C (Jurewicz et al. 1995). The maximum smelting pressure is ~20–80 bars, depending upon the mafic-silicate mg; lower mg implies a higher pressure to forestall smelting (Warren and Kallemeyn 1992). At the lower end of the temperature range under consideration (990 °C), the limiting pressure would be considerably lower, only of order 1–10 bar (Warren and Kallemeyn 1992). There is no guarantee that any significant portion of the parent asteroid(s) passed through such an area of P-T space. The near-surface regions of any body tend to remain at below-average temperature. In a 200 km radius (R) asteroid with a small core (~10–20 wt%), only ~17% of the noncore volume is at P < 80 bar, and 5 vol% is at P < 20 bar (Fig. 10; pressure-depth relationships calculated after Turcotte and Schubert 1982). Assuming R = 300 km, these volumes shift to 8% and 2%, respectively. Even at its maximum bulk temperature, the ureilite parent asteroid presumably had a conductive boundary layer at average temperature much lower than the T of the underlying ureilite partial-melt zone. In the case of the
lowest-mg ureilites that would smelt at the highest pressures (~80 bar), the ureilite $T$ was ~1210 °C. Of the zone in a large ($R = 200$–$300$ km) asteroid that qualified for smelting in terms of pressure, probably at least half, and quite conceivably all, would never be hot enough for smelting. In summary, it is possible but hardly inevitable that some small subvolume of the parent asteroid was at one time both shallow and hot enough to undergo true smelting.

**Asteroidal Setting for Ureilite Petrogenesis**

As noted by Warren and Kallemeyn (1992) and Scott et al. (1993), there is little reason to assume that all of the ureilites are products of a single parent asteroid. Goodrich et al. (2004) note that the polymict-breccia ureilites collectively show a similar spectrum of olivine-core mg as that from the population of monomict ureilites. A close match, especially if found in just a single individual polymict ureilite, would be consistent with a single parent asteroid. To account for a close match in a multiple-parent-asteroid model would require pervasive mixing of debris from originally separate ureilite asteroids; and yet the mixing would have to be selective (i.e., the original orbits would have to be assumed remarkably similar) because the polymict ureilites contain very little of anything other than ureilitic debris. The mg population agreement is far from perfect, however. Out of several hundred olivine cores that have been characterized from ~8 polymict ureilites (105 from North Haig alone) (Berkley et al. 1980), only two grains have been reported to have mg > 90 mol%: one in North Haig (Berkley et al. 1980) and one in Elephant Moraine (EET) 83309 (Warren and Kallemeyn 1989). The overwhelming majority of polymict ureilite olivine cores have mg < 85 mol% (Berkley et al. 1980; Jaques and Fitzgerald 1982; Ikeda and Prinz 2001; Goodrich et al. 2004). In contrast, 12/108 (11%) of the monomict ureilites have olivine-core mg > 90 mol%. More studies of polymict ureilites are warranted, but the implications from the present database for the issue of one versus multiple primary parent asteroids are far from clear.

Provided the Wilson and Keil (1991) basalt blow-away mechanism is as effective as their physical modeling implies, the main prerequisites for a parent asteroid are that it be heated to a low-moderate degree of anatexis; that it be rich in carbon (fuel for explosive volcanism); and that it be moderately large—large enough to not be widely smelted until a sudden transition (by inference, a major, partially disruptive impact) causes a sharp drop in pressure, and at about the same time, a sharp increase in cooling rate. Aside from these prerequisites on the state of the primary parent asteroid just before the disruptive (impact?) event, the parent material’s evolution to that state is constrained to some degree. Ordinary chondrites of low thermal-metamorphic type often have much higher C concentrations than their counterparts of high thermal-metamorphic type. In the data...
set of Jarosewich (1990), the incidence of C being >0.5 wt% is 12/32 (38%) for type 3, versus just 3/132 (2%) for types 4–6; C being >0.9 wt% is 7/32 (22%) for type 3, versus 0/132 for types 4–6. The detailed mechanism of the metamorphic carbon depletion is unclear (cf. McSween and Labotka 1993), but it probably involved thermally triggered oxidation into CO gas. The temperature of metamorphism where most of this C-loss occurred (i.e., where type 3 grades near to type 4) cannot be precisely gauged, but it was probably not >>600 °C (Sears et al. 1995). In the case of the ureilites, the original material somehow managed to reach silicate-anatectic temperatures (~1200–1300 °C) with a still very high (~3 wt% average) C concentration. The avoidance of early thermal-metamorphic C depletion may have been only partially effective in some batches of protoureilitic material, but for the most part, the ureilite parent materials managed to assemble into quite large bodies with high enough prevailing pressure to inhibit oxidation of solid C into CO gas before their interiors warmed to >>600 °C. The limiting pressure, at temperature of order 600–1000 °C, would be of order 1–10 bar (Warren and Kallemeyn 1992), so assuming most of the material avoids C depletion (say, three-fourths of it; i.e., the ultimate starting material averaged 4 wt% C instead of 3 wt%), the implied size attained before heating to >>600 °C is of order R ~ 20–60 km.

The implied temperature-size evolution seems consistent with models by Shensu and Matsui (2004) for the gradual internal heating of a family of planetesimals destined to accrete into one large, partially molten asteroid, with R = 250 km and roughly half of its interior at T = 1200 °C. However, as the metamorphosed ordinary chondrites demonstrate, survival of the high ureilite C concentration was far from inevitable. The HED parent asteroid, with its major proportion of basaltic (eucritic) crust, clearly was not prone to the highly explosive (Wilson and Keil 1991) style of volcanism that is inferred to have depleted basalt and Al from the ureilite asteroid(s). This profound difference in style of volcanism suggests that much higher proportions of the fuel for CO-gas production (i.e., fine-grained “C-matrix” that could be entrained in out-percolating basaltic melts) were present in the ureilites than existed in the HED-asteroidal mantle. That difference might stem from early nebular fractionation effects on the C contents of the parent materials. But it also might stem from a disparity in the pressure conditions (i.e., planetesimal sizes) of ~600–1000 °C thermal metamorphism. To have reached a state of extensive anatexis with a still large (~3 wt%) proportion of C, the protoureilitic materials must have accreted into large (of order 20–60 km) planetesimals before being heated to >>600 °C.

CONCLUSIONS

Three different mass-balance problems arise from the often-cited hypothesis that pressure-buffered equilibrium smelting played an important role in producing the mafic-silicate-core mg diversity of ureilites. In order of increasing severity, these problems concern solid carbon (including its C isotopes); Fe metal (and total Fe, and siderophile elements); and most importantly the mass and especially the implied volume of CO gas. The proportion of gas required to account for the ureilites’ entire 21 mol% range in olivine-core mg is ≥85 vol%. Even to account for one-fourth of the range in olivine-core mg would require a gas yield of ≥65 vol%. Obviously, such high proportions of gas could never be sustained, at equilibrium, within the interior of even a very small asteroid.

Even a CO-leaky variant of the smelted-cores model would leave unmitigated the carbon and Fe metal mass balance problems. Also, by Le Châtelier’s principle, and moreover in consequence of the loss of asteroidal mass (by blow-out and blow-off of basalt) that would likely accompany initiation of significant smelting, a CO-leaky smelting process would probably become a runaway. Indeed, based on the remarkably stepwise cooling history inferred from ureilite texture and mineralogy, a runaway, CO-leaky process that can loosely be termed smelting appears to have occurred, probably triggered by a major impact. However, the only “smelting” in this scenario was a short-lived disequilibrium process that reduced only the rims, not the cores, of the ureilite olivines; and the ureilites were cooling, not melting, during the abortive “smelting” episode.

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Ureilite petrogenesis: A limited role for smelting


