

PRIMARY IGNEOUS CARBON IN UREILITES: PETROLOGIC AND GEOCHEMICAL  
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Recent hypotheses for the origin of ureilites (carbonaceous olivine pyroxene achondrites) portray these rocks as primarily igneous ultramafic assemblages formed by fractional crystallization and silicate mineral accumulation in the upper crustal regions of the parent body [1,2]. As a first approximation this hypothesis successfully accounts for gross textural features and certain mineral composition properties and trends [1,2,3,4] but less adequately accounts for more problematic features such as (i) the origin of carbonaceous matrix (C-matrix; mainly graphite with minor diamond lonsdalite), (ii) V-shaped chondrite-normalized REE patterns [5], and (iii) high planetary-type noble gas contents [6,7]. We have evaluated these problems using electron microprobe, neutron activation, and petrographic data, and thermochemical calculations bearing on the nature and physical significance of redox reactions for a carbon saturated silicate melt in equilibrium with mafic silicate minerals and graphite. We conclude that the problems and features cited above can be adequately explained within the conceptual framework of a closed-system cumulate body.

Competing hypotheses for the origin of C-matrix in ureilites include (a) forceful solid state carbon injection, possibly during an impact event [2,5,7,8] and (b) primary intercumulus incorporation during igneous crystallization and cumulate formation [1,4]. The problems of REE and noble gas patterns are intimately associated with the origin of C-matrix, thus [5] concluded that LREE enrichments arise by secondary LREE introduction along with injected C-matrix and [7] proposed a similar mechanism for incorporating planetary noble gases. It is improbable that C-matrix entered ureilites by forceful injection as detailed by [1]. This conclusion is further corroborated by new microprobe data showing qualitative indications of significant C in ureilite kamacite and kamacite-sulfide spherules of igneous origin. Furthermore, delicate graphite crystals (Fig. 1) observed in grain boundary interstices and as inclusions in silicate grains in the virtually unshocked (e.g., no diamonds) ureilite ALHA78019 suggest that most graphite crystallized in situ from intercumulus liquid. This observation effectively precludes violent carbon injection into ureilites.

However secondary introduction may be required to explain the enrichment of LREE since no known single-stage primary mechanism could produce the highly fractionated V-shaped REE patterns in ureilites [5,1]. Irvine [9] recently stressed the requirement that relatively rare adcumulate formation in terrestrial layered intrusions is accompanied by significant infiltration of- and reaction with- the unconsolidated cumulate pile by lower-level silicate fluids. Ureilites are adcumulates, thus by analogy to terrestrial systems, they may have acquired their LREE, noble gas, and some C content by infiltration metasomatism from below. The low absolute abundances of REE [5] also stem from the adcumulate nature of ureilites because adcumulates contain little or no material representing REE-rich intercumulus liquid. LREE [5] and noble gases [7] are concentrated in the C-matrix of ureilites, a factor that is consistent with secondary intergranular introduction of these components, possibly in the manner described above.

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Given that carbon constituted a significant component in the ureilite parent melt as we propose, we have calculated the effect of C on Fe/Mg ratios in mafic silicate minerals (using olivine as representative) for petrologically relevant temperatures (1200 and 1600°K). At fixed T and melt composition, olivine composition is largely controlled by oxygen fugacity (see [10]) according to the reaction  $\text{MgSi}_{0.5}\text{O}_2(\text{ol}) + \text{FeSi}_{0.5}\text{O}_2(\text{ol}) = \text{Fe}(\text{metal}) + 0.5 \text{O}_2(\text{g}) + \text{MgSiO}_3(\text{px})$ . In a graphite-bearing system  $f_{\text{O}_2}$  is dominantly controlled by a reaction similar to  $3\text{C}(\text{s}) + 2\text{O}_2(\text{g}) = 2\text{CO}(\text{g}) + \text{CO}_2(\text{g})$  (for  $P_t = P_{\text{CO}} + P_{\text{CO}_2}$ ). This equilibrium allows calculation of  $f_{\text{O}_2}$  for any given P,T condition (Fig. 2). Calculated  $f_{\text{O}_2}$  in equilibrium with known ureilite olivine compositions are plotted in Fig. 2 and yield rough total pressure estimates of < 25 bars, consistent with previous estimates [1,8] of relatively low pressures of formation. Assuming an approach to equilibrium conditions (reasonable, considering equilibrated silicates) the C-CO-CO<sub>2</sub> reaction should fix mafic silicate compositions for a given T and melt composition, preventing "runaway reduction" of the magmatic system.

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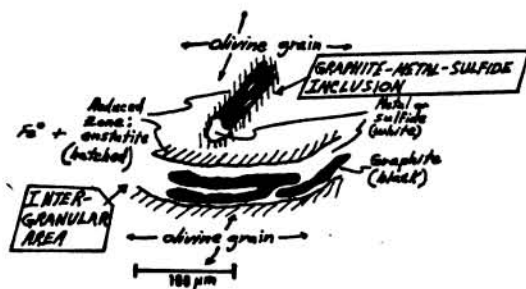


Fig. 1. Schematic sketch of textural relationships in C-matrix areas in ALHA78019.

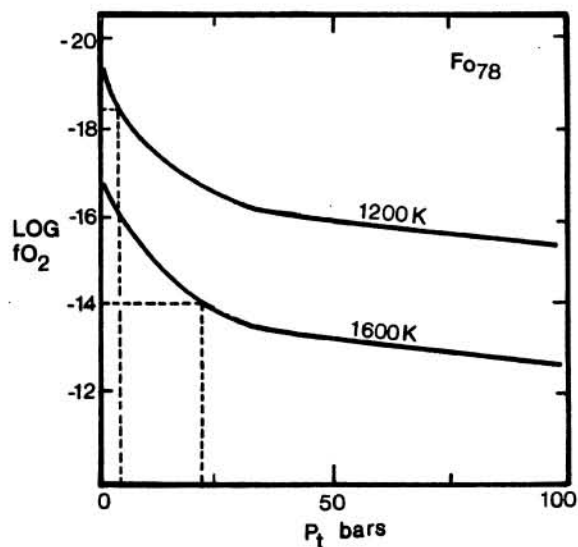


Fig. 2. Equilibrium curves for system C-CO-CO<sub>2</sub> at 1200 and 1600°K. Dashed lines show  $f_{\text{O}_2}$  in equilibrium with olivine (Fo78) and corresponding P of formation at specified T's.