DIAMONDS IN UREILITES FROM MARS.

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Introduction: Ureilites are an enigmatic class of meteorite (see review by Goodrich et al. [1]). After HEDs from Vesta, they are the most common achondrite. Based on ε^{50}Ti and ε^{54}Cr anomalies, ureilites formed in the inner solar system [2], at about 2.7-2.8 AU [3]; yet they are far richer in C (graphite ~3wt%) than other inner solar system bodies (< 1wt%), and as C-rich as the most C-rich carbonaceous chondrites [1].

The ureilite parent body (UPB) melted but only experienced partial (~15%) extraction of silicate melt [1], and some S-rich metal [4]. Based on pigeonite-olivine thermometers, the UPB reached ~1200°C. Olivine cores in ureilites exhibit a wide range of Mg# (74-96, strongly peaked at 80), often attributed to pressure-sensitive 'smelting' reactions (reduction of FeO in silicates to Fe metal by reaction with C), such as [5]:

$$(Fe,Mg)_2SiO_4 \text{ (olivine)} + CaO + SiO_2 \text{ (in melt)} + C \rightarrow 2\,(Mg,Ca)SiO_3 \text{ (pigeonite)} + Fe \text{ (metal)} + CO \text{ (gas)}.$$

Many properties correlate with Mg#: oxygen isotopes and FeO/MnO of olivines [6], carbon isotopes of associated graphite [6], and Cr valence states of olivine [7].

The UPB was catastrophically disrupted [1] early in its history (the youngest samples formed at $t = 5.4$ Myr after CAIs [8]), while at ~1200°C. Microns-thick reduction rims around olivines speak to a release of pressure, followed by a rapid cooling over hours [1,9]. The UPB (and impactor) reassembled into numerous smaller ureilite daughter bodies (UDBs), from which ureilite meteorites derive. Neither the largest remnant nor its collisional family has been identified yet.

Within the graphite in ureilites are abundant nanodiamonds (< 100 nm) likely formed by shock during the impact [10]. Graphite in the polymict ureilite Almahata Sitta also holds larger (~100 μm) diamonds argued to have formed at static high pressures > 2 GPa [11], much higher than the highest pressures in asteroids, ~0.1 GPa. Recently, [12] analyzed small (< 100 nm) Fe-Ni-P-S inclusions within these diamonds, concluding they formed from decomposition of the phase $(Fe_{0.932}Ni_{0.068})_3(P_{0.12}\,S_{0.88})$, stable only at pressures > 21 GPa [13] characteristic of planetary interiors. [12] suggested the UPB was a Mercury- to Mars-sized body, now lost. This would be inconsistent with partial melting on the UPB.

All of these features about ureilites are mysterious. Here we present a unifying hypothesis that explains them. We especially argue that the C and diamonds in ureilites are largely exogenous, deriving from Mars.

Production of Diamonds in Mars: Mars is known from Hf-W [14] and ^{60}Fe-^{60}Ni [15] systematics to have accreted mostly between t = 1 to 3 Myr, very likely by pebble accretion [16]. It therefore accreted cold (< 1000°C), but quickly heated by ^{26}Al decay, producing a global magma ocean [17,18]. We predict Mars first reached the Fe-S eutectic temperature (988°C) and formed a S-rich core with high-pressure eutectic composition (14.4wt% S); given Mars's S inventory [19], the core at first had only ~3/4 of Mars's Fe. Immiscibility of S and C in metallic melts limited the C dissolved in the melt to ~1/4 of Mars's C inventory. Further heating then yielded a whole-mantle magma ocean [17,18], delivering the remaining metal and the remaining ~3/4 of Mars's C to the core, by $t = 3$ Myr.

As diapirs of the last, C-rich metal joined the S-rich metallic core at the core-mantle boundary (CMB), at pressure 22 GPa, diamonds would be produced. In experiments, when S-rich and C-rich metallic melts combine at > 7.5 GPa, diamonds spontaneously nucleate and grow at rates ~1 μm/hr [20,21]. We calculate that if diapirs sank ~ 10 m into the core, the diamonds would have grown to ~100 μm in size. We calculate the abundances of Fe, Ni, S and P in the two metallic melts, using partitioning coefficients of [22] to find that 30% of Mars's P entered only the second, C-rich melt. We find a 50-50 mixture of the two melts would yield exactly the unusual stoichiometry of the metallic inclusions in the large Almahata Sitta diamonds.

We calculate the densities of melt in the whole-mantle magma ocean assuming an adiabat $T = 1440°C + (30°C)(P\ /\ 1\ \mathrm{GPa})$. The diamonds were positively buoyant in the core and lower mantle ($P > 5.7$ GPa) and were advected upward by convection. Above the 6.0 GPa, $T = 1620°C$ level, diamond was unstable and transformed to lower-density graphite at known rates [23]; diamonds reaching the surface were ~30% graphite and positively buoyant relative to the melt; being > 20 μm in size (the largest size particle that could remain in suspension in the convecting martian magma ocean [24]), they fell upward out of suspension and collected near the surface. By $t = 3$ Myr, about 1/4 of Mars's C resided in a thick graphite-diamond layer (up to 10vol%) in Mars's upper mantle/crust, as chondritic material continued to accrete onto Mars's surface.

Ejection of the Martian diamonds: The Borealis basin impact was one of the largest impact events in the solar system, and ejected ~ 0.01 Mars masses of material from the surface down to >200 km depth (2.5 GPa) [25]. It produced over 100 fragments >100 km, many unmelted, that would have reached 2.9 AU [25]. If the impact occurred at *t*~5 Myr, fragments would have sampled the surface before mantle overturn [26], including crystallized martian magma ocean (MMO), plus carbonaceous chondrites, plus the diamonds formed at Mars's CMB. A mix of 55% MMO, 20% CV and 25% CI chondrite would have olivines with Mg#77 and Δ^{17}O=-0.4‰. This mixture matches one end-member composition in ureilites identified by [6].

The UPB before the Collision: We argue the UPB formed with olivines with Mg#80-85, FeO/MnO=43, Δ^{17}O=-0.9‰, and some C with δ^{13}C=-7‰. It would be well approximated by a mix of 63% H, 33% CV, and 4% CI chondrite, which would have olivines with Mg#75, FeO/MnO~45 and Δ^{17}O=-0.7‰, and ~0.4wt% C with δ^{13}C=-7.7‰. The UPB would have resembled Vesta, modeled as 70% H + 30% CV [27]. Smelting reactions with C and silicate melt (likely CAI melt) would have generated olivines with higher Mg#. Such smelting processes would lead to observed correlations of oxygen isotopes and Fe/Mn with Mg# [6]. Based on the fraction of olivines not smelted due to high pressure, we estimate the UPB had radius 168 km.

Collision with the UPB: We argue that at t≈6 Myr, a fragment from Mars collided at 5 km/s with the UPB at ~2.7 AU. The impactor and UPB catastrophically disrupted and mixed to form UDBs. UDB silicates would sample either specific depths in the UPB, or the martian surface. Based on the fraction of ureilites with olivines with Mg# <80, we estimate the impactor had radius 113 km. Within each UDB, metal from the impactor and metal from the UPB would have melted and flowed; metal would match the mix identified by [4]. Flowing metal would have mobilized graphite from the impactor, distributing the large martian diamonds.

The Largest UDB: The asteroidal source of ureilites is unknown. Based on the trajectory of meteoroid 2008 TC_3 (i.e., Almahata Sitta), [29] calculated it came from either the ν_6 resonance at 2.05 AU or the 3:1 resonance at 2.50 AU; the ε^{54}Cr anomaly of ureilites [3] suggests an origin beyond 2.5 AU. Although Almahata Sitta spectrally resembles F type asteroids [29], it was a rare polymict ureilite; more common monomict ureilites spectrally resemble S(III) asteroids [30]. Based on the sizes of the UPB and impactor and the collision velocity, we use the formalism of [28] to estimate the largest fragment has radius 135 km. We therefore seek an S(III) asteroid ~135 km in radius at ~2.7 AU, with an extensive collisional family that is 4.5 Gyr old.

The S(III) asteroid 15 Eunomia has radius ~132 km, and orbits at 2.64 AU. It has an extensive collisional family with thousands of members; assuming thermal conductivity k = 0.1 W/m/K, its age is 4.5 Gyr [31]. Eunomia is non-spherical, with one end rich in olivine, the other rich in pyroxene. Olivine is commonly associated with material launched from Mars, e.g., A type asteroids and martian Trojans [32]. The ν_6-ν_5+ν_{16} secular resonance can transport UDBs from 2.64 AU to 2.54 AU. The F type asteroid 438 Zeuxo orbits at 2.55 AU. With k = 0.1 W/m/K, fragments the size of 2008 TC_3 could Yarkovsky drift 0.05 AU within Almahata Sitta's cosmic ray exposure age of 20 Myr [33], from 2.55 AU to 2.50 AU, and be delivered to Earth.

Other samples of Mars in the asteroid belt: The 0.01 Mars masses ejected by the Borealis basin impact exceeds the total mass of the asteroid belt today. Besides the fragment that collided with the UPB, we suggest A type asteroids [32] and two eclogitic clasts in CR chondrites [34,35] as deriving from Mars at *t*~5 Myr.

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