A large planetary body inferred from diamond inclusions in a ureilite meteorite

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Planetary formation models show that terrestrial planets are formed by the accretion of tens of Moon- to Mars-sized planetary embryos through energetic giant impacts. However, relics of these large proto-planets are yet to be found. Ureilites are one of the main families of achondritic meteorites and their parent body is believed to have been catastrophically disrupted by an impact during the first 10 million years of the solar system. Here we studied a section of the Almahata Sitta ureilite using transmission electron microscopy, where large diamonds were formed at high pressure inside the parent body. We discovered chromite, phosphate, and (Fe,Ni)-sulfide inclusions embedded in diamond. The composition and morphology of the inclusions can only be explained if the formation pressure was higher than 20 GPa. Such pressures suggest that the ureilite parent body was a Mercury- to Mars-sized planetary embryo.
Asteroid 2008 TC₃ fell in 2008 in the Nubian desert in Sudan, and the recovered meteorites, called Almahata Sitta, are mostly dominated by ureilites along with various chondrites. Ureilite fragments are coarse grained rocks mainly consisting of olivine and pyroxene, originating from the mantle of the ureilite parent body (UPB) that has been disrupted following an impact in the first 10 Myr of the solar system. High concentrations of carbon distinguishes ureilites from all other achondrite meteorites, with graphite and diamond expressed between silicate grains.

There are three mechanisms suggested for diamond formation in ureilites: (i) shock-driven transformation of graphite to diamond during a high-energy impact, (ii) growth by chemical vapor deposition (CVD) of a carbon-rich gas in the solar nebula, and (iii) growth under static high-pressure inside the UPB. Recent observation of a fragment of the Almahata Sitta ureilite (MS-170) revealed clusters of diamond single crystals that have almost identical crystallographic orientation, and separated by graphite bands. It was thus suggested that individual diamond single crystals as large as 100 μm existed in the sample, which have been later segmented through graphitization. The formation of such large single-crystal diamond grains along with ¹⁵N sector zoning observed in diamond segments is impossible during a dynamic event due to its short duration (up to a few seconds), and even more so by CVD mechanisms, leaving static high-pressure growth as the only possibility for the origin of the single-crystal diamonds.

Owing to their stability, mechanical strength and melting temperature, diamonds very often encapsulate and trap minerals and melts present in their formation environment, in the form of inclusions. In terrestrial diamonds, this has allowed to estimate the depth of diamond formation, and to identify the composition and petrology of phases sampled at that depth. Therefore, diamonds formed inside the UPB can potentially hold invaluable information about its size and composition.

In this study, we investigated the Almahata Sitta MS-170 section using transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS). We studied the diamond–graphite relation and discovered different types of inclusions that were chemically characterized by energy dispersive X-ray (EDX) spectroscopy, crystallographically by electron diffraction, and morphologically by TEM imaging. The composition and mineralogy of these inclusions points to pressures in excess of 20 GPa inside the UPB, which in turn implies a planetary body ranging in size between Mercury and Mars.

**Results**

**Diamond–graphite relationship.** The diamond matrix shows plastic deformation as evidenced by the high density of dislocations, stacking faults and a large number of [111] deformation twins. Despite no sign of graphitization for uninterrupted twins, the deformation twins that intersect an inclusion transform to graphite. This is further confirmed by the constant and stoichiometric bulk chemical composition of these inclusions. In order to avoid any sampling bias in such multicomponent inclusions, the composition was measured only on those grains that were completely embedded inside the diamond host determined by electron tomography, leaving aside those that had been partially cut during focused ion beam (FIB) preparation. We found an average molar (Fe + Ni)/(S + P) ratio of 2.98±0.36 from 29 sulfide inclusions (Supplementary Table 2), which corresponds to an (Fe,Ni),S, Fe,Ni,P-chalcocite and (Fe,Ni),S have the same space group (tetragonal I4) and their lattice parameters are very close, allowing them to form a solid.

**Iron–sulfur type inclusions in diamond.** The overwhelming majority of inclusions are iron-rich sulfides, found either as isolated grains with sizes up to a few 100 nanometers, or as trails of small particles ranging from 50 nm down to a few nanometers (Fig. 3 and Supplementary Fig. 4). All the inclusions are faceted indicating that they were trapped as solid crystalline phases rather than melts. However, they show evidence of transformation to low-pressure phases during decompression, similarly to those found in deep terrestrial diamond inclusions. Both chemical and crystallographic analysis (Supplementary Table 1 and Supplementary Fig. 5) show that the sulfide inclusions have dissociated to three phases (Fig. 2c): FeS-troilite, (Fe,Ni)-kamacite, and minor amounts of (Fe,Ni),P-chalcocite. The latter either dissociates to a separately detectable phosphide phase in larger inclusions (Fig. 3 and Supplementary Fig. 4), or concentrates at grain boundaries in smaller inclusions (Supplementary Fig. 4). It is noteworthy that troilite, kamacite, and schreibersite are never found as isolated mono-mineralic inclusions in the diamonds, but always together inside a very sharply defined polyhedral arrangement; two arguments promoting the idea that these inclusions crystallized as a single-Fe–Ni–S–P phase during diamond formation, that later decomposed into different phases.

**Graphitization of diamond along twinning directions.** The overwhelming majority of inclusions are iron-rich sulfides, found either as isolated grains with sizes up to a few 100 nanometers, or as trails of small particles ranging from 50 nm down to a few nanometers (Fig. 3 and Supplementary Fig. 4). All the inclusions are faceted indicating that they were trapped as solid crystalline phases rather than melts. However, they show evidence of transformation to low-pressure phases during decompression, similarly to those found in deep terrestrial diamond inclusions. Both chemical and crystallographic analysis (Supplementary Table 1 and Supplementary Fig. 5) show that the sulfide inclusions have dissociated to three phases (Fig. 2c): FeS-troilite, (Fe,Ni)-kamacite, and minor amounts of (Fe,Ni),P-chalcocite. The latter either dissociates to a separately detectable phosphide phase in larger inclusions (Fig. 3 and Supplementary Fig. 4), or concentrates at grain boundaries in smaller inclusions (Supplementary Fig. 4). It is noteworthy that troilite, kamacite, and schreibersite are never found as isolated mono-mineralic inclusions in the diamonds, but always together inside a very sharply defined polyhedral arrangement; two arguments promoting the idea that these inclusions crystallized as a single-Fe–Ni–S–P phase during diamond formation, that later decomposed into different phases. This is further confirmed by the constant and stoichiometric bulk chemical composition of these inclusions. In order to avoid any sampling bias in such multicomponent inclusions, the composition was measured only on those grains that were completely embedded inside the diamond host determined by electron tomography, leaving aside those that had been partially cut during focused ion beam (FIB) preparation. We found an average molar (Fe + Ni)/(S + P) ratio of 2.98±0.36 from 29 sulfide inclusions (Supplementary Table 2), which corresponds to an (Fe,Ni),S, Fe,Ni,P-chalcocite and (Fe,Ni),S have the same space group (tetragonal I4) and their lattice parameters are very close, allowing them to form a solid.
solution at high pressures as \((\text{Fe,Ni})_3(\text{S,P})\)\(^{16,17}\) across the entire compositional S–P join.

The pressure stability of the \(\text{Fe}_3(\text{S,P})\) phase depends\(^{18}\) on its composition (Supplementary Note 2 and Supplementary Fig. 6), and ranges from 21 GPa for the \(\text{Fe}_3\text{S}\) to room pressure for \(\text{Fe}_3\text{P}\), allowing to use the \(P/(S+P)\) ratio as an internal thermobarometer. Phosphorus has no effect on the stability for \(P/(S+P)\) between 0 and 0.2, \(\text{Fe}_3(\text{S,P})\) is only stable above 21 GPa\(^{18}\) (Supplementary Fig. 6) just like \(\text{Fe}_3\text{S}\). The average \(P/(S+P)\) of the inclusions observed here is 0.12±0.02 (Supplementary Table 2), and therefore these can only have formed above 21 GPa. Similarly, the inclusions contain nickel, with \(\text{Ni}/(\text{Fe}+\text{Ni}) = 0.068 \pm 0.011\), which could also have an effect on the stability pressure of \((\text{Fe,Ni})_3(\text{S,P})\), with \(\text{Ni}_3\text{S}\) (isostructural with \(\text{Fe}_3\text{S}\))\(^{19}\) stable only above 5.1 GPa. We lack the experimental work to evaluate the pressure effect of Ni substitution for Fe, but assuming a linear dependence of pressure stability on Ni content, the \((\text{Fe,Ni})_3(\text{S,P})\) inclusions would only form above ~20 GPa (Supplementary Note 2 and Supplementary Fig. 7). It is noteworthy that pressure-composition phase diagrams are often concave downward, and there could be, just as with S–P substitution, no effect on pressure at those low Ni concentrations, so that 20 GPa is actually a lower bound for the inclusions’ formation pressure (Supplementary Fig. 7).

**Chromite and phosphate inclusions in diamond.** A second type of inclusions, \(\text{Cr}_2\text{FeO}_4\) chromite, are rare (with only a few identified in the samples) but rather large with grains a few hundred nanometers across (Supplementary Fig. 8). The mineralogy of chromite grains is well preserved and chemical analysis confirms a stoichiometric \(\text{Cr}_2\text{FeO}_4\) chromite (Supplementary Note 3), with no Mg

![Fig. 2](image_url) Inclusion trails imaged inside diamond fragments. **a** HAADF-STEM image from diamond segments with similar crystallographic orientation. Dashed yellow lines show the diamond–graphite boundaries. **b** High-magnification image corresponding to the green square in **a**. Diamond and inclusion trails are cut by a graphite band. The dashed orange line shows the direction of the inclusion trails.

![Fig. 3](image_url) Electron micrograph and compositional maps of diamond inclusions in ureilite. HAADF-STEM images (**a**, **b**, **c**, and **d**) and associated Fe and S elemental maps (**e**, **f**, **g**, and **h**) of inclusions in diamond. All chemical (EDX) maps show Fe (light blue) and S (red) distribution. Kamacite and troilite phases appear as light blue and reddish-pink respectively.
Fig. 4 Electron micrograph and chemical map of an inclusion in a graphitized region. a Bright-field (BF) STEM image and b chemical (EDX) map from graphite growth in diamond matrix around an inclusion. Blue dashed lines indicate the diamond–graphite boundary. The yellow arrows point out the Fe-S-rich regions in graphite. Notice the clear rounded form of the inclusion in graphitized part indicating partial melting.

or Al substitution for Fe and Cr, respectively. While chromite is often observed in meteorites, Mg- and Al-free end-members are only found in iron meteorites. It has been proposed that such end-members must form in a metallic melt with low Cr and O concentration close to the Fe–FeS join. Therefore, these chromites must have formed in an iron-rich environment.

Finally, rare Ca–Fe–Na phosphate inclusions were found, roughly ~20 nanometer or smaller (Supplementary Fig. 8), which were only characterized chemically due to their small size (not structurally due to overlap with the surrounding diamond). These inclusions are chemically similar to the ones observed in iron meteorites where they are the most common companions of pure Cr$_2$FeO$_4$ chromites (Supplementary Note 3).

Iron–sulfur type inclusions in graphite. Whereas the polyhedral shapes and consistent bulk composition of inclusions in diamond shows that these phases were a single-homogeneous solid phase at the time of diamond formation, the morphology of inclusions in neighboring graphitized bands shows evidence of melting (Fig. 2a and 4, Supplementary Fig. 9). Indeed, Fe- and S-bearing phases of varying composition and arbitrary shapes are dispersed in the graphitized areas and between graphite layers (Fig. 2a and 4, Supplementary Fig. 9), which provides an evidence for melting of inclusions at the time of graphitization, and yet another indication that graphitization is subsequent to diamond formation. This also provides an explanation for the transformation of original (Fe,Ni)$_3$(S,P) solid solution to kamacite, troilite and schreibersite phases while keeping the polyhedral shape and bulk composition of the initial parental phase. Graphitization is likely caused by a shock event, which is followed by separation from the parent body and, therefore, a pressure drop. That same shock event should melt the inclusions, which then recrystallize after the pressure drop as kamacite, troilite and schreibersite, which are the equilibrium phases at low pressures. The volume change during melting would also add to the strain concentration around them, which in turn facilitates the graphitization process.

Discussion

The segment sizes of diamonds are not measured in this study; however, the segments we used for sample preparation were all over 10 μm in diameter. Our results also confirm the previous suggestion that the large diamond crystallites are later segmented through graphitization during a shock event. Thus, considering previous studies using electron backscatter diffraction, we can conclude that there were diamond grains as large as 100 μm in this particular meteorite. The surprisingly large size of diamond grains and specifically $^{15}$N sector zoning is incompatible with formation by shock metamorphism. Indeed, laboratory shock experiments are generally done in nanoseconds and natural shocks by impact in the solar system have durations ranging from microseconds up to at most a few seconds. The typical grain size for shock produced diamond is in the order of few nanometers up to few tens of nanometers. Diamond composite aggregates can reach several hundreds of microns in exceptional cases like Ries and Popigai craters where graphitic precursors are known. However, the crystallite size in these aggregates never exceeds 150 nm. In contrast, the diamond grain size we observe in Almahata Sitta MS-170 samples are 2–4 orders of magnitudes larger than the shock produced diamonds. Such large diamonds are even less likely to grow by CVD in the solar nebula. Moreover, the existence of inclusions in these diamonds and the pressure required to form them (above 20 GPa) clearly rules out the CVD growth mechanism. Therefore, we can distinguish two distinct types of diamond in ureilites: Multigrain diamond resulting from shock events producing clumps of nm-sized individual diamonds, and large diamonds up to 100 μm in diameter growing at high-static pressure inside the proto-planet subsequently broken down to equally oriented segments of several tens of micrometer in diameter.

Ureilites are unique samples from the mantle of a differentiated parent body. It has been shown that temperature inside the UPB was higher than the Fe–S eutectic temperature (~1250 K at ambient pressure, ~1350 K at 21 GPa) (~1400 K at ambient pressure). Therefore, an Fe-S melt must have percolated and segregated to form a sulfurbearing metallic core, but the temperature was never high enough for complete melting of silicates and metallic iron, and the core formation process continued until the UPB’s mantle reached 20–30 vol% of melt fraction.

The composition of chromite inclusions in diamonds shows that they have formed from iron-rich composition without any interaction with silicates. Otherwise, chromite would have accommodated Mg and Al in its composition similarly to the previously reported chromites in ureilite meteorites. This corroborates the formation of the sulfide, chromite, and phosphate inclusions in a metallic liquid.

Moreover, the Fe–C binary system also has a eutectic point (~1400 K at ambient pressure). Fe–C and Fe–S liquids are immiscible at ambient pressure, but the miscibility gap closes by increasing the pressure above 4–6 GPa (depending on the
monds have formed from an Fe–P–S system at pressures. It has been recently shown that large terrestrial diamonds form at the core-mantle boundary, the UPB would be Mars-sized. The lower-bound for its size is for them to form at the solidus of (Fe,Ni)3(S,P) inclusions in diamond which is unlikely to take place by diffusion inside a graphic precursor.

There is considerable debate on the size of the UPB. A body about 1000 km in diameter was recently suggested to account for the pressure required to form diamond (above 2 GPa) in the depths of its mantle. Here we show that these diamonds contain inclusions that can only form above 20 GPa, which can only be attained in a large planetary body. If the diamonds formed at the core-mantle boundary, the UPB would be Mars-sized. The lower-bound for its size is for them to form at the center of the UPB, and a 20 GPa center is consistent with a Mercury-sized body.

Although this is the first compelling evidence for such a large body that has since disappeared, their existence in the early solar system has been predicted by planetary formation models. Moon- Mars-sized planetary embryos have formed either by runaway and oligarchic growth of planetesimals or by pebble accretion in the first million years of the solar system. Mars-sized bodies (such as the giant impactor that formed the Moon) were common and either accreted to form larger planets, or collided with the Sun or were ejected from the solar system. This study provides convincing evidence that the ureilite parent body was one such large “lost” planet before it was destroyed by collisions.

Methods
Focused ion beam sample preparation. Samples for TEM investigations were prepared using the conventional in situ lift-out technique in a Zeiss Nvision 40 dual beam instrument. The polished surface of the MS-170 section from Almahata Sitta was milled with Ga ions at 30 kV starting with 27 nA current and going down to 700 pA, until we obtained a ~1 μm thick slice. This slice was then transferred onto a copper grid with a carbon deposition. To make the slice electron transparent (~100 nm in thickness), it was thinned down with low-beam currents (ranging from 700 pA down to 80 pA). At the end the slice was polished with Ga+ ions at 5 kV and 2 kV using 30 pA and 25 pA beam currents, respectively. Five thin sections were prepared for transmission electron microscopy (TEM) studies.

Energy electron loss spectroscopy. EELS analysis was performed on a FEI Tecnai Themis TEM operated at 300 kV. The carbon K-edge was recorded by electron spectroscopic imaging (ESI) in scanning TEM (STEM) mode using 30 pA and 25 pA beam currents, respectively. Five thin sections were prepared for transmission electron microscopy (TEM) studies.

Data availability. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
F.N. and P.G. planned the research. F.N. performed STEM imaging and EDX analysis. F.N. and M.C. prepared the sample with FIB. We are grateful to Dr. Richard Gaal for the scientific discussions about this research. This work was supported by the Swiss National Science Foundation through FND grant 200021_140474.

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