

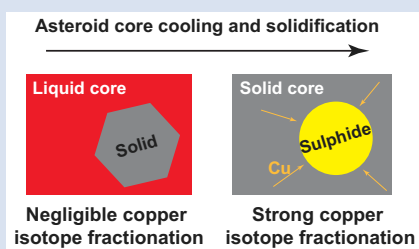
Copper isotope fractionation during asteroid core solidification

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Abstract



Moderately volatile elements (MVE) and their isotopic compositions are powerful tools to understand the origin of volatiles on terrestrial planets, including Earth. The ⁶⁵Cu/⁶³Cu ratio of Cu, one of the MVEs, has been found to be relatively high in the bulk silicate Earth (BSE), which potentially was caused by either evaporative loss or partitioning into Earth's inaccessible core. Iron meteorites are the accessible cores of differentiated planetesimals whose creation involved processes similar to Earth's in the early Solar System. Measurements of their Cu isotope composition currently yield a large range of values that reveal little about core-forming processes. Here, we determine the equilibrium Cu isotope fractionation between solid and liquid metal and quantify the partitioning of Cu between troilite and metal, showing that the latter is a more significant factor in fractionating the Cu isotopes when planetesimal cores cool. Our experiments also call for verification of existing data for equilibrium Cu isotope fractionation between silicate–sulphide and silicate–metal to support current models using sulphide segregation to explain the heavy Cu isotope enrichment in bulk silicate Earth and Moon.

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Introduction

The terrestrial planets in our Solar System are vastly different from each other in internal structure and composition due to their distinct accretion and formation histories. Earth, when compared with the bulk Solar System composition as represented by the CI chondrites, exhibits a prominent depletion in moderately volatile elements, such as alkali elements, Cu, and Zn (McDonough and Sun, 1995). With a half condensation temperature of ~1030 K (Lodders, 2003; Wood *et al.*, 2019), Cu is one of the moderately volatile elements that could be susceptible to evaporative loss during the early stages of Earth accretion. On the other hand, Cu is also a moderately siderophile element (*e.g.*, Mahan *et al.*, 2018), indicating that its depletion in the Bulk Silicate Earth (BSE) could be due to core formation.

One potential way to understand the relative importance of the above two effects on Cu abundance in the BSE is to examine Cu isotope fractionation. Measurements of mid-ocean ridge basalts, ocean island basalts, komatiites, and peridotites defined a robust and precise BSE $\delta^{65}\text{Cu}$ (defined as the per mil difference in ⁶⁵Cu/⁶³Cu with respect to NIST SRM 976) value of 0.07 ± 0.10 ‰ (2 s.d.), significantly heavier than the estimated

initial bulk Earth composition of -0.24 ± 0.09 ‰ (2 s.d.) based on chondrites (Savage *et al.*, 2015).

Despite the potential application of Cu isotopes to tracing planetary processes experienced by Earth, experimental studies on equilibrium Cu isotope fractionation are limited to only a few studies on silicate–metal and silicate–sulphide fractionation. These studies found limited fractionation between silicate melt and metallic liquid, but relatively large fractionations between silicate melt and sulphide liquid (up to 0.33 ‰, Xia *et al.*, 2019; ~1 ‰, Savage *et al.*, 2015), leading the authors to conclude that late segregation of a sulphide-rich liquid to the core has contributed to the heavy Cu isotope composition of the BSE (Savage *et al.*, 2015), and the bulk silicate Moon (BSM) (Xia *et al.*, 2019).

Core crystallisation is another process commonly experienced by differentiated asteroids and terrestrial bodies. Recent experiments by Ni *et al.* (2020) demonstrated that core crystallisation could introduce Fe isotope fractionation due to solid metal–liquid metal differentiation. This fractionation trend was observed in magmatic iron meteorites originated from the metallic cores of differentiated extinct asteroids (Ni *et al.*, 2020). Compiled copper isotope data of iron meteorites show large variations in their $\delta^{65}\text{Cu}$ from -6 ‰ to $+1$ ‰ (Figure 1), raising the

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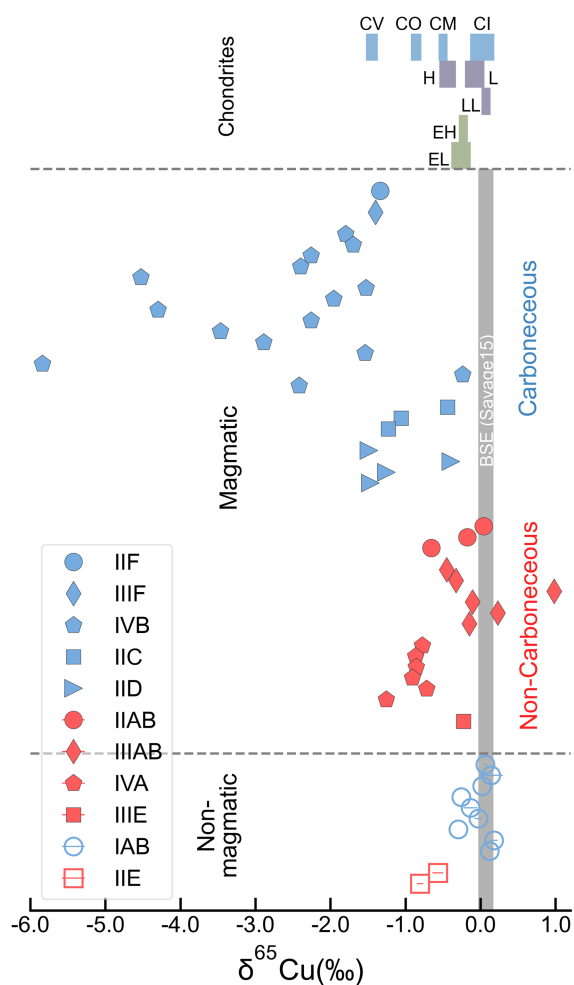


Figure 1 Copper isotope data for chondrites and iron meteorites. Data for different types of chondrites from [Savage et al. \(2015\)](#) and iron meteorites from [Luck et al. \(2005\)](#), [Bishop et al. \(2012\)](#), and [Chen et al. \(2016\)](#) are plotted. The bulk silicate Earth (BSE) composition is from [Savage et al. \(2015\)](#).

need to quantify the effect of core crystallisation on causing the variation. In this study, we conducted solid–liquid metal equilibrium experiments to constrain the degree of Cu isotope fractionation during core crystallisation in iron meteorite parent bodies. The experimental data are combined with a kinetic model to explain Cu isotope variations in iron meteorites. Our results are also used to indirectly assess existing Cu isotope exchange experiments that suggested a late-stage sulphide segregation in causing the bulk silicate Earth and Moon to be heavy in Cu isotopic composition.

Methods

Solid–liquid metal equilibrium experiments were conducted at the Johns Hopkins University Applied Physics Laboratory to simulate the core crystallisation process following the approach in [Chabot et al. \(2017\)](#) utilising vacuum-sealed silica tubes and vertical furnaces. Major element composition of the phases was analysed with a JEOL 8530F electron microprobe at the Carnegie Institution for Science. The quenched solid and liquid metal phases were sampled for Cu isotope measurements using a micromill equipped with tungsten carbide drill bits. Column purification of Cu was performed using in-house custom-made quartz glass columns following the procedure previously

reported by [Ni et al. \(2021\)](#). Isotopic compositions of the purified Cu solution of the solid and liquid metal phases were measured using a Nu Plasma II Multi-Collector ICP-MS at the Carnegie Institution for Science in wet plasma mode. Analyses were conducted using ERM-AE633 as the bracketing standard, and all isotope results are reported relative to NIST SRM 976 after correcting a -0.01 ‰ difference between ERM-AE633 and NIST SRM 976 ([Moeller et al., 2012](#)):

$$\delta^{65}\text{Cu} = \left[\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{Sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{SRM976}}} - 1 \right] \times 1000 \text{ ‰}.$$

Modelling of the partitioning, diffusion, and isotopic fractionation of Cu between metal and troilite grains in iron meteorites was performed assuming one-dimensional diffusion in spherical coordinates and an asymptotic cooling history. Details about the experimental and analytical methods and the kinetic model are available in the [Supplementary Information](#).

Results and Discussion

A total of ten solid–liquid metal equilibrium experiments were conducted at 1260–1425 °C to study Cu isotope fractionation during iron meteorite core crystallisation. Sulphur content of the liquid metal was intrinsically controlled by the temperature following the Fe–Ni–S phase diagram ([Hsieh and Chang, 1987](#)), with higher sulphur in the liquid at lower temperatures. Microscopic images of one experiment (S20-Cu1) are shown in [Figure S-1](#) as an example. The quenched sample charges show distinct regions of solid metal (Fe–Ni alloy) and liquid metal (Fe–Ni–S), the latter with characteristic dendritic textures formed during quench. The quenched liquid metal contains 0.8 to 3.3 wt. % Cu while the solid metal contains 0.3 to 0.6 wt. % Cu ([Table S-1](#)). Calculated Cu partition coefficients between the solid and liquid metal vary from 0.11 to 0.62 as a function of sulphur content, generally consistent with literature data ([Figure S-2](#); [Chabot and Jones, 2003](#); [Chabot et al., 2009](#)).

Although the Cu partitioning data indicate chemical equilibrium between the solid and liquid metal, it was not the case for Cu isotope exchange. Copper isotopic difference between the solid and liquid metal phases in these ten experiments vary significantly from 0.35 ± 0.04 ‰ to 1.75 ± 0.08 ‰. Further investigation of the experimental data showed that isotopic equilibrium was only reached for high-sulphur experiments at temperatures lower than 1350 °C (S15-Cu1, S20-Cu1, S25-Cu1, S25-Cu2, S25-Cu3). For low-sulphur experiments at higher temperatures (S5-Cu1, S5-Cu3, S10-Cu1, S15-Cu2, S15-Cu6), Cu isotopic composition was significantly affected by evaporation of Cu to the interior of the vacuum-sealed quartz glass tube. The initial bulk $\delta^{65}\text{Cu}$ was 0.45 ± 0.02 ‰ as measured on the Cu powder used for doping the experiments and the starting mixture for S15-Cu1 ([Table S-2](#)). The low-sulphur, high-temperature experiments reached isotopic compositions as heavy as 1.39 ± 0.19 ‰ for the solid metal and 1.75 ± 0.08 ‰ for the liquid metal ([Figure S-3](#)). Evaporative loss of the Cu occurs primarily in the liquid metal with higher mobility for the elements, driving it towards heavier $\delta^{65}\text{Cu}$ compositions. Copper diffusion in the solid metal limits its isotopic exchange with the liquid metal, causing its Cu isotope composition to exhibit a lighter value. This is evidenced by duplicated sampling and analyses of the same experiments, which yielded identical $\delta^{65}\text{Cu}$ composition for the liquid metal but different compositions for the solid metal in both cases (S5-Cu1, S10-Cu1; [Table S-2](#)). The evaporative loss of Cu is further proved by measuring the acid leachate of the tube inner wall of the most affected experiment (S15-Cu2). The Cu leachate yielded an extremely light Cu isotopic composition of -1.51 ± 0.06 ‰,

consistent with light Cu being preferentially lost during evaporation and later condensed on the low-temperature end of the quartz glass tube.

Due to the complications caused by Cu evaporation, equilibrium Cu isotope fractionation data are limited to the low-temperature experiments with 20 wt. % or more sulphur in the liquid metal (Figure S-4). Isotopic equilibrium between the solid and liquid metal was assessed by: 1) a set of time-series experiments conducted at the lowest temperature (1260 °C) for durations of 1, 2.75, and 5 days; 2) departure of the bulk Cu isotopic composition from the estimated initial composition ($\delta^{65}\text{Cu} = 0.45\text{‰}$). The time-series experiments yielded fractionation factors within error from each other, suggesting that isotopic equilibrium was reached within one day at 1260 °C (Figure S-3). For the low-temperature experiments with 20 wt. % or more sulphur, the bulk $\delta^{65}\text{Cu}$ varies between $0.36 \pm 0.04 \text{‰}$ and $0.69 \pm 0.03 \text{‰}$, within $\sim 0.2 \text{‰}$ from the estimated initial of $0.45 \pm 0.02 \text{‰}$ (Table S-2). We suspect the offset to the light composition was the consequence of isotopic heterogeneity within the Cu powder used for doping the experiments because Cu evaporation would only drive the bulk composition toward heavy values. The shift toward the heavy composition can be attributed to either isotopic heterogeneity or a small degree of Cu evaporation that was compensated by sufficient diffusive re-equilibration.

With the above considerations, five of the ten experiments with sulphur contents over 20 wt. % can be concluded to have reached isotopic equilibrium. All five experiments gave Cu isotope fractionation factors of $\sim 0 \text{‰}$, indicating limited fractionation between solid and liquid metal (Figure 2; Table S-2). With a weighted average of $0.01 \pm 0.04 \text{‰}$ for $\Delta^{65}\text{Cu}_{\text{solid-liquid metal}}$ ($\Delta^{65}\text{Cu}_{\text{solid-liquid metal}} = \delta^{65}\text{Cu}_{\text{solid-metal}} - \delta^{65}\text{Cu}_{\text{liquid-metal}}$), crystallisation of the parent core of magmatic iron meteorites does not cause significant isotope fractionation in Cu. This is different from the case of Fe (Ni *et al.*, 2020), where fractionation of over 0.1 ‰ occurs throughout the core crystallisation process. Such a low $\Delta^{65}\text{Cu}_{\text{solid-liquid metal}}$ conclusively excludes core crystallisation as a potential source of large Cu isotope variations in magmatic irons (Figure 1).

Another process common to the parent bodies of all magmatic iron meteorites that could affect their Cu isotope composition is the diffusive exchange between Fe metal and troilite. This process occurs at much lower temperatures than core crystallisation and would be separate from it. As a chalcophile element, Cu tends to partition into the troilite phase, especially

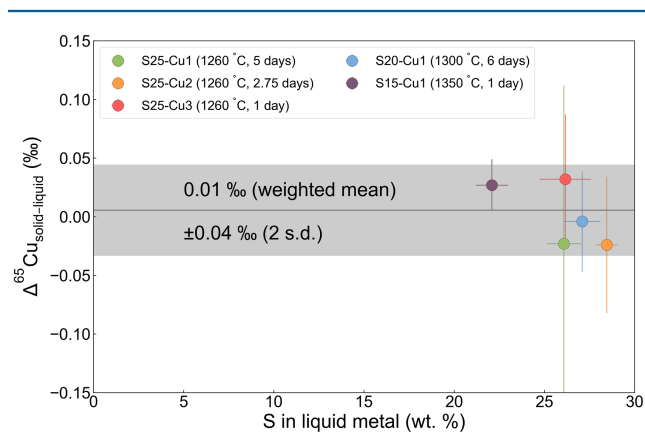


Figure 2 Equilibrium Cu isotope fractionation between solid and liquid metal during core crystallisation. A plot of all experimental data is available in Figure S-5. Error bars represent 2 standard deviations of the mean.

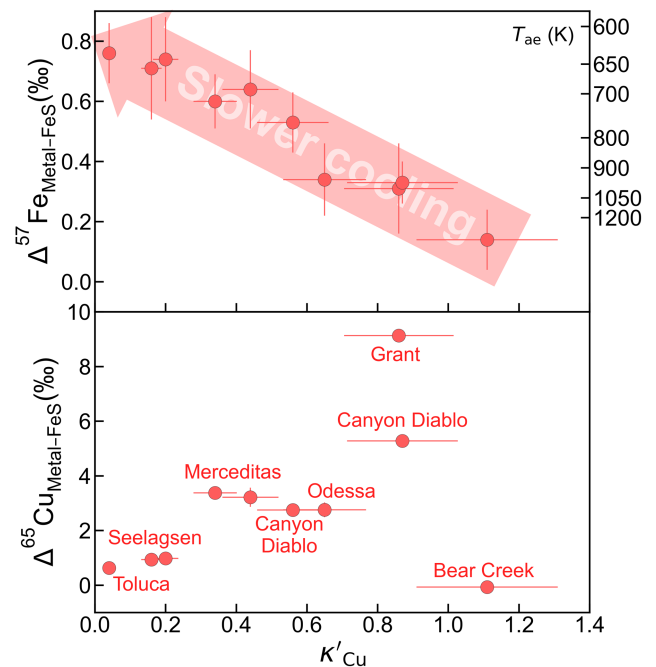


Figure 3 Iron and Cu isotope fractionation between metal and troilite in iron meteorites. Figure reproduced based on Williams and Archer (2011). The apparent partition coefficient of Cu is defined as $K'_{\text{Cu}} = C_{\text{FeS}}(\text{Cu})/C_{\text{Meteorite}}(\text{Cu})$. Calculated apparent equilibrium temperature (T_{ae}) for Fe isotope fractionation is plotted on the right side of y-axis (see Supplementary Information).

as the temperature decreases. Direct measurements of troilite grains in iron meteorites found them to be as light as -9‰ in $\delta^{65}\text{Cu}$ (Williams and Archer, 2011). Such large fractionation can potentially explain the large Cu isotope variations seen in iron meteorites. According to the authors, this significant fractionation is likely the result of a kinetic process. As shown in Figure 3, Williams and Archer (2011) measured both Fe and Cu isotopes of troilite in iron meteorites. The fractionation of iron isotopes between the Fe-Ni alloy matrix and troilite was found to correlate with apparent Cu partition coefficient (calculated as Cu concentration of troilite divided by bulk meteorite Cu concentration) and kamacite bandwidth, which is related to cooling rate.

Iron meteorites that cooled down faster had less time to develop the Widmanstätten pattern and therefore tend to show narrower kamacite bands in general, although Ni and P concentrations also play a role. Chemically, a faster cooling rate would also limit the length scale of diffusion, “freezing” equilibrium Fe isotope fractionation and Cu partitioning that happened at higher temperatures. Iron meteorites with slower cooling rates, on the other hand, would have time to grow wider kamacite bands and allow for chemical re-equilibration between the metal and troilite until much lower temperatures. Our calculated apparent equilibrium temperatures based on Fe isotope fractionation factors from Dauphas *et al.* (2012) (see Supplementary Information) vary between 630 and 1200 K, which are generally consistent with the upper limit of troilite stability (Hsieh and Chang, 1987) and the lower end of Widmanstätten pattern nucleation (Yang and Goldstein, 2005).

Copper isotope compositions measured in the same samples (Williams and Archer, 2011) show much larger fractionations than possible equilibrium effects at magmatic temperatures (Figure 3). Unlike Fe, which is a primary component of both the metal and troilite phases in iron meteorites, Cu is a trace element that experiences significant redistribution between

these phases as it becomes more chalcophile upon cooling (Figure 3). Such redistribution requires mass transfer by diffusion in solid metal, potentially leading to large kinetic isotope fractionation. It has been proposed by Williams and Archer (2011) that the range of Cu isotope composition for troilites was the product of partial isotope equilibrium from an initial kinetically-caused, light signature.

We developed a quantitative model to simulate the diffusive exchange of Cu between the metal and troilite phases, aimed at assessing the extent of light Cu enrichment in the troilite from the cooling and redistribution of Cu within the iron meteorite parent body. The isotopic composition of the troilite is modelled as a function of cooling time scale (τ_c) and shown in Figure 4. The simulations were conducted assuming a troilite radius (a) of 2 mm, a metal matrix radius (b) of 40 mm, and a B value of $-75,000$ to characterise the temperature dependence of the partition coefficient (κ). At 1100–1200 K when troilites first form, Cu is approximately evenly distributed between metal and troilite, as evidenced by the highest apparent partition coefficient (κ) of ~ 1 in the meteorite Bear Creek (Figure 3) and solid metal–liquid metal–troilite equilibrium experiments (Shread *et al.*, 2024).

If an iron meteorite cooled down at extremely high cooling rates (e.g., $\tau_c = 10$ years), the troilite exhibits only minor Cu isotopic fractionation due to the limited Cu exchange between the metal and troilite, “freezing” its elemental partition and Cu isotope fractionation at high-temperature equilibrium. This could be the case for the Bear Creek meteorite, which recorded a high Cu partition coefficient and low degrees of Fe and Cu isotope fractionation (Figure 3). With slightly longer cooling time scales, ranging from 0.1 to 100 ka, Cu will have time to diffuse from metal to sulphide. The diffusion front entering the troilite phase would be enriched with light Cu isotopes, quickly overwriting the initial Cu isotope signal that was dominated by equilibrium fractionation. This would decrease the $\delta^{65}\text{Cu}$ composition of the troilite to be as light as -10 ‰. At even longer cooling time scales, from 1 to 1000 Ma, the heavier Cu isotope in the metal matrix has more time to diffuse into the troilite, thus bringing its isotopic composition back to ~ 0 ‰, representing equilibrium fractionation (Figure S-5).

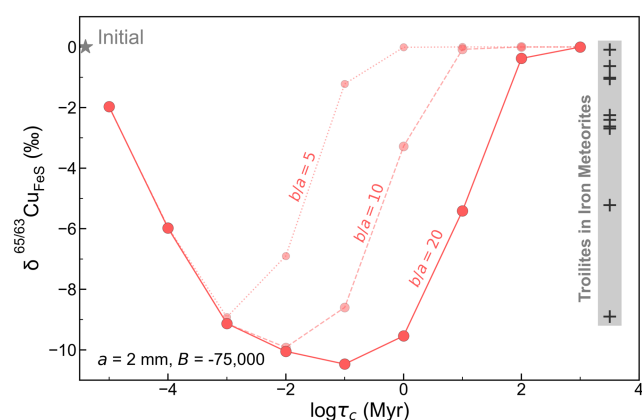


Figure 4 Modelled Cu isotope fractionation in troilite as a function of cooling time scale. The model was conducted assuming a troilite radius (a) of 2 mm, and a temperature dependence of the partition coefficient (B) of $-75,000$. Measured Cu isotope composition of troilites in iron meteorites is plotted on the right-hand side of the figure for comparison. Details of the model are described in the main text and in the [Supplementary Information](#).

Simulations assuming smaller b/a ratios of 10 and 5 produced similar outcomes, albeit with the peak fractionation occurring at different cooling time scales. Our model offers a semi-quantitative explanation for the Cu isotope compositions observed in troilites from iron meteorites, demonstrating a non-monotonic dependence on cooling rate, as shown in Figure 4. The modelling results align with the observed trend turnover and the overall magnitude of fractionation depicted in Figure 3b.

Previous studies report a small positive fractionation between metal–silicate and relatively large negative fractionation between sulphide–silicate (Savage *et al.*, 2015; Xia *et al.*, 2019). Combining those results and assuming equilibrium conditions at ~ 1350 °C in all experiments would predict a 0.4 ‰ fractionation in $\delta^{65}\text{Cu}$ between metal and Ni-free sulphide, and 0.1 ‰ between metal and Ni-rich (~ 27 wt. %) sulphide. This contrasts with our measured fractionation of 0.01 ± 0.04 ‰ at 1260 °C. This discrepancy can be attributed to the lack of isotope equilibrium in previous experiments (see [Supplementary discussion](#)), a composition dependence that is not yet fully understood, or systematic differences between different experiment setups. A careful re-evaluation of Cu isotope fractionation will be necessary to support the current models of sulphide segregation in explaining the heavy Cu isotope composition of the bulk silicate Earth and the Moon.

Conclusion

We demonstrate through solid–liquid metal equilibrium experiments that core crystallisation of iron meteorite parent bodies does not result in measurable Cu isotope fractionation. Instead, the observed variations in Cu isotopes among iron meteorites are likely attributable to diffusive Cu enrichment into troilite from the metal matrix as the parent bodies cooled. Our quantitative model illustrates that this process can account for the observed magnitude of Cu isotope fractionation in troilite, as well as the general relationship between the fractionation and the cooling rate of iron meteorites. Interpreting the Cu isotope composition of iron meteorites’ parent cores requires careful evaluation, correction, or possibly complete avoidance of the influence of troilites. Our experiments also illustrate the potential for isotopic disequilibrium, even when elemental partitioning appears to have reached equilibrium. This highlights the necessity of verifying existing experimental data on Cu isotope fractionation between silicate–metal and silicate–sulphide, which is crucial for substantiating the prevailing theory that late-stage sulphide segregation explains the Cu isotope composition of the bulk silicate Earth and the Moon.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2432>.



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