

An Experimental Investigation of the Pressure effect on Stable Isotope Fractionation at High Temperature; Implications for Mantle Processes and Core Formation in Celestial Bodies. S. Mikhail^{1,2}, A. Shahar³, S.A. Hunt⁴, A.P. Jones¹ and A.B. Verchovsky². ¹Department of Earth Sciences, University College London, UK (s.mikhail@ucl.ac.uk); ²Planetary and Space Sciences Research Institute, The Open University, UK; ³Geophysical Laboratory, Carnegie Institution of Washington, Washington DC, USA (ashahar@ciw.edu); ⁴Mineral Physics Institute, Department of Geoscience, Stony Brook University, NY, USA

Introduction: The origin and primordial isotopic composition of the terrestrial and Martian light volatile elements (i.e. carbon) is commonly investigated using the stable isotopes of primary magmatic and mantle minerals (for Earth see ref [1] and for Mars see ref [2]). This is in part because the stable isotopes were not thought to considerably fractionate at mantle temperatures [3] and therefore they would be indicative of their source composition.

The relationship between temperature (T) and stable isotope fractionation factors (expressed as $1000 \cdot \ln(\alpha) \approx \delta \text{‰}$) is one of a negative and exponential trend with increasing T and decreasing $1000 \cdot \ln(\alpha)$ with the magnitude of the effect increasing with decreasing mass number of the element in question (first theorised by Urey [5] and demonstrated in Figure 1). However more recent theoretical work [6-7] demonstrated that at $T > 2000$ K there can be significant fractionation (several ‰) for the light stable isotopes of carbon (Figure 1). For example, Schauble [8] calculated the fractionation factors at high T using Density Functional Theory for isotopic fractionation between various light elements and metallic phases and noted the following: The light isotopes preferentially partition into the metallic phase. Light-element coordination in the metal phase may significantly affect fractionation, for instance Fe_3C (8-fold coordination) is predicted to be about 0.6‰ lighter than $\eta\text{-Fe}_2\text{C}$ (6-fold coordination) at 2000 K for carbon (Figure 1). If a significant part of a light-element reservoir partitions into a planetary or planetesimal core the residual silicate (i.e. BSE) will have isotopic compositions that are distinct from the whole body (primordial). Residual isotopic signatures of core formation may be easiest to detect in elements where the composition of the bulk planetary reservoir can be constrained. This is the rationale behind the conclusions of Georg et al. [4] in noticing that the Earth (and moon) were almost consistently distinct from various chondritic meteorite classes and attributed core formation as the mechanics that produced a BSE to be distinct from an initial primordial composition that was akin to the chondrites and the premise was experimentally confirmed at 1 GPa and circa 2100 K [9].

This has implications that complicate any modeling of isotopic fractionation between the mantles and

proto cores of both large and small celestial bodies during metal-silicate partitioning of the light stable isotopes, especially if one assumes Rayleigh type partitioning. Should the partitioning of the heavy element between the metal and silicate occur at different depths it will also be at a different T and this will therefore yield a different fractionation factor.

However with greater depth in celestial bodies there is also a P change. Horita et al. [10] observed a P effect at much lower PT conditions for D/H fractionation (15 to 800 megapascals and circa 380 K). Therefore the following must be considered; is the P effect (magnitude and influence) quantifiable for heavier elements?

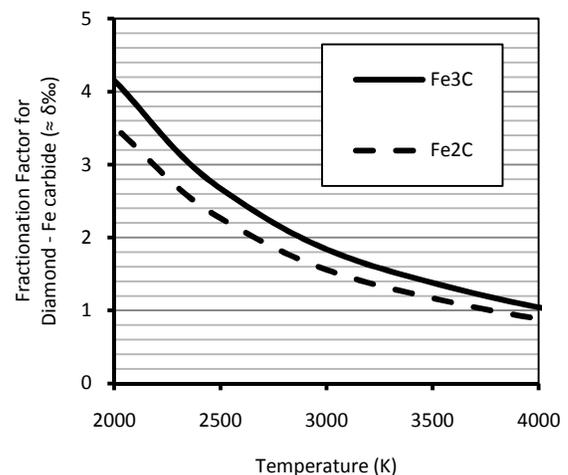


Fig 1: The calculated fractionation factors as a function of reaction temperature for diamond – Fe carbide at 0 GPa [8].

Carbon systems in nature:

To find an adequate system to test we first investigated the literature and then natural terrestrial samples. Deines and Wickman [11] observed a near constant fractionation factor between graphite and cohenite in Fe-meteorites of circa +12 ‰ with the cohenite being depleted in ¹³C. Recent work has shown that a similar fractionation factor exists between Fe-carbide and mantle diamond of circa +7 ‰ [12]. This is not surprising as one expects the fractionation factor to decrease with increasing T and the presence of diamond is suggestive of higher T (but also higher P). This warranted an experimental investigation in the system FeC-C at various P-T conditions akin to the terrestrial

mantle as a preliminary investigation to test the following 2 possibilities: 1- Carbon incorporation during core formation has the potential to fractionate the BSE from the primordial BE $\delta^{13}\text{C}$ value and 2- That pressure may have an effect on the fractionation factor for a given T and therefore complicate the modelling of the isotopic effect of C incorporation into the core and during deep planetary magmatic processes. Here we present work on carbon in the system Fe-C from 1 to 25 GPa and for T within the range of 1400-2000 K.

Analytical techniques: The HPHT experiments were performed in both piston cylinder (1-2 GPa) and multi anvil press (5-25 GPa) apparatus. The reaction was a solid state to avoid the formation of a liquid phase with dissolved C instead of a Fe carbide mineral phase. The furnaces used were graphite (with the exception of the 25 GPa runs where Re was used as both furnace and sample chamber) and the sample powder was graphite + Fe powder (molar 1:1 mix) within a BN or MgO sealed capsules. Phases were identified using powder XRD and texture investigated using uncoated samples in an SEM. Experimental run products were analysed using stepped combustion static vacuum mass spectrometry on the finesse machine (Open University, UK) where the Fe-carbide ($\text{Fe}_3\text{C}/\text{Fe}_7\text{C}_3$) and diamond/graphite have been found to combust at different temperatures (<650 and >700 °C respectively).

Results: The results to date are shown in figure 2 below.

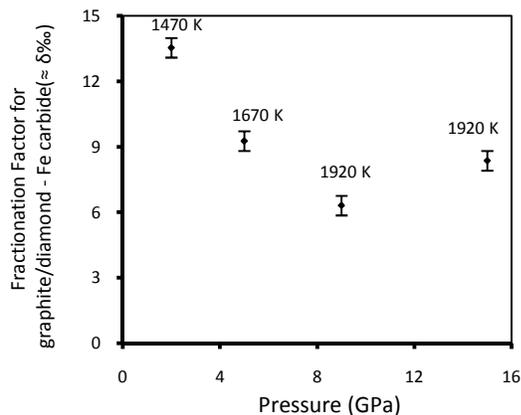


Fig 2: Results to date expressed in graphical form showing synthesis pressure vs. the fractionation factor. The temperature of synthesis is shown in bold text next to the data points and error bars are for 1 σ . Note the increase in the fractionation factor from 9-15 GPa at a given T. This is suggesting that P has an effect at a given T (> 2 ‰ for a 6 GPa increase in P).

Broad implications: This study demonstrates that the fractionation factor for ^{13}C in the system Fe-C un-

der mantle conditions is strongly influenced by temperature. It also suggests that pressure can reduce the temperature effect even at $T = > 1900$ K (Figure 2). The reason, magnitude and full nature for this is not fully understood at present and more experiments are planned to better constrain this effect.

Where in the Earth did the partitioning of C into metallic (core bound) diapirs occur? I.e. The fractionation factor computed in the model is dependent upon the PT conditions of equilibration (i.e. depth). To model the deviation from the primordial value due to core formation the primordial value must be assumed. Is the Earth's primordial $\delta^{13}\text{C}$ value (AKA the Bulk Earth Value) circa -5 or -25 ‰? Noteworthy is that the magmatic $\delta^{13}\text{C}$ values for Mars, Vesta and the Moon are not around -5 ‰, but -25 ‰. Grady et al. [2] used this observation to pose the question; 'why should the Earth's primordial value be any different?' Given the shape of the terrestrial geotherm (and for other planets) a P effect has important implications. As with depth >150 km and to depths of the core mantle boundary the P increase is > than the T increase. Therefore one may postulate at this point that fractionation factors can increase with depth? Should Grady et al [2] be correct in that the Earth has a primordial $\delta^{13}\text{C}$ values akin to Mars (circa -25 ‰) then the size of the planet and not the carbon concentration of the core could be the reason for the shift in the terrestrial $\delta^{13}\text{C}$ value from circa -25 to -5 ‰, whilst preserving the Martian primordial value of circa -25 ‰ post carbon incorporation into the core with both planets having the same ratio of carbon in the core/mantle. The Earth is almost twice as large as Mars and therefore should isotopic equilibrium during core formation be reached in the Earth's lower mantle ($P = 25$ -150 GPa) then the fractionation factor could be considerably larger than that obtainable on Mars (<25 GPa). This would produce a much larger shift in the $\delta^{13}\text{C}$ value of the residual silicate proportion of the Earth relative to Mars and hence the discrepancy in the bulk silicate $\delta^{13}\text{C}$ values for both planets starting at the same primordial value and possibly having the same core/mantle ratio for carbon.

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