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Comment

Comment on "Reconciliation of the excess ^{176}Hf conundrum in meteorites: Recent disturbances of the Lu-Hf and Sm-Nd isotope systematics" [Geochim. Cosmochim. Acta 212 (2017) 303–323]

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In a recent paper, Bast et al. (2017) present an impressive set of mineral and whole rock isochrons and use them to investigate the cause(s) of excess ^{176}Hf in eucrite and angrite meteorites. They argue that during terrestrial weathering of these samples, phosphates present as isolated grains or inclusions underwent partial dissolution during which Lu was mobilized more effectively than Hf. If this residual, unsupported Hf were not effectively excluded from analyses, then the data points would be shifted above the actual isochron, creating scatter and potentially spurious Lu-Hf ages. Bast et al. (2017) conclude that: (1) diffusive fractionation of Lu from Hf during a thermal metamorphic event on the parent body, as suggested by Bloch et al. (2017) and Debaille et al. (2011), did not contribute significantly to the anomalous Lu-Hf ages, and (2) terrestrial weathering effects are the primary cause of the older-than-solar-system Lu-Hf mineral ages retrieved from some eucrites and angrites (e.g. Bast et al., 2012; Bizzarro et al., 2012; Lapen et al., 2015; Sanborn et al., 2015). We find these conclusions to be unjustified in light of the authors' selective and incomplete consideration of results from the modeling by Bloch et al. (2017).

Bast et al. (2017) reject the hypothesis that diffusive decoupling of Lu from Hf contributed to isochron steepening based on the timing of thermal metamorphism on Vesta:

``Bloch et al. (2017) argued that diffusive Lu loss from pyroxene to a partial melt might have steepened the px-WR isochrons for Millbillillie and Piplia Kalan. They proposed that the observed offsets for these samples (Fig. 4a and c) could have been caused, e.g., by a 1 Myr period of reheating above 1050 °C at 4.2 Ga. However, if such events only occurred before 4.47 Ga, the Lu-Hf dates should not exceed the real crystallisation ages by >0.1 Gyr. Thus diffusion in response to protracted high temperature conditions cannot fully explain the observed disturbances in achondrite Lu-Hf systematics."

Although we did provide the results of a simulation that assumed thermal metamorphism took place at 4.2 Ga (Fig. 8 from Bloch et al. (2017)), *we also reported model results that impose thermal metamorphism occurring as early as 4.554 Ga, which directly address the issue raised by Bast et al. (2017)*. The broad range of permissible values reflects the disagreement in the literature over when exactly global thermal metamorphism on Vesta occurred (Prinzhofer et al., 1992; Kunz et al., 1995; Nyquist et al., 1997; Tera et al., 1997; Bogard and Garrison, 2003; Kleine et al., 2005; Dietderich et al., 2013; Iizuka et al., 2015). These results are not only discussed in the text of Bloch et al. (2017) (section 4.3) but are also summarized in Fig. 10 of that paper.

In short, a period of reheating prior to 4.47 Ga, as preferred by Bast et al. (2017), is well within the realm of plausible scenarios for diffusive perturbation of Lu-Hf mineral ages, given the uncertainties in parameters such as the

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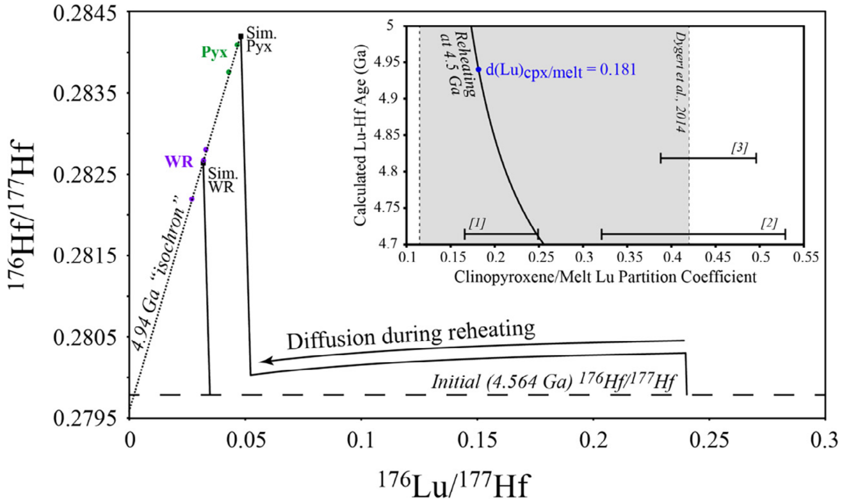

Fig. 1. Example output of a model simulation for the development of the pyroxene-bulk rock Lu-Hf isochron of the eucrite Millbillillie. This simulation imposes a clinopyroxene/melt Lu partition coefficient of 0.181 and a reheating temperature of 1050 °C sustained for 1 Myr at 4.5 Ga. Solid curves in the inset show the calculated Lu-Hf age as a continuous function of clinopyroxene/melt Lu partition coefficient, if metamorphism occurred at 4.5 Ga. Metamorphism occurring at a different time would produce a different curve, as illustrated in Fig. 10 of Bloch et al. (2017). The shaded area shows the range of experimentally determined clinopyroxene/melt Lu partition coefficients from Dygert et al. (2014). Horizontal bars show the range in experimental clinopyroxene/melt Yb (a proxy for Lu) partition coefficients reported by [1] Blundy and Dalton (2000), [2] Johnston and Schwab (2004), [3] Laubier et al. (2014). Whole-rock (WR) and pyroxene (Pyx) data are from Bast et al. (2017). See Bloch et al. (2017) for a detailed description of these simulations.

clinopyroxene/melt Lu partition coefficient and relative initial $^{176}Lu/^{177}Hf$ ratios in pyroxene and the bulk rock. For example, Fig. 1 shows the result of a simulation that imposes thermal metamorphism of the eucrite Millbillillie at 4.5 Ga. Using a clinopyroxene/melt Lu partition coefficient of 0.181, we obtain an apparent Lu-Hf age of 4.94 Ga. This simulation is identical to those reported in Bloch et al. (2017), with the exception that we slightly altered the bulk rock Lu and Hf concentrations in order to reflect the values reported by Bast et al. (2017). If reheating occurred even earlier, for example at 4.554 Ga, then a Lu partition coefficient of 0.114 could be used to calculate an age of 4.945 Ga in an otherwise identical simulation. Because these partition coefficients are well within the range of permissible values (Fig. 1), the premise upon which Bast et al. (2017) rule out diffusive decoupling of Lu from Hf as a plausible contributor to the disruption of Lu-Hf ages is unsubstantiated.

Bast et al. (2017) also state, in section 4.3.1 of their paper, that "Bloch et al. (2017) have experimentally determined Lu diffusion rates only for clinopyroxene and do not explain the scatter observed among the other minerals." While it is true that we did not model the effects of diffusion on Lu-Hf systematics in other minerals, mainly due to the lack of relevant diffusion and/or partitioning data for these phases, we did discuss this issue in section 4.3 of our paper, where we pointed out that the nature of the scatter among the other phases is qualitatively consistent with the proposed redistribution of parent and daughter nuclides during high temperature metamorphism. We were, and still are, reluctant to make stronger statements until the data needed to model the effects of diffusive resetting on other phases become available.

Lastly, we make clear that despite our objection to the selective analysis of our model results by Bast et al. (2017), we did not, and still do not, claim that diffusive decoupling of Lu from Hf must be solely responsible for the observed Lu-Hf systematics in the eucrites Millbillillie and Piplia Kalan. As discussed in section 4.5 of Bloch et al. (2017), the uncertainty in both the clinopyroxene/melt Lu partition coefficient, and the time at which metamorphism of Millbillillie and Piplia Kalan occurred, prohibits us from concluding that diffusive redistribution of Lu was solely responsible for the Lu–Hf ages of these samples. Although our model demonstrates that diffusive decoupling of Lu from Hf is capable of producing the observed ages, it is also possible that diffusion caused only part of the age disruption (inset in Fig. 1; and Fig. 10 from Bloch et al. (2017)) and that another mechanism such as terrestrial weathering, metasomatic fluid infiltration (Jones et al., 2014) or some other as yet unidentified process also contributed to the pre-solar apparent ages of these samples. In summary, while we do not unequivocally reject the hypothesis that terrestrial weathering and incomplete removal of weathered material during sample preparation could have had some impact on the Lu-Hf systematics of these samples, we find the arguments provided by Bast et al. (2017) against the generation of anomalous Lu-Hf ages via diffusive decoupling of Lu from Hf to be unfounded at this juncture.

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