CONSTRAINING VOLATILE ELEMENT LOSS PROCESSES BY GERMANIUM ISOTOPES IN IRON METEORITES. E. Wölfer[1*], C. Burkhardt[1], C. J. Renggli[2], P. Pangritz[2], and T. Kleine[1], [1]Max Planck Institute for Solar System Research, Justus-von-Liebig-Weg 3, 37077 Göttingen, Germany. [2]Institute for Mineralogy, University of Münster, Corrensstraße 24, 48149 Münster, Germany. *Corresponding author. Email: woelfer@mps.mpg.de

Introduction: The concentrations of Ge and other moderately volatile elements (MVE) in iron meteorites vary by orders of magnitude, a feature that has been key for defining the major iron meteorite groups [1]. However, the origin of these MVE depletions is not well understood. They may reflect heating processes in the disk that led to MVE depletions in a parent body's precursor material [e.g., 2]. Alternatively, the MVE depletions may result from magma degassing and/or vaporization during planetesimal formation [e.g., 3-6]. For instance, the extreme MVE depletions of group IVA irons have been proposed to reflect evaporative losses from exposed molten iron cores after collisional stripping of their silicate mantles [5,6]. Such degassing is expected to result in mass-dependent isotope fractionation, but until now no clear evidence for such isotope fractionation has been found among those iron meteorites that sample protoplanetary cores.

We measured the Ge isotopic compositions of a comprehensive set of iron meteorites to search for mass-dependent isotope variations among variably MVE-depleted iron meteorite parent bodies. To evaluate these data within the framework of degassing from molten protoplanetary cores, we also measured Ge depletions and isotopic fractionation in controlled metal melt degassing experiments. Together, the new data provide constraints on the origin and processes of MVE depletion among iron meteorite parent bodies.

Samples and Methods: In total, three IAB, four IC, eight IIAB, five IID, one IIE, nine IIIAB, and one IIIE iron meteorites were investigated for their Ge isotopic composition. All samples were digested in $cHNO_3$, followed by chemical separation and purification of Ge by ion-exchange column chromatography [7,8]. Germanium isotopic compositions and concentrations were measured on a Neptune Plus MC-ICP-MS at the University of Münster using a ^{70}Ge-^{73}Ge double-spike. The Ge isotopic data are reported in $\delta^{74/70}$Ge values as the permille deviations from the NIST SRM 3120a Ge standard. To evaluate the effect of melt degassing on the Ge isotopic composition of the residue, we performed controlled degassing experiments of Ge from a metallic Fe melt, both in vacuum and at atmospheric pressure. For the experiments, metal pellets with known Ge starting concentration and isotopic composition were placed in a graphite capsule and heated in a vertical gas-mixing furnace at different temperatures, pressures, and time periods.

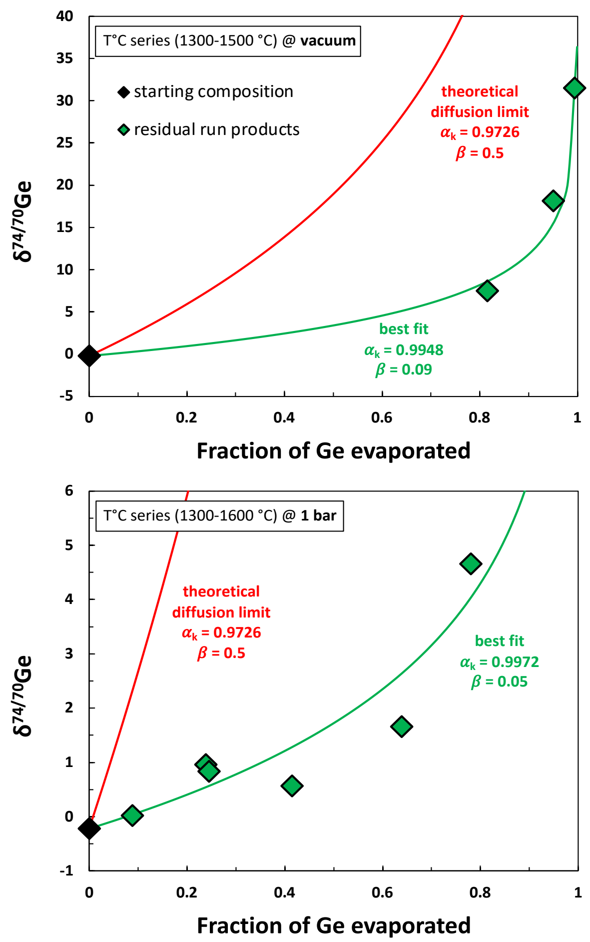

Fig. 1. Experimental results from Ge evaporation experiments from metal melts in vacuum (top panel) and at atmospheric pressure (bottom panel). Green lines indicate modelled best fits for kinetic isotope fractionation, while red lines represent the theoretical limit of Ge loss and isotope fractionation into vacuum.

Results: The experimental run products display significant Ge depletions relative to the starting composition (e.g., from ~10% up to >99%), and as expected for a kinetic isotope effect, the $\delta^{74/70}$Ge values of the residual run products become increasingly heavier with increasing evaporation and loss of Ge. The isotope fractionation during vaporization into vacuum can be modelled with a kinetic fractionation factor α_k = 0.9948 (i.e., β = 0.09 since $\alpha_k = (m_{70Ge}/m_{74Ge})^{\beta}$), whereas evaporation at atmospheric pressure yields α_k = 0.9972 (i.e., β = 0.05) (Fig. 1). Fractionation in both settings is significantly below the theoretical limit for Graham's law of diffusion into vacuum (i.e., $\beta = 0.5$ by definition, such that $\alpha_k = (m_{70Ge}/m_{74Ge})^{0.5} = 0.9726$).

The Ge concentrations of the iron meteorites of this study determined by isotope dilution are consistent with literature data [1] and range from ~35–40 ppm for IIIAB and IIIE irons up to ~370 ppm for some of the IAB irons. The magmatic irons of this study have relatively uniform Ge isotope compositions with $\delta^{74/70}$Ge values of ~1 (Fig. 2). These results agree well with prior results from IIAB and IIIAB irons [7,8] and show that other magmatic irons such as the IC, IID, and IIIE irons (for which no Ge isotopic data have been reported previously) all share a very similar Ge isotopic composition. By contrast, the non-magmatic IIE iron meteorite Miles exhibits a very different $\delta^{74/70}$Ge value of –0.4 (Fig. 2), which again is consistent with literature data for this group of meteorites [7,8].

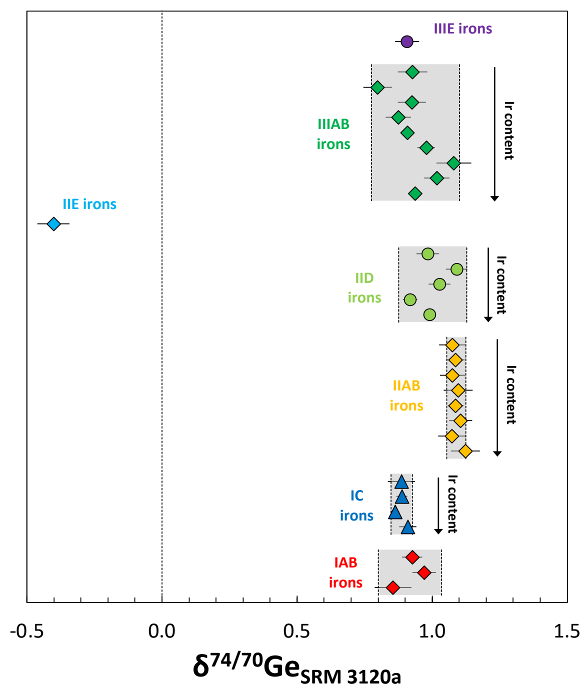

Fig. 2. Germanium isotopic compositions of the analyzed iron meteorites relative to the NIST SRM 3120a solution standard. Note that within each group, samples are sorted according to their Ir content, which is an often-consulted proxy for constraining fractional crystallization. With the exception of the IIE iron meteorite Miles, all other investigated samples show $\delta^{74/70}$Ge of ~1.

Among the magmatic iron meteorite samples investigated so far, there is no resolved within-group variability for most of the groups. Only the IID and IIIAB irons seem to show some internal variability, which for the IIIAB irons is correlated with the Ni content of the samples.

Discussion: *Origin of within-group Ge isotope variations.* The Ge isotope variations among the IIIAB and IID irons can neither be attributed to fractional crystallization of their parental cores (e.g., $\delta^{74/70}$Ge is not correlated with Ir contents; arrows in Fig. 2) nor to cosmic ray exposure effects (e.g., $\delta^{74/70}$Ge is not correlated with ε^{196}Pt). Instead, these variations likely reflect a small-scale sampling bias between kamacite and taenite, as is evident from a correlation of $\delta^{74/70}$Ge with Ni content among the IIIAB irons of this study.

Lack of Ge isotope variations among magmatic iron groups. Despite large differences in Ge concentrations, the different groups of magmatic irons display no significant Ge isotopic variations. Thus, the Ge depletion of iron meteorites is not associated with the large kinetic isotope fractionation, which can be observed for instance in the degassing experiments and which may be expected for evaporative Ge loss from exposed molten cores. However, isotope fractionation during evaporation from molten planetesimals may have reached near-equilibrium conditions, in which case much smaller isotope effects are expected [9]. Clearly, further experimental studies are needed to better understand Ge isotope fractionation under these conditions.

Ge isotope fractionation in IIE irons. The light Ge isotopic composition for the IIE iron Miles is consistent with the results of [7,8], who reported highly variable $\delta^{74/70}$Ge values for five IIE irons that are correlated with Ge concentrations. Interpreting this correlation to reflect evaporative Ge loss yields an $\alpha_k = 0.9948$ (i.e., $\beta = 0.09$), in excellent agreement with the kinetic isotope fractionation factor obtained from the vacuum degassing experiments of this study. Evaporation from a metallic melt can thus readily explain the $\delta^{74/70}$Ge systematics of the IIE irons, consistent with the idea that these non-magmatic iron meteorites formed by impact-related processes that induced local melting and metal-silicate fractionation [10].

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