CONSTRAINTS ON THE NATURE AND TIMING OF POST-FORMATION ALTERATION OF CHONDRITIC METEORITES FROM $^{87}Sr/^{86}Sr$ AND $^{143}Nd/^{144}Nd$ SYSTEMATICS. G. R. Eppich[1], L. E. Borg[1], and C. Burkhardt[2] [1]Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA, USA (eppich1@llnl.gov); [2]Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm Klemm-Strasse 10, 48149 Münster, Germany.

Introduction: Chondrites, long utilized as proxies for initial bulk Earth composition, contain an abundance of petrologic (e.g., [1]) and isotopic [2] evidence indicative of one or more post-formational metamorphic events. Investigation into the timing of these events provides insight into the nature of early solar system processes including protoplanetary accretion and planetary bombardment. Previous studies to constrain the timing of post-formational metamorphic events using Rb-Sr [2] and Ar-Ar [3] have suggested that metamorphism may have occurred around 4.50 to 4.54 Ga. We report new Rb-Sr data alongside previously-reported Sm-Nd data [4] for enstatite and ordinary chondrites in order to further constrain the early histories of these objects.

Samples and Methods: The majority of the samples analyzed in this investigation were the same as those analyzed by [4] and included eleven ordinary chondrites (six H, two L and three LL), six enstatite chondrites (three EL and three EH), and the brachinite-like achondrite NWA 5363. These meteorites are equilibrated chondrites and belong to petrologic classes 4–6. They were chosen to minimize the isotopic effects associated with incomplete dissolution of refractory presolar components and to minimize potential disturbances through terrestrial alteration. In addition, four Antarctic meteorites including GRO95502 (L3), LAR06252 (EH3), QUE97030 (H3), and WSG95300 (H3) were analyzed for Rb-Sr. Several samples were analyzed multiple times and represent separate digestions that were processed though chemistry at different times and run on separate filaments. About 2 g of each meteorite was powdered and digested in a $HF–HNO_3–HClO_4$ mixture and aqua regia in 90 ml Savillex teflon vials for about 10 days on a hotplate at 170 °C. After several drydowns and ultrasonication steps, the samples were redissolved in HCl forming a clear solution from which 5% was taken for Rb, Sr, Sm, and Nd isotope dilution and/or isotopic compositions measurements. Strontium was purified using Sr spec resin in 4N HNO_3 and water. Rubidium was purified using AG50-x8 cation resin and 0.6N HCl. Strontium was run on a Thermo Triton thermal ionization mass spectrometer at LLNL using a three cycle multi-dynamic routine that yielded dynamic isotope ratio measurements for both $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$. Individual analyses consisted of 600 ratios run at 6 to 9 volts ^{88}Sr (10^{11} ohm resistors). Instrumental fractionation was corrected using the exponential law assuming $^{86}Sr/^{88}Sr = 0.1194$. The average $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$ ratios determined on N = 39 measurements of NBS-987 during the course of this investigation were 0.7102521 ± 46 and 0.0564956 ± 37.

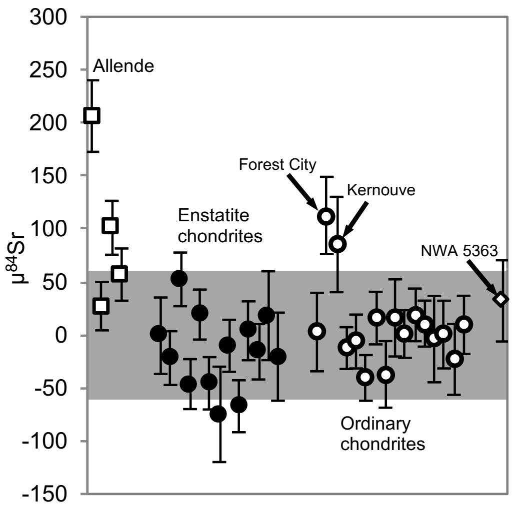

Figure 1. Measured ^{84}Sr isotopic anomalies in enstatite chondrites, ordinary chondrites, and the Allende meteorite. Uncertainty of NBS 987 is given as the gray shaded area.

Strontium isotopic composition: The nuclide ^{84}Sr is generated exclusively by the p-process and has been found to be variable in early solar system materials such as CAIs [5]. If similar anomalies in ^{84}Sr are present in chondritic samples, they could account for some of the scatter observed in Rb-Sr isochron plots [2] because they would produce small deviations in measured $^{87}Rb/^{86}Sr$ ratios. Likewise, if ^{84}Sr anomalies are a manifestation of fractionation correction to an incorrect $^{86}Sr/^{88}Sr$ value, the measured $^{87}Sr/^{86}Sr$ values could be incorrect [6-7]. Figure 1 demonstrates that almost all of the enstatite and ordinary chondrites measured in this investigation have $\mu^{84}Sr$ values that are indistinguishable from the terrestrial standard value. The exceptions are the Forest City ($\mu^{84}Sr = +113 \pm 36$) and Kernouve ($\mu^{84}Sr = +85 \pm 45$) samples (Fig. 1). Four analyses of Allende demonstrate enrichment in $\mu^{84}Sr$, likely caused by its abundance of ^{84}Sr-enriched CAIs [5]. The fact that enstatite chondrite $\mu^{84}Sr$ values are similar to terrestrial values is consistent with the hypothesis that the bulk Earth formed from enstatite chondrite-like material [7]. The lack of detectable ^{84}Sr anomalies in these samples stands in contrast to the observed ^{145}Nd, ^{148}Nd, and

^{150}Nd anomalies in these same samples [4], reflecting the fact that (*i*) there is less natural variation in ^{84}Sr compared to stable Nd isotopes and (*ii*) ^{84}Sr is more challenging to measure precisely given it low natural abundance.

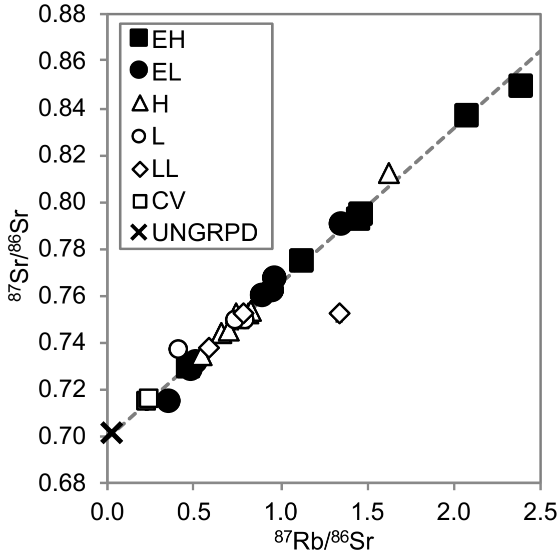

Figure 2. Rb-Sr isochron diagram of all measured chondrites. Dashed line is 4.567 Ga reference isochron through BABI [6]. Uncertainties are smaller than symbols.

Rb-Sr systematics: While a handful of the Rb-Sr measurements reported here fall along a 4.567 Ga isochron intersecting with an initial $^{87}Sr/^{86}Sr$ equal to BABI [6], many fall outside of uncertainty of this isochron (Fig. 2). Moreover, replicate analyses of individual meteorites yield results that differ outside analytical uncertainty. These findings indicate that post-formational metamorphic events have likely altered the $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios of each meteorite on a small scale consistent with the sampling volume. Ordinary chondrites tend to be more disturbed in Rb-Sr systematics than enstatite chondrites, perhaps reflecting the fact that they probably originate from three distinct parent bodies (H, L, and LL) that may have had distinct post-formational metamorphic histories.

The measured $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios of replicate analyses were averaged to produce a "whole-rock averaged" isochron for enstatite chondrites (Fig. 3). The slope of a line regressed through these data corresponds to an age of ~4.52 Ga. There is significant scatter on this plot with Abee and Blithfield falling farthest from the regression. Although the significance of the age is unclear, it is broadly consistent with Ar-Ar ages determined for enstatite chondrites by [8]. This implies that the metamorphism responsible for disturbing the Rb-Sr system occurred fairly late in solar system history, at least tens of millions of years after solar system formation. Furthermore, the fact that Rb-Sr system does not define a linear array suggests metamorphism was heterogeneous, both adding and removing Rb and Sr from different portions of the samples, and/or occurring over a significant period of time.

Comparison to Sm-Nd systematics: Burkhardt *et. al.* (Extended Data Figure 2 in [2]) observed that the enstatite chondrites (with the exception of Atlanta and Blithfield) plot along a 4.567 Ga isochron, suggesting: (*i*) that the Sm-Nd systematics are recording the age of formation of these samples; and (*ii*) that Sm-Nd are minimally affected by post-formation alteration events, such as impact events associated with the brecciation and shock metamorphism. These findings are consistent with the Rb-Sr system being more affected by metamorphic events than Sm-Nd because the chemical behavior of Sm and Nd are similar in most metamorphic conditions, whereas Rb is both more volatile and more fluid-mobile than Sr.

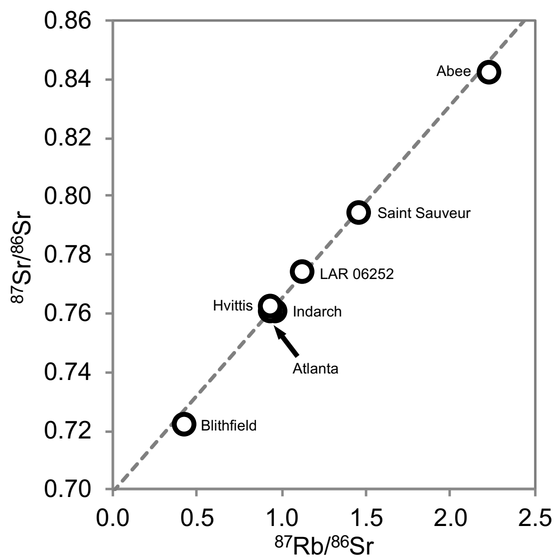

Figure 3. ~4.52 Ga Rb-Sr isochron diagram for enstatite chondrites. Uncertainties are smaller than symbols.

References: [1] Rubin A. E. (2015) *Chem. Erde 75*, 1-28. [2] Minster J.-F. et. al. (1979) *Earth Pl. Sc. Lett., 44,* 420-440. [3] Bogard et. al. (2010) *MAPS, 45*, 723-742. [4] Burkhardt C. et. al. (2016) *Nature 537*, 394-398. [5] Brennecka et al (2013) *PNAS, 110,* 17241-17246. [6] Hans et al. (2013) *EPSL* 374, 204-214. [7] Papanastassiou & Wasserburg (1978) *GRL* 5, 595-598. [8] Javoy M. (1995). *JGR, 22*, 2219-2222. [9] Dixon et al. (2004) *GCA* 3779-3790. Work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344. This research was an outgrowth of Laboratory Directed Research and Development project 17-ERD-001., "Uncovering the Origins of the Solar System with Cosmochemical Forensics".