Utilizing Stable Isotopes and Isotopic Anomalies to Study Early Solar System Formation Processes. J. I. Simon, Center for Isotope Cosmochemistry and Geochronology, Astromaterials Research and Exploration Science Division, EISD-XI3, NASA Johnson Space Center, Houston, TX 77058, USA (justin.i.simon@NASA.gov).

Introduction: Chondritic meteorites contain a diversity of particle components, i.e., chondrules and calcium-, aluminum-rich refractory inclusions (CAIs), that have survived since the formation of the Solar System. The chemical and isotopic compositions of these materials provide a record of the conditions present in the protoplanetary disk where they formed and can aid our understanding of the processes and reservoirs in which solids formed in the solar nebula, an important step leading to the accretion of planetesimals.

Isotopic anomalies associated with nucleosynthetic processes are observed in these discrete materials, and can be compared to astronomical observations and astrophysical formation models of stars and more recently proplyds, e.g., [1]. The existence and size of these isotopic anomalies (e.g., [2]) are typically thought to reflect a significant state of isotopic heterogeneity in the earliest Solar System, likely left over from molecular cloud heterogeneities on the grain scale [3], but some could also be due to late stellar injection (e.g., [4]). The homogenization of these isotopic anomalies towards planetary values can be used to track the efficiency and timescales of disk wide mixing, e.g., [5-7].

Mass-dependent fractionation recorded by the isotopic compositions of early formed solids is primarily controlled by chemical volatility. Evaporation/sublimation are well understood through both theory and experimental work, but until recently we've only had a qualitative understanding about the fractionation effects of condensation (see [8, 9]).

I will present several "case studies" that emphasize the useful insights that can be had, and the complexity of the stable isotope records contained in early formed astromaterials. These isotopic records reflect the temperatures, pressures, and gas compositions in which early formed solids originated, as well as, the timing in which these particles exchanged with different nebular gas reservoirs. In combination with theoretical models of isotopic fractionation, these results can be used to critically test assumptions and input parameters (i.e., temperature, pressure, nebular gas composition, and timescale) of contrasting astrophysical models of protoplanetary disk evolution.

Analytical Background: Many current isotopic discoveries are possible because of improvements in analytical methods. These either reflect advancements in precision (e.g., calcium, [9]), spatial resolution (e.g., oxygen [10]), or a bit of both (e.g., magnesium [11]). It is common for these measurements to be made in conjunction with radiogenic dating methods (see Wadhwa, this workshop) and we strive to integrate all of these isotopic measurements into their petrological context.

Theoretical Background: The anomalous distribution of oxygen isotopes among planetary materials is a fundamental chemical feature of the Solar System [12]. Mass independent variations in ^{16}O relative to ^{17}O and ^{18}O (expressed as deviations from the terrestrial mass-fractionation line, $\Delta^{17}O$) is commonly ascribed to photochemical self shielding by CO, which produces ^{16}O-depleted H_2O, and because this H_2O gas readily exchanges with silicate minerals. The isotopic signature of CO self shielding is likely a function of position and time in the protoSolar disk [13]. It can be argued that heterogeneities in early formed solids reflect their evolutionary history in the nebula, although later parent body alteration can certainly obscure this history.

Theoretical and experimental studies imply that evaporative residues must have been heated at low pressures for appreciable mass dependent isotopic fractionation to be preserved [14-22], e.g., the heavy Mg isotope enrichments of many CAIs imply that they experienced evaporation at low pressures ($<10^{-4}$ bar), conditions that are thought to be typical near the protoSun.

The isotopic consequences of condensation from a nebular gas can be considered in terms of the kinetics of condensation, the degree of undercooling, and potential reservoir effects [8, 9]. The magnitude of fractionation is controlled mainly by the transformation from vapor to solid with the exact identity of the solid phase(s) being of less importance. Ultimately, the relative importance of equilibrium versus the potentially much larger kinetic effects in the isotope fractionation depends on the degree of "overstepping" thermodynamic equilibrium, which can be equated with a temperature difference (i.e., undercooling).

Oxygen isotopes: In general, CAIs are understood to start ^{16}O-rich relative to chondrules and other "more" planetary materials and to record the isotope composition of solar nebular gas from which they grew. Recent high spatial resolution oxygen isotope measurements afforded by ion microprobe analysis across the margins and rims of CAIs reveal systematic variations in $\Delta^{17}O$, which suggests formation from a diversity of nebular environments [10, 23]. The variability implies that CAIs probably formed from several oxygen isotopic reservoirs. The observations support early and short-lived fluctuations of the environment in which CAIs formed,

either because of transport of the CAIs themselves to different regions of the solar nebula or because of varying gas composition near the protoSun.

Recently, NanoSIMS oxygen isotopic imaging of a primitive spinel-rich CAI spherule (27-2) from the MIL 090019 CO3 chondrite has confirmed the existence of outward enrichment of ^{16}O [24], indicating that at least some CAIs exchanged with ^{16}O-poor nebular gas followed by a more ^{16}O-rich gaseous reservoir. Likewise, the observed radial oxygen isotopic heterogeneity among multiple occurrences of the same mineral in this inclusion strongly supports interpretations of interactions with distinct nebular oxygen reservoirs.

Magnesium (and Silicon) isotopes: Significant advances in measuring moderately volatile Mg (and Si) have been made by coupling a short-pulsed laser with a MC-ICPMS. In particular, this *in situ* approach affords the measurement of detailed intra-particle isotope zoning profiles across the margins of inclusions and rims that make up the outer portion of most CAIs [11]. Because Mg isotope zoning across melilite at the margins of CAIs can be decoupled from the chemical zoning of the melilite (typically dropping from the relatively heavy Mg isotopic enrichments indicative of the cores to normal Mg isotopes at the margins), the Mg isotope zoning profiles are interpreted to reflect solid-state diffusive exchange with the gas attending growth of their rims [25]. Furthermore, the near normal Mg isotopic compositions observed in the rims indicate that these mineral layers are in part condensates that formed at relatively high gas pressures (P_{H2} and/or P_{Mg}) while the heavy Mg isotopic enrichments of the interiors of igneous CAIs (once molten in space) show that they are evaporative residues formed at lower gas pressures (P_{H2}) [11].

Fractionation of Mg isotopic compositions in rims, e.g. [11], has not been quantified. These rims can have lower Mg isotopic compositions than typical of planetary materials and are not convincingly explained by parent body processes. Using a new fractionation theory for condensation [9] it can be shown that these rims likely formed by small (0.5-1.0 ^{o}C) degrees of non-equilibrium condensation (i.e., undercooling) from a gas with a "normal" planetary Mg isotopic composition.

Because silicon is also a moderately volatile element, the comparison of Mg with Si isotope measurements to models for the chemical and isotopic effects of evaporation of molten CAIs can be used to produce a univariant relationship between pressure (P_{H2}) and time during melting [20]. These results show that igneous CAIs were molten for short periods of time (hours to days). In some cases, subsolidus heating sufficient to produce diffusion-limited heavy isotope enrichment at the margin is required [20, 25]. The cumulative timescale for the sublimation history is longer, years to 100's years, but not as long as the 10^3 to 10^4 years required for the inward diffusive exchange computed by modeling the "normal" Mg isotopic zoning and O isotopic zoning commonly seen in other CAIs [23, 25].

Calcium and Titanium isotopes: Using isotopic compositions of the refractory elements Ca and Ti to understand the isotopic effect of condensation allow us to more accurately assess the initial isotopic ratios of the more volatile Mg and Si potentially overprinted by later evaporation events. Furthermore, these results allow us to assess whether a given CAI is a primary condensate from a homogeneous solar gas or instead represents a mixture of materials from a variety of early reservoirs.

Although substantial work remains, it is clear that many "normal" CAIs, and/or their precursor materials, record a multi-step/source condensation history [2, 9]. The extreme depletions of Ca isotopes and slight enrichments of Ti isotope effects measured in a fine-grained CAI exemplify the complicated condensation history of early formed solids. Such fine-grained textures are often assumed to signify a primitive nature for nebular materials, but they may in fact reflect condensation from relatively evolved (fractionated) nebular gas. An origin as primordial condensates might be incorrect. Additionally, the discovery of Ca isotopic zoning [9] in a Type B1 igneous CAI likely involves condensation from an evolving gaseous reservoir, presumably after now extinct ^{26}Al was added to the Solar System, but before its moderately volatile element isotopic signatures were set. Thus, the existence of Ca isotopic zoning in this inclusion implies that a majority of its Mg isotope record pertains to a later, likely subsolidus, nebular history.

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