THE IMPORTANCE OF ISOTOPE ANOMALIES: A HISTORICAL PERSPECTIVE.

D. A. Papanastassiou, Science Division, Jet Propulsion Laboratory, MC 183-335, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109 (dimitri.a.papanastassiou@jpl.nasa.gov).

There is a current emphasis on the measurement of whole meteorite samples to establish isotope anomalies and characterize nucleosynthetic components. Sometimes these measurements are coupled with the study of leaches and residues of whole meteorites. The purpose of whole rock analysis is ostensibly to identify also different regions of the solar nebula, characterized by specific isotope signatures. However, the early and important measurements have been those which have identified large isotope anomalies and nucleosynthetic effects and which serve to interpret the very small residual effects in whole meteorite samples. The large effects have consisted of: a) identification and confirmation of the Ne-E component; b) identification of the ^{16}O-rich component in carbonaceous meteorites; c) identification of Mg isotope anomalies, followed by the discovery of ^{26}Al; and d) the discovery of FUN inclusions and the measurement, in a relatively quick progression, of correlated isotope anomalies in Mg, Sr, Ba, Nd, Sm and for many of the elements in the vicinity of the Fe abundance peak (i. e., for Ca, Ti, Cr, Fe, and Zn). Some have called the FUN inclusions oddballs and "hard to interpret", and have instead concentrated on "normal" CAIs and on whole meteorite measurements. However, the excitement of the FUN inclusions was clear, even though they have been rare and unique. They contain the evidence for many distinct nucleosynthetic components, over wide regions of the chart of nuclides. Their discovery was also serendipitous and the inclusions were almost used up for less momentous investigations. Inclusion Allende C-1 was analyzed first for Rb-Sr and was found to have relatively high Rb/Sr and ^{87}Sr/^{86}Sr. Since it was of no importance for the determination of a primitive initial ^{87}Sr/^{86}Sr, much of it was ground to face powder to be used as a check of analytical reproducibility for Rb-Sr; luckily that intent was not followed. Similarly, most of Allende EK-1-4-1 was used for the measurement of distribution coefficients for REE between plagioclase and pyroxene. Because C-1 was a large inclusion, one of the splits was shared with R. N. Clayton, who originally disliked the inclusion, because it fell of the 1:1 oxygen correlation line. However, he also recognized the importance of this behavior when he subsequently measured EK-1-4-1, found a similar behavior, and then generously shared EK-1-4-1 with us. While the original two FUN inclusions may have appeared unique, a second group of inclusions, identified as Pink Spinel-rich Inclusions (PSI) was chosen based on unique mineralogy and have all been characterized by isotope anomalies for Ca, Ti and Cr, effectively identical to the FUN inclusion C-1. Hence, FUN inclusions can be identified and may not be as rare or "odd", as generally assumed. The isotope geochemistry community has failed to avail itself of sufficiently detailed searches for rare FUN components. By contrast, there has been a revolution in the study of isotope anomalies based on preserved refractory grains, produced by extensive leaching of primitive meteorites. This revolution came based on the perseverance of Ed Anders and Roy Lewis, despite some less than complimentary early comments by some, including at Caltech. The unique importance of the refractory chemical residues was identified by work on noble gases (Kr, Xe) and then exploded based on the collaboration between Anders and Zinner and many more. This collaboration was critically dependent on developments for ion microprobes and also in instrumentation of coupled sputtering by ion beams, followed by resonant ionization mass spectroscopy, as developed at ANL by Pellin and his colleagues, including the important link provided by A. M. Davis. Based on this work and over a couple of decades, it is clear that refractory grains (SiC, graphite, diamond) have preserved important evidence of their production in AGB stars and in supernovae. This evidence has supported the chemical memory proposals of D. D. Clayton, even though the original proposals to interpret the evidence of the in situ decay of ^{26}Al in the solar system as chemical memory were wrong. We now know that refractory grains have been preserved in the formation and evolution of the solar nebula. We also know that marble-sized refractory inclusions also contain significant effects and hence significant amounts of specific components, which were not mixed. Effects are much, much smaller once processing of materials on small planetesimals has occurred. The exception has been the evidence for significant isotope anomalies for platinum group elements (Ru, Os) and Mo in iron meteorites, which are products of large scale planetary differentiation. Hence, there must be mechanisms for siderophiles, which encapsulated and preserved early, presumably refractory components. The key issues to address are:

a) How refractory grains survived their ejection from their stellar environments, including SN shock fronts;
b) How Ca-Al refractory inclusions were formed and were able to accumulate more of these grains, with diverse isotope components, before homogenization;

c) How components for siderophiles were preserved within the nebula, presumably as refractory, siderophile “smoke” particles, so they could be incorporated in FeNi and preserved though both the condensation of FeNi and planetary differentiation;

d) How, while evidence of isotope anomalies has been preserved, whole meteorites have almost normal, average isotope compositions, requiring a good average over mm to cm scale, which is the typical size for a whole meteorite analysis.

e) How many components and of what nature have been preserved. For example, are the FUN Ti anomalies in CAIs of similar origin as the Ti anomalies in SiC and compatible with an s-process or instead with neutron-rich equilibrium burning, based on the well-defined correlation for FUN inclusions of isotope anomalies (both excesses and deficits) for the neutron rich isotopes of Ca, Ti, Cr, Fe, and Zn;

f) Are the deficits in C-1 and PSI in the neutron-rich isotopes in the Fe abundance peak, indicative of an initial condition, with the deficits being filled-in for the average solar system material by a more massive contribution of these neutron-rich isotopes;

g) There is as yet no clear correlation of nucleosynthetic anomalies with short-lived chronometers, so the time scale for introduction and incomplete mixing is unknown. For Cr, an isotope anomaly in ^{53}Cr for EK-1-4-1 provides evidence for heterogeneity in ^{53}Cr which could affect the application of the ^{53}Mn-^{53}Cr chronometer in FUN inclusions and interfere with chronology; and

h) There is still no understanding of the connection between F (mass dependent isotope fractionation) and UN (nucleosynthetic anomalies) for FUN inclusions.

The isotope measurements of FUN and of SiC are real and reproducible. Some effects for whole rock measurements are at the limit of analytical precision and in need of confirmation. If bulk meteorites have isotope anomalies, is it due to the last-minute introduction of large anomalies from presolar grains or early-formed FUN inclusions, etc. being diluted by normal material? Or do the very small whole meteorite isotope anomalies represent mixtures of many components that were averaged out? These two possibilities have fundamentally different implications for processes in the early solar system. If the bulk anomalies are due to minor components and most material is "normal", then it is reasonable to infer that most matter that makes up meteorites and planets was processed in the solar system efficiently to destroy most of the presolar dust. If the latter is the case and the small anomalies in bulk meteorites are due to slightly different mixtures of a large number of components, this implies that a large fraction of nebular dust was inherited from the presolar cloud and was not processed in the solar system. Both types of processes need to be investigated even though most investigators are more comfortable with the solar system material being mostly well-mixed with some last minute salt and pepper addition. Processes that reveal preservation of isotope anomalies despite planetary-scale processing, e. g., effects in Ru, Mo, and Os, are harder to envision but are clearly important. If the molecular cloud had many different components with different thermal stability, and these components had different isotopic compositions, then thermal processing in the nebula could separate components and reveal isotopic shifts.

This overview is based on close to three decades of work by a myriad of investigators. A reference list is impossible. I acknowledge the many contributions of the following, although the list is of necessity incomplete: C. J. Allègre, S. Amari, E. Anders, R Andreasen, J.-L. Birck, M. Bizzarro, D. Black, A. Bouvier, C. A. Brigham, R. W. Carlson, J. H. Chen, D. D. Clayton, R. N. Clayton, H. C. Connolly, N. Dauphas, A. M. Davis, P. Eberhardt, T. Elliott, C. M. Gray, A. N. Halliday, P. Hoppe, G. R. Huss, I. D. Hutcheon, S. B. Jacobsen, M. T. McCulloch, T. Kleine, T. Lee, R. S. Lewis, G. Lugmair, F. Moynier, F. R. Niederer, S. Niemeyer, L. Nittler, U. Ott, M. Pellin, F. A. Podosek, L. Qin, G. Quitté, M. Regelous, L. Reisberg, A. Shukolyukov, F. Stadermann, R. C. J. Steele, F. Tera, A. Trinquier, J. Voelkening, R. M. Walker, R. J. Walker, G. J. Wasserburg, Q. Yin, E. Zinner.

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