CA ISOTOPE ANOMALIES IN ORGUEIL LEACHATES AND IMPLICATIONS FOR THE CARRIER PHASES OF CA and CR ANOMALIES. Frederic Moynier[1], Justin I. Simon[2], Frank Podosek[1], Joyce Brannon[1] and Donald J. DePaolo[2] [1] Department of Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St Louis, One Brookings Drive, St Louis, MO 63130, USA [2] Center for Isotope Geochemistry, Earth and Planetary Science, University of California, Berkeley, CA 94720, USA.

Introduction: Carbonaceous chondrite meteorites, especially the CI class, are often regarded as the most primitive samples of solar system materials available for laboratory examination. CI meteorites such as Orgueil may have originally incorporated presolar (molecular cloud) solids relatively unmodified by nebular processes and likely represent our best means of studying presolar materials.

One manifestation of these generalizations is that carbonaceous chondrites are prominent (though not exclusive) hosts for several known varieties (diamond, graphite, silicon carbide, corundum, silicon nitride) of circumstellar grains [1, 2] inherited from the solar system's parental molecular cloud with little or no evident modification by nebular processes. Such grains are recognized as presolar primarily on the basis of radically anomalous isotopic compositions plausibly attributable to nucleosynthesis in specific stellar environments.

When whole-rock Orgueil samples are progressively dissolved (leached) in a series of reagents [3-6] the different fractions show large isotopic anomalies in ^{54}Cr. Initial treatment with acetic and nitric acids is found to dissolve most of the Cr (and other cations as well); the Cr thus dissolved is nearly uniform in composition but deficient (with respect to normal composition) in ^{54}Cr by some 5-6 ε. Further treatment with hydrochloric acid and then other reagents liberates the remainder of the Cr, which has variable composition, mostly with excess ^{54}Cr (up to more than 200 ε). There being no known way to generate such isotopic variations within the solar system, this effect must be interpreted in terms of isotopic anomalies, i.e., non-homogenization of distinct presolar nucleosynthetic components

The simplest interpretation of the ^{54}Cr enrichment suggests a nucleosynthetic signature, as may be expected from Type Ia supernovae [7, 8], carried by some form of presolar grain whose Cr has not been homogenized, on the microscopic scale, with the other (complementary) nucleosynthetic components that make up the solar normal mix.

Measuring the relative abundances of isotopes of other elements produced by the same process can provide useful constraints on the origin of the isotopic anomalies. Associated isotopic enrichments or depletions in other Fe-group elements (in particular Ca, Fe, and Zn) may thus be expected, especially in the neutron-rich isotopes of these elements.

We recently found small isotopic anomalies in Ca isotopes in the mass range 40-44 in meteorites at the bulk sample scale and in a couple refractory inclusions that are most compatible with variable proportions of material derived from Type II supernovae [9] .

The carrier(s) of these effects are poorly understood and therefore provide additional motivation for the current investigation. In this work we measured the relative isotopic abundances of ^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca, ^{46}Ca, and ^{48}Ca from Ca separated from the exact same leachates in which [3] measured the ^{54}Cr anomalies to search for possible collateral effects.

Samples and Methods: The leachates of Orgueil used here were described in detail in [3], designed as O-I. The leaching procedure was carried out on ~200 mg of Orgueil powder which was treated sequentially from weak acids to total dissolution in 10 progressive steps [3].

The bulk of the Ca was leachated in O-I steps 1-3. Subsequent steps contained very little Ca and accurate measurements were not available for every step. Up to now, we only have been able to measured the Ca isotopic composition of O-I dervied from steps 1 to 7.

We also report new bulk rock data for Murchison, Allende, a Vigarano CAI, and the geostandard BCR-1 as well as the ^{46}Ca/^{44}Ca and ^{48}Ca/^{44}Ca data for several of the chondrites presented in [9].

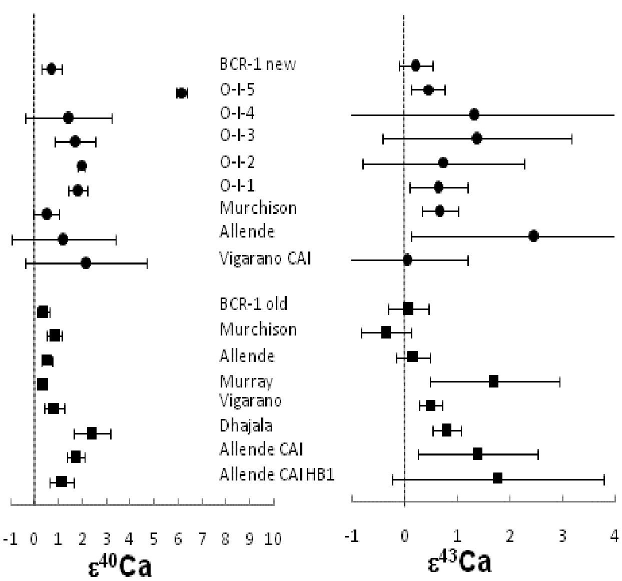
We used the Thermo-Finnigan Triton TIMS instrument at the Center for Isotope Geochemistry, University of Califronia, Berkeley, to perform the Ca isotopic measurements. The analytical procedure is similar to that described in [9] with the exception that masses 46 and 48 were also measured. Due to the large dispersion angle between masses 40 and 48 and the low abundances of mass 46, this requires two static cup configurations and longer run times. Ca isotope ratio data were collected in 17 groups of 30 cycles each, over a period of about 360 minutes. Potential Ti interferences have been carefully monitored and for the most part were negliable. The exceptions include O-I steps 4, 6, and 7 where limited Ca was available. As reported by Simon et al. [9] the detector efficency in the Faraday cup used to measure ^{40}Ca can gradually change. To account for the evolution of this cup, our sample ^{40}Ca/^{44}Ca ratios are normalized to stable blocks of running averages of the SRM915A standard. During the course of this study no cup replacement has been performed. Based on our analyses of the SRM915A standard (~1 year, n=27), the reproducibility of our measurements is ±0.71 ε-units (SD) for ε^{40}Ca, ±1.18 ε-units (SD) for ε^{43}Ca, ±6.0 ‰ for δ^{46}Ca (SD), and ±2.32 for ε^{48}Ca (SD). Uncertainties that are typically equal to or significantly larger than the internal precision of individual sample measurements and the standard error (σ) of replicate sample averages.

Results: The Ca isotope composition of the different samples are reported in the Figure 1. We used the conventional ε notation in part per 10,000. The data are normalized to ^{42}Ca/^{44}Ca =0.31221 using an exponatial law (see details in [9]). In addition to the data reported in Simon et al. [9], we report ^{46}Ca/^{44}Ca (ε^{46}Ca), and ^{48}Ca/^{44}Ca (ε^{48}Ca).

The new bulk sample measurements of Murchison (ε^{40}Ca=0.50±0.25 and ε^{43}Ca=0.67±0.17) and Allende (ε^{40}Ca=1.21±1.09 and ε^{43}Ca=2.45±1.16) confirm our previous finding that bulk carbonaceous chondrites yield anomalous ^{40}Ca and ^{43}Ca isotopic abundances. As for Allende CAIs [9], the Vigarano CAI exhibits fairly large anomalies on ε^{40}Ca (2.16±1.26), but surprisingly no resolvable anomalies on ε^{43}Ca (0.06±0.57).

Our new ε^{46}Ca and ε^{48}Ca data do not show any resolvable effects on bulk meteorites at our current analitical level of resolution. However, one of the Allende CAIs shows large enrichement in ^{48}Ca; the second Allende CAI and the Vigarano CAI have some Ti interferences which prevent us from using the data at this stage.

Fig. 1: Ca isotope composition for the samples analyzed in this study (black dot). The black squares are our previous data from Simon et al. (2009). The errors are 2se.



All leachates of Orgueil show small isotopic effects on ^{40}Ca and possibly in ^{43}Ca, ^{46}Ca and ^{48}Ca. A mass balance of the different leaching steps shows that bulk samples of Orgueil clearly exhibit anomalous ^{40}Ca and ^{43}Ca.

Discussion: *Bulk samples:* Our new results for Murchison and Allende confirm that CV and CM have isotopically heterogeneous abundances of ^{40}Ca and ^{43}Ca when normalized to ^{42}Ca/^{44}Ca. The new data on Orgueil, show that at the bulk sample scale, CI are also heterogeneous for Ca isotopes.

Refractory Inclusions: New results for a Vigarano CAI and previously unpublished 46 and 48 data for two Allende CAIs included in [9] confirms the excess of neutron rich nuclides in CAIs [10].

Stepwise leachings: The stepwise leaching show that not all the components of Orgueil have the same Ca isotope composition. However, the magnitude of these enrichments is significantly lower than those observed for Cr [3], and are comparable to those observed in other bulk chondrite data [9] and significantly lower than the enrichments for the isotope effects in these elements observed in CAIs [9, 11], in particular the FUN inclusions [11].

Correlated enrichments and depletions of the neutron-rich isotopes of Ca and Cr (and also Fe and Zn) have indeed been measured in a variety of inclusions, in particular FUN CAIs. Growing evidence shows smaller, but similar effects in the carbonaceous chondrites. These enrichments have been attributed to material having formed under nuclear stastical equilibrium conditions (see [12] for review). While the effects in CAIs and in ^{54}Cr-rich phase may be related, the fact that the carrier phase of Cr anomalies does not contain large isotopic anomalies in Ca isotopes implies that that the ^{54}Cr is an isolated effect. ^{54}Cr has to be either produced in articular zones in Type Ia's, enriched predominantly in Cr and ^{54}Cr and not mixed with other zones, or, ^{54}Cr has been produced together with other neutron-rich nuclides and there has been subsequent decoupling of this material in the star, in the solar system or in the laboratory.

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