CORRELATED Ca, Ti, and Cr ISOTOPIC ANOMALIES IN METEORITES. J. H. Chen[1], D. A. Papanastassiou[2], J. Zhang[3], N. Dauphas[3,4], and A. M. Davis[3,4], [1,2]Science Division, [1]MS 183-601, [2]MS 183-335, Jet Propulsion Lab, Caltech, 4800 Oak Grove Dr., Pasadena, CA 91109, [3]Dept. Geophysical Sciences and [4]Enrico Fermi Institute, The University of Chicago, 5734 South Ellis Ave., Chicago, IL 60637. (James.H.Chen@jpl.nasa.gov)

Introduction. Recently new data on isotopic anomalies of ^{50}Ti, ^{54}Cr and ^{48}Ca have been reported in both bulk and components of a few members of different classes of meteorites [1-5]. The isotopic heterogeneity can be explained by the presence of exotic presolar carrier grains or a significant contribution of late stellar inputs during the accretion of the solar system [6, 7]. We present ^{48}Ca anomalies in the same samples from 10 meteorites, which show ^{50}Ti anomalies [8] and examine if they are also coupled with ^{54}Cr effects.

Analytical methods. Aliquots of solutions were first analyzed for Ti at the University of Chicago. The cuts, which contain most of the Ca, were analyzed at JPL. High purity Ca, free from Ti, is essential for precise Ca isotopic measurements. A substantial effort was required to purify Ca, due to large amounts of added boric acid in the Ca cuts from the Ti chemistry. We checked any interferences in the Ca-Ti mass region using an electron multiplier. Any signal at mass 49 was assumed to be all from ^{49}Ti and required a negligible correction on ^{48}Ca (<0.1 εu, Table 1). Because of the large mass difference for Ca isotopes we did not measure the high intensity ^{40}Ca ion beam and measured ^{42}Ca to ^{48}Ca using 2 dynamic, multiple cup configurations. The data were normalized for mass fractionation using $^{42}Ca/^{44}Ca = 0.31221$.

Results. The new Ca isotopic data are shown in Table 1 in epsilon units (1 εu =10^{-4}). We also show the ε^{48}Ca *vs.* ε^{46}Ca data (Fig. 1). In this graph the effect of Ti interferences on Ca would displace points along the solid line from the origin. While, with the larger uncertainties for ^{46}Ca, some samples appear to be on the calculated Ti interference line, no sample supports the presence of Ti interferences, since the limit for an interference at ^{48}Ca is <0.1 εu. All meteorite samples except Lancé, Leoville, and Orgueil plot within the error envelopes for normal ^{46,48}Ca. These three samples require a distinctly anomalous ^{48}Ca isotopic composition. In an ε^{48}Ca *vs.* ε^{50}Ti diagram (Fig. 2a), 4 samples (Camel Donga, Ausson, Orgueil, and Lancé) show a correlation line with slope ~0.77. Leoville plots above this line and several other meteorites, with essentially normal ^{48}Ca plot below it. All three carbonaceous chondrites show distinctly positive ε^{48}Ca and ε^{50}Ti anomalies while all other samples show different patterns. In Fig. 3, we compared the new ε^{48}Ca with ε^{54}Cr from Qin et al. [3] and Trinquier et al. [1-2]. Only a few of the samples plotted, in Fig. 3, have been analyzed for both Ca and Cr (Orgueil, Lancé and Leoville). For the other samples shown, we have used the ^{54}Cr data for *each group* of meteorites and not from the individual specific meteorites. These data generally show the same coupled positive-negative relationships but not as well correlated as for ^{48}Ca-^{50}Ti. Future Ca and Cr isotopic work on the same samples may help to clarify this matter. Schiller et al. (2011)[9] have shown good correlations of ^{48,46,43}Ca and ^{54}Cr. In general, the effects for Ca are definitely less pronounced than effects for ^{50}Ti and ^{54}Cr, and, hence, correlations may remain elusive.

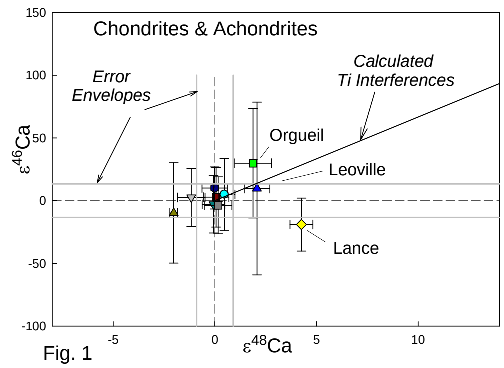

Fig. 1

Discussion. Our new Ca data on meteorites appear

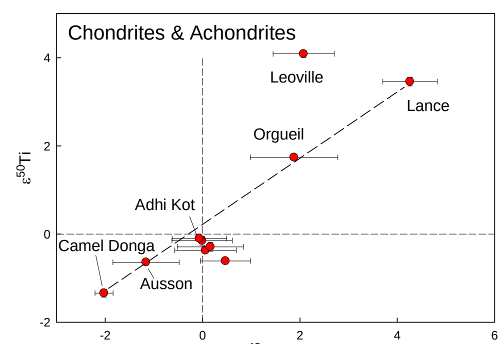

Fig. 2a

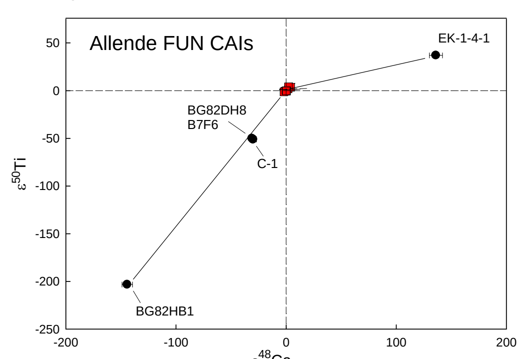

Fig. 2b

to support the recently reported correlation among ^{48}Ca, ^{50}Ti and ^{54}Cr in differentiated meteorites [4]. The stellar source of the most neutron-rich Cr and Ti isotopes can be produced from a neutron-rich subset of Type Ia sypernovae (nSNe Ia, [10]) or in asymptotic giant branch (AGB) stars via slow neutron capture s-process[11-13]. The correlation with ^{48}Ca effects and especially the absence of large s-process effects in ^{46}Ca, exclude an AGB provenance. The Ca data appear to be compatible with a nSN Ia explosion [10].

Considerable effort has been expended for the identification of large ^{54}Cr effects and of their carrier, ultimately as nano-oxide grains (nano-spinels) of supernova origin [6, 7]. By contrast, the measurement of very small isotope anomalies in whole rock samples addresses the goal to identify the degree of preserved isotope heterogeneity in the early solar nebula, in bulk materials, with the hope to use even small isotope effects, to differentiate individual classes of meteorites and their possible provenance from specific regions within the early solar nebula. For identifying correlations in neutron-rich isotopes, we already know that there are good correlations observed for FUN Allende inclusions for ^{48}Ca, ^{50}Ti, ^{54}Cr, ^{58}Fe, and ^{66}Zn. We show in Fig. 2b the correlation for FUN inclusions for ^{48}Ca and ^{50}Ti. This is a remarkable correlation, as it includes, by comparison with whole meteorite analyses, large effects, corresponding to correlated excesses and deficits. The real questions then become: a) are the small effects observed for whole meteorites simply indicators of admixed, small amounts of FUN inclusions, and b) are the small effects in whole meteorite samples potentially indicative of different components than preserved and manifested in the early-formed condensates in the solar system, recognized as Ca-Al-Ti-rich inclusions. Based on this work and the de-amplification of Ca isotope anomalies as compared to Ti and Cr anomalies, the answer to both questions remains elusive and it not clear whether more whole rock Ca measurements will be useful, given the low abundances of most Ca isotopes. The issue which is of high importance is the extent to which the significant deficits observed for ^{48}Ca, ^{50}Ti, ^{54}Cr, ^{58}Fe should be considered as the initial solar nebula isotopic composition. If this is the case, a large addition of neutron-rich isotopes is required to fill up the "holes". This was addressed for Ti, for 2-component mixtures, by Hinton et al. [14]. Furthermore, to the extent that evidence of significant deficits in the whole meteorite measurements is absent, the neutron-rich material must have been very efficiently mixed into the early solar nebula with tell-tale large deficits being preserved only in a few, earliest formed (FUN) CAI, in addition to large effects in preserved interstellar grains.

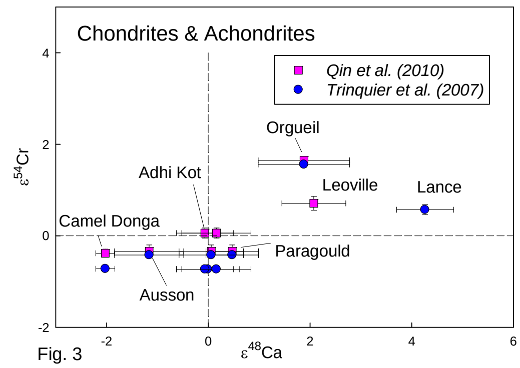

Fig. 3

References. [1] Trinquier A. et al. (2007) *Ap J. 655*, 1179. [2] Trinquier A. et al. (2009) *Science 324*, 374. [3] Qin L. et al. (2010) *GCA* 74, 1122. [4] Chen H.W. et al. (2011) *ApJ Lett. 743*, L23. [5] Moynier F. et al. (2010) *ApJ Lett. 718*, L7. [6] Dauphas N. et al. (2010) *ApJ 720*, 1577. [7] Qin L. et al. *GCA 75* 629. [8] Zhang J. et al. (2012) *Nature Geosci.* (in press). [9] Schiller M. et al. (2011) In *Formation of 1st Solids in Solar System*, #9064. [10] Woosley S. E. (1997), *ApJ 476*, 801. [11] Hoppe P. et al. (1994), *ApJ 430*, 870. [12] Woosley, S. E. et al. (2002), *Rev. Mod. Phys. 74*, 1015. [13] Lugaro, M. et al. (2004) *Mem. Soc. Astron. It. 75*,723.[14] Hinton R.W. et al. (1987) *ApJ 313*, 420.

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Table 1. Ca and Ti isotopic composition in chondrites and achondrites

Sample		$\varepsilon^{43}Ca$		2σ	$\varepsilon^{46}Ca$		2σ	$\varepsilon^{48}Ca$		2σ	$\varepsilon^{48}Ca$*		2σ	$\varepsilon^{50}Ti$		2σ
Carbonaceous chondrites																
Orgueil	CI	0.31	±	0.65	29.81	±	43.51	1.93	±	0.91	1.88	±	0.90	1.74	±	0.05
Lance	CO	0.82	±	1.41	-19.00	±	21.10	4.29	±	0.56	4.26	±	0.56	3.46	±	0.10
Leoville	CV	0.04	±	1.32	9.68	±	68.88	2.08	±	0.62	2.07	±	0.63	4.09	±	0.08
Ordinary chondrites																
Paragould	LL5	-0.34	±	0.88	4.97	±	28.54	0.49	±	0.52	0.47	±	0.52	-0.61	±	0.07
Ausson	L5	0.36	±	0.52	2.58	±	23.24	-1.16	±	0.68	-1.16	±	0.68	-0.64	±	0.05
Kesen	H4	0.05	±	0.59	2.79	±	23.78	0.08	±	0.63	0.06	±	0.63	-0.37	±	0.05
Achondrites																
Camel Donga	Eucrite	0.21	±	0.73	-9.75	±	40.00	-2.02	±	0.19	-2.02	±	0.19	-1.34	±	0.09
Cumberland	Aubrite	0.21	±	0.73	10.10	±	16.80	0.01	±	0.63	-0.01	±	0.62	-0.15	±	0.10
Enstatite chondrites																
Adhi Kot	EH4	0.67	±	0.46	-2.94	±	22.78	-0.05	±	0.56	-0.07	±	0.56	-0.10	±	0.04
Jajh	EL6	-0.10	±	0.58	-3.71	±	22.73	0.25	±	0.68	0.16	±	0.68	-0.29	±	0.10

* Corrected for ^{48}Ti interference.