Nb-Ta RATIOS IN THE ALLENDE CV CHONDRITE; THE RELATIONSHIPS BETWEEN CALCIUM-ALUMINIUM-RICH INCLUSIONS, CHONDRULES AND MATRIX. R. D. Ash[1], M. Lipella[1], W.F. McDonough[1] and R.L.Rudnick[1]. [1]Department of Geology, University of Maryland, College Park, MD 20742, USA (rdash@geol.umd.edu).

Introduction: Niobium and tantalum are refractory lithophile elements with similar geochemical behaviour. Their condensation temperatures are also predicted to be similar (1517K and 1543K, respectively [1]). Both are predicted to substitute into perovskite, hence we may expect the cosmochemistry of these elements to be similar. In a recent paper [2] Nb/Ta of chondritic meteorites was used to constrain models involving the evolution of the Earth-Moon system. This required the determination of the primordial Solar System ratio of Nb to Ta and this was accomplished by the measurement of chemically primitive meteorites. In making determinations of these chondrites it was found that most exhibit a uniform Nb/Ta value of 19.9+/-0.6, which was then used to represent the bulk Solar System value. The most notable exceptions to this uniformity in undifferentiated materials were the CV chondrites, which have a mean Nb/Ta of 16.5+/-0.6. This lower ratio was attributed to the high abundance of Calcium Aluminium-rich Inclusions (CAI) in the CV chondrites. However the available literature data for niobium and tantalum in CAI is generally old and limited, with data often gathered by different techniques on different inclusions; some implying a low Nb/Ta [1] and others indicating a solar value [3].

Similarly hafnium and zirconium is a pair of highly refractory elements (50% condensation T 1690K and 1717K respectively [1]) with similar geochemical properties. These show less whole-rock variation than Nb/Ta [2], perhaps reflecting their more refractory nature.

In order to further understand the cosmochemical evolution of Nb and Ta, and to test the validity of the Nb/Ta fractionation in CAI we have undertaken a survey of Nb/Ta and Hf/Zr in components in the Allende CV3 meteorite.

Methods: Samples of the Allende meteorite were selected from the Smithsonian Institution collections, and thick sections and probe mounts prepared for *in situ* chemical analysis. Chondrules from previous studies of oxygen isotope and trace element analysis [4] were also available for this study.

Major element abundances were determined using a JEOL electron microprobe and Ca, Ti, Nb, Ta, Hf and Zr abundances measured using laser ablation ICP-MS. Material was ablated into a He stream using a New Wave 213nm quadrupled Nd-YAG laser, and introduced into a ThermoElectron Finnigan Element 2 single collector magnetic sector ICP-MS. Spot sizes varied from 20 to 120 microns.

Results: Initially two CAIs (3529-61-RR1 and 3529-63-RR1 – hereon 61RR and 63RR) were selected as appropriate targets for Nb-Ta analysis. 63RR is a brecciated Type B CAI, with 50-250μm fragments in a fine-grained matrix of typical CAI material. 61RR is an altered Type A CAI with well-developed rims.

Laser ablation analysis is inherently less precise than solution methods. Errors are typically in the range of 4-7%, depending upon count rates and signal/noise ratio. For ratios this translates to a cumulative error of *ca*. 10%.

		Nb (ppm)	*Ta (ppm)*	*Nb/Ta (wtd mean)*
3529-63-RR1	*CAI*	*2.3*	*0.51*	*5.0*
3529-61-RR1	*CAI*	*1.3*	*0.46*	*4.7*
Allende A7	*chondrule*			*23.2*
Allende A6	*chondrule*			*17.0*
Allende A5	*chondrule*			*10.4*
Allende A4	*chondrule*			*3.8*
Allende A3	*chondrule*			*8.7*
Allende	*matrix*			*16.2*
Allende	*matrix*			*20.5*
Tieschitz	*chondrule*	*0.21*	*0.011*	*19.1*
Tieschitz	*chondrule*	*0.38*	*0.018*	*21.1*
Solar System	*[2]*	*0.52*	*0.03*	*19.9*

Table 1. Nb-Ta data for Allende CAIs, matrix and chondrules. Also Tieschitz chondrules and Solar System (chondritic) values from [2]

Both CAI are enriched in both Nb and Ta (Table 1). The mean of the measured Nb/Ta are 5.0 for 63RR and 4.7 for 61RR. Both CAI exhibit heterogeneous Nb/Ta values, ranging from 1 to 12.7, but the majority of 63RR analyses lie between 2.7 and 4.0, and 61RR between 1.0 and 3.2.

Hafnium and zirconium data for 63RR show that both of these elements are enriched, with mean Zr of 16.1ppm and Hf 0.37ppm (*viz*. 5.4 and 0.16 respectively for the preferred chondritic values [2]). Within error data for 61RR show no clear enrichments in the abundances of Hf or Zr, giving mean abundances close to bulk chondrite. Both CAIs show heterogeneous Zr/Hf between analytical spots.

The chondrules from Allende also show a range in Nb/Ta, though within individual chondrules, where measured, there is no evidence for internal heterogeneity. The range is somewhat more limited than observed in CAIs, from a chondrite-like 23, down to a CAI-like value of 3.8, the latter for an Al-rich chondrule. As Figure 1 shows there is little evidence for fractionation of Hf-Zr in the chondrules, with a mean value of 37.5 +/-3.2 (*viz*. chondritic 34.3 [2]).

Two analyses of Allende matrix yield abundances close to chondritic for all four refractory elements and Nb/Ta of 16.2 and 20.5, closely bracketing the bulk Solar System value. Similarly the Zr/Hf of 34.7 and 41.0 are close to the chondritic value and identical to the mean chondrule values.

Discussion: These CAI data demonstrate that CAIs in the Allende chondrite do indeed have Nb/Ta values that are sub-chondritic as suggested to explain the sub-Solar values imprinted upon the bulk CV chemistry [2]. However the data show that it is not only CAIs that bear the imprint of Nb-Ta fractionation, but also a sub-set of Allende chondrules. The two matrix analyses bracket the bulk Solar System value.

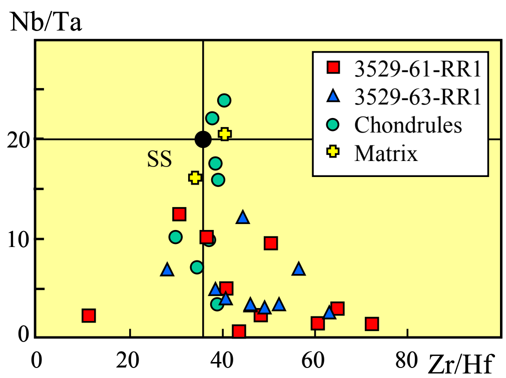

Figure 1. A plot of Nb/Ta against Hf/Zr for Allende objects. Also show is the Solar System (SS) value from [2]. Errors on the ratios are typically ca. 10%.

Implications for CAI-chondrule relations: The relationship between chondrules and CAIs remains uncertain. Our Nb-Ta data suggest that, in the case of Allende and, presumably other CVs, the chondrules and CAIs may have some genetic relationship. The presence of low Nb/Ta values in bulk CVs was used to suggest that these low ratios would be found in CAIs, the argument being that the CVs had far more CAIs than other chondrite types, hence would be the meteorites that would exhibit the signature most clearly. However, we have measured a population of chondrules within the CVs that also show comparably low Nb/Ta values. Either chondrule forming processes can also fractionate Nb-Ta or some chondrules inherited their Nb-Ta characteristics from their cohabiting CAIs.

If there were Nb-Ta fractionation of chondrules during chondrule formation it would require the ordinary, enstatite and carbonaceous (*sans* CV) heating to be a entirely local, closed system events with any chondrule variation from Solar System bulk values to be counterbalanced by an opposite effect in the matrix – an exhibition of the chondrule matrix complementarity.

In another study we have measured Nb-Ta ratios in two chondrules from the ordinary chondrite Parnallee – both of them have values that match, within error, that of mean chondrites (19.9 and 21.1). Although this is a small number of analyses of a very limited number of chondrules we find no evidence for fractionation of Nb from Ta during ordinary chondrite chondrule formation. Thus it appears that, barring a unique chondrule forming mechanism in the CV chondrite-forming region, it is difficult to account for the fractionation of Nb-Ta without inheritance from CAIs.

Signatures for CAI inheritance in CV chondrite chondrules abound, and include oxygen isotopes (^{16}O-rich chondrules abound in the CV chondrites) and REE signatures, with all types of CAI REE signatures represented in CV chondrules yet only rarely observed in ordinary chondrite chondrules. More controversially, it has been suggested that some live ^{26}Al was inherited, by some chondrules, from CAIs within the chondrule-forming region. The above features are all more abundant in chondrules from the CV chondrites, which contain a plethora of CAIs.

Collectively, these observations suggest that CAIs were indeed more abundant in the CV chondrite-forming region during the time of chondrule formation, not just at the time of accretion. This indicates chondrules were locally produced with respect to their parent bodies – there is no evidence for the admixture of the chondrules of the ordinary chondrites into carbonaceous chondrite materials, nor *visa versa*. Similarly the enstatite chondrites contain only enstatite chondrite chondrules without the presence of any other chondrule types. This limit on the degree of mixing between groups has implications for the degree of post-chondrule formation mixing in the nebula environment.

References: [1] Kornacki A.S. and Fegley B. (1986) *EPSL*, 79, 21. [2] Münker *et al*. (2003) *Science* 301, 84. [3] Wänke *et al*., (1974) *EPSL* 23, 1. [4] Ash et al. (2003) *LPSC* 34 [5]