EXPLORATION OF METHODS TO REMOVE TERRESTRIAL HIGHLY SIDEROPHILE ELEMENT CONTAMINATION FROM DESERT METEORITES.

K. S. Almas[1] and R. J. Walker[1], [1]Department of Geology, University of Maryland, College Park, Maryland, USA 20742 (kalmas@umd.edu).

Introduction: The majority of meteorite finds worldwide are increasingly limited to cold deserts (i.e., Antarctica) and hot deserts (e.g., Sahara) today. These meteorites have had residence times ranging from thousands to > 1 million years [1]. In most such meteorites, desert residency has led to some degree of open-system behavior with respect to chemical and isotopic compositions. For example, study of Antarctic meteorites has revealed variable effects of cryptic chemical alteration, even within individual mineral grains [2]. Meteorites found in hot desert environments have been shown to be even more prone to alteration than meteorites collected from cold [3, 4]. The effects of open-system behavior can be quite important, as they can make characterization of some aspects of the meteorite's parent body difficult or impossible to ascertain.

While numerous studies have focused on the movement of lithophile elements in desert meteorites [5, 6], one group of elements whose terrestrial alteration effects have been little studied are the highly siderophile elements (HSE; Re, Os, Ir, Ru, Rh, Pt, Pd, Au). The absolute and relative abundances of these elements in primitive meteorites have been used to assess nebular condensation and evaporation processes. These elements are also used to examine crystal-liquid fractionation in iron meteorites, and core formation and mantle-crustal processes occurring in the silicate portions of the parent bodies of achondrite meteorites. The HSE includes the ^{187}Re-^{187}Os radiometric system ($^{187}Re \rightarrow ^{187}Os + \beta^-$; λ for ^{187}Re = $1.666*10^{-11}$ yr^{-1}), which has proven useful for studying planetary mantle evolution [7] and the effects of late accretion to planetary bodies [8].

Studies of HSE in chondrites, ureilites, shergottites and brachinites have reported variability in the relative abundances of HSE, some of which likely resulted from open-system behavior in the terrestrial environment [9-12]. In particular, Re/Os and ^{187}Os/^{188}Os ratios appear to be highly sensitive to terrestrial alteration. These variations have commonly been attributed to Os loss or gain of Re [12]. The exact mechanisms of open-system behavior for HSE are currently poorly constrained.

Limited attempts have been made to circumvent the effects of terrestrial alteration on HSE in meteorites. In one study of shergottites, ultrapure acetic acid was used as a leaching agent to remove alteration [7]. Five out of 7 reported leachates were strongly enriched in Re by a factor of ten or more relative to that of the residue and the un-leached bulk samples, suggesting that Re was added to the desert meteorites, most likely by dust transport, followed by aqueous infiltration. To our knowledge, no further work has been conducted to explore methods to remove alteration of HSE from desert meteorites.

In this study ordinary chondrites are used to examine the effects of mild leaching on primitive meteorites, with the ultimate objective to remove terrestrial alteration without disturbing primary phases. Variable leaching times were used to identify the effects of acetic acid, the leaching agent, on the samples. Both a chondrite with a long residence time in the Sahara and a recent fall are examined to compare the amount of HSE removed per leach step.

Samples and Analytical Methods: Two ordinary chondrites were investigated: NWA 869 (L3-6, find), and Viñales (L6, fall). A major objective was to compare the effects of leaching on an altered find (W1 [13]) relative to a rapidly recovered fall (W0). Portions of the chondrites were crushed (>15 g pieces) using an alumina mortar and pestle, which was cleaned between samples using quartz sand. 50-100 mg powder aliquots were used in each analysis.

Sample aliquots were leached at room temperature with 1 mL *TraceMetal* grade glacial acetic acid from *Fisher Scientific*. The sample and acetic acid mixtures were manually agitated for 2 minutes, followed by variable resting times in order to identify the chronologic effect of the leaching agent on the bulk meteorites. Resting times of 4 minutes, 6 minutes, 1 hour, 4 hours, 1 day, and 1 week for each chondrite, were investigated.

After the resting period, the acetic acid (hereafter referred to as the leachate) was pipetted into a separate beaker and treated as unique sample. The leachates were then dried down and treated with ~1mL double-quartz-distilled concentrated HCl three times to remove organics. The residues were also dried under a heat lamp, as they retained trace amounts of acetic acid once the leachate was removed. The residues were also treated with concentrated HCl three times.

Following the HCl treatment, the residues and leachates were picked up in concentrated HCl and spiked with appropriate amounts of mixed ^{190}Os-^{185}Re, and platinum group element (^{191}Ir, ^{99}Ru, ^{194}Pt, ^{106}Pd) spikes. The samples were then processed to extract and purify the HSE following previously established procedures [14-16]. In brief, samples were transferred to *Pyrex* Carius tubes and sealed after the addition of doubly Teflon distilled HNO_3. They were then heated in an oven to 260°C for at least 36 hours. The Os was extracted from the resulting liquid phase using CCl_4 and microdistilled to further purify the Os before concentrations and isotopic ratios were measured using a *ThermoFisher Triton* thermal ionization mass spectrometer. Platinum, Ir, Re, Ru, and Pd were separated from the remaining liquid phase using anion exchange chromatography and were measured using a *Thermo Neptune Plus* multi-collector inductively coupled plasma mass spectrometer.

Results: The HSE and Re-Os systematics of bulk samples of both meteorites are similar to reports for other L chondrites. The Os concentration in leachates positively correlates with the length of the leaching time (**Fig. 1**). Data for other HSE in leachates of NWA869 also show a positive correlation with the length of the leaching time.

The leaching results show that the shorter leaching times (4 minutes-1 hour) preferentially remove small amounts of Os from phases characterized by low $^{187}Os/^{188}Os$ ratios (**Table 1**). The subchondritic ratios are not the result of terrestrial alteration, as terrestrial crustal Os is characterized by strongly suprachondritic Os. Subchondritic ratios have previously been reported for primary nonmagnetic phases in H chondrites [17]. As the leaching time increased, the Os accessed by the leachate evolved to a composition more representative of the bulk meteorites.

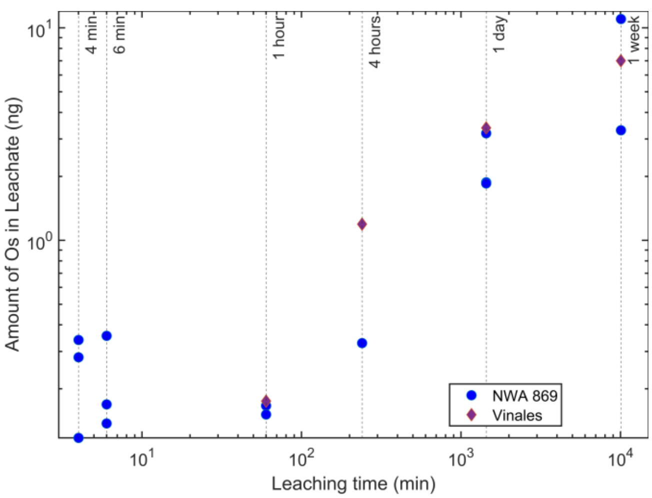

Fig. 1. Log-log plot of the amount of Os released from the sample in ng with leaching times.

Discussion: The Os data show an increasing effect of the leaching agent on the meteorites over time, leading to elevated Os abundance in the leachate. Given that Viñales is a fall and has experienced minimal terrestrial weathering, this indicates that primary phases are being dissolved.

The subchondritic $^{187}Os/^{188}Os$ ratios of the shorter term leachates in particular are not terrestrial in nature. Rather, a primary phase with a low $^{187}Os/^{188}Os$ ratio is being accessed; further Re analysis will clarify whether the disturbed phase would plot on a primordial isochron or Re and Os are being differentially leached from different phases. Easily soluble early solar system phases are being accessed by this mild leach; a more conservative leaching agent may be needed for chondrites.

Leach Length	NWA 869		Viñales	
	Leachate	Residue	Leachate	Residue
4 min	0.1217(3) n=3	0.1276(4) n=2	N/A	N/A
6 min	0.1145(9) n=3	0.1299(2) n=3	N/A	0.1282(1) n=1
1 hour	0.124(3) n=3	0.121(9) n=1	0.099(2) n=1	0.1261(3) n=1
4 hours	0.1236(1) n=1	N/A	0.1241(1) n=1	0.1271(1) n=1
1 day	0.1283(2) n=3	0.123(2) n=1	0.1233(2) n=1	0.1207(2) n=1
1 week	0.1297(1) n=2	0.1291(1) n=1	0.1294(1) n=3	0.1315(1) n=1
Bulk	0.1292(2) n=4		0.1254(5) n=3	

Table 1. $^{187}Os/^{188}Os$ ratios of leachates, residues, and bulk meteorites. Currently not available data are signified by N/A.

Conclusions: The initial methodology attempted does not appear to be appropriate for removing terrestrial HSE signatures from hot desert meteorites. While acetic acid is a mild leaching agent, evidence from both meteorites examined indicate removal of a primary, early solar system phase or phases. Additional HSE analyses of the leachates and residues will elucidate whether Re and Os are being affected similarly. Other leaching agents will be investigated that target specific altered phases commonly found in chondrites. Applications of this method will be extended to achondrites as they will not contain the easily dissolved phases accessed in this study.

References: [1] Welten, K. C. et al. (1997) *Meteorit Planet Sci*, 32(6), 775-780. [2] Floss, C. and Crozaz, G. (1991) *EPSL*, *107(1)*, 13-24. [3] Crozaz, G. and Wadhwa, M. (2001) *GCA*, *65(6)*, 971-977. [4] Crozaz., G et al. (2003) *GCA*, *67(24)*, 4727-4741. [5] Stelzner, T. H. et al. (1999) *Meteorit Planet Sci*, *34(4)*, 787-794. [6] Korochantseva, E. V. et al. (2005) *Meteorit and Planet Sci*, *40(9-10)*, 1433-1454. [7] Brandon, A. D. et al. (2012) *GCA*, *76*, 206-235. [8] Smoliar, M. et al. (1996) *Sci*, *271(5252)*, 1099-1102. [9] Walker, R. J. et al. (2002) *GCA*, *66(23)*, 4187-4201. [10] Rankenburg, K. et al. (2007) *GCA*, *71(9)*, 2402-2413. [11] Fischer-Godde, M. (2010) *GCA*, *74(1)*, 356-379. [12] Day, J. M. et al. (2012) *GCA*, *81*, 94-128. [13] Connolly, H.C. (2006) *Meteorit Planet Sci Archives*, *41(9)* 1383-1418. [14] Shirey, S. B. and Walker, R. J. (1995) *Anal. Chem.*, *67(13)*, 2136-2141. [15] Cohen, A. S. and Waters, F. G. (1996) *Anal. Chim. Acta*, *332(2-3)*, 269-275. [16] Birck, J. L. et al. (1997) *Geostand. Newsl.*, *21(1)*, 19-27. [17] Horan, M. F. et al. (2009) *GCA 73(22)*, 6984-6997.