CHARACTERIZATION OF THE DISTRIBUTION OF SIDEROPHILE AND HIGHLY SIDEROPHILE ELEMENTS IN THE MILTON AND EAGLE STATION PALLASITES

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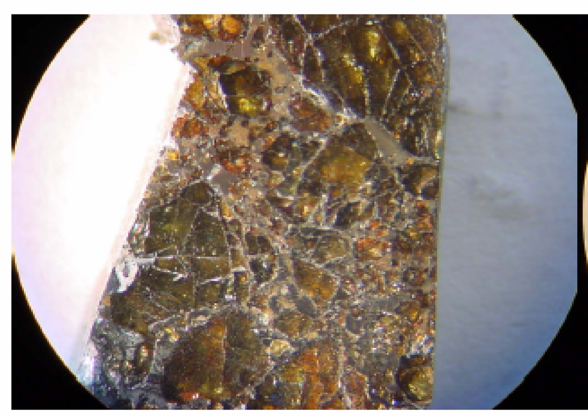
Introduction:

Pallasite meteorites may provide important information regarding the partitioning of siderophile and highly siderophile elements (HSE) between metal and silicate phases in magmatic systems. This information may in turn be used to predict the abundances of these elements present in the silicate portions of planetesimals and asteroids that segregated metallic cores.

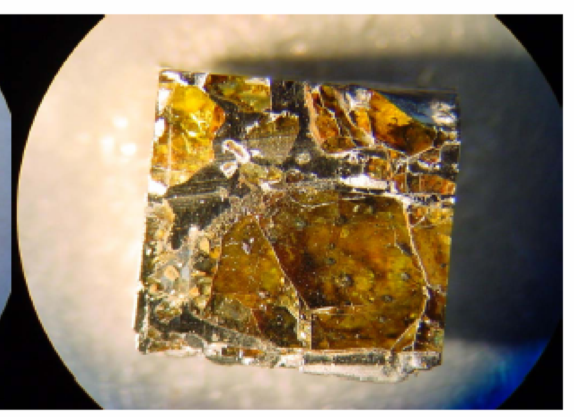
Here, we examine, through *in situ* techniques and isotope dilution measurements, the partitioning characteristics of several siderophile element and HSE in the Eagle Station and Milton pallasites to determine if the $D^{Metal/Silicate}$ in natural systems are comparable to the $>10^4$ range determined through study of synthetic materials [1].

Samples:

Eagle Station station is genetically grouped with two other pallasites, Itzawisis and Cold Bay, to form the Eagle Station grouplet [e.g. 2]. These three meteorites share common O isotopic compositions. Milton is not presently known to be genetically linked to any other pallasite [3].

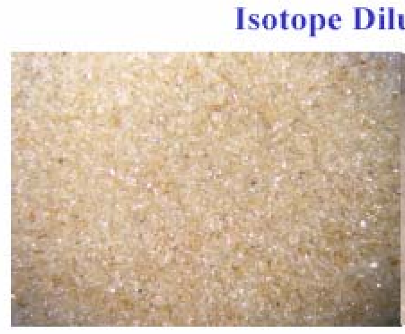


Milton: 1.5cm x .5 cm



Eagle Station: 1cm x 1cm

Isotope Dilution Samples



Eagle Station Olivine

Eagle Station Metal

Milton Olivine

Milton Metal

Eagle Station and Milton are particularly appropriate for this type of study because previous studies have shown that bulk samples of these meteorites have much higher abundances of siderophile elements and HSE than bulk samples of main group pallasites or mesosiderites [2-3]. Thus, the expectation that initiated this study was that the abundances of at least some elements of interest present in the silicate phases may be at levels sufficiently high to be determined via *in situ* spot analysis using laser ablation ICP-MS.

Analysis Methods

Samples of the Eagle Station and Milton pallasites were prepared for analysis by polishing using a 3 step procedure including 600 grit sanding paper, 0.3µm aluminum polishing compound, followed by a 0.1 µm aluminum polishing compound to achieve a smooth, pit free surface. Polished samples were carbon coated and analyzed using a JEOL *JXA-8900* Electron Microanalyzer for major and minor elements in the metal phases (Fe, Ni, Co, Cu, and Cr) and olivine (Mg, Fe, Ca, Mn, Ni, Cr and Si). The following conditions were employed: accelerating voltage of 15 keV, 10 nA sample current, and a 5 µm diameter beam. Peak and background intensities were measured for all elements, and raw intensities were compared to intensities from natural standards, and corrected using a CIT-ZAF algorithm.

Laser Ablation Parameters

- Analysis conducted using laser ablation ICP-MS
  - 213 nm Nd:YAG laser coupled to an *Element 2*, magnetic sector ICP-MS
- Small volume in-house developed ablation cell
  - Flushed with He (~1.2 mL/min) and Ar (~0.6 mL/min)
- Optimum maximum signal intensity of ~ 10^6 cps
- Time-resolved spectra
  - Acquisition of ~20 seconds of gas background followed by 40-80 seconds of signal.
- Spot Sizes:
  - Range between 20-60µm for metal and up to 160µm for olivine.

Analyses of unknowns were evaluated using a range of standard materials (i.e., NIST glasses and metals, Hoba and Filomena meteorites, and an in-house PGE-bearing sulfide standard). Siderophile and highly siderophile element concentrations were determined for sampling sites that were first examined via electron probe microanalysis. To minimize contamination during ablation, the olivine crystals in each pallasite were analyzed prior to the metals.

Results

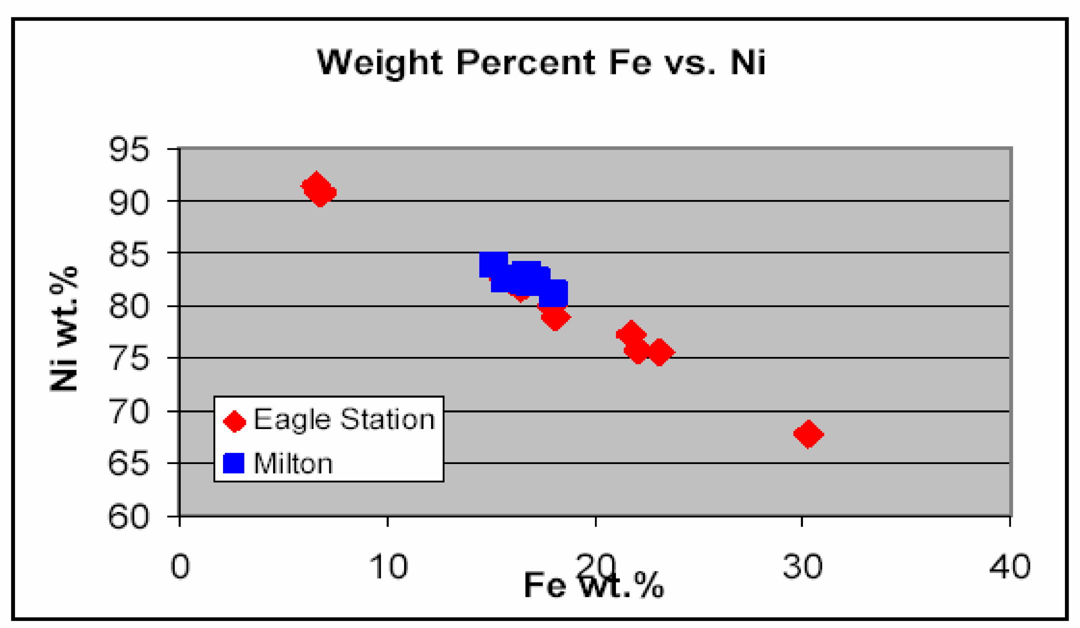
Electron probe microanalysis of olivines in Eagle Station and Milton show that their Fo contents (Fo=atomic % Mg/(atomic % Mg + atomic % Fe) x 100) are 84.1±0.4 (2σ) and 80.4±0.4 (2σ) respectively (Table 1). Major element weight percents determined by electron probe microanalysis show slight deviations from average in the olivine crystals of both pallasites. Data for metal phases reveal that Milton is generally homogeneous

Table 1. Electron microprobe data summary for olivine and comparison to previously reported data.

Milton	MgO	MnO	CaO	SiO2	FeO	Cr_2O_3	NiO	Total	Fo
Average Wt. %	45.2	0.13	0.17	39.2	15.2	0.06	0.05	100.1	84.1
St. Dev (2-sig.)	0.69	0.05	0.11	0.34	0.44	0.03	0.02		0.4
Jones *et al.* (2003)	44.3	0.13	0.12	39	16.4	0.09			82.8
Eagle Station	**MgO**	**MnO**	**CaO**	**SiO2**	**FeO**	**Cr2O3**	**NiO**	**Total**	**Fo**
Average Wt. %	42.7	0.19	0.05	38.7	18.5	0.03	0.05	100.25	80.4
St. Dev.	0.78	0.06	0.03	0.57	0.55	0.01	0.02		0.41
Mittlefehldt (1898)	49.1	0.2	0.1	38.7	19.0	0.0			79.8

while Eagle Station has a much more heterogeneous taenite (Figure 1).

Figure 1. Fe wt.% vs. Ni wt.% of Eagle Station and Milton.



The concentrations of major, minor, and trace elements show significant variation in the olivine phases of both meteorites (Table 2). Eagle Station shows a high degree of heterogeneity in olivines, as indicated by a range of concentration values. While Milton shows similar patterns, its olivine heterogeneity is less extensive for most elements. Milton metal is generally homogeneous, whereas metal compositions have large variations in Eagle Station. Concentrations of minor and trace elements for metal and silicate are provided in Table 2. Of note, the concentrations of most HSE, including; Ru, Rh, Pd, Re, Os, Ir, Pt, and Au, were detected at the ppt level in both pallasites. Analysis of bulk metal show Os concentrations in the taenite of both pallasites are roughly 10% greater than that of LA-ICP-MS values (Table 3). As such, the iron meteorite Coahuila will be analyzed via ICP-MS and used to further calibrate data. Concentrations of Os in bulk olivine separates are significantly higher than that determined through LA-ICP-MS. This is a result of metal or sulphide inclusions remaining in the olivine after purification.

Table 2. Concentration data for olivines and metal.

(ppt)	Eagle Station		Milton			Eagle Station		Milton	
Olivines	average	±	average	±	Metals	average	±	average	±
Sc*	2.9	0.4	4	0.4	Fe %	80.5	4.7	82.5	0.3
V*	9.9	0.5	17	1	Co*	6660	668	8790	38
Cr*	156	34	574	133	Ni %	17.6	4.9	16.5	0.5
Mn*	1470	10	1230	10	Cu*	80	4	256	20
Fe %	14.4	0.22	11.8	0.17	Ga*	--	--	33	10
Co*	20	1	31	5	Ge*	129	132	55	9
Ni*	49	1	84	21	As*	75	44	7.2	1.5
Olivines	**min**	**max**	**average**	**±**	Mo*	--	--	14	2
Ru	600	1000	320	200	Ru*	2.3	1.4	31	5
Rh	100	1600	50	40	Rh*	2.4	1.3	5	1
Pd	40	2300	280	180	Pd*	3.5	0.5	5.2	0.1
W*	4000	79000	14.2	0.1					
Re	100	2000	610	310	W*	46	53	1.2	0.1
Os	10	150	180	40	Re*	0.5	--	5.1	0.6
Ir	10	190	130	20	Os*	18	13	51	3
Pt	70	6500	140	40	Ir*	14	11	45	2
Au	20	620	120	0.03	Pt*	1.6	1.9	33	1
Scans	7		5		Au*	--	--	130	130

*Concentrations in ppm

Red: Inclusion w/ Pt=510±175ppt and Au=390±330ppt

Table 3. Os concentrations and $D^{metal/silicate}$ calculated from LA-ICP-MS and isotope dilution of bulk samples.

Sample	Isotope Dilution Os (ppb)	Laser Ablation Os (ppb)
Coahuila 1	10123	---
Coahuila 2	10119	---
Eagle Station Metal	15099	9000-33000
Eagle Station Olivine	12.24	.01-.15
Milton Metal	46554	51000
Milton Olivine	24.6	0.18
D-values		
Eagle Station	1.23E+03	6.96E+05
Milton	1.89E+03	2.79E+05

Calculated metal/silicate partition coefficients are variable between the two pallasites (Table 4). Siderophile elements, including Ni, Co, and W in both pallasites fall within the 10^2-10^4 range with the exception of W in Milton which has a $D^{metal/silicate}$ of 8.5×10^1. All of the HSE $D^{metal/silicate}$ fall within the proposed 10^4-10^6 range with the exception of Re, Au, and possibly Pd.

$^{187}Os/^{188}Os$ ratios were also determined during the bulk analysis of Eagle Station and Milton (Table 5). These ratios show that Eagle Station metal is in isotopic equilibrium with olivine. This isotopic equilibrium could indicate mixing during the formation of the meteorite or metal contamination during the purification process. This, however, is not the case for Milton. Metal and olivine in Milton have significantly different $^{187}Os/^{188}Os$ ratios of 0.1371 for metal and 0.1308 for olivine.

Table 4. Minimum Metal/Olivine D-values based on concentration data.

	Eagle Station	Milton
Fe	5.81.E+00	6.99.E+00
Co	3.70.E+02	2.51.E+02
Ni	2.90.E+03	1.96.E+03
Cr	---	2.53.E-02
Ru	6.11.E+04	5.26.E+04
Rh	8.58.E+04	1.03.E+05
Pd	6.75.E+03	2.49.E+04
W	1.36.E+03	8.45.E+01
Re	8.27.E+03	8.39.E+03
Os	6.96.E+05	2.79.E+05
Ir	9.98.E+05	3.52.E+05
Pt	1.40.E+04	2.42.E+05
Au	6.03.E+03	1.11.E+03

Table 5. Isotopic ratios of Coahuila, Milton, and Eagle Station determined through isotope dilution of bulk samples.

Sample	$^{187}Os/^{188}Os$
Coahuila 1	0.14152
Coahuila 2	0.14155
Eagle Station Metal	0.12477
Eagle Station Olivine	0.1251
Milton Metal	0.13711
Milton Olivine	0.1308

Discussion

Metal/silicate partition coefficients for siderophile and HSE in Milton and Eagle Station, are broadly similar to those determined for synthetic materials [1]. Some Metal/silicate D-values for HSE including Pd, Re, and Au in Eagle Station are below 10^4, while the remaining HSE are between 10^4-10^5. All HSE in Milton have metal/silicate D-values within the 10^4-10^5 range, with the exception of Re and Au.

At face value, the results for Eagle Station and Milton suggest that some silicates in contact with metal in planetary bodies retain relatively high concentrations of siderophile elements and HSE. Nonetheless, the relative abundances of the HSE would be highly fractionated from chondritic.

Conclusions:

1. It is now possible to directly measure the concentrations of siderophile and HSE elements in the silicate phases of some pallasite meteorites.
2. Metal-silicate partition coefficients for siderophile and HSE obtained for Milton and Eagle Station are broadly similar to values determined for synthetic systems with the exception of Pd, Re, and Au [1].
3. Metals and olivine in Eagle Station have similar $^{187}Os/^{188}Os$ ratios whereas, the $^{187}Os/^{188}Os$ ratios in the metal and olivine of Milton are significantly different.

References:

[1] Borisov A. & Palme H. (1997) *GCA* 58, 705-716. [2] Wasson J.T. and Choi B.-G. (2003) *GCA* 67, 3079-3096. [3] Jones R. (2003) *LPSC XXXIV*, 1683

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