Age-dating and Trace Element Analysis of Pallasite Meteorites

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ABSTRACT

This study hopes to investigate the age and formation conditions of two pallasite meteorites, Esquel and Springwater. The olivine and metal phases of the samples were separated and each analyzed for lead isotope ratios, uranium and lead isotope concentrations, and trace element concentrations. The lead isotope ratios and uranium and lead concentrations were done using a Thermal Ionization Mass Spectrometer, while the trace element concentrations were analyzed with an Inductively Coupled Plasma Mass Spectrometer. Initial age estimates suggest that the accretion of the pallasite parent bodies occurred 4.5×10^9 yr ago, and the core-formation of the Esquel parent body could have possibly occurred 4.3×10^9 yr ago.

INTRODUCTION

METEORITES

Occasionally one can spot a meteor as it runs across the night sky. Most often these fragments moving around our solar system burn up as they encounter the earth's atmosphere, but larger ones sometimes remain intact and are known as meteorites. Though not always easily recognized, meteorites can hold valuable information about the history of other bodies in the solar system, and even earth itself (Dalrymple 1991, p 257).

Three major classifications of meteorites are recognized. Meteorites in the first category, stony meteorites, are generally grouped together due to their high content of silicate minerals. These are further divided into chondrite and achondrite types. Chondrites typically have not undergone differentiation and include small, millimeter-scaled globules of silicate minerals known as chondrules, which are thought to contain some of the solar system's most primitive material. Achondrites, however, contain no chondrules and have been altered by one or more processes, no longer representing primitive material. They are composed of silicate minerals and closely resemble igneous rocks found on earth, suggesting that they would have occupied the mantle of a differentiated parent body. Stony meteorites represent the greatest percentage of meteorite falls (documented sight and recovery of a meteorite), but do not have a high percentage of meteorite finds (no sighting of the fall) since they are more fragile and blend in with terrestrial rocks better than the other types of meteorites (Dalrymple 1991, p 264-272).

Iron meteorites are more easily found on earth due to their composition. The nickel-iron alloy they are composed of is more stable in the earth's environment and gives them a unique appearance. This category is divided into groups based on two factors, the structure and the chemistry. These meteorites are thought to represent the core of differentiated bodies or trapped metallic melts (Dalrymple 1991, p 265,274).

The third type, the stony-iron meteorites, are a combination of properties of the two other groups. The have roughly equal parts of silicate and metallic nickel-iron alloy, with the silicate dispersed in the metal matrix throughout the meteorite. The presence of both these phases in the meteorite would suggest its formation at the core-mantle boundary of its parent body.

PALLASITES

One group of stony-iron meteorites, the pallasites, are composed mainly of olivine (often gem quality) and nickel-iron alloy. Based on their exact compositions they are divided into three subgroups, the pallasite main group (PMG), the Eagle Station grouplet, and the pyroxene grouplet. It has been suggested that the meteorites in each subgroup share the same parent body (a differentiated asteroid), though geochemical analysis shows that some anomalous meteorites may have their own individual origins (Mittlefehldt 1999).

Some studies of pallasites attribute their formation to one or more impacts (or other energetic events) on the parent body that resulted in the mixing of solid olivine in the mantle with liquid metal from the core. This idea seems to be based solely on the observation that the olivine crystals are somewhat angular and therefore were fragmented at some time. The competing idea is that the pallasites formed from incomplete separation during more equilibrium conditions (Ulff-Møller, et al. 1998).

This study focuses on the age determination of pallasites using lead isotopes and also on the conditions of meteorite formation using information gathered from trace element concentrations.

EXPERIMENTAL PROCEDURE

Two pallasite main group (PMG) meteorite samples, Esquel and Springwater, were selected to be analyzed. Ranchers in Argentina found the Esquel pallasite in 1951. The amount available for study was roughly 2 g from the main mass of 680 kg. This sample included both the metal matrix and gem quality subangular olivine crystals. Other minor mineral phases that have been reported by others in Esquel are troilite, chromite, and schreibersite (Ulff-Møller, et al. 1998).

The Springwater pallasite was recognized in 1931, after being discovered just 100 miles west of Saskatoon in Saskatchewan, Canada, near the town of Springwater. At least three separate masses of 39 kg, 19 kg, and 10 kg have been found (Nininger 1971). 3 g were available for this study, which contained both rounded to subrounded olivine and metal. Other minor mineral phases found in Springwater by others are schreibersite and troilite (Nininger 1971). The rare phosphate mineral farringtonite was also discovered in Springwater (Hsu 2003).

SAMPLE PREPARATION

Mineral Separation

The olivine and metal phases in both samples were separated, using a small hammer to break out olivine pieces, and cutters to take off a piece of metal from the Esquel sample (the Springwater sample was already broken). Each piece was viewed beneath the microscope to ensure that the olivine was free of metal and inclusions, and that the metal contained no other phases. It was necessary to soak the Esquel pieces in acetone to remove the epoxy coating present. The Esquel and Springwater olivine samples were then cleaned in 2% HNO_3, and the metal samples were cleaned with methanol. An agate mortar and pestle was used to grind up the olivine crystals into a powder. All samples were taken into the clean lab to be weighed. The mass of the samples was as follows: Esquel olivine 0.04175 g, Springwater Olivine 0.03676 g, Esquel metal 0.26965 g, Springwater metal 0.10751 g.

Mineral Dissolution

These known amounts of sample were then dissolved. The olivines were dissolved in 2 ml of 47% HF, along with about 1/10 ml of 7N HNO_3 so that a soluble salt would form. The metal samples were dissolved by adding 2 ½ ml of 6N HCl. An olivine blank and a metal blank were also created at this point, undergoing every step the same as the samples. After the samples dissolved in the acid, they were evaporated to dryness.

The samples were then divided by dissolving them again in 2.5 ml of 2.5N HCl and going through a process of weighing an empty clean beaker, adding the sample, weighing again, pouring part into a new beaker, and then weighing the beaker one last time. The amount of sample contained in each beaker was then calculated from this. The samples were each divided twice, resulting in a total of four parts for each of the four samples and two blanks. The mass of sample in each part has been listed in FIGURE 1.

Sample Description	Sample Designation	Mass (grams)
Esquel Olivine	EO1A	0.00895
	EO1B	0.00892
	EO2A	0.00944
	EO2B	0.01443
Springwater Olivine	SO1A	0.00875
	SO1B	0.00906
	SO2A	0.01151
	SO2B	0.00744
Esquel Metal	EM1A	0.07546
	EM1B	0.05554
	EM2A	0.09017
	EM2B	0.04848
Springwater Metal	SM1A	0.01850
	SM1B	0.02433
	SM2A	0.03602
	SM2B	0.02866

FIGURE 1: Mass of Sample in Divisions

One division was set aside for lead isotope ratio analysis, another for isotope dilution analysis, and a third for trace element analysis. The fourth part was saved for further research.

LEAD ISOTOPE RATIO

Lead Columns

The samples designated for lead isotope ratio analysis were evaporated to dryness and then dissolved again with 0.5N HBr (0.5 ml for all but the larger Esquel metal sample, to which was added 1 ml). Lead ion exchange columns were set up to use for the separation

of lead from the other elements in the sample. Resin was placed in the stem of the column and then it was cleaned and conditioned with the following series of acids, described in FIGURE 2 below:

Cleaning, add:		
	1.0 ml	0.25N HNO_3
	1.0 ml	0.25N HNO_3
	0.5 ml	6N HCl
Conditioning, add:		
	0.2 ml	0.5N HBr
	0.2 ml	0.5N HBr
	0.2 ml	0.5N HBr

FIGURE 2: Lead Column Cleaning and Conditioning Acid Steps

After conditioning and cleaning, the sample (dissolved in 0.5N HBr) was loaded onto the column. An additional 0.5 ml of 0.5N HBr and 0.2 ml of 2N HCl were added (separately) to the column. These acids stripped off other elements from the sample, which, at that point, was being held by the resin. Clean beakers were put in place and 0.7 ml of 6N HCl was put through the column. This released the lead from the resin and it was collected in the beakers, which were then evaporated to dryness.

This process was repeated in order to ensure that the lead was isolated. All steps were the same except the last, where 1.5 ml of 0.4N HCl was used to collect the lead, instead of the 0.7 ml of 6N HCl used on the first run.

LEAD AND URANIUM ISOTOPE DILUTION

Uranium Columns

After division, a lead and uranium spike was added to the isotope dilution portion of the samples, and a lead calibration and uranium calibration sample was also made. They were then evaporated to dryness and later dissolved in 0.5 ml of 7N HNO_3.

The uranium ion exchange columns were assembled and filled with resin. They were then cleaned and conditioned by adding a series of acids, shown in FIGURE 3 below.

Cleaning, add:		
	3 ml	7N HNO_3
	3 ml	7N HNO_3
	2 ml	QD H_2O
	3 ml	6N HCl
	3 ml	6N HCl
	2 ml	QD H_2O
Conditioning, add:		
	1 ml	7N HNO_3
	1 ml	7N HNO_3

FIGURE 3: Uranium Column Cleaning and Conditioning Acid Steps

A new beaker was put in place as the addition of the next acids, 0.5 ml of 7N HNO_3, 0.625 ml of 7N HNO_3, and 2 ml of 6N HCl, separated lead from the sample. This solution was then evaporated to dryness and put through the lead columns in the same manner as described above (though only one time through was necessary). The uranium from the sample was then collected in a new beaker by adding 0.6 ml of 1N HBr and another 0.6 ml of 1N HBr. This was also evaporated to dryness.

THERMAL IONIZATION MASS SPECTROMETRY

Filament Making and Loading

The Thermal Ionization Mass Spectrometer (TIMS) (which uses a current to heat the sample and give off ions) used to analyze the lead isotope ratios and lead and uranium isotope dilutions requires the samples to be loaded onto filaments. Single filaments were made using rhenium ribbon. After cleaning in a degasser, droplets of silica gel and H_3PO_4 were placed on the center of the filament and then about 1 μl of sample was dropped on top. The filament was heated by a current to dry this mixture. The samples were then loaded into the magazine and analyzed in the TIMS machine.

TRACE ELEMENT CONCENTRATION

Standard Preparation

A standard solution was prepared that contained 100 ppb of each element requiring analysis. These elements are listed below in FIGURE 4.

Niobium	Uranium	Iron	Lead	Nickel
Chromium	Cobalt	Copper	Gallium	Manganese
Molybdenum	Tantalum	Titanium	Vanadium	Zinc
Iridium	Gold	Germanium	Indium	

FIGURE 4: Elements for Concentration Analysis

The solution was made from the addition of 1 ml of each element's standard (in 10 ppm) and then diluted 100 times by adding 2 % HNO_3. The iron standard had to first be diluted to 10 ppm, however. The entire standard solution was then diluted 100 times again.

The samples were dissolved with a little 2% HNO_3 and then diluted with more 2% HNO_3 to make a solution of 100 ml. A portion of these samples was then diluted again by 1000 times with 3% HNO_3.

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

The Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used to analyze the trace element concentrations. This machine produces ions by aspirating the sample solution into a stream of argon plasma. The samples were analyzed for the 19 elements mentioned above (FIGURE 4), as was the standard solution. The analysis of a few elements that indicated a counts per second value that was too large was done with the sample portion that had been diluted an additional 1000 times.

RESULTS

LEAD ISOTOPE RATIO RESULTS

Data was obtained from the run of the Esquel olivine, Esquel metal, and Springwater olivine samples (FIGURE 5). The Springwater metal sample, however, did not produce satisfactory results and will be redone.

Sample Name	Pb 206/204 ratio	Pb 207/204 ratio
EO2B	18.77	15.56
EM2A	17.81	15.07
SO2A	18.83	15.63

FIGURE 5: Lead 206/204 and 207/204 Ratios

These ratios were used with the following equation to calculate the age of the samples:

$$\frac{\Delta\, {}^{206}Pb/{}^{204}Pb}{\Delta\, {}^{207}Pb/{}^{204}Pb} = \frac{1}{137.88} \frac{(e^{\lambda 238\, t} - 1)}{(e^{\lambda 235\, t} - 1)}$$

(This equation was arranged from the decay equations of ${}^{238}U$ to ${}^{206}Pb$ and ${}^{235}U$ to ${}^{207}Pb$. $\lambda 238$ and $\lambda 235$ are the decay constants of ${}^{238}U$ and ${}^{235}U$, with values of 1.55125×10^{-10} yr^{-1} and 9.8485×10^{-10} yr^{-1}, respectively. The initial lead ratio values are assumed to be those of the Canyon Diablo Troilite, with values of 206/204 = 9.31 and 207/204 = 10.29)

The lead ratio values were graphed (FIGURES 6 & 7), along with the Canyon Diablo Troilite values.

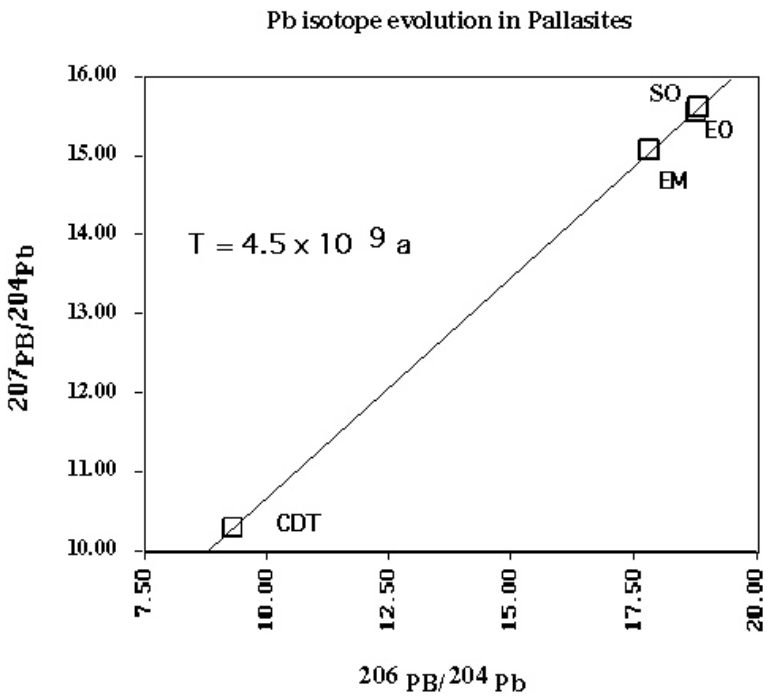

FIGURE 6: Pb Isotope Evolution in Pallasites

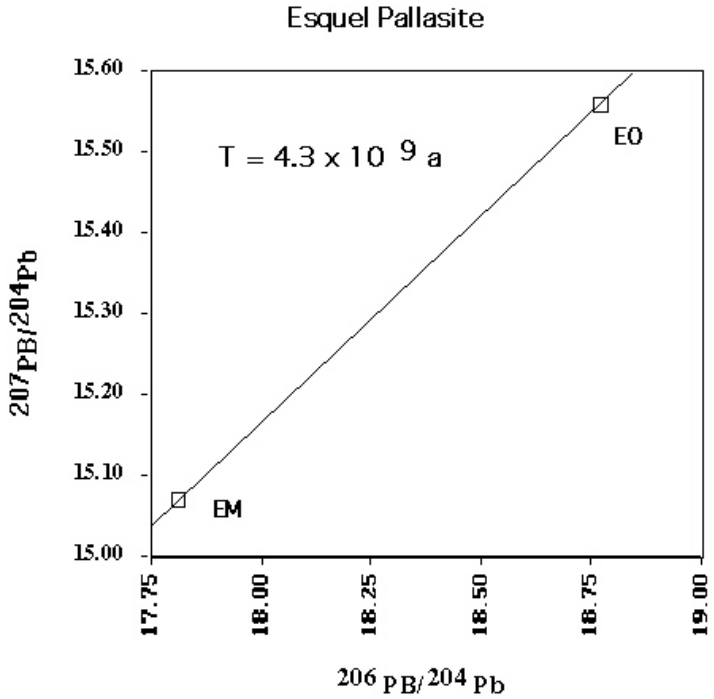

FIGURE 7: Esquel Pallasite

The slope of the best-fit line between them corresponds to the second part of the equation mentioned above. Since this equation cannot be directly solved for t, a process of trial and error was used, inputting different values of t to narrow in on the observed slope. This process has not been completed, but initial estimates indicate that all three samples had the same lead ratios 4.5×10^9 yrs ago, and the Esquel metal and Esquel olivine samples had the same ratios 4.3×10^9 yrs ago.

LEAD AND URANIUM ISOTOPE DILUTION RESULTS

Satisfactory data has not been obtained from the lead and uranium isotope dilution samples on the TIMS machine, though work will continue so that results can be provided in the future.

TRACE ELEMENT CONCENTRATION RESULTS

Interpretation of the data from the trace element analysis with the ICP-MS has not been completed. This will be done and available at a future date.

CONCLUSION

Even with the preliminary results reported here, much has been learned about the Esquel and Springwater pallasite meteorites. The 4.5×10^9 yr age estimate probably represents the last time that the material was together; in this case, that might be the age of accretion of the parent bodies. The 4.3×10^9 yr age estimate could be how long ago core formation occurred on the Esquel parent body, assuming equilibrium separation and not mixing due to a high-energy event. The lead and uranium isotope dilution data will provide a way to check these ages, while the trace element concentrations will present ways to get more information about the conditions of the formation of pallasites. Also in the future it is hoped to use the last portion of the samples to date the timing of their formation after the formation of the heavy elements in the solar system. This will be done by measuring ^{182}W and using the decay of ^{182}Hf to ^{182}W as the dating clock. This should bring new insight on the history of pallasite meteorites and their parent bodies in the solar system.

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