

# Comparative Partitioning of Hf and W in Silicates: A Key to Understanding Radiogenic W in Terrestrial Planets

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## Introduction

In contrast to the W isotope signature of basalts from Earth (1), some lunar and Martian samples have a radiogenic W signature, i.e.  $\epsilon^{182}\text{W} > 0$  (2). This radiogenic W isotopic signature may originate from early Hf-W fractionation during core formation or from early Hf-W fractionation during differentiation or magma ocean crystallization. The former process is relatively well understood because Hf is lithophile and W is siderophile;. Over 100 metal-silicate partition coefficients have been determined for W (e.g., 3). In this study, we investigate the partitioning behavior of W in a variety of silicates that may have been stable in magma ocean environments, evaluate their role in generating W isotopic signatures observed in lunar rocks and speculate about the early differentiation of the terrestrial planets and the Moon.

## Experimental-Analytical Approach

Experiments were conducted in a 1/2" non end-loaded piston cylinder apparatus (10-20 kb) and Walker-style multi-anvil press (40-100 kb) at the University of Arizona. Experimental details are presented elsewhere [4]. Three silicate compositions were used: a calc-alkaline basalt for olivine-, augite- and plagioclase-liquid equilibrium, and alkali basalt for garnet-liquid and pyroxene-liquid equilibrium, and a synthetic eucrite basalt for orthopyroxene-liquid, and garnet-liquid equilibrium. Each composition was doped with ~ 0.5 wt%  $\text{WO}_3$ . Oxygen fugacity in each run was monitored with a sliding redox sensor of Co-(Co,Mg)O. Phases produced in all experimental charges were analyzed using a CAMECA SX-50 electron microprobe, with operating conditions as outlined in [4]. All solid phases were analyzed with a point beam. Some liquids did not quench to a glass and thus were analyzed with a rastered beam (10  $\mu\text{m}$  x 10  $\mu\text{m}$ ). Equilibrium was monitored in these experiments by measuring olivine-liquid and garnet-liquid MgO-FeO Kd's. Tungsten was measured in the crystalline and glass phases using the Cameca ims 4f operated on the University of New Mexico campus by a UNM-Sandia National Laboratories consortium. Analyses were made using primary  $\text{O}^-$  ions accelerated through a nominal potential of 12.5 kV. A primary beam current of 25 nA was focused on the sample over a spot diameter of 20  $\mu\text{m}$ . Sputtered secondary ions were energy filtered using a sample offset voltage of 120 V and an energy window of  $\pm 50$  V. Initial analyses involved repeated cycles of peak counting on  $^{182}\text{W}$ ,  $^{184}\text{W}$ ,  $^{186}\text{W}$  and  $^{30}\text{Si}$ . The analytical procedure included counting on a back-

ground position to monitor detection noise. Absolute concentrations of each element were calculated using empirical relationships of  $\text{W}/^{30}\text{Si}^+$  ratios (normalized to known  $\text{SiO}_2$  content) to element concentrations as derived from daily calibration. A calibration curve was constructed using a series of W-bearing glasses synthesized in the lab (Figure 1) and analyzed independently using the electron microprobe. Determination of W in individual mineral phases assumes that ionization efficiency is the same as the glass standards. Additional studies evaluating this assumption are currently being made.

## Results and discussion

D's for W partitioning between garnet-melt, olivine-melt, orthopyroxene-melt, clinopyroxene-melt, and plagioclase-melt were measured. The initial ion probe results combined with results from previous studies indicate that many of the phases will not significantly fractionate Hf from W during the crystallization of a basaltic melt. Pyroxene will fractionate Hf from W, although the extent of fractionation is dependent upon the pyroxene composition (i.e. Ca in the M2 site). To a smaller degree, garnet may also fractionate Hf from W. Ilmenite is also capable of fractionating Hf from W [5], and this will be important for interpreting lunar data where ilmenite is present in the source region. These initial observations suggest that the crystallization of ilmenite and high-Ca pyroxene from the lunar magma ocean (LMO) was capable of producing W anomalies in the lunar mantle. Because ilmenite and high-Ca pyroxene crystallized during the very late-stages of LMO evolution [6], these late-stage cumulates carried the radiogenic W signature. In addition, the radiogenic W values measured in Martian samples may be produced by combined garnet and clinopyroxene fractionation, also supported by other isotope systems.

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