

# INITIAL TUNGSTEN ISOTOPIC COMPOSITIONS FOR ANGRITES OBTAINED FROM PHOSPHATES

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**Introduction:** Hafnium-tungsten chronometry is useful to determine the timing of planetary accretion and core formation as well as also to determine ages of crystallization and metamorphism [1]. Important constraints on any isochron are placed by sampling the most radiogenic phase and the least radiogenic phase available in a meteorite. An important challenge for Hf-W chronometry of achondrites is the dearth of metal, usually the phase with the least radiogenic W. Angrites are among the most ancient basaltic meteorites with U-Pb ages of 3-8 Ma [2]. Recent Hf-W dating of angrites established ages of core formation on the Angrite Parent Body (APB), and provided constraints on the ages of CAIs [3, 4]. In these Hf-W studies, clinopyroxene was found to have the highest Hf/W ratio, consistent with experimental partition coefficients for Hf and W [5]. However, the fraction with the lowest Hf/W was usually a set of fines, with  $180\text{Hf}/184\text{W}$  only slightly lower than that of the bulk rocks [3, 4].

Shirai et al. [6] determined the internal distribution of moderately siderophile elements, including W, in angrites by LA-ICP-MS. They reported verbally that the main carrier phase for W in angrites was phosphates, either whitlockite ( $\text{Ca}_3(\text{PO}_4)_2$ ) (NWA 4801) or a silico-phosphate (NWA 4590), and that these phases have low Hf/W ratios. Therefore, phosphates permit accurate determination of initial W isotopic compositions for angrites, and potentially other achondrites. Here we report elemental compositions of phosphates from NWA 4590, NWA 4801, SAH 99555, LEW 86010, and ADOR. We also report a low-blank procedure to extract W, and the first results of W isotopic composition of these fractions in NWA 4590 and D'Orbigny.

**Analytical methods:** Analytical details for the laser ablation procedure followed Shirai et al. [6], and are not repeated here. Analytical details for the leaching and W isotope composition determination are reported below. About 1 g of the angrites NWA 4590 and D'Orbigny were gently crushed and sieved into four size fractions, <143  $\mu\text{m}$ , 143-350  $\mu\text{m}$ , 350-500  $\mu\text{m}$  and >500  $\mu\text{m}$ . Two fractions (143-350  $\mu\text{m}$  and 350-500  $\mu\text{m}$ ) were put through magnetic separation to obtain pyroxene.

Chemical leaching on each of the four different size fractions was performed as follows. To extract metal and sulfide, the samples were first leached with 6M HCl and 1%  $\text{H}_2\text{O}_2$  in an ultrasonic bath for 30 min.

The silico-phosphates of terrestrial analogs were found to be soluble in conc.  $\text{HNO}_3$  with trace HF added. To remove whitlockite from the samples, concentrated  $\text{HNO}_3$  and 0.1%  $\text{H}_2\text{O}_2$  was used. Then, concentrated HCl and 1%  $\text{H}_2\text{O}_2$  was applied for 3 hrs. To extract the silico-phosphates concentrated  $\text{HNO}_3$  and 0.01% HF was applied for 2.5 hrs at  $150^\circ\text{C}$ . In order to insure quantitative recovery of the W in solution, the residues were washed with 2%  $\text{HNO}_3$  and 0.1%  $\text{H}_2\text{O}_2$  in an ultrasonic bath after each leaching step, and this solution was combined with the main leachate. Elemental abundances of these solutions was determined by Finnigan Element<sup>TM</sup> ICP-MS.

Separation of W from sample matrix was carried out by using anion exchange resin following procedures used in W isotope determinations of meteorites [7]. We noted that Ca was not efficiently removed by the anion exchange step, so a small cation exchange column (0.5 ml Bio-Rad AG50-X8) was used for final cleaning prior to mass spectrometry. The sample was added in 0.1N  $\text{HNO}_3$  with 1%  $\text{H}_2\text{O}_2$ , and the W was eluted from the column with the same solution. Tungsten isotopic analyses were made using a Thermo NEPTUNE multicollector ICP-MS at the NHMFL. An APEX<sup>TM</sup> desolvating nebulizer was used to introduce W solutions into the plasma. We obtained ~2 V signal from a 15 ppb W solution, and collected 60 ratios for each analysis. Measurements of each sample were bracketed with multiple measurements of the NIST SRM 3163 W standard. Instrumental mass fractionation was corrected by normalizing to  $^{184}\text{W}/^{183}\text{W} = 2.033$  using the exponential law. Osmium interferences on masses 186 and 184 are corrected by monitoring  $^{188}\text{Os}$  and  $^{190}\text{Os}$ , but Os interference was negligible. Tungsten isotope compositions of the samples are as  $\epsilon^{182}\text{W}$  relative to measurements of SRM 3163.

**Results:** Phosphates from angrites concentrate many incompatible lithophile elements, including lanthanides, W, Th and U, but are low in high field strength elements (HFSE) including Ti, Zr, and Hf. Figure shows Th vs. W in individual mineral phases in six angrites. It can be seen that W is concentrated by about 3 orders of magnitude. Since phosphates constitute about 0.1% by mass fraction of angrites, they account for 30-50% of the W budget in angrites.

Figure 2 shows P, W and Th contents recovered in successive leaching steps applied to NWA 4590 and D'Orbigny. Most of the sample's P was recovered in

the first leaching step (6M HCl and 0.1 % H<sub>2</sub>O<sub>2</sub>). Proportions of W and Th decrease with each successive leaching step. The dissolution patterns for W and Th are parallel to that of P for most cases, implying that W and Th are partitioned in phosphate. Thus our leaching technique successfully extracted phosphate from angrites.

Figure 3 shows a plot of W isotopic composition vs. age of the angrites, and is modified from Markowski et al. [3]. W isotopic compositions of two leachates from D'Orbigny plot close to the previous value obtained from the isochron [3]. The leachates from NWA 4590 show a more complicated pattern. The isotopic compositions of three leachates ranged from -1.7 to -0.1, indicating that some of the leached W was potentially derived from terrestrial contaminants. Kleine et al. [4] found that NWA 4590 showed evidence of disturbance or terrestrial contamination. Our leachate data obtained a least radiogenic W consistent with the value obtained from the isochron of [4], and also extracted components that were more radiogenic.

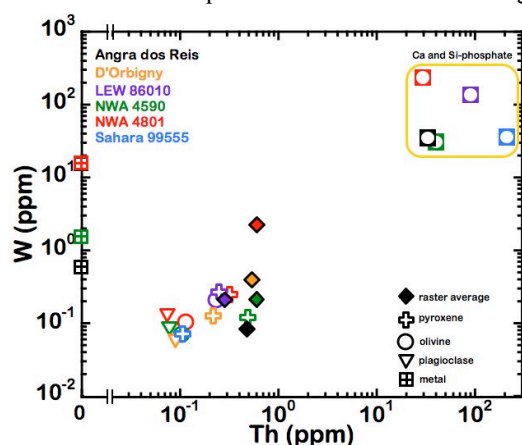


Fig. 1 W vs. Th abundances for raster average and some minerals for angrites.

Fig. 2 Distribution patterns for P, W and Th of each leaching stage in <143 $\mu$ m fraction of NWA 4590 (solid symbol) and D'Orbigny (open symbol).

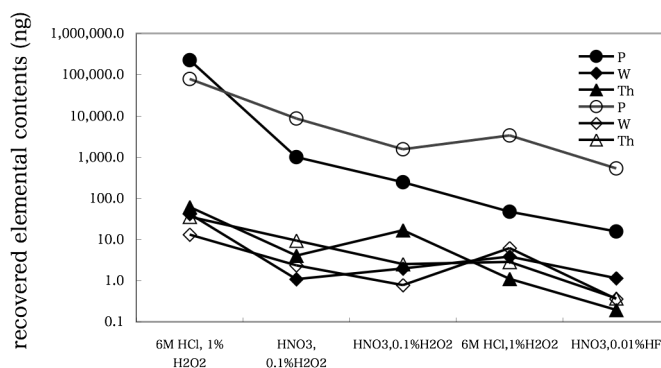


Fig. 2 Distribution patterns for P, W and Th of each leaching stage in <143 $\mu$ m fraction of NWA 4590 (solid symbol) and D'Orbigny (open symbol).

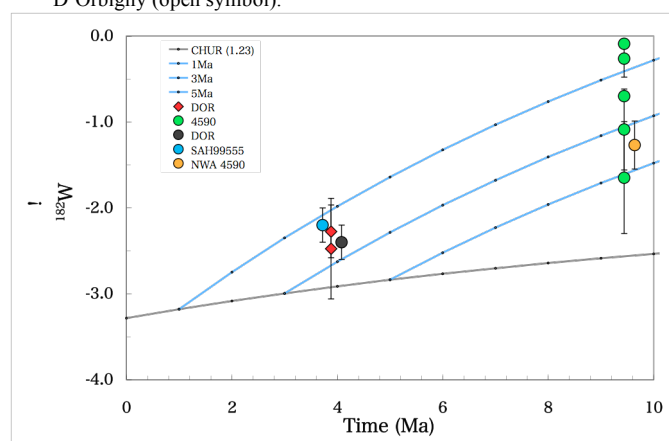


Figure 3. Model of  $\epsilon^{182}\text{W}$  evolution of the source of angrites, after [M]. Black line represents the W isotopic evolution of a chondritic reservoir. The blue lines represent the evolution of angrite parent magma sources having  $\text{Hf}/\text{W} = 4.6$ , and differentiating at 1, 3, and 5 Ma, after CAI formation. Literature data for NWA 4590 [4] and D'Orbigny and SAH 99555 [3] have been displaced by 0.2 Ma for presentation purposes. Two leachates of D'Orbigny plot within error of the initial value obtained from an isochron [3]. The least radiogenic leachate from NWA 4590 is within error of the initial value obtained from an isochron [4], while more radiogenic leachates indicate potential terrestrial disturbance of this desert meteorite.

**References:** [1] Kleine et al. (2009) *GCA* 73, 5150-5188. [2] Amelin Y. (2007) *LPSC XXXVIII*, #1669. [3] Markowski A. et al. (2007) *EPSL* 262, 214-229. [4] Kleine T. et al. (2008) *LPSC XXXIX*, #2367. [5] Righter K. and Shearer C. K. (2003) *GCA* 67, 2497-2507. [6] Shirai N. et al. (2009) *LPS XL*, #2122. [7] Kleine et al. (2004) *GCA* 68, 2935-2946.