

## INFLUENCE OF ALTERATION CONDITIONS ON TUNGSTEN ISOTOPE FRACTIONATION.

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**Introduction:** Radiogenic tungsten (W) isotopes have been commonly used for more than 20 years to date early differentiation processes in the solar system. Recently, the study of W stable isotope fractionation has started following analytical improvements. Most chondrites show evidence of relatively low temperature alteration that affected their components [1]. The presence of hydrous and anhydrous minerals such as serpentines, clays, sulfates, oxides, sulfides, halides, and oxyhydroxides prove that these rocks have undergone aqueous alteration [2], be it on the parent body or on the Earth. At the same time, the <sup>182</sup>Hf-<sup>182</sup>W short-lived radiochronometer applied to CR2 metal-rich chondrites yields intriguing results: the isochron of the most altered sample, Renazzo, seems to be disturbed [3]. Given that non-traditional stable isotopes are potential tools to better apprehend the conditions and pathways of alteration processes [e.g. 4-6], we decided to study the mass dependent isotope fractionation of W in a variety of chondrites showing different degrees of alteration.

**Samples:** Carbonaceous chondrites (petrographic types 1 to 3) have been analyzed with some emphasis on CV3 chondrites as they are known to present various degrees of alteration going along with variations in textures, matrix abundance and metal preservation. We also analyzed L6 and H5 ordinary chondrites previously studied for their Fe isotope composition [7] and known to have suffered from terrestrial weathering in deserts of Morocco and Algeria. The study of antarctic meteorites is under progress.

**Results and Discussion:** All carbonaceous chondrites are enriched in heavy W isotopes relative to the NIST SRM 3163 standard. CV3 chondrites show large variations in their signatures ; the tungsten isotope fractionation seems to be related to the degree of alteration, and so is the Hf/W ratio of the samples. Considering Vigarano as one of the most primitive chondrites, representative of the reduced starting material, we propose that the trend observed for Allende and Axtell is due to the progressive loss of W relative to Hf during increasing alteration processes on the parent body. The W-bearing solution resulting from the alteration is enriched in light W isotopes, and the remaining rock thus enriched in heavy isotopes as observed. Ordinary chondrites altered in terrestrial deserts also display some isotope variability, even if the spread is smaller. Once again, the isotope composition seems to be related to the degree of weathering as approximated by the S content of the meteorite. Thus, the Hf/W ratio as well as the W isotope fractionation appear to be potential proxies for the extent of aqueous alteration in chondrites, which has strong consequences on the <sup>182</sup>Hf-<sup>182</sup>W chronometry.

**Laboratory experiments and thermodynamical modeling:** In parallel to the analysis of natural samples, we also decided to perform laboratory experiments to investigate the behavior of W during fluid-rock interactions in a more systematic way and to establish W stable isotopes as a new tracer of alteration. Even if W is moderately siderophile and thus mostly present in metal, silicate is of prime importance as it is the most abundant phase in meteorites, displaying the highest Hf/W ratios. The expected Hf-W fractionation due to fluid-rock interactions is then larger in silicates, resulting in a larger potential disturbance of the isochron. Among silicates, olivine, pyroxene and plagioclase are the most common minerals in extraterrestrial samples. Short-term dissolution tests have been performed as a function of pH. All experiments were conducted at a constant liquid to solid ratio (L/S =10), at ambient temperature (21 ± 2 °C) and pressure (1 atm). Element concentrations were measured with a quadrupole ICP-MS, while isotope compositions were determined using a MC-ICPMS. In parallel, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDS), and Raman analyses were used to characterize and compare fresh and altered samples in order to give insights regarding the surface morphology, the mechanisms of alteration, and the formation of secondary mineral phases.

These experiments confirmed that W is much more mobile than Hf, resulting in a strong Hf/W fractionation during alteration processes. It also appears that the mineral dissolution (mainly olivine and pyroxene) is incongruent concerning W. Last but not least, both experiments and modeling using PHREEQC indicate that the dissolution-precipitation equilibria are not controlled by the saturation in W of the solution but rather by adsorption and coprecipitation on/with secondary phases, as tungsten is a trace element in the minerals under consideration.

### References:

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