

## Aerosol trace metal fractional solubility and chemical composition of marine aerosols at the CVAO

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The atmosphere and ocean interact in various ways that significantly affect the local and global climate. Mineral dust deposition onto the oceans plays a vital role as it provides key nutrients to the ocean biota and thereby influence the oceanic biogeochemical cycle and thus oceanic emissions. In this work we present chemical and trace metal composition of marine aerosol at the Cape Verde Atmospheric Observatory (CVAO) obtained during periods of and without Saharan dust storms.

The data were collected during intensive field campaigns and continuous measurements from January 2007 until now. During this period PM10 samples were collected using a 5-stage Berner impactor for size-resolved measurements and a high volume DIGITEL DHA-80 sampler with PM<sub>10</sub>-inlets.

Our observations show that about 45% of the year are dominated by remote conditions while the rest was influenced by continental and Saharan dust air masses. Continental air masses contained significant amounts of Saharan dust with trace metals and organic carbon compared to marine air masses. Dust events were observed mostly during the winter months of the year. During the events, the contribution of sea salt to the total PM<sub>10</sub> mass was found to be low. The sea salt and Saharan dust in the particle were found in the coarse mode fractions while the organics and non-sea salt components were observed mostly in the submicron fraction. Interannual and seasonal variability were observed for nearly all aerosol constituents. Strong seasonal trends were observed for ammonium and non-sea salt sulfate with peaks observed in the spring and summer, respectively.

Significant differences were observed in the trace metal composition (especially iron) between days of Saharan dust outbreaks (about 20.0 Fe, 16.4 Ca, 2.3 Ti, and 0.3 Mn  $\mu\text{g}/\text{m}^3$ ) and days without (less than 10.0  $\text{ng}/\text{m}^3$ ). Mn was found to be the most soluble trace metal followed by Zn and Fe. Iron was mostly present in Fe (III) form with Fe (II) often found only at lower pH. Dissolution experiments at varying pH (from 5.5 to 2) showed significant increase in metal solubility at lower pH with an increase of over 3 orders of magnitude for both Fe (II) and Fe(III) and about two orders of magnitude for Cu and Mn.

## The unexpected 'compatible' behavior of W during mantle melting: Implications for the W/U ratio of the lunar mantle

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The timing of core formation is essential for understanding the early differentiation history of the Earth and the Moon. Because Hf is lithophile and W is siderophile during metal-silicate segregation, the decay of <sup>182</sup>Hf to <sup>182</sup>W (half-life of 9 Ma) has proven to be a useful chronometer of these major planetary differentiation events. A key parameter for the interpretation of the <sup>182</sup>Hf/<sup>182</sup>W chronometer is the Hf/W ratio of the primitive (i.e. undepleted) mantle. Since W is incompatible during mantle melting, its ratio relative to U and other similarly incompatible elements in basalts (e.g. Th, Ba) may be used as proxies for their mantle sources. However, the assumption that W and U are equally incompatible may be flawed for petrological systems that equilibrated over a large range of  $f\text{O}_2$ . Although W is typically perceived as being homovalent, evidence suggests that U is heterovalent over the range of  $f\text{O}_2$  experienced in the mantle of the Earth and the Moon respectively.

Here we report partitioning data for W, U, high-field strength elements (HFSE), and Th between clinopyroxene, orthopyroxene, olivine and silicate melt. In agreement with previous studies, we show that these elements behave as homovalent elements at  $f\text{O}_2$  higher than QFM. However, both W and U become more compatible at  $f\text{O}_2$  lower than QFM, indicating a change in their redox state.

This result is particularly unexpected, because W is thought to be hexavalent even at very low  $f\text{O}_2$ . However, the much higher compatibility of W<sup>4+</sup> as compared to W<sup>6+</sup>, means that even a small fraction of W<sup>4+</sup> will increase the overall compatibility of W. Our results imply that under the reducing conditions in which lunar differentiation is thought to have taken place (i.e. ~IW-1), W is likely to become fractionated from U. These newly obtained partitioning data carry with them the potential implication that the W-to-U ratio of lunar basalts does not directly represent their mantle source. More high-precision measurements of W and U abundances in lunar rocks are needed to more precisely estimate the Hf/W of the Moon and thus, the age of the Moon itself.