Exploring a 60-year record of Mn deposition by comparing atmospheric dispersion models to soil chemistry profiles in Ohio (USA)

M.R. CARTER[1]* AND S.L. BRANTLEY[1]

[1]Geosciences Dept., The Pennsylvania State Univ., University Park, PA 16802 (*mcarter@psu.edu)

Atmospheric deposition of metals emitted by anthropogenic activities has been a significant source of metal loading into soils worldwide. A ferromanganese refinery, located in Marietta, OH, is currently the largest US emission source of manganese (Mn) into the atmosphere. Particulate emissions during production are up to 35% manganese oxide (MnO) by weight and predominantly range in diameter from 0.05 to 0.4 μm, making them both highly mobile and respirable. In order to assess the role of soils in Marietta as sinks for atmospherically-derived Mn, a series of soil cores were collected at a range of distances (1-45 km) from the refinery. The results show that enrichment of soil-surface Mn is 10 times that of the parent material and decreases in surface concentration as a function of increasing distance from the refinery. Total mass of Mn added to soils per unit land area integrated over the soil depth was calculated to be 75 mg Mn cm^{-2} near the refinery. In contrast, a net loss of Mn was found in soil profiles at a distance of 45 km from the facility. Enrichment of chromium (Cr) by more than a factor of 3 was also found in surface soils near the refinery, consistent with the production of ferrochromium at the Marietta plant. Mn deposition rates were also estimated with an atmospheric dispersion model (SCIPUFF) using recent meteorological data and emission rates for the refinery. When scaled appropriately, this model-derived deposition can reproduce the soil-derived value as long as deposition rates in previous decades were more than 3 orders of magnitude greater than today's rates. This model-soil discrepancy may be due to enforcement of air quality standards, such as the Clean Air Act. We are furthermore exploring other possible explanations for the discrepancy. These results suggest that coupling soil measurements with atmospheric dispersion modelling could help identify locations where deposition rates have changed dramatically.

Nb/Ta decoupling under low fo_2

C. CARTIER[1], T. HAMMOUDA[1], M.A. BOUHIFD[1],
M. BOYET [1] AND J.L. DEVIDAL[1]

[1] Laboratoire Magmas et Volcans, UBP, CNRS UMR 6524, 5 rue Kessler, 63038 Clermont-Ferrand, France.
Correspondence: (c.cartier@opgc.univ-bpclermont.fr)

The high field strength elements Nb and Ta are thought to behave like geochemical twins since they have similar ionic radii and the same valence (5+) and thus should not be fractionated during magmatic processes. As both elements are refractory, the bulk Earth is thought to have a chondritic Nb/Ta ratio (=19.9±0.6, [1]). However, and in contrast to Mars and other asteroids, lunar and terestrial rocks all display a subchondritic ratio (Nb/Ta=14±0.3 and 17.0±0.8 respectively, [1]). One way to explain this paradox is to invoke the incorporation of Nb by the core during a high pressure segregation (>25GPa) and moderately reducing fO_2 (IW-1.5), because in these conditions Ta is lithophile whereas Nb is moderately siderophile [2].

Here we present new metal/silicate melt trace element partition coefficients obtained on enstatite chondrite material at 5 GPa and under variable oxygen fugacities (IW to IW-8). Experiments have been conducted in the multianvil apparatus between 1580 and 1850°C, using doped material. Trace elements were analyzed using laser ablation ICP-MS on metal and silicate liquid phases.

Our result show that below about IW-4 and at 5GPa, both Nb and Ta are siderophile. When plotted as a function of oxygen fugacity, metal/silicate partition coefficients display slopes that depend on the valence state of the element in the silicate liquid. Our results show that under extremely reducing conditions (<IW-4) Nb is changing from Nb^{5+} to Nb^{2+} and Ta is changing from Ta^{5+} to Ta^{3+} in the silicate melt. This valence contrast generates a fractionation of the Nb/Ta ratio in the silicate, that consequently presents Nb-depleted Nb/Ta ratios.

These results suggest that Nb and Ta can be extracted by metal/silicate separation at low pressure (5GPa) and fractionated in the silicate if the segregation occurs at low oxygen fugacity (<IW-2). Since proto-Earth probably created from differenciated small bodies before undergoing high pressure events, these new results should then be considered in the Earth's accretion models.

[1] Münker *et al*. (2003), *Science* ***301***, 84-87. [2] Wade and Wood (2001*), Nature* ***409***, 75-78.

DOI: 10.1180/minmag.2013.077.5.3