Fractionation of Sulfur and Oxygen isotopes during SO_2 photolysis

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The discovery of sulfur mass-independent fractionation (S-MIF) in ancient sedimentary rocks [1] has created the opportunity for quantitative constraints on the composition of the early atmosphere. Laboratory experiments have shown that S-MIF occurs during SO2 photodissociation at a variety of UV wavelengths [2, 3]. The source of the S-MIF in experiments at wavelengths ~ 200 nm is self-shielding in SO2 [4, 5]. Sulfur isotope substitution produces shifts in the locations of vibronic bands (see Fig. 2 in [4], and Fig. 5.2b in [5]). During photolysis saturation in the rovibronic lines of the most abundant SO2 isotopologue ($^{32}SO_2$) results in a non-mass-dependent rate of photolysis in the rare isotopologues (i.e. self-shielding). Modeling SO_2 photolysis in an atmosphere shows that after ~10% of SO_2 has been dissociated, S-MIF signatures of $\Delta^{33}S$ ~ 10 ‰ are obtained, depending on the column abundance of SO_2. The corresponding model $\Delta^{36}S/\Delta^{33}S$ ratios are ~ -3 to -0.5, depending on both the SO_2 and CO_2 column abundances in the model atmosphere.

The oxygen isotopologues of SO_2 will also undergo vibronic band shifts and self-shielding, and large O-MIF effects should be produced during SO_2 photolysis. I am presently computing synthetic spectra for SO18O and SO17O isotopologues by the same method used for the sulfur isotopologues [4, 5], and will determine the magnitude of O-MIF expected. Oxygen exchange reactions must also be included. For example, SO_2 exchange with H_2O has been estimated to be rapid [6], and may be fast enough to preclude O-MIF from surviving in sulfates in the geologic record. In laboratory photolysis experiments oxygen exchange between SO_2 and O may limit the magntiude of O-MIF in photolysis products such as O2. The sensitivity of O-MIF to these exchange reactions will be reported.

[1] Farquhar *et al.* (2000) *Science* **289**, 756-758. [2] Farquhar *et al.* (2001) *J. Geophys. Res.* **106**, 32829-32840. [3] Wing *et al.* (2004) abstract 228th meeting of Amer. Chem. Soc., Philadelphia, PA, 22-26 Aug. [4] Lyons (2007) *Geophys. Res. Lett.* **34**, L22811. [5] Lyons (2008*) Adv. Quantum Chem.* **55**, 57-74. [6] Holt *et al.* (1983) *Atmos. Environ.* **17**, 625-632.

Discovery of tazheranite (cubic zirconia) in the Allende meteorite

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During a nano-mineralogy investigation of the Allende meteorite, we found Y-rich tazheranite (cubic zirconia) [$(Zr,Ti,Ca,Y)O_{1.75}$] in a refractory inclusion within an amoeboid olivine aggregate. Synthetic cubic zirconia is well known in the field of materials science. Tazheranite [$(Zr,Ti,Ca)O_2$] is a rare, naturally occurring cubic zirconia, discovered in the Tazheran massif, Russia in 1969 [1]. We report here its first occurrence in a meteorite, as an ultra-refractory mineral likely formed at the beginning stage of our solar system.

FE-SEM revealed that tazheranite occurs as subhedral grains (350 nm – 1.2 μm in dia.) along with zirconolite and Fe-Ni and alloys dominant in Os-Ir-Mo-W, occupying the core area in a refractory inclusion with a rim consisting of fassaite (cpx), surrounded by olivine (Fig. 1). The mineral was only found in one polished section, prepared from a 1-cm-diameter Allende fragment. The mean chemical composition of the zirconia phase determined by electron microprobe analysis is (wt%) ZrO_2 49.76, TiO_2 28.45, CaO 9.94, Y_2O_3 6.15, HfO_2 2.23, FeO 2.00, Al_2O_3 0.96, MgO 0.47, Sc_2O_3 0.43, sum 100.39, giving an empirical formula: $(Zr_{0.38}Ti^{4+}_{0.33}Ca_{0.17}Y_{0.05}Fe_{0.03}Al_{0.02}Hf_{0.01}Sc_{0.01}Mg_{0.01})_{\Sigma 1.01}O_{1.75}$, No other elements with atomic number greater than 4 were detected. *In situ* electron back-scatter diffraction analysis revealed that the zirconia phase has a fluorite-type *Fm3m* structure, identical to that of tazheranite [2] and synthetic cubic zirconia, showing a = 5.11 Å and Z = 4. This zirconia is Ti-rich, having a Ca- and Y-stabilized cubic structure.

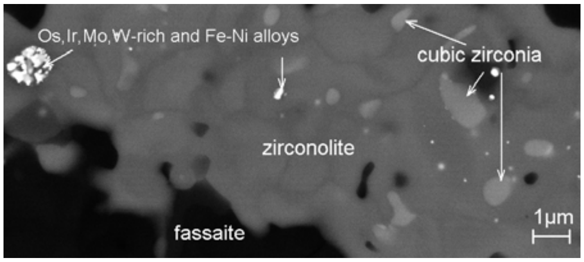

Figure 1: SEM image showing cubic zirconia in Allende.

[1] Konev *et al*. (1969) *Doklady Akad. Nauk* **186**, 917–920. [2] Rastsvetaeva *et al*. (1998) *Doklady Akad. Nauk* **359**, 529–531.