EXPERIMENTAL AND PETROLOGIC STUDIES OF SCHREIBERSITE CORROSION

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Introduction: Schreibersite, $(Fe,Ni)_3P$, is a common meteoritic mineral. Phosphorus in schreibersite is reduced relative to orthophosphate, PO_4^{3-}, the stable oxidation state on the surface of the Earth. Consequently, P in schreibersite is oxidized by water and atmospheric O_2. The only known mineral associated with the oxidation of schreibersite is cassidyite, $Ca_2(Ni,Mg)(PO_4)_2{\times}2H_2O$, a poorly studied mineral associated with the Wolf Creek meteorite [1]. Since nearly all P on the surface of the Earth is orthophosphate, schreibersite corrosion products may serve as an indicator of extraterrestrial impacts.

Samples and Methods: Schreibersite corrosion was studied by a series of experiments in which ~1g of a synthetic iron phosphide (Fe_3P) powder or ~7 g samples of the Seymchan or Canyon Diablo meteorites were oxidized in water at 25°C for 1 day to 1 month. Oxidation took place both under air and under an inert Ar atmosphere to elucidate the effects of O_2. The aqueous corrosion products were analyzed by ^{31}P NMR, EPR, and MS techniques [2,3].

NWA 4194 is a weathered enstatite meteorite with 20µm-200µm grains of schreibersite surrounded by P-rich rust. A section of NWA 4194 was analyzed by EMPA (Sx50), with a focus on P chemistry in the rust.

Results and Discussion: Schreibersite corrodes to phosphite (HPO_3^{2-}), orthophosphate (HPO_4^{2-}), hypophosphate ($HP_2O_6^{3-}$), and pyrophosphate ($HP_2O_7^{4-}$) in aqueous solution. The oxidation state of P in these compounds ranges from 3+ to 5+, and their formation proceeds by a free radical pathway [3].

Schreibersite in NWA 4194 is surrounded by a hydrous Fe, Ni, Ca, P-rich oxide. The oxide is highly heterogeneous, and is enriched in P relative to Fe and Ni. Ca was introduced from the terrestrial environment during weathering. The O:P ratio is ~ 3:1 ($R^2 = 0.883$), which may indicate that the P is reduced relative to orthophosphate.

These heterogeneous phases are incompletely characterized, but may represent a new group of reduced P minerals. If so, these minerals would demonstrate the formation of reduced P oxides on Earth. Since reduced P compounds are derived almost exclusively from extraterrestrial sources and crustal P is uniformly orthophosphate, detection of phosphite or hypophosphate in soil or rock samples may serve as an indicator of ancient meteorite impacts or meteoritic flux.

Finally, schreibersite was a highly reactive source of P on the early Earth and may have primed the environment with reduced P compounds, which react with organics to form phosphorylated compounds, enabling the origin of life. Several species of bacteria can use reduced P as their sole P source [4], which may be an ancient genetic indicator of the environment of the early Earth.

References: [1] White J.S. et al. 1967 *American Mineralogist* 52:1190-1197. [2] Pasek M.A. and Lauretta D.S. 2005 *Astrobiology* 5:515-535. [3] Pasek M.A. et al. 2007 *Geochimica et Cosmochimica Acta* 71:1721-1736. [4] Kononova S.V. and Nesmeyanova M.A. 2002 *Biochemistry (Moscow)* 67: 220-233.