

Dark production of reactive oxygen species in freshwaters

B.M. VOELKER^{1*}, R. MARSICO¹, R. SCHNEIDER¹,
C.M. HANSEL² AND T. ZHANG²

¹Department of Chemistry and Geochemistry, Colorado
School of Mines, Golden, CO 80401, U.S.A.
(*correspondance: voelker@mines.edu)

²Marine Chemistry and Geochemistry Department, Woods
Hole Oceanographic Institution, Woods Hole, MA 02543,
U.S.A.

Reactive oxygen species (ROS) superoxide (O_2^-), hydrogen peroxide (H_2O_2) and hydroxyl (OH) can affect metal redox speciation and organic carbon cycling in natural waters. In this study, we focus on hydrogen peroxide, the product of superoxide reduction and the source of strong oxidants including hydroxyl, via Fenton's reaction.

We measured production and decay rates of hydrogen peroxide in dark incubations of freshwater samples from a variety of systems. Dark production was found to be a ubiquitous feature of freshwater environments, and both production and decay rates were generally related to the concentrations of microorganisms in the samples. Production rates ranged from undetectable to greater than 200 nM hr^{-1} , with large temporal fluctuations in two field sites that were sampled repeatedly. Filtering decreased, but did not always eliminate, production of hydrogen peroxide, indicating chemical as well as biological sources of ROS. Our results suggest that metal reactions involving ROS are likely to occur even when photochemical ROS production is minimal.

The dependence of siderophile element partitioning on Pressure, Temperature, fO_2 and S-content

VOGEL, A.K.¹; RUBIE, D.C.¹; FROST, D.J.¹,
AUDÉTAT A.¹ AND PALME, H.²

¹Bayerisches Geoinstitut, Universität Bayreuth, D-95440
Bayreuth, Germany, antje-kathrin.vogel@uni-bayreuth.de

²Forschungsinstitut und Naturmuseum Senckenberg, D-60325
Frankfurt, Germany

The partitioning of siderophile elements between liquid metal and liquid silicate provides information about the conditions that dominated during core formation in the Earth and other terrestrial planets. In particular high pressure – high temperature experiments, performed in a multianvil apparatus, and the quantification of the partitioning behaviour in the form of partition and exchange coefficients yield conclusions about former pressure, temperature and oxygen fugacity conditions.

We have chosen a broad range of elements for our experiments, namely the refractory elements Ni, Co, W and Mo, as well as the moderately volatile elements Ag, As, Au, P, Ge, Cu and Sb and the volatile elements Sn and Pb. We have investigated the partitioning behaviour over the P - T range 11-23 GPa and 2200-2800 K respectively. Oxygen fugacities of -2 to -5 log units relative to the iron-wüstite buffer have been determined, enabling us to draw additional conclusions about the valence state of the elements of interest in the silicate melt. In addition, we have investigated the effect of the S content of liquid metal on partitioning because S contents were likely significant, especially during the late stages of accretion.

The most siderophile of the studied elements, gold, exhibits the strongest temperature dependence with exchange coefficients varying over one log unit within a temperature range of 2400-2600 K. Other elements, in particular Pb, show no significant dependence on temperature. The partitioning behaviour of Pb furthermore seems to be unaffected by pressure. With 10 wt% S in the starting material, the exchange coefficient for Sn decreases by 0.5 log units, and converges with the exchange coefficient of Pb, a condition that has to be fulfilled because Pb and Sn are depleted by the same extent in the Earth's mantle.

The results are being incorporated into an accretion/core formation model in order to understand the timing of volatile element addition to the Earth.