Hydrothermal processes beneath the Merensky Reef and UG2 Chromitite, Bushveld Complex, RSA

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Pegmatites in the Bushveld Complex occur as veins/pipes comprised of quartz-andesine-biotite intergrowth. Mineral thermometry indicates minimum equilibration temperatures of 610-740ºC. Mossbauer spectroscopy of biotite Fe^{3+}/Fe^{2+} ratios constrain fO_2 within 1 log unit of FMQ. The Cl isotope composition of biotite is consistent with a mantle source ($\partial^{37}Cl$ = -0.15‰ to 0.84‰). $^{40}Ar/^{39}Ar$ dating of biotite indicates pegmatite crystallization ages ranging from 2044 (±23) to 2023 (±12) Ma; therefore, late stage volatile activity persisted well beyond the accepted crystallization age of the layered rocks (2054.4±1.3 Ma[1]).

Quartz and andesine contain primary inclusions of magmatic origin, varying from early low salinity two-phase aqueous to late, nearly anhydrous NaCl-CaCl2-dominant halide melt inclusions. Silicate melt inclusions (high K-rhyodacitic) are also present, and are unambiguously coeval with the halide melt inclusions, demonstrating that the late stage felsic liquid was saturated in this salt melt. Trace element modelling shows formation of these pegmatites by low degrees of fractional crystallization (~1 vol%) of the melt composition trapped in the inclusions.

Pegmatite cores contain base metal sulfides hosting primary inclusions of Pd-bearing melonite [$(Ni, Pd)Te_2$]. Normative abundance patterns are most similar to those from the Platreef, showing a marked enrichment in Pd relative to Pt (Pd/Pt > 8), Cu relative to Ni (Cu/Ni > 20) and significant depletion in Ir. Analyses of melt inclusions by LA-ICP-MS indicate high concentrations of precious metals such as Pd and Au (0.2-0.6 ppm range) at the time of their entrapment.

We show direct evidence that relatively oxidizing, halide melt-saturated silicate residues were ore metal-bearing at the time of entrapment. Ore/accessory metal ratios in the melt inclusions and sulfide assemblages in the pegmatites are consistent with the bulk rock metal ratios of the pyroxenite cumulates below the Merensky Reef, suggesting that metals were scavenged from those cumulates. Quantitative modelling suggests that the residues significantly impacted metal tenor and ratios in the Upper Critical Zone magma.

[1] Scoates, J., Friedman, R., (2008), *Econ. Geol.* **103**, 456.

Electron and proton transfer equilibria of reducible moieties in humic substances

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Humic substances (HS) can act as electron acceptors and electron transfer mediators and play an important role in biogochemical redox processes and in reductive pollutant transformations. Yet, key redox properties of HS remain poorly characterized. Using a novel electrochemical approach, we previously demonstrated largely reversible electron transfer to HS in reduction-O_2 reoxidation cycles and a linear correlation of electron accepting capacities with aromaticities for different HS [1]. These findings suggested quinones as major redox active moieties. The aim of this work was to characterize the electron and proton transfer equilibria of reducible moieties in HS by extending on the electrochemical methods presented in [1].

In a first step, we determined the effect of pH on the coupling of protons to electrons (molar ratios m_{H+}/n_{e-}) transferred to selected humic acids during electrochemical reduction. m_{H+}/n_{e-} gradually decreased from 1.1 to 1.0 at pH 6 to 7 to values < 0.8 at pH 10. The trend in m_{H+}/n_{e-} was consistent with increasing deprotonation of formed hydroquinones with pH, supported by the pH dependence of m_{H+}/n_{e-} during the reduction of selected model quinones. Consistent with the m_{H+}/n_{e-} ratios, potentiometric E_h-pH titration curves for HS reduced to different extents had slopes of $\Delta E_h/\Delta pH \approx -60$ mV.

In a second step, we determined the distribution in standard reduction potentials ($E_h^{0\prime}$ at pH 7) of reducible moieties in HS by fitting the decrease in E_h with increasing number of electrochemically transferred electrons, n_{e-}, using a model assuming i types of redox active sites with $E_h^{0\prime}(i)$. Attainment of redox equilibria was facilitated by addition of small amounts of radical electron transfer mediators (e.g. diquat). The E_h-n_{e-} curves showed pronounced redox buffering over a wide E_h range. The fitted $E_h^{0\prime}(i)$ distributions were in good agreement with the standard reduction potentials of naphthoquinones and anthraquinones, suggesting that benzoquinone moieties were already present as reduced hydroquinones in the non-pretreated HS.

The proton and electron transfer equilibria of the studied HS support quinones as major reducible moieties in HS and allow, for the first time, estimating free energies of electron transfer reactions involving HS and placing HA on the redox ladder of biogeochemical redox couples and of organic and inorganic pollutants.

[1] Aeschbacher, Sander & Schwarzenbach (2010), *ES&T* **44**, 87-93.