Sulphate reduction induced by hydrogen under hydrothermal conditions

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Abiotic redox reactions induced by hydrogen are of prior importance in numerous fields of investigation in geoscience where hydrogen is produced either naturally or indirectly via industrial activities: e.g. nuclear waste storage [1], underground storage of hydrogen [2], hydrogen generation during serpentinization and related redox reaction [3], early earth, termochemical sulphate reduction (TSR) [4].

In this experimental study we focus on sulphate reduction induced by hydrogen under hydrothermal conditions. We provide kinetic data as a function of temperature (125°C-300°C), pH, hydrogen pressure, sulphate speciation (HSO_4^-, $MgSO_4°$, $CaSO_4°$), surface catalysts or additional electron donor (Hastelloy C273, Ni (0), Fe (0), magnetite). This parametric approach on simplified systems allow us to probe the reaction mecanism and to discriminate electron donors: i.e. native metal, mixte oxide, atomic hydrogen or H_2. In addition, we provide kinetic data that can be apply in numerical simulations. In presence of these catalysts, the reaction rate is one to two order of magnitute higher than in diphasique systems [4] i. e: aqueous sulphate + dissolved hydrogen. However, low pH are required in presence of Hastelloy or Ni (0) to reduced sulphate within hours in the temperature range 250-300°C. Under these conditions hydrogen is not necessary but the reaction rate is enhanced in its presence. We suppose that hydrogen radicals generated by alloy or metal corrosion are the main electron donors. In presence of magnetite, the reaction occurs at low temperature (125°C) but only under restricted conditions: low sulfate concentration, pH around magnetite PZC and hydrogen partial pressure. We further reveale that sulphide reaction initiation is not a necessary condition providing that these catalytic surfaces are present in the system.

The results of this study are discussed in the light of kinetic data and reaction pathways obtained in previous studies using hydrocarbons as electron donor instead of H_2.

[1] Truche *et al.* (2009) *GCA*, **73**, 4824–4835. [2] Panfilov (2010) *Transp. in Porous Media*, **85**, 841–865. [3] Fu *et al.* (2007) *GCA*, **71**, 1982–1998. [4] Truche *et al.* (2010) *GCA*. **74**, 2894–2914.

Platinum-group elements in basaltic rocks from the Etendeka province in N.W. Namibia

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The continental flood basalts and intrusive rocks of the Paraná – Etendeka Large Igneous Province have been reasonably well studied, giving a good foundation for more specific questions. One aspect of special interest in LIPs and their mantle source (s) concerns the behavior of platinum group elements (PGE). These elements and their isotopes can help distinguish mantle components (lithospheric, asthenospheric, deep-mantle) and they have obvious economic significance. Some Phanerozoic flood basalt provinces are associated with important Cu-Ni-PGE ore deposits (Emeishan, Siberia), whereas others appear to lack them (Karoo, Deccan and Paraná-Etendeka). Whether this difference relates to conditions in the magma source region or to the nature of crustal assimilation is debated, but sulfur is seen to play a critical role.

We present new PGE concentration data for lavas, dolerite dikes and gabbroic intrusions from the southern Etendeka region of Namibia. The rocks represent the low-Ti magma series, with examples from both tholeiitic and alkaline groups. MgO contents range from 5 to 18 wt.%. PGE concentrations were measured on 5g samples by Ni-sulphide fire assay followed by ICPMS. The results give very low values compared with basalts from other LIPs, with 1 to 6 ppb total PGE, but in agreement with a previous study of Karoo and Etendeka rocks [1]. Primitive mantle-normalized PGE concentrations are below 1 and PGE abundance patterns show moderate to high fractionation (Pt/Ir = 5-30). Ratios of Cu/Pd are high (10^4 to 10^5). There appear to be no systematic differences in abundance or PGE patterns in the tholeiitic vs. alkaline magma series.

The low PGE contents in these rocks may relate to retention of sulphides in the mantle source as argued by [1] or to removal by sulphide saturation of the magma during ascent and evolution. Bulk-rock ratios of chalcophile-lithophile trace elements (e.g. Cu-Zr) in the samples suggest the latter but additional evidence will come from analyses of S and trace elements in olivine-hosted melt inclusions.

[1] Maier *et al.* (2003) *Contributions to Mineralogy & Petrology* **146**, 44–61.