

Constraints on Archaean and Palaeoproterozoic pO_2 levels based on multicomponent reactive transport modelling of chemical weathering in the Hekpoort palaeosol

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Leaching of iron in the uppermost portions of a number of Archaean and Palaeoproterozoic palaeosols have led workers to suggest that atmospheric oxygen levels 2.2 Ga were significantly lower than they are today. For example, the top portion of the *c.* 2.22 Ga Hekpoort palaeosol in South Africa is depleted in Fe relative to the parent rock in all of the sections we have studied. The Fe/Ti ratio in all of the samples from the uppermost 2 meters of the profile in the BB8 core through the palaeosol is less than 50% of the Fe/Ti ratio in the unaltered basaltic andesite protolith. Below 2 meters, there is an approximately 1 meter thick zone characterized by Fe-enrichment, i.e. a higher Fe/Ti ratio. This Fe-enrichment zone gives way downward to unaltered protolith. Various methods have been used to estimate the likely pO_2 levels which could produce this kind of Fe leaching (e.g. Pinto and Holland, 1988) and redistribution (Rye *et al.* 1995). However, we believe it may be possible to further constrain atmospheric pO_2 levels through a somewhat more sophisticated calculation of the physical and chemical processes operating during Archaean and Palaeoproterozoic weathering.

Modelling approach

In this study, we use a multicomponent reactive transport model capable of handling partially saturated conditions to simulate elemental changes in the Hekpoort palaeosol in South Africa. The simulations are carried out with the code GIMRT (Steefel and Yabusaki, 1996), modified to include diffusion of multiple gases in the air phase and equilibrium partitioning between the air and liquid phase. The calculations are carried out by including 45 aqueous species along with the gases O_2 , CO_2 , and CH_4 . Thirteen minerals either initially present in the basaltic andesite protolith or allowed to precipitate as

secondary phases are considered. The initial mineralogy of the basaltic andesite is obtained by carrying out a CIPW norm calculation based on major element analyses of the protolith and assuming subsequent isochemical metamorphism. Altered rock compositions, to which we compare the model results, are obtained by correcting for rock density and/or compaction by assuming that Ti is immobile. Fluid boundary conditions are based on the assumption that the infiltrating rainwater is dilute and in equilibrium with the Palaeoproterozoic atmosphere. pH-dependent dissolution rates for all of the primary minerals in the protolith are taken from recent experimental studies (see various chapters in White and Brantley, 1995). Despite the large uncertainties associated with the estimation of reactive surface areas in the basaltic andesite, the use of carefully determined laboratory rates (including their pH dependence) suggests that the relative rates of reaction of the various primary minerals (if not their absolute rates) will be captured in the simulations. In the simulations, we consider atmospheric pO_2 values ranging from present day values down to 10^{-7} atmospheres and atmospheric pCO_2 values ranging from present day to 30 times present day (Rye *et al.*, 1995).

Representative water saturation profiles versus depth are generated using typical values of the van Genuchten parameters which relate saturation to the relative permeability and the capillary pressure in the rock (van Genuchten, 1980). The saturation profiles are obtained by solving the steady state version of the Richards equation (Lichtner, 1995). The steady state Richards equation assumes that the gas phase is immobile, so that gas transport is via diffusion only. The high rates of gas diffusion in the air phase, however, produce significantly different results in the simulations with partially saturated conditions from those simulations which assume fully saturated conditions.

Preliminary results

Preliminary results from the modelling suggest that Archaean oxygen partial pressures must have been significantly lower than present day values. A best model fit for Fe/Ti ratios (and for the weight percentage of Fe) in the Hekpoort palaeosol is obtained by using a pO_2 of 10^{-7} atmospheres, a pCO_2 30 times the present day value, and an erosion rate of 0.4 mm/year (Fig. 1). This result is not strictly unique, however, and is subject to a number of uncertainties. The detailed positions and widths of the alteration zones in the palaeosol are affected by a number of uncertain parameters, including the rate of infiltration into the weathering profile, the saturation profile, the rates of reaction of the minerals, and the erosion rate. The overall widths of the alteration zones are controlled by the ratio of reaction rates to infiltration rates (e.g. faster reaction rates or slower infiltration rates will tend to compress the alteration zones). Since erosion has the effect of removing the topmost portion of the weathering profile, the results show some (relatively minor) sensitivity to the value used for the erosion rate. However, the topology of the alteration zones in the palaeosols, as indicated for example by the changes in the Fe/Ti ratio vs depth shown in Fig. 1, provides a much more robust constraint than do the actual positions of the reaction fronts. The preliminary simulations indicate that at atmospheric O_2 levels at or above 10^{-6} atmospheres (and even more strikingly at levels at or above 10^{-5} atmospheres), a substantial thickness of ferric iron hydroxide is developed at the top of the weathering profile, no matter what (reasonable) pCO_2 value is used. In the simulations at 10^{-6} atmospheres, Fe-leaching occurs below the ferric iron hydroxide layer because oxygen is depleted and the solution pH rises in the iron hydroxide zone. Only in simulations using pO_2 values at or below 10^{-7} atmospheres is there little to no accumulation of iron hydroxide at the top of the profile, in agreement with the data from Hekpoort (Fig. 1). Note that the model results also capture the distinctive enrichment in Fe immediately below the Fe-depleted zone (Fig. 1). This enrichment is the result of the precipitation of Fe-rich smectite in the simulations. The present mineralogy of this zone in the Hekpoort palaeosol is dominated by Fe-rich chlorite and quartz. These minerals are most likely the products of the breakdown of the original Fe-rich smectite during lowermost greenschist facies metamorphism (Rye *et al.*, 1995). The modelling provides no constraints on minimum pO_2 values. These preliminary model results are broadly consistent

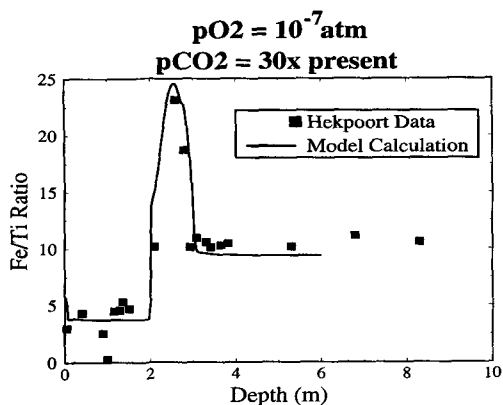


FIG. 1. Modelled Fe/Ti ratios vs data for the Hekpoort palaeosol. See text for parameters used in the simulation.

with previous estimates of Archaean and Palaeoproterozoic atmospheric oxygen and carbon dioxide levels (e.g. Pinto and Holland, 1988; Rye *et al.*, 1995). If anything, the model may indicate that oxygen levels were lower than earlier estimates required. Such a downward revision of atmospheric oxygen levels prior to 2.2 Ga would be consistent with the presence of a substantial amount of atmospheric methane at that time, which may be required to compensate for the early faint sun (Rye *et al.*, 1995).

References

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