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Evolution of Different Redox Couples During the Weathering of Mine Waste

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A temporal and spatial hydrogeochemical monitoring programme has been carried out on waters draining a waste heap at the former gold mine of Chéni, France (Bodénan *et al.*, 2000). The main water-rock interaction process corresponds to oxidation of pyrite and arsenopyrite traces in the heap. Particular emphasis has been placed on studying the behaviour of various redox couples. Based on speciation calculations, the aim was to identify the couple(s) that may influence the redox potential of the environment. The software program used was EQ3NR (Wolery, 1992), the database of which was extended by Gaskova *et al.* (1999) to include minerals and aqueous species of arsenic.

Redox potential and speciation were measured *in situ* before sampling (Bodénan *et al.*, 2000). The redox couples analysed were Fe^{II}/Fe^{III}, As^{III}/As^{V}, S^{IV}/S^{VI} and N^{-III}/N^{V}, and the results show that these were generally in thermodynamic disequilibrium in natural aqueous solutions (Lindberg and Runnells, 1984; Criaud and Fouillac, 1986). It should be noted, in the case of Chéni, that the spatial evolution of the calculated redox potential for each couple is similar to that of the measured redox potential (Fig. 1). This observation concerns both oxidation and reduction processes. In the upstream part of the site (pz1), the waters become progressively oxidised down to the saturated zone (pz2) of the second terrace where oxidation reaches its maximum. Similarly, all the measured redox couples reflect a clear oxidation trend. The measured Eh values decrease downstream of the saturated zone (pz5 and pz3). Higher Eh values were recorded near the river (pz4). Again, all the redox couples reflect to varying degrees the variations recorded by the measured redox potential of groundwater. The measured redox potential variations are everywhere higher than those calculated for the different redox couples, except for iron, which shows a greater deviation at point bbt (Fig. 1). The global impression is nevertheless that the dynamics suggested by the redox potential of the solution are higher than those represented by the different redox couples.

Two groups of redox couples are defined. The first corresponds to couples tending towards oxidising conditions, namely Fe^{II}/Fe^{III} and N^{-III}/N^{V}. Concerning the most oxidising conditions (pz2), the Eh values obtained on the basis of iron speciation suggest equilibrium of the Fe^{II}/Fe^{III} couple. Even under such conditions of partial equilibrium with respect to iron, the measured potential remains different from the speciation results. The few measurements for the N^{-III}/N^{V} couple suggest more oxidising conditions.

The second group of redox couples reflects less oxidising - more reducing conditions, and is represented by As^{III}/As^{V} and S^{IV}/S^{VI}. As for the case of iron demonstrated by the first group, arsenic shows redox equilibrium in the waters of pz2. Nevertheless, the measured Eh values remain distinct from those of As^{III}/As^{V} equilibrium.

In a context of oxidation of mine waste, it is difficult to attribute the redox potential measurements to a specific couple, despite the observation of the partial equilibrium of certain couples (Fig. 1). The only area where the iron data may coincide with the measured Eh values is at the point of maximum oxidation (pz2). The Fe and As concentrations in the waters show a minimum that would correspond to the precipitation of iron hydroxides accompanied by adsorption/co-precipitation of arsenic. It is clear that redox disequilibrium, increasingly detected in natural and anthropic aqueous systems, needs to be taken into account in models of reactive transport (Azaroual *et al.*, 2000).

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The Oxygen Geochemical Cycle: Dynamics, Stability and Evolution

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The timing of and the cause(s) for the rise(s) of atmospheric oxygen have been debated, but nearly everyone agrees that the atmospheric oxygen level has been essentially constant within a range of 0.5-1.5 PAL (present atmospheric level) for the last 600 Ma. We have revealed the mechanisms controlling the atmospheric oxygen level.

The atmospheric oxygen level has been controlled by the balance between (P) the rate of O_2 production (= the burial rate of organic matter in sediment) and (C) the rate of O_2 consumption by oxidation of carbon (and S and Fe) of rocks during soil formation and by oxidation of reduced volcanic gas. The values of (P) and (C) can ultimately be related to the following parameters: (a) the initial levels of atmospheric O_2 and CO_2; (b) the size of the reactive continental surface area; (c) the average depth of soil zone; (d) the average erosion rate of soils on land and the average rate of clastic sedimentation in ocean; (e) the average size of organic matter in sediments; and (f) the composition and flux of volcanic gas which depend on the mantle redox state and the rate of subduction.

For various combinations of the above input parameters, we have computed the changes with time in the following output parameters: (g) the atmospheric pCO_2 and pO_2; (h) the burial fluxes and contents of organic C and carbonate C in new sediments; (i) carbon isotopic compositions of organic C and carbonate C in new sediments; (j) the total masses and isotopic compositions of the organic C and carbonate C reservoirs in the crust; and (k) the organic C content of soil. Our model is not a steady-sate box model, but a dynamic one. It incorporates the observed relationships among the organic burial flux, dissolved O_2 content of deep ocean, and clastic sedimentation rate, the three-box model ocean (Sarmiento, 1992), the equilibrium ocean-atmosphere-carbonate model of Kump and Arthur (1999), the kinetic data of oxidation of coal (Chang and Berner, 1999) as a proxy for the oxidation of kerogen in sedimentary rocks, and the dynamics of soil formation and erosion (Lasaga et al., 1994).

Our computations have revealed that the atmospheric pO_2 level has been maintained primarily by the coupling of two negative feedback mechanisms: (1) the increase of O_2 production rate with decreasing pO_2 and with increasing rate of clastic sedimentation; and (2) the increase of O_2 consumption rate with increasing pO_2 and with increasing rate of erosion. The stability of the oxygenated atmosphere is demonstrated by a worst-case scenario in which the flux of reduced volcanic gas (H_2, CH_4, H_2S, CO, etc.) is increased to 5 times the present flux for a period of 10 Ma. In this scenario, the pCO_2 drops to 0.03 PAL but the pO_2 drops only to 0.6 PAL in 10 Ma. Both the pCO_2 and pO_2 rebound to today's values in ~20 Ma after the cessation of the increased volcanism.

Many researchers suggest that the Archean atmosphere was essentially free of O_2 because the consumption rate of O_2 by reduced volcanic gas was higher than the O_2 production rate. However, our computations suggest that such a scenario would have resulted in a nearly complete loss of atmospheric CO_2 and a nearly complete conversion of the carbonate reservoir to organic C. In contrast, under a moderate flux (e.g., ~3 X the present flux) of reduced volcanic gas and with an initial pCO_2 of 100 PAL, a stable, oxygenated atmosphere with today's pO_2 develops in about 3 Ma since the first appearance of cyanobacteria. That is, a sudden and dramatic rise of atmospheric oxygen is likely to have occurred before 2.7 Ga according to the molecular fossil evidence (Brocks et al., 1999) and possibly before 3.5 Ga according to the morphological fossil evidence (Schopf, 1993).

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