A framework for understanding the first and second rises of O_2

DAVID C. CATLING[1]

[1]Dept. Earth and Space Sciences/ Astrobiology Program, Univ. of Washington, Box 351310, Seattle WA, USA

Oxygenation of the atmosphere and oceans was determined by key source and sink fluxes of O_2. In terms of reductants, key fluxes are: (1) the escape of hydrogen to space F_E, (2) the 'net' flux of O_2 associated with the burial of organic carbon and sulfide derived from sulfate, F_B, (3) the flux to the atmosphere of aerial volcanic and metamorphic gases F_{VM}, (4) the continental oxidative weathering flux F_W, which depends on atmospheric pO_2, (5) reductants associated with seafloor volcanism F_{OV}, and (6) seafloor weathering F_{OW}. The last two fluxes connect seafloor redox to the surface environment. The seafloor weathering flux depends on pO_2 through downward mixing of O_2 and marine sulfate.

I propose a model where the relative magnitude of these fluxes determine three redox stages of Earth history with different mean states: I. anoxic (before 2.4 Ga), III. oxic (Proterozoic) and III. highly oxic (after late Neoproterozoic).

In state I, an anoxic atmosphere is relatively rich in hydrogen-bearing species, by definition, and so F_E is non-negligible. Thus, $F_B < F_{VM}$ and $F_E \approx F_{VM} + F_{OV}$. Since F_E is (to first order) proportional to the concentration of atmospehric CH_4, a model solution gives 100s to 1000s of ppmv CH_4 for reasonable $F_{VM} + F_{OV}$. The transition from I to II is reached when F_B exceeds F_{VM}. These two fluxes are small compared to gross biogenic gas fluxes, but the redox state of the atmosphere is set by small differences between large fluxes. In state II, enough O_2 allows continental weathering, and F_W is non-negigible. F_E (though persistent for probable mid-Proterozoic CH_4 levels) is small compared to other fluxes. A balance is $F_B \approx F_{VM} + F_{OV} + F_{OW} + F_W$. Seafloor volcanic and weathering fluxes buffer O_2 in the deep ocean to low levels. F_W depends on O_2 and a model solution in state II gives O_2 mixing ratios of 0.2-2% absolute. In state III, seafloor buffering is exhausted and the dominant balance is $F_B \approx F_{VM} + F_{OV} + F_W \approx F_W$, allowing Phanerozoic O_2 levels of 10-30%.

Driving state I to II are hydrogen escape [1] and possible geologic evolution affecting volcanic fluxes [2, 3]. The possible drivers of state II-III include hydrogen escape and sulfide burial and subduction [4].

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Archaeological practices validating mineralogical and geochemical analyses in metal provenance studies. The gold mines from central Gaul (France) case study

B. CAUUET*[1], C.G. TAMAS[2], S. BARON[1] AND J. MILOT[1]

[1] TRACES-CNRS, 5, allées A. Machado, 31058 Toulouse Cedex 09, France. (*corresponding author: cauuet@univ-tlse2.fr)

[2] University Babes-Bolyai, 1, M. Kogalniceanu str., 400084 Cluj-Napoca, Romania

A quality protocol regarding the selection of materials used and/or formed during the chaîne opératoire from the ore of an Ancient mine to the produced metal is proposed. This protocol, based on many archaeological findings during the 90ies is applied here for Limousin (France) Au province exploited during Gaul times.

The Gaul mining in Fouilloux deposit (3rd to end of 1st c. BC) was focused on a quartz vein with native gold, electrum and sulfides (arsenopyrite, stibnite etc.) with a N60 strike and a dip of 62o to the NW. The exploitation started in an open pit with several benches going down to a depth of 20 m and afterwards continued in underground closely following the ore body on another 10 m depth. The underground stope follows the dip of the ore body and has 2 to 2.5 m width. Pillars have been preserved within the ore body by the Gaul miners for safety reasons. The pillars are high grade (around 90 g/t Au) and represent a certified archaeological ore occurrence which is used for metal tracing.

Ore treatment workshops were discovered nearby with remnants of the Ancient metallurgy (e.g. archaeological roasted ore) and remainders of the produced gold. A low open furnace for the gold metallurgy and a touchstone preserving golden traces was discovered in Fouilloux, as well as crucibles in Cros Gallet-Nord gold mine situated nearby. These artifacts allowed reconstitution of the various operations of the chaîne opératoire of gold production from La Tène in Limousin and will be used for metal tracing.

Archaeo-Metallurgical experimental operations using gold ore from a third Gaul mine, Laurieras allowed us to produce materials which will be also analyzed, i.e. raw ore, grilled ore, slags, and gold brought out directly from the crucible.

Mineralogical and geochemical analyses are ongoing on the materials obtained through experimental works on Au ore from Laurieras. The results obtained on experimental products will be compared with the results on archaeological materials discovered in Fouilloux and Cros Gallet-North Gaul mines.

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