

## Seawater-ocean crust interaction and Proterozoic oxidation

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The redox evolution of the Earth surface depends on both exogenic processes and coupling with Earth's interior. The continuous production of oceanic crust (OC) generates a reactive reservoir of reducing potential, controlled by the high ferrous iron content. Reactions in the ocean-crust interface zone act as an important global redox sink [1, 2]. Exogenic redox processes (largely the burial of organic carbon) must generate oxidative potential equal to the reduction rate by SW-crust interaction simply for the Earth surface oxidation state to remain constant. Net oxidation of the ocean-atmosphere system requires that oxidants be produced faster than they are consumed by SW-crust interaction, as well as by other sinks. The rate of SW reaction with the reduced OC reservoir depends on the extent of fluid-rock interaction, which is partly a function of the thermal state of the crust. The thickness, thermal gradient and Fe content of the OC are a function of mantle potential  $T$  that has declined over time [3].

The rate of redox reactions between the OC and SW depend on the composition of the OC and content of oxidized species in the oceans, as well as the reaction pathways. Oxidation currently largely takes place in the OC, as  $O_2$ ,  $NO_3^-$  and  $SO_4^{2-}$  are present in deep SW that infiltrates the upper OC. Under conditions with low or absent deep ocean oxidants, the locus of reaction is moved out of the OC and into the water column. Dissolved Fe is generated by reactions between oxidant-depleted fluid and the OC, and introduced into deep water. In the absence of an analog environment, reaction path modeling can be used to constrain the flux of Fe from the OC to SW. The magnitude of the OC redox sink in a low oxidant ocean is dependent on this flux. A critical threshold occurs when the deep ocean becomes oxidizing and redox reactions move into the OC from the water column. A better understanding of this critical term in global redox evolution requires improved representations of the thermal, hydrologic and geochemical processes under conditions different from the present.

[1] Lecuyer and Ricard (1999) *EPSL* **165** 197-211.  
[2] Hayes and Waldbauer (2006), *Phil. Trans Roy. Soc. B* **361** 931-950. [3] Herzberg et al. (2010) *EPSL* **292** 79-98.