

## **Emerged Archaean oceanic crust and its role for regulating the composition of the early atmosphere.**

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The first geochronological date obtained one century ago by Rutherford via the measurement of accumulated helium (He) from radioactive decay of uranium (U), while spectacular and elegant, was compromised by the tendency of He to diffuse from the U-bearing mineral. The report by Rutherford nevertheless further ignited the already fiery debate about the age of the Earth and how to best determine it. In 1907, Boltwood concluded from a survey of U-rich minerals that the final decay product of U must be lead (Pb). Arthur Holmes thus investigated the possibility of dating rocks with the U-Pb method. Namely, after elapse of sufficient time the quantity of Pb that had accumulated from decay of U could be used to estimate the age of the mineral. This phenomenon made it possible for Holmes to extract the first U-Pb geochronological date of 370 million years from a U-rich rock from Norway. During WW1, with the realisation that the final decay product from radioactive Th was also Pb, it became necessary not only to determine the concentrations of U, Th and Pb, but also the exact atomic weight of Pb. From this, an estimate of the contribution of the then known two Pb isotopes to the overall Pb extracted from the mineral was possible. This gravimetric mass 'spectrometry' allowed researchers at Vienna's Radium Institute to determine the age of minerals with a high degree of accuracy.

From the late 1950ies, mass spectrometers made it possible for chemists and physicists to determine the isotopic make-up of Pb more and more accurately. This opened the discipline of plumbo-tectonics. Namely, it was realised that minerals that do not contain significant U and Th, but are quite rich in indigenous Pb, can be used to extract information about the geological setting that a rock had formed in. As the international database for Pb isotopes in ores expanded, it was further realised that the global picture contained information about how the Earth differentiated over its 4.568 Ma life time. Important advances in modelling terrestrial differentiation were made by Zartman&Haines (1988) and more recently by Kramers&Tolstikhin (1997).

A significant implication of combined modelling of terrestrial Pb and Nd isotopes is that the mass of continental crust has increased with time in a sigmoidal fashion that saw the largest net growth during the late Archaean and early Proterozoic. However, the hypothesis of small Archaean continents and limited weathering and recycling of continental crust causes a problem for observations relevant to the atmosphere. Namely, the geological evidence for liquid water in the early Archaean (pillowed basalts) implies that the faintness of the young Sun was counter-acted by a dense atmosphere of greenhouse gases, mostly CO<sub>2</sub>. Yet by 2.3 Ga, there is excellent evidence for widespread glaciation, which implies that virtually all of the CO<sub>2</sub> from the early atmosphere had gone through the Urey cycle. This refers to the draw-down of CO<sub>2</sub> via weathering into sediments. This is where the paradox of a small Archaean continental crust arises. Namely, there does not appear to have been sufficient exposure of continental rocks to draw-down sufficient CO<sub>2</sub>. Should this problem be interpreted to question Kramers&Tolstikhin's (1997) finding of slow increase of

continental volume (Harrison et al., 2005), or is this a true paradox that requires an alternative explanation, such as what I propose here?

Analyses of the rare earth elements (REE&Y) in precipitates from seawater (cherts, stromatolites and banded iron formation) have now demonstrated that the ocean's REE&Y characteristics appear to have remained largely unchanged since 3.7 Ga. Lawrence&Kamber (2006) have recently shown that the shale-normalised REE&Y pattern of seawater is created in the estuary, where organo-metallic complexes from freshwater destabilise in the face of the high ionic strength of seawater. The important implication of this discovery is that for as long as the marine REE&Y pattern has existed there must have been land, rivers, estuaries and a sea.

In fact, the exact shape of the marine REE&Y pattern is influenced by the balance between REE&Y input from hydrothermal vents into the deep ocean and input from land via rivers and dust. Neither of these inputs are fully constrained for the geological past but what is clear is that the mass of continental crust imposed by Nd and Pb isotope systematics of the Earth is not sufficient to provide the necessary REE&Y input seen in Archaean chemical sediments. Nd and Pb isotope systematics are in agreement with the marine Sr isotope record, which also requires low continental inputs.

The solution to this paradox is simple. The Archaean land area did not only consist of continents but also of emerged oceanic 'land'. The amount of oceanic 'land' required by REE&Y modelling is ca. 50% of the present land at 3.7 Ga and ca. 70% at 2.5 Ga, after which this type of land probably started disappearing. There are two attractive aspects to this solution. First, it is not in conflict with Sr isotopes because the relatively short lifespan of oceanic crust did not permit ingrowth of significant radiogenic Sr such that the marine Sr isotope record cannot discriminate between hydrothermal input and input from exposed oceanic crust. Second, due to its short lifespan, exposed oceanic crust is also an ideal candidate for CO<sub>2</sub> draw-down from the atmosphere. Unlike the continents, which can have extremely ancient surfaces, oceanic plates are replaced at a steady rate and allow the recycling of CO<sub>2</sub> into the mantle.

How exactly exposed oceanic crust would have looked remains a matter of speculation. However, the higher inferred upper mantle potential temperature of the Archaean necessarily created much thicker oceanic plates, which, under the right circumstances, apparently sometimes emerged and helped to balance the composition of the atmosphere.

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