The evolving nature of terrestrial crust from the Hadean, through the Archaean, into the Proterozoic

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The ancient rock and mineral records show that Hadean crust could persist for 500-700 Ma. Notwithstanding the general longevity of evolved crust, the well-established major Precambrian time boundaries remind us that terrestrial geology did not proceed in a uniform manner. The Hadean-Archaean boundary witnessed the near-complete destruction of the Hadean crust. This crust was chemcially diverse, and at least the zircon bearing magmas formed at relatively low T and had interacted with the hydrosphere. Opinions diverge as to whether these attributes imply plate tectonics. Advocates of the existence of Hadean continental lithosphere have yet to propose a plausible mechanism by which this lithosphere was destroyed. Those who appeal to internal differentiation of largely basaltic crust, aided by volcanic resurfacing, can appeal to the episodic collapse of early planetary crustal lids to explain the disappearance of Hadean crust.

Regardless of this unresolved debate, agreement exists that the entire Archaean record is dominated by greenstone-granitoid terrains. The much-improved greenstone belt geochronological database demonstrates that most of these edifices grew vertically, by repeated eruptions of new volcanic sequences on top of older ones. Although they do not represent oceanic crust, the existence of subduction and subductable oceanic lithosphere can be inferred from a variety of observations, ranging from granitoid geochemistry to diamond inclusions. It is thus proposed that the Archaean represents the era of three types of plates: continental and oceanic lithosphere as well as prominent oceanic plateaus.

The Palaeoproterozoic rock record differes in many ways. Greenstone belts have disappeared, platform sediments have become abundant and the first very high-P rocks are preserved at the Earth's surface. These phenomena reflect a change in the mechanical stength of the continents, which increased due to less internal heat production and redistribution of K, Th and U. However, the disappearance of komatiites and the unexpected lack of increase in extent of mantle depletion from 2.7 Ga to 2.0 Ga argue for mantle reorganisation. It is here proposed that a mechanical and thermal boundary layer existed in the mantle transition zone until the end of the Archaean. This led to severe depletion in the upper mantle, promoted build up of heat plumes and prevented recycling of oceanic plates into the deep mantle. Accordingly, the onset of deep recycling is dated by the ca. 2 Ga 'age' of OIB sources.

A first-order deep time reconstruction of the marine Sr/Ba ratio from microbial carbonate

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The upper crust is enriched in Sr and Ba where they occur at a mass ratio of ca. 1.25. The dissolved river load has a Sr/Ba of ca. 1.8, whereas residual weathering profiles have a Sr/Ba of ca. 0.9, showing that Sr is more easily released. In our estuarine transects both elements behave conservatively. Once in the ocean, the fates of Ba and Sr diverge sharply. Sr has a long residence time and is homogenously distributed whereas dissolved Ba concentration in seawater is very low and varies systematically with depth [1] (very depleted in the shallow ocean and more enriched at depth). The overall depletion and the depth structure are explained by Ba-removal as biogenic marine barite in organisms and its partial re-release at depth. Hanor [2] predicted that this type of barite formation may not have been constant through time and that marine Ba could be a proxy for sulphate concentration.

Our data from Holocene microbial carbonate faithfully record the very high but variable Sr/Ba (400-1,200) of very shallow seawater. In situ LA-ICP-MS of partly dolomitised samples clearly indicate that dolomitisation greatly increases the Ba content and our deep time reconstruction was conducted on best preserved calcite only. The reconstruction shows a very clear first-order Sr/Ba topology. The ratio remained very high (>>200) back to 555 Ma, decreased rapidly throughout the Proterozoic to 2-5 until the Great Oxygenation Event, before which it was quite constant at 10. This evolution is interpreted as a three step increase of marine sulphate levels. A second-order control on the shape of the Sr/Ba topology can be inferred from the absolute Sr and Ba concentrations in the microbial carbonate, which, for Sr, was much lower for most of the Precambrian but increased strongly after the Marinoan. This is important as it suggests a much reduced nutrient load to the Precambrian ocean with wide implications for other deep time studies (e.g. Mo in shale) that assume variable removal but constant supply of metals.

[1] Griffith and Paytan (2012) *Sedimentology* **59**, 1817-1835.
[2] Hanor (2000) *Rev. Min. & Geochem.* **40**, 193-275.

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