



## A relatively reduced Hadean continental crust

Xiaozhi Yang (1), Fabrice Gaillard (2), and Bruno Scaillet (2)

(1) State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210046, PR China (xzyang@nju.edu.cn), (2) Institut des Sciences de la Terre d'Orléans, CNRS/Université d'Orléans/BRGM, 1a rue de la Férollerie 45071, Orléans cedex 2, France[

Among the physical and chemical parameters used to characterize the Earth, oxidation state, as reflected by its prevailing oxygen fugacity ( $f\text{O}_2$ ), is a particularly important one. It controls many physicochemical properties and geological processes of the Earth's different reservoirs, and affects the partitioning of elements between coexisting phases and the speciation of degassed volatiles in melts. In the past decades, numerous studies have been conducted to document the evolution of mantle and atmospheric oxidation state with time and in particular the possible transition from an early reduced state to the present oxidized conditions. So far, it has been established that the oxidation state of the uppermost mantle is within  $\pm 2$  log units of the quartz-fayalite-magnetite (QFM) buffer, probably back to  $\sim 4.4$  billion years ago (Ga) based on trace-elements studies of mantle-derived komatiites, kimberlites, basalts, volcanics and zircons, and that the  $\text{O}_2$  levels of atmosphere were initially low and rose markedly  $\sim 2.3$  Ga known as the Great Oxidation Event (GOE), progressively reaching its present oxidation state of  $\sim 10$  log units above QFM. In contrast, the secular evolution of oxidation state of the continental crust, an important boundary separating the underlying upper mantle from the surrounding atmosphere and buffering the exchanges and interactions between the Earth's interior and exterior, has rarely been addressed, although the presence of evolved crustal materials on the Earth can be traced back to  $\sim 4.4$  Ga, e.g. by detrital zircons.

Zircon is a common accessory mineral in nature, occurring in a wide variety of igneous, sedimentary and metamorphic rocks, and is almost ubiquitous in crustal rocks. The physical and chemical durability of zircons makes them widely used in geochemical studies in terms of trace-elements, isotopes, ages and melt/mineral inclusions; in particular, zircons are persistent under most crustal conditions and can survive many secondary processes such as metamorphism, weathering and erosion. Thus, zircons in granites of shallow crust may record the chemical/isotopic composition of the deep crust that is otherwise inaccessible, and offer robust records of the magmatic and crust-forming events preserved in the continental crust. In fact, due to the absence of suitable rock records (in particular for periods older than  $\sim 4.0$  Ga), studies in recent years concerning the nature, composition, growth and evolution of the continental crust, and especially the Hadean crust, have heavily relied on inherited/detrital zircons. Natural igneous zircons incorporate rare-earth elements (REE) and other trace elements in their structure at concentrations controlled by the temperature, pressure,  $f\text{O}_2$  and composition of their crystallization environment. Petrological observations and recent experiments have shown that the concentration of Ce relative to other REE in igneous zircons can be used to constrain the  $f\text{O}_2$  during their growth.

By combining available trace-elements data of igneous zircons of crustal origin, we show that the Hadean continental crust was significantly more reduced than its modern counterpart and experienced progressive oxidation till  $\sim 3.6$  billions years ago. We suggest that the increase in the oxidation state of the Hadean continental crust is related to the progressive decline in the intensity of meteorite impacts during the late veneer. Impacts of carbon- and hydrogen-rich materials during the formation of Hadean granitic crust must have favoured strongly reduced magmatism. The conjunction of cold, wet and reduced granitic magmatism during the Hadean implies the degassing of methane and water. When impacts ended, magma produced by normal decompression melting of the mantle imparted more oxidizing conditions to erupted lavas and the related crust.