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A relatively reduced Hadean continental crust and implications for the early atmosphere and crustal rheology

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ABSTRACT

It is widely believed that the Earth was strongly reduced during its early accretion, however, the transition from the reduced state that prevailed during Earth's early period to the modern oxidized crust and mantle has never been captured by geochemical surveys on Earth materials as old as ~4.0 billion years ago. 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 ~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 chondritic addition during the late veneer. Inputs of carbon- and hydrogen-rich chondritic materials during the formation of Hadean granitic crust must have favored strongly reduced magmatism. The conjunction of cold, wet and reduced granitic magmatism during the Hadean implies the production of methane-rich fluids, in addition to the CO- and H_2-rich volcanic species produced by degassing of hot reduced basaltic melts as modified by delivered materials during the late veneer. When the late veneer events ended, magma produced by normal decompression melting of the mantle imparted more oxidizing conditions to erupted lavas and the related crust, emitting CO_2- and H_2O-rich gases. Our model suggests that the Hadean continental crust was possibly much weaker than present-day, facilitating intrusion of underplating magma and thus allowing faster crustal growth in the early Earth.

1. Introduction

Among the physical and chemical parameters used to characterize the Earth, oxidation state, as reflected by its prevailing oxygen fugacity (fO_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 (Collerson and Kamber, 1999; Delano, 2001; McCammon, 2005; Zahnle et al., 2010). In the past decades, numerous studies have been conducted to document the evolution of mantle and atmospheric oxidation states with time in an effort to elucidate possible transitions from an early reduced state to present oxidized conditions. So far, it has been established that the oxidation state of the uppermost mantle is within ±2 log units of the quartz–fayalite–magnetite (QFM) buffer, probably back to ~4.4 billion years ago (Ga) based on trace-elements studies of mantle-derived komatiites, kimberlites, basalts, volcanics and zircons (Canil, 1997; Delano, 2001; Li and Lee, 2004; Trail et al., 2011). It has been also established that the mantle becomes increasingly reduced with depth, reaching fO_2 as low as QFM-4 at ~200 km (McCammon, 2005; Rohrbach et al., 2007). The atmosphere also experienced changes in fO_2, being initially low, and rising markedly at ~2.3 Ga, during the so-called Great Oxidation Event (GOE) (Collerson and Kamber, 1999; Holland, 2002; Zahnle et al., 2010), progressively reaching its present oxidation state of ~10 log units above QFM (McCammon, 2005). In contrast, the secular evolution of oxidation state of the continental crust, an important boundary layer separating the underlying upper mantle from the atmosphere and buffering the exchanges and interactions between the Earth's interior and exterior, has rarely been addressed, though the presence of evolved crustal materials on the Earth can be traced back to ~4.4 Ga in particular via detrital zircons (e.g. Wilde et al., 2001).

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 (e.g. Hawkesworth et al., 2010). 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

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persistent under most crustal conditions and can survive many secondary processes such as metamorphism, weathering and erosion (Harrison, 2009; Hawkesworth et al., 2010). 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 ∼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 (Wilde et al., 2001; Valley et al., 2002; Harrison, 2009; Hawkesworth et al., 2010). Natural igneous zircons incorporate rare-earth elements (REE) and other trace elements in their structure at concentrations controlled by temperature, pressure, fO_2 and melt composition (Hanchar and van Westrenen, 2007). Petrological observations (e.g. Ballard et al., 2002) and recent experiments (Trail et al., 2011, 2012; Burnham and Berry, 2012) have shown that the concentration of Ce relative to other REE in igneous zircons can be used to constrain the fO_2 during their growth. In this report, the change of crustal oxidation state with time is evaluated by using reported trace-elements data for igneous zircons of inferred crustal origin.

2. Ce-based zircon oxybarometers

Available Ce-based zircon oxybarometers include:

$$\ln\left(\mathrm{Ce}/\mathrm{Ce}^*\right)_{CHUR} = (0.1156 \pm 0.0050) \times \ln(fO_2) + \frac{13\,860 \pm 708}{T} - (6.125 \pm 0.484) \quad (1)$$

$$\ln\left(\mathrm{Ce}/\mathrm{Ce}^*\right)_{CHUR} = (0.0433 \pm 0.008) \times \ln(fO_2) + \frac{7123 \pm 1309}{T} - (3.113 \pm 1.072) \quad (2)$$

$$\log\left(\mathrm{Ce}/\mathrm{Ce}^*\right)_{CHUR} = (0.1625 \pm 0.0143) \times \left(\log(fO_2) - \mathrm{QFM}\right) + (0.274 \pm 0.053) \quad (3)$$

where $(\mathrm{Ce}/\mathrm{Ce}^*)_{CHUR}$ is the chondrite-normalized Ce anomaly in zircon and T is the zircon crystallization temperature (K). Eqs. (1) and (2) were obtained with experiments conducted at 10 kbar and 800–1300 °C on hydrous peraluminous and peralkaline granitic melts, respectively (Trail et al., 2011, 2012), whilst Eq. (3) is an empirical form (Supplementary Material) derived from experiments conducted at 1300 °C and 1 bar on a dry andesitic melt (Burnham and Berry, 2012).

Crystallization of zircon requires that its parental melt must be Zr-saturated, and considering the average Zr concentration in the upper mantle, ∼5 ppm (Workman and Hart, 2005), Zr saturation in nature would be mostly, if not only, achieved in felsic, non-peralkaline derivatives (Watson, 1979), agreeing with the general knowledge that natural zircons are almost ubiquitous in crustal materials and the Hadean crustal zircons probably grew from felsic granitic melts (e.g. Harrison, 2009). In this study, we have mostly used Eq. (1), because partial melting of standard crustal protoliths (e.g. Rapp and Watson, 1995; Montel and Vielzeuf, 1997) yields either metaluminous or peraluminous silicic liquids, not peralkaline. The occurrence of strongly peraluminous minerals as inclusions in Hadean crustal zircons, in particular muscovite (e.g. Hopkins et al., 2008), indicates that their original melts were most likely metaluminous or peraluminous (Harrison, 2009). Metaluminous/peraluminous silicic melts reach zircon saturation at reasonable values (<100 ppm), while natural peralkaline melts have very high Zr solubility (thousands of ppm to several wt%), which prevents them from crystallizing zircons (Watson, 1979) in the temperature range recorded by most, if not all, crustal zircons, e.g. 650–900 °C (Fu et al., 2008). In addition, Ce-anomalies in zircons from peralkaline melts are less sensitive to changes in oxygen fugacity and are thus unlikely to yield robust constraints on the oxidation state of natural magmas (Trail et al., 2012). Eq. (3) is calibrated on a less felsic (andesitic) metaluminous composition and at high temperature (1300 °C) only: it illustrates that zircon can also record redox conditions in mafic magmas, however, it cannot be applied directly to low-temperature zircons (Burnham, 2013).

In addition to the above mentioned Ce-based zircon oxybarometers, there are also a few experimentally calibrated Eu-based zircon oxybarometers (Burnham and Berry, 2012; Trail et al., 2012), which may be equally used to place constraints on the prevailing oxygen fugacity of the environment during the growth of igneous zircons. However, the use of Eu is less straightforward than that of Ce, because, in addition to fO_2, the crystallization of feldspar, a major phase for hosting Eu, can also strongly affect the partitioning of Eu into coexisting zircon. Therefore, although experimental studies have demonstrated that the Eu anomaly, Eu/Eu*, in igneous zircons is not affected by crystallization temperature (Trail et al., 2012), application of Eu-based oxybarometers calibrated from zircon-only (+ glass) experiments, is unlikely to be valid in systems crystallizing abundant feldspar such as the continental crust (Supplementary Material).

3. Data compilation of igneous crustal zircons

Igneous zircons of crustal origin were compiled from previous reports (Table 1), totaling more than 300 data points (see Supplementary Materials for more details). These zircons, from a range of lithologies, encompass a wide range of formation ages from ∼4.4 Ga to almost the present (∼40 Ma). All these zircons were used to study the composition/evolution/growth of the continental crust in previous studies (Hoskin and Ireland, 2000; Ballard et al., 2002; Whitehouse, 2003; Whitehouse and Kamber, 2003; Cavosie et al., 2006; Bouvier et al., 2012; Mueller and Wooden, 2012).

To ensure the calculation and comparison of fO_2 between different periods, the following criteria were applied: (1) the well-studied Hadean Jack Hills and Hadean to Archean Wyoming Province detrital zircons and post-Hadean inherited zircons, typical of continental crust origin, were selected; (2) the contents of REE and other trace elements of the zircons were measured *in situ* by ion microprobe or laser-ablation inductively-coupled-plasma mass-spectrometry; (3) the selected zircons are of typical igneous origin, as evaluated by their textures and/or by their REE patterns (Fig. 1) and other trace-elements features as summarized by Hoskin and Schaltegger (2003), including depleted light-REE relative to heavy-REE, positive Ce-anomaly, negative Eu-anomaly and reasonable total REE abundance (in rocks of mantle affinity, zircon usually has much lower total REE abundance); (4) for the Hadean detrital zircons, only grains with typical crustal-δ^{18}O values, e.g., higher than 5.3 ± 0.3‰ for normal mantle (Trail et al., 2011), were chosen (see also Cavosie et al., 2006).

We excluded the following categories of zircons: (1) zircons with abnormal contents/patterns of REE and other trace elements, including data from likely altered zircon grains/domains (e.g. Type 2 zircons of Cavosie et al., 2006, which were excluded because of their too high La contents (e.g. >0.3 ppm) relative to igneous crustal zircons (<0.1–0.2 ppm), see Hoskin and Schaltegger, 2003); (2) zircons of the Hadean ages, where grain-/domain-scale age information is not available or whose trace-elements contents and/or O-isotopic compositions are not reliable (e.g., the data in parentheses in Cavosie et al., 2006 who stated that "parentheses around age or δ^{18}O data indicate a value that is not considered reliable"), were discarded.