



The redox geodynamics linking basalts and their mantle sources through space and time



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ABSTRACT

The Earth's mantle redox state regulates the fate and transfer of metals by magmatism, buffers the igneous inputs of volcanic gases in the atmosphere and controls the depth of mantle melting. It therefore strongly affects ore forming processes, biogeochemical cycles and deep geodynamic processes. This paper reviews the current knowledge on the redox state of the upper mantle and of magmas produced by mantle melting. The geochemical processes likely to control and modify it through space and time are discussed.

We analyze the link between the redox state of magma and that of their mantle source and we conclude that melts produced in the mantle may well all equilibrate in a narrow range of oxidation state, where the speciation of sulfur in basalts shifts from sulfide to sulfate, that is, $FMQ+1 \pm 1$ (1 log unit below and above the oxygen fugacity buffered by the assemblage fayalite–magnetite–quartz). Subsequently, degassing and partial crystallization of melts can affect their redox states, producing most of the range of redox states observed on magmas reaching Earth's surface. The asthenosphere sourcing basaltic magmas may therefore be more oxidized than the $FMQ-1$ value generally assumed.

We also discuss redox transfers from the mantle to the atmosphere via volcanic degassing and the backward fluxes via subduction processes of the hydrothermalized oceanic lithosphere. Arc-magmas are oxidized (up to $FMQ+4$) but it is unclear when this feature is acquired since strongly oxidized primary arc-basalts have yet to be found. The oxidizing event may be the assimilation of slab-derived SO_3 -rich fluids by primary basalt generated by decompression melting in the mantle-wedge.

Overall, subduction must result in a transfer of oxygen from the Earth's surface down to the mantle. This must imply that subduction and its initiation can hardly be the trigger of the great oxidation event at the end of the Archaean. In contrast, the cooling of the Earth's interior through time must have impacted on the redox state of basalts, by decreasing the depth of mantle melting. According to the long-established vertical stratification of the Earth's mantle, ancient primary magmas are therefore likely to have been more reduced (i.e. $<FMQ-3$) than present-day ones. However, geochemical observations on ancient basalts suggest a constant oxidation state since the early Archaean.

We conclude that large uncertainties in the calibration of mineralogical oxygen barometer probably explains why we have difficulties in identifying (i) ancient primary basalts being more reduced than recent ones and (ii) primary basalts from subduction zones being as oxidized as arc-lavas reaching the surface. Finally, the degree of mantle melting is certainly a key issue for the interpretation of the mantle oxidation state. Extremely oxidized melts, enriched in C–H–S volatile species, produced by very low degrees of mantle melting may be indicative of an Earth's mantle more oxidized than usually considered.

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1. Introduction: oxygen fugacity and redox transfers

The redox state of the Earth's mantle is of prime interest as it fuels numerous processes such as the behavior and fate of metallic elements involved in ore deposits (Mungall, 2002; Mungall et al., 2006; Ganino

et al., 2008; Jenner et al., 2010; Zajacz et al., 2013; Richards, in press), the depth of partial melting and associated mantle weakening (Rohrbach and Schmidt, 2011; Dasgupta et al., 2013; Stagno et al., 2013; Sifre et al., 2014), and the speciation of magmatic gases that are conveyed to the atmosphere by volcanic degassing (Holland, 2002; Edmonds, 2008; Gaillard et al., 2011; Iacono-Marziano et al., 2012a; De Moor et al., 2013; Gaillard and Scaillet, 2014; Moussallam et al., 2014; Yang et al., 2014). In this paper, we focus on igneous redox processes, leaving aside near surface redox processes intimately tied to

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life such as H_2 ($\pm \text{CH}_4$) production associated with serpentinization of oceanic crust (Sleep et al., 2011; Russell et al., 2013) or sulfate reduction in sediments (Lyons and Gill, 2010).

Identifying variations in mantle redox state both in time and space and capturing the parameters that control redox state inside the Earth is the kernel of a wide and active debate in Earth and planetary sciences (Ballhaus et al., 1991; O'Neill et al., 1993; Ballhaus and Frost, 1994; Canil, 1997; Delano, 2001; Canil, 2002; McCammon, 2005; Frost and McCammon, 2008; Hirschmann, 2009; Kelley and Cottrell, 2009; Scaillet and Gaillard, 2011; Trail et al., 2011; Foley, 2012; Lee et al., 2012; Keller and Schoene, 2012; Bali et al., 2013; Yang et al., 2014). The second issue is about whether the redox state of basalts and associated volcanic gases reflects their mantle source regions (Carmichael and Ghiorso, 1986; Carmichael, 1991; Lee et al., 2005; Mallman and O'Neill, 2009; Kelley and Cottrell, 2012; Moussallam et al., 2014), and if not, what are the processes likely to change magma redox state upon ascent to the Earth's surface (e.g., Carmichael and Ghiorso, 1986; Carmichael and Ghiorso, 1990; Gaillard et al., 2011; Iacono-Marziano et al., 2012b; Kelley and Cottrell, 2012; Moussallam et al., 2014). So far, iron, owing to its high abundance and variable oxidation state, has been identified as the main redox buffer in mantle rocks and mantle-derived magmas (Wilke, 2005; Behrens and Gaillard, 2006; Rohrbach et al., 2007; Frost and McCammon, 2008). However, volatile elements such as hydrogen, carbon and sulfur have tremendously variable oxidation states (Behrens and Gaillard, 2006; Jugo, 2009; Rohrbach and Schmidt, 2011; Evans, 2012), and are therefore likely to locally affect, and even buffer, mantle and magma redox states.

The redox state of mineral, rocks, melts and fluids is conventionally related to oxygen fugacity, f_{O_2} , a thermodynamic parameter that gauges the availability of oxygen in a given system. High f_{O_2} characterizes oxidized systems (Frost, 1991). Several processes are likely to modify the f_{O_2} of rocks. The most intuitive is via a change in the oxygen/cation ratio of the rock, occurring in an open system, in which oxygen is truly gained or lost producing either an increase or a decrease in the oxygen/cation ratio of the system (Cooper et al., 1996; Behrens and Gaillard, 2006; Evans, 2008). A typical example is a fluid or melt interacting with a rock and generating reactions that can oxidize or reduce the pervaded system by rising or decreasing its oxygen/cation ratio. Such phenomena are documented in all geodynamic settings and are usually termed fluid–rock interactions as observed in mantle metasomatism (Menzies, 1983; Woodland et al., 1996; Coltorti et al., 1999; McCammon et al., 2001; O'Reilly and Griffin, 2012) and hydrothermal processes (Honnorez, 2003; Evans, 2008).

Variations in f_{O_2} also happen in closed systems when a phase change occurs. Melting, or mineralogical transitions are typically able to modify the f_{O_2} of a rock (and the oxygen/cation ratios of the individual phases), while degassing and crystallization can modify the f_{O_2} of a melt, even in absence of change of the oxygen/cation ratio of the bulk system (Carmichael and Ghiorso, 1986). An example is the decompression of graphite-saturated systems inducing graphite volatilization and the reduction of the system (Sato, 1978; Iacono-Marziano et al., 2012b; Shirayev and Gaillard, 2014). Yet, redox changes in a closed system may also occur via the modifications of properties of one or several phases constituting the rocks without phase transitions. Upon a change in pressure or temperature, the ability of a phase to preferentially take a reduced or oxidized species can vary. This in turn induces a change in oxygen availability in the system, which translates into a change in the equilibrium f_{O_2} (i.e., the f_{O_2} of the rock–melt–fluid involved in the system) whereas the oxygen/cation ratio of the bulk system remains unchanged. For instance the decompression of sulfur-bearing volcanic gases drives the system toward more reducing conditions (Burgisser and Scaillet, 2007; Gaillard et al., 2011; Kelley and Cottrell, 2012; Moussallam et al., 2014). Another example is the decompression of garnet-bearing peridotites leading to increasingly oxidizing conditions (Woodland and Koch, 2003; Rohrbach et al., 2007; Frost and McCammon, 2008; Rohrbach and Schmidt, 2011; Stagno et al., 2013; see Section 3.2).

Because the oxygen fugacity of systems with a given oxygen/cation ratio changes with changing pressure and temperature, f_{O_2} is conventionally expressed relatively to that buffered by a relevant mineral assemblage. The f_{O_2} of mantle rocks is usually calculated in log-units relative to that of the fayalite–magnetite–quartz redox buffer, FMQ (Frost, 1991). The f_{O_2} of most mantle rocks and magmas is conveniently over ca. 2 log-unit across the FMQ buffer (Carmichael, 1991; Frost and McCammon, 2008; Foley, 2011) but secular changes as well as regional controls significantly extend this range (Scaillet and Gaillard, 2011; Iacono-Marziano et al., 2012b).

This paper reviews the current knowledge on mantle f_{O_2} , (i) how it controls the f_{O_2} of mantle-derived magmas and impacts on volcanic gas compositions, (ii) how it varies with depth and (iii) how it may be modified by global geodynamics. The main purpose is to capture the processes that may have induced secular variations in redox state of the mantle and related magmas. Whenever possible, the link with the redox evolution of the atmosphere is emphasized.

2. The early redox story of the Earth's mantle and its magmatism

2.1. Magma ocean redox geodynamics: internal- and self-oxidation

It is well accepted that temperature was hot enough during planetary accretion, so as to permit large scale melting (magma oceans), and that conditions were reducing enough to trigger Fe-metal saturation from a molten silicate (e.g., Walter and Tronnes, 2004; Wood et al., 2006), that is, ca. 6 log-units below the present-day estimated/observed lithospheric mantle f_{O_2} . It is believed that several magma ocean events occurred during planet growth, from the earliest planetesimal stage to the ultimate planet-size, stage, including the Moon forming event (O'Neill, 1991; Greenwood et al., 2005). The temperature and depth of the magma ocean, hence the pressure at the bottom of the magma ocean, both increase with planet size (Wood et al., 2006; Rubie et al., 2011). For various reasons that we expose below, it is generally accepted that such an increase in pressure and temperature triggers/is accompanied by a progressive shift from strongly reduced to moderately reducing conditions. The enstatite chondrite model of Javoy (1995) has recently been rejuvenated by several workers (Wood et al., 2006; Javoy et al., 2010; Ricolleau et al., 2011; Rubie et al., 2011), based on the observation that laboratory-based metal–silicate partitioning coefficients better explain the depletion level of various chemical elements in the Earth's mantle (relative to their chondritic parents) if oxygen fugacity increased during accretion from ca. IW–5 to IW–2; the latter value has been inferred from the fairly uniform FeO content of the Earth's mantle requiring an f_{O_2} at IW–2 at Fe-metal saturation (Wood et al., 2006; Frost et al., 2008; Gaillard and Scaillet, 2009). An increase in f_{O_2} can be justified by the fact that at high P and high T, Si becomes soluble in metal according to the following reaction:



Recent modeling indicates that between 2 and 8 wt.% Si can be incorporated into the forming core (Ricolleau et al., 2011), which translates into a significant gain in FeO content of the coexisting silicate melt (at the base of the magma ocean). As long as metal and silicate melt coexist, the oxygen fugacity of the magma ocean is controlled by the following fundamental reaction:



Equilibrium (2) implies that any increase in the FeO content of the silicate melt is accompanied by an increase in f_{O_2} , which therefore affects partitioning of all elements between the silicate mantle and the metal core. The Enstatite chondrite model of Javoy (1995) implies an initial oxygen fugacity 5 orders of magnitude lower than that imposed by the iron–wüstite redox buffer (Fig. 1). Under such conditions, equilibrium (2) predicts that no FeO would be dissolved in the magma

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