

The Oxygen Budget of the Earth and the Oxidation State of the Archean Upper Mantle

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Knowledge of the oxygen fugacity (fO_2) of the mantle rocks is fundamental to any hypothesis regarding to the early history of the Earth (Arculus, 1985;), the composition of Earth's primitive atmosphere (Kasting, et al., 1993) and the composition of gases, exsolved by the terrestrial magmas in the upper layers of the Earth (Kadik, 1996; Javoy, 1995). Current models are based on the assumption that the redox state of the upper mantle has not changed, so that mantle volatile species and volcanic gas composition has remained approximately constant with time. We argue that this assumption is probably incorrect and the upper mantle was originally more reduced than today, although not as reduced as the metal arrest level, and has become progressively more oxidized. This work provides a data set on the fO_2 's recorded by the ancient rocks and minerals that indicate the redox state of the ancient lithosphere and the upper mantle as estimated from the electrochemical measurements and the mineralogical oxygen geobarometers: 1) the diamond-bearing peridotite and eclogite (an age of 3.3 - 3.5 Ga; 2) the "dry" mantle-xenolith sampled from several localities in Northeastern Eurasia (Mongolia, Baikal, Tien- Shan (an age of around 2 -2. 5 Ga); 3) the zircon crystals from the oldest orthogneisses of the Siberia (an age of 3.5 Ga) and from the granite - greenstone association of the middle Pridneprov'e (an age of 3.0 Ga). The fO_2 's of ancient rocks support idea that the upper mantle redox state has changed with time. The oxidation could be considered as the main trend of the upper mantle evolution. The process of mantle oxidation was slow, so that reduced conditions could have prevailed for as much as half of the Earth's history (Kasting et al. 1993; Kadik,1997) The observed oxidation of the ancient lithosphere is closely linked to the evolution of volatile species. In reduced areas, a separate carbon - saturated fluid, if it were stable, would be CH_4 . Volcanic gases could have been more reduced in the past if the magmas from which they were evolved had a lower fO_2 . As the planet evolved, it underwent a substantial change in the direction of increased oxygen potential

contraction of the free-carbon stability field, and correspondingly an increase in the proportions of oxidized carbon compounds such as CO_2 and also of H_2O in relation to the reduced compounds CH_4 , CO , and H_2 . An evolving mantle redox state would have important implications. The transition from a reducing to an oxidizing atmosphere near 2.5 Ga could be explained as the result of an increase in the oxidation state of volcanic gases. Some investigators debate whether this transition actually occurred at this time. The oxidation of the Earth's upper mantle was probably a mixture of complex physical and chemical processes: 1) the multi-stage mechanism of accretion, production of the upper mantle oxidized iron via the auto-redox process (Allègre et al., 1995; Javoy, 1995); 2) the solid-liquid mantle differentiation of the outer carbon-bearing layers of the primitive mantle, progressive oxidation occurred resulting perhaps largely from the preferred loss of hydrogen and carbon (Kadik, 1997); 3) the recycling of surface volatiles through the mantle and the fluxing of substantial volumes of fluids into the mantle (Arculus 1985). The plausible way to explain the present oxidized state of the most part of upper mantle is of surface volatiles recycling through the mantle followed by the subduction of seafloor from time about 2.5 Ga. Acknowledgements. This study was supported by Russian Fond of Fundamental Investigations (grant N 99-05-65479).

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