

**Electrochemical measurements of oxygen fugacity of rocks and meteorites.**

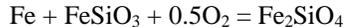
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Oxygen fugacity ( $fO_2$ ), along with temperature and pressure, is an important thermodynamic parameter, which allows researchers to describe the Red-Ox conditions of the formation and evolution of both terrestrial and meteoritic matter. Basically,  $fO_2$  is estimated indirectly with the use of the oxybarometers, i.e. by the presence of the phase equilibrium that fixes oxygen fugacity, and by the chemical composition of these phases. Another method to estimate oxygen fugacity is electrochemical measurements (EMF-method) that allow the direct measurement of  $fO_2$ .

The EMF-method is widely used to measure  $fO_2$  in the systems where the chemical potential of oxygen is fixed by oxygen buffers (Fe/FeO, Ni/NiO etc.). Sato [1] introduced the concept of intrinsic oxygen fugacity –  $fO_2$  of the monomineral fraction of rock. This concept can be grasped by considering the metal M that forms two stable oxides, MO and MO<sub>2</sub>. Then MO is only stable at  $fO_2$  (MO) such that  $fO_2$  (M/MO) <  $fO_2$  (MO) <  $fO_2$  (MO/MO<sub>2</sub>). Despite the stoichiometry of MO, the actual M/O ratio vary within narrow limits, and each composition correspond to a unique value of  $fO_2$  (MO). EMF-measurements conducted on several different monomineral fractions will result in a series of curves in terms of  $fO_2$ -T, and their intersection point will represent the conditions at which the studied rock was formed [1].

The main issue is that monomineral fraction itself cannot fix oxygen fugacity. The measured  $fO_2$  value depends on extensive parameters of the system: sample weight, the inner volume of the EMF cell, the amount of oxygen that the cell can absorb. It should be noted that the isolation of a truly monomineral fraction is a difficult process. The presence of additional phases will lead to a significant distortion of the results [2], up to the establishment of parasitic binary or triple equilibria that will shift  $fO_2$ . The surface area of the phase, determined by the degree of its grinding, may also affect the results [3]. However, even when these factors are taken into account, the angle of intersection of the obtained  $fO_2$ -T curves is too small, and the accuracy the coordinates of the intersection point is low.

On the other hand, an electrochemical measurement of  $fO_2$  in the bulk samples of meteorites and rocks is possible when the phases buffering the chemical potential of oxygen are present. In such case, extensive parameters will not affect the resulting  $fO_2$ . An example of a buffering reaction is the equilibrium between metallic iron, olivine and pyroxene, which is typical of ordinary chondrites:



In this equilibrium, all phases are multicomponent solid solutions, which greatly complicates the calculation of  $fO_2$  from corresponding thermodynamic models. The EMF-method allows to measure oxygen fugacity directly and does not require information on the exact chemical composition of the sample or auxiliary thermodynamic data.

[1] Sato M (1972) *Memoirs - Geological Society of America*. pp 289–308. [2] Kersting AB, Arculus RJ, Delano JW, Loureiro D (1989) *Contributions to Mineralogy Petrology* 102:376–388. [3] Righter K, Arculus RJ, Paslick C, Delano JW (1990) *Geochimica et Cosmochimica Acta* 54:1803–1815.