

Nanoscale Effects on the Thermodynamics of Oxidation-Reduction Equilibria in Transition Metal Oxide Systems

ALEXANDRA NAVROTSKY^{1*}

¹Peter A. Rock Thermochemistry Lab, University of California Davis, Davis, CA 95616 USA, anavrotsky@ucdavis.edu

Keynote Speaker

Many low temperature aqueous geochemical processes involve the precipitation, dissolution, and redox reactions of fine - grained (nanophase) transition metal oxide minerals. Because phases with different oxidation states have different structures and, often, different surface energies, their redox phase boundaries can be significantly shifted in oxygen fugacity - temperature space at the nanoscale. We have shown, for example, that FeO (wustite) has no stability field at the nanoscale, and that the stability field of magnetite is expanded relative to both reduction (to iron) and oxidation (to hematite) for small particles. A current calorimetric study suggests that fayalite has a higher surface energy than the assemblage magnetite plus quartz, thus shifting the QFM buffer to more reducing conditions for nanoparticles. In the manganese oxides, the phase field of Mn₃O₄ (hausmannite) is expanded relative to reduction to MnO and oxidation to Mn₂O₃, and the Mn₂O₃-MnO₂ equilibrium is also affected. Furthermore, there appears to be complex involvement of water in these redox reactions, with possible reversible formation of hydrated amorphous layers at the nanoscale. The thermodynamic effects of particle size on reactions at bulk and nanoscale in the system magnetite - maghemite - ulvöspinel are also under investigation. Thus significant nanoscale thermodynamic effects are a general phenomenon and must be considered, in addition to kinetic factors, in redox reactions in mineral and mineral - water systems at low temperature.

Amphiboles from the subcontinental lithospheric mantle of the Northern Victoria Land (Antartica): implications for the water activity and metasomatism

S. NAZZARENI^{1*}, C. BONADIMAN², P. COMODI¹, B. FACCINI², P.F. ZANAZZI¹, M. COLTORTI², AND G. GIULI³

¹ Department Earth Sciences, University of Perugia, Italy
sabrina.nazzareni@unipg.it

² Department Earth Sciences, University of Ferrara, Italy

³ Scuola di Scienze e Tecnologia, University of Camerino

Spinel-bearing lherzolites and wehrlites from Baker Rocks (Northern Victoria Land, Antarctica) have pargasitic amphiboles as metasomatic phase [1]. We investigated the amphiboles in order to estimate the physico-chemical conditions of their formation and, combined with the H₂O content in coexistent pyroxenes, to estimate the total water budget of this mantle domain. The samples were analysed by Single-Crystal XRD, EMPA, SIMS and XANES to have an accurate crystalchemical formula and to calculate the fH₂ and ultimately the fO₂ and aH₂O. The crystalchemical data showed that these amphiboles have similar composition, irrespective of the textural position and lithotype. The high equivalent thermal factor and cation off-centering suggest partition of Ti at M1 site. The high M3 site distortion and low <M3-O> distances suggest the presence of Fe³⁺ at M3 site. Starting from the crystallographic data we calculated dehydrogenation using the Oberti et al.'s method [2], whereas Fe³⁺/Fetot was measured by Fe K-edge XANES spectroscopy at GILDA beamline. Dehydrogenation varies from 0.80 to 1.07 a.f.u., with the lowest values for samples with lowest Ti and Fe. The measured Fe³⁺/Fetot and the crystallographic data suggest that dehydrogenation occurred by Ti-oxy substitution with only a minor Fe-oxy component. These data were used to estimate the aH₂O and the fO₂ of the mineral assemblage, following Lamb & Popp [3] and Ballhaus et al. [4] methods. Pressure estimates indicate a relatively shallow lithospheric mantle (P: 0.5-1.6 GPa) and T in the range of 800-1000 °C, implying an aH₂O for the amphibole formation in the range of 0.01- 0.02. The calculated aH₂O values are quite low if compared with those reported for the stability field of the reaction in the T-aH₂O diagrams [3]. Δlog fO₂ values relative to FMQ buffer range from -1.4 to -0.4. This range perfectly overlaps that of anhydrous samples from a locality nearby, as well as those obtained from peridotite xenoliths from continental setting [Δlog (FMQ) = -1.5 - +1.5; T=900-1100; P= 1.0-1.5 GPa. The low water content of amphibole is in agreement with that of the coexisting pyroxenes, which are about two times lower than those from other intraplate off-craton mantle xenolith [5], discharging the hypothesis that their low H₂O contents may have resulted from the OH being preferentially partitioned in amphibole. This fact confirms the anomalously low whole-rock water content shown by the Antarctic sublithospheric mantle domain in a rifting setting.

[1] Coltorti et al.(2004) *Lithos*, **75**, 115-139. [2] Oberti et al. (2007) *Rev. Mineral MSAGS*, **67**, 125-164. [3] Lamb & Popp (2009) *Am. Mineral*, **94**, 41-59; [4] Ballhaus et al. (1991) *Contrib. Mineral. Petrol.*, **78**, 27-40 [5] Bonadiman et. Al. (2009) *Eur. J. Min.*, **21**, 637-647