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Solubility of Ti^{+4} in Olivine in High Pressure Experiments - Revisited with Ab Initio Calculations.

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Interest in studying the solubility of Ti^{+4} in olivine was triggered by the discovery of olivine from the Alpe Arami peridotite massif (Switzerland) which had a high concentration of $FeTiO_3$ exsolution lamellae. It was proposed that this massif had been exhumed from depths of >300 km and it was much deeper than previously thought [1]. This was considered highly controversial; see the review [2] described this controversy. After this discovery in 1996 a series of high pressure and high temperature experiments were carried out in a multianvil apparatus. These experiments showed that the TiO_2 concentration in olivine is almost negligible (<0.1wt.%) at T=1400K and P=5GPa, however at T=1700K it increases from 0.4wt.% at 8GPa, 0.5wt.% at 10GPa and to 1wt.% at 12GPa [3]. Now, almost 25 year later, we explore the thermodynamics of titanium incorporation into olivine under varying pressure conditions using the latest density functional theory approaches. Our analysis reveals significant insights into the dissolution of titanium on the silicon sublattice and iron on the magnesium sublattice of beta-olivine (Mg_2SiO_4), alongside the precipitation processes of $FeTiO_3$. The enthalpy changes (Delta H) for the dissolution are computed to be 1.404eV (135.4 kJ/mol) at 10GPa and 2.036eV (196.5 kJ/mol) at ambient pressures, indicating a relatively more favorable condition for the dissolution under high pressure. By balancing the chemical equation and applying computational thermodynamics, we deduce that the positive reaction enthalpy at high pressures is offset by entropy contributions, allowing the calculation of solubility limits for Ti^{+4} in olivine. Our findings demonstrate a solubility of 0.38mol.% (0.40wt.%) at 10GPa and 1700K, and a markedly lower solubility of 0.0051mol.% at ambient pressure and the same temperature. The data obtained by the calculations agree reasonably well with the results of experiments. Therefore, this research provides critical insights into the geochemical behavior of titanium in olivine. The calculated solubilities under different conditions underscore the influence of pressure and temperature on the geochemical distribution of titanium.

REFERENCES

1. Dobrzhinetskaya, Green & Wang (1996), *Science* 271, 1841-1845.
2. Green, Dobrzhinetskaya & Bozhilov (2010), J. *Earth Sci*. 21, 731-743.
3. Dobrzhinetskaya, Bozhilov & Green (1999), *Chem. Geol.*160, 357-370.