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Redox state of the subducting slab: Thermodynamic constraints from multicomponent phase equilibria

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Oxybarometry of natural peridotite xenoliths and shifts in phase equilibria, which include incorporation of ferric iron in silicate phases, suggest a progressively decreasing oxygen fugacity of the upper mantle. In contrast, metasomatized mantle xenoliths and those from arc settings record relatively oxidizing conditions. In order to understand origins of the high oxidation state in the mantle, we evaluate changes in the redox state of the subducting slab during progressive metamorphism and release of C-H-O fluids. Phase equilibrium calculations were conducted in the SiO_2-TiO_2-Al_2O_3-FeO-MgO-CaO-Na_2O-K_2O-H_2O-CO_2-O_2 system, which allows us to assess, in particular, the Al-Fe^{3+} exchange in hydrous and anhydrous aluminosilicates and the stability of Fe-Ti oxides during subduction. We use a three layer slab model consisting of global oceanic subducting sediment, oceanic basalt supercomposite and serpentinized harzburgite. The relationship between oxygen fugacity and the whole-rock Fe^{3+}/Fe^{tot} ratio is strongly non-linear for all lithotypes. Oxygen fugacity remains buffered over certain ranges of the Fe^{3+}/Fe^{tot} ratio (generally less than 0.5) in dependence on whole-rock composition and amount of H_2O. In carbonate-bearing protoliths, the lower limit of oxygen fugacity is defined by graphite/carbonate equilibrium (ΔQFM = 0 to 1), whereas in serpentinized ultramafics the lower limit corresponds to iron/ferrous silicate equilibrium. There is no unique upper limit of oxygen fugacity; owing to the progressive transformation to ferric oxide and silicates and, subsequently, the saturation with an O_2-bearing aqueous-carbonic fluid phase. The phase equilibrium calculations of progressive metamorphism and devolatilization of three main slab lithologies demonstrate that: (1) the initial redox state of oceanic sediments, sea floor

basalts and harzburgites with incipient serpentinization is ΔQFM = 2-3; completely serpentinized harzburgites provide a strongly reducing environment at ΔQFM up to -7; (2) aqueous fluids released during slab devolatilization are dominated by H_2O, with lesser amounts of CO_2, which occur above 800 ^{o}C and 50 kbar. Concentrations of H_2 become only significant in low-temperature serpentinite fluids. Comparative calculations of episodic devolatilization *vs.* retainment of pore fluids show no significant effect of the devolatilization mechanism on the slab redox state. However, above 500 ^{o}C and 35 kbar transfer of fluids from the slab to the mantle leads to significant oxidation of peridotites; (3) the location of major dehydration reactions, e.g., breakdown of lawsonite, is sensitive to the whole-rock Fe^{3+}/Fe^{tot} ratio; a change of Fe^{3+}/Fe^{tot} by 0.4 units shifts the onset of dehydration by $\sim$150 ^{o}C or 9 kbar; (4) changes in the redox state during metamorphism are driven by Fe-Mg and Fe^{3+}-Al substitutions in silicates. In addition, variations in the oxygen fugacity are affected by transformations of iron oxides near 400-500 ^{o}C and their subsequent breakdown in favour of acmitic pyroxene and ferric garnet at eclogite facies. Upon complete devolatilization, the oxidation state of metasediments and metabasalts remains close to ΔQFM = 4 whereas that of harzburgites is ΔQFM = 2. The oxygen fugacity of the subducting slab does not decrease with pressure and it is 6-8 orders of magnitude higher than that of garnet-bearing peridotites in the surrounding mantle.