The oxygen content of sulphides in the mantle and a geothermometer for diamond formation

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Sulphides are ubiquitous accessory minerals in mantle rocks and form the most prevalent type of inclusion in diamonds. Diamond sulphide inclusions are trapped as sulphide melts that crystallise on cooling to form Fe-Ni monosulphide solid solution (MSS) and ultimately recrystallizes to assemblages containing pyrrhotite, $Fe_{(1-x)}S$ (x = 0 to 0.2), pentlandite, $(Fe,Ni)_9S_8$, and sometimes pyrite (FeS_2). Sulphide inclusions are also found in many xenoliths but those which are hosted by diamonds provide potentially the most pristine samples from the lithospheric mantle and deeper. Previous experiments indicate that oxygen partitions into sulphide melts and although sparse, some measurements of natural sulphide inclusions from mantle xenoliths indeed show measurable and in some cases relatively high oxygen concentrations. If the parameters that control sulphide oxygen concentration can be determined then they could be potentially used to understand conditions in the mantle and in particular in sublithospheric diamonds. The oxygen content of sulphides separating to the core during core formation could have also influenced the oxygen fugacity of the early mantle.
We have measured the oxygen contents of sulphide melts within experimentally produced mantle assemblages at high pressures and temperatures. A series of multi-anvil experiments were conducted to equilibrate a peridotite assemblage with molten sulphide (FeS) at pressures between 3 –11 GPa and temperatures of 1300 ˚C –1700 ˚C. The effects of pressure, temperature, oxygen fugacity and composition have been investigated. Oxygen fugacity was determined in some experiments by saturating the sulphide in Ir to produce a separate Ir-Fe metal alloy, for which the Fe content is a function of oxygen fugacity. The results show that sulphide melt oxygen contents can range up to 16 weight % FeO, at mantle conditions. Moreover, the content of oxygen in the sulphide is found to be not controlled by fO_2 or fS_2, which is in disagreement with previous experimental studies conducted at ambient pressure conditions. The experiments indicate that the oxygen concentration is mainly controlled by the FeO activity in coexisting silicates phases and the temperature, although further work is still required to calibrate effects of Ni and Cu. In order to fit the data and to account for the FeO dependence, we developed a thermodynamic model using an end-member equilibrium between olivine, pyroxene and FeO in the sulphide melt. The resulting relationship can be used as a geothermometer based on sulphide inclusion oxygen contents and could be particularly useful for determining diamond formation temperatures for sub lithospheric diamonds.

Keywords: Sulfide, Oxygen, Geothermometer