



Thermodynamic forecast for dry C-O-S fluid and possible link with 2012-2013 Tolbachik eruption.

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Carbon and sulfur transfer in the upper mantle and lower crust can be coupled due to the stability of their mutual compounds COS and CS₂. These components are registered in the volcanic gases in the rather minor quantities [Symonds et al., 1994] due to the effects of decompression, oxidation and hydration. At the same time in the dry reduced conditions at the elevated pressures these components along with CO may comprise more than half of carbon bearing fluid as shown by thermodynamic calculations [Simakin, 2014]. Carbon monoxide and COS were suggested as potential carriers for Ni and PGE in reduced carbonic fluids at magmatic PT conditions. Moreover at the unrealistically reduced for the Earth oxygen fugacities $fO_2 < 10^{-5}$ experimentally registered CO solubility in the basic melts is thought to be accomplished via Fe(CO)₅ complexes [Wetzel et al., 2013].

To get first insight into conditions of the carbonyls and COS stability we consider thermodynamics of some related reactions at the elevated PT. Fugacity coefficients of the carbonyls at the elevated pressures are not known therefore our estimates are preliminary and needs experimental verification. By setting some reasonable fugacity coefficients and assuming ideal mixing of the non-ideal components we find that nickel carbonyl possesses the highest stability in reaction $Ni + 4CO = Ni(CO)_4$. At the upper crustal pressure ($P=3$ kbar) it is expected to be stable at the temperature up to 670°C. This temperature fairly exceeds temperature 550°C of the natrocarbonatite lavas at Oldoinyo Lengai volcano, Tanzania, where enhanced fluid transport of Ni as a carbonyl is anticipated [Teague et al., 2011]. At 10 kbar stability temperature of Ni(CO)₄ is approaching magmatic one above 1000°C. Observation of the elemental carbon and native alloys Ni-Fe-Co dispersed in the volcanic gasses collected from the active lava flow at the Tolbachik 2012-2013 yrs eruption (Zelensky, in preparation) can be explained by disequilibrium processes in accordance with reaction: $NiS+5C+2.5O_2 = Ni(CO)_4+COS$. This reaction proceeds to the right at magmatic PT conditions ($P=1-2$ kbar, $T=1150^\circ C$) at the relatively high oxygen fugacity around NNO+0.5 fairly above CCO buffer. At the decomposition of Ni(CO)₄ native alloys may form. However, simple thermodynamic estimate shows, that iron carbonyl Fe(CO)₅ stability is substantially lower than Ni(CO)₄ excluding its existence at magmatic temperatures even at high P. Mixed Ni-Fe carbonyls or more complex compounds including COS can be involved. Degassing of the reduced basic magma containing dissolved sulfur and CO₂ is opposite to the magma sulfurization at the elevated pressure by the dry COS bearing fluid as envisaged in [Simakin, 2014]. In accord to the simple thermodynamics during the initial stage of degassing of the magma close to Ol-Opx cotectic composition and high S²⁻ content COS generates with ratio of COS/CO₂ in the fluid reaching 100-200. At the same time for the olivine saturated compositions and low S₂- content pure CO₂-CO mixture generates with COS/CO₂ ratio dropping to 0.001.

Literature.

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