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Extreme pressure dependence of sulfur solubility in silicate melts (experimental data)

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Sulfide-silicate demixing of silicate melts on immiscible silicate and sulfide liquids occurs at magma sulfur saturation. This type of liquation plays an important role in geochemistry of mantle magmas, in processes of magmatic differentiation, and in ore deposit formation. The major parameter defining sulfide-silicate stratification of silicate melts is solubility of sulfur in magmas at sulphide saturation. Presence of magmatic sulphides in rocks and minerals of various facies of depth, from inclusions in diamonds to near-surface land's and ocean floor's lavas, are evidence of existence of sulfide-silicate magmas in a wide range of depths in the upper mantle and earth's crust. In this connection researches on influence of pressure on solubility of sulfur have a great interest. Influence of pressure on solubility of sulphur is still controversial [*Mysen* and *Popp*, 1980; *Wendlandt*, 1982; *Mavrogenes* and *O'Neill*, 1999]. In most cases experiments were carried out in natural or modeling "dry", not containing H_2O, CO_2 silicate systems. In many cases these systems haven't been saturated by sulfide and studied at atmospheric pressure. Physicochemical conditions of sulphur concentration within fluid-bearing magmas in the upper mantle and the earth crust during sulphide-silicate immiscibility are very important for understanding of origin of magmatic sulphide deposits.

We studied influence of pressure on the SCSS (sulphur concentration at sulphide saturation) in H_2O and H_2O+CO_2-bearing silicate melts.

Experiments were carried out in an internal-heated pressure vessels at P=0.1-0.8 GPa; on the piston-cylinder at P=1-2.5 GPa; on the anvil-with-hole apparatus at P=4.0 GPa by a quenching technique. We used Pt-peridotite ampoules filled with powder of olivine basalt and synthetic sulphide $Fe_{30}Ni_{30}Cu_{30}S_{10}$ as starting compositions. The total volatile in system were 3-5 wt. %. Source of H_2O was the water containing glasses and the distilled water. Source of H_2O+CO_2 - dihydrate oxalic acid ($H_2C_2O_4$x$2H_2O$). Fugacity of sulphur buffered by Pt-PtS buffer, and fugacity of oxygen buffered by Ol-Opx-Pt-PtS association: $[Fe_2SiO_4]$ Ol + 1/2 S_2 (f) = $[FeSiO_3]$ Opx + FeS + 1/2 O_2 (f).

The temperature is measured by a Pt30Rh/Pt6/Rh thermocouple. At high temperature, pressure is calibrated using a curve of balance quartz - coesite. Uncertainties are ± 5ºC for temperature and ± 0.1 GPa for pressure measurements [*Litvin*, 1991]. Duration of experiments were 8-12-24 hours. Products of experiments were studied by PC-controlled scanning electron microscope Tescan VEGA TS 5130MM with detector of secondary and backscattered electron on the YAG-crystals and energy dispersive X-ray microanalyzer with semi-conductor Si(Li) detector INCA Energy 350.

The highest concentrations of sulphur were 0.88-1.01 wt.% in H_2O-bearing silicate melts at 1.5-2.0 GPa (Fig. 1). The minimum concentrations were 0.1-0.2 wt.% both at low (0.1-0.8 GPa) and high (2.5-4.0 GPa) pressure. Negative dependence of solubility of sulfur on pressure was observed in olivine basalt melts in the range of P=2.0-2.5 GPa. At T=1300°C solubility of sulfur decreased from 1.01 ± 0.09 wt. % at P=2.0 GPa to 0.20 ± 0.03 wt. % at P=2.5 GPa. At the further increase in pressure to 4.0 GPa solubility of sulfur changed slightly, about 0.1-0.2 wt. %. Concentration of sulfur increases from 0.09 ± 0.04 to 0.32 ± 0.04 wt. % in the field of low pressure (from 0.1 to 0.5 GPa) at T=1200-1300°C in water containing basalt melts (8-12 wt. % MgO, 50-56 wt. % SiO2). This data has once again confirmed the conclusions drawn earlier about extreme pressure dependence of SCSS with a maximum in 1.5-2.0 GPa [*Gorbachev* et all., 2005].

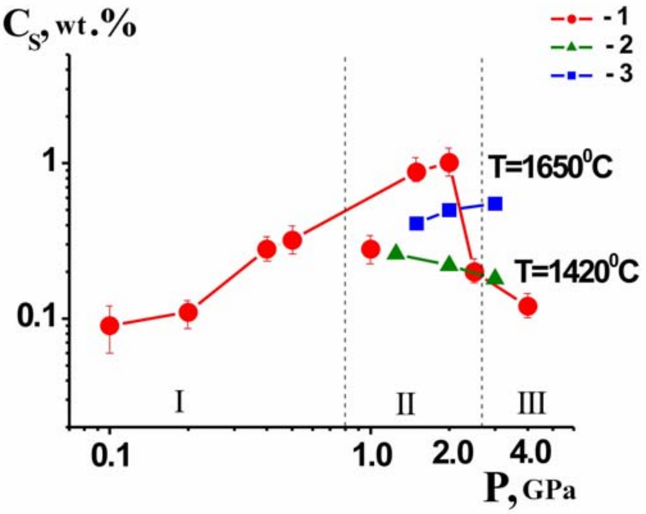

Fig. 1. Relationships between pressure and SCSS in H_2O-bearing sulfide-saturated (1) and "dry" (2, 3) silicate melts. 1-extreme pressure dependences of sulfur concentration with a maximum at 1.5-2.0 GPa and T=1350□C, our data; 2-Wendlandt (1982); 3-Myson, Popp (1980). I, II, III – experimental assemblies.

Experiments with H_2O+CO_2–fluid were carry out in the range of P=1.0-2.5 GPa and T=1250ºC. As well as in H2O-bearing melts, extreme pressure dependences of SCSS was observed in basalt melts with a maximum at P=2.0 GPa (fig. 2). However, concentration of sulfur were essentially more low (in 1.5-2 times), than in water containing silicate расплавах. With increase in pressure from 1.0 to 2.0 GPa concentration of sulfur increased from 0.08 ± 0.03 to 0.17 ± 0.05 wt. %, and then, at increase in pressure up to 2.5 GPa decreased up to 0.11 ± 0.06 wt. %.

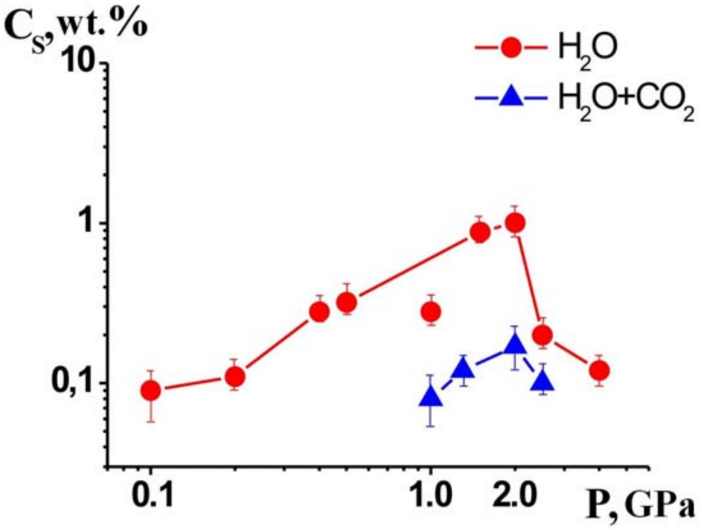

Fig. 2. Relationships between pressure and SCSS in H_2O- and H_2O+CO_2-bearing silicate melts.

Inversion of relationships between pressure and SCSS in H_2O- and H_2O+CO_2-bearing silicate melts at P=1.5-2.0 GPa can be related to the inversion of volume effect of reactions and speciation of C, O, H and S in basalt melts at different pressure. Such inversion can play an important role in transport of sulphide sulphur and ore elements from the deep magmatic centres to the upper levels of the Earth crust where most of known sulphide ore deposits were discovered.

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