Interaction between (alumino)silicates and SO$_2$-containing gas: experiment and thermodynamic model

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Results of investigation in the 'SO$_2$–rock' system are important in solving a problem of silicate rocks alteration under the influence of C-O-H-S fluids. SO$_2$ is one of the main components of emitted volcanic gases. Due to its interaction with host rocks the latter undergo strong metasomatic changes, causing formation of secondary quartzites in ultimate case. Studying of such processes on natural objects (fumarols, solfataras) represents great difficulties owing to variety of physical and chemical conditions and overprint of the formed mineral associations replacing each other at temperature changes.

In planetary sciences the problem of volcanic SO$_2$ emissions is of high interest due to the presence of sulfur compounds in atmospheres of Venus and the Jupiter satellite Io. Surfaces of such planets as Venus, Mars and Io consist of the rocks which are similar to basic rocks. For example, solid phases containing Na and S are found out on the Io surface. Such phases can be formed by reactions of SO$_2$ or S$_2$ with silicate lavas as well as in volcanic channels at Io conditions. The nature of formation process of these «Na-S» phases on the Io surface, is discussed [*Kargel, et al,* 1999, etc.]. Experimentally proved that Na-sulfate can be formed during interaction of SO$_2$ with volcanic glasses of different compositions (at 850°C) [*Johnson, Burnett,* 1993]. In turn one of the open key questions of Venus is the phenomenon of "super-greenhouse" effect [*Fegley,* 2003]. SO$_2$ is one of the main greenhouse gases in Venusian atmosphere, and its interaction with Ca-containing surface rocks represents special interest [*Fegley, Treiman,* 1992, etc.].

Interaction between sulfur-containing gases and rocks is considered as a problem of capture and storage of greenhouse gases in geological formations [*Palandri, et al,* 2005, etc.]. Basic and ultrabasic rocks are the most favorable for the greenhouse gas storage because of high content of Ca and Mg, which potentially can form stable carbonates and sulfates [*Goldberg, et al.,* 2008, etc.]. For example, greenhouse gas storage in basalt formation is already under process in Iceland (CarbFix project). Investigation, concerning similar technology on recycling of pure SO$_2$, is not carried out by now. There is a number of works where model of combined storage of CO$_2$ and SO$_2$ (5-10 %) is studied [*Xu, et al,* 2007, etc.]. It is shown that the presence of sulfur-containing gases in fluid leads to formation of such minerals as pyrite and alunite. However, these experimental and theoretical studies are not enough for gaining full information about processes of interaction between SO$_2$ and rocks.

The aim of the present study is to show the results of investigation in system SO$_2$–(alumino)silicates. Temperature and gas phase composition are considered as important parameters in calculations. The first part of our investigation is an experimental studying of interaction between SO$_2$ and pure minerals (Ab, An, Ol, Px) as well as natural basalt at T = 450–850°C and P(SO$_2$+O$_2$) ≈ 3-10 bar. An effective supplementing method is thermodynamic modeling of equilibrium composition in multicomponent system SO$_2$–(alumino)silicates. Therefore, the second part of our work was to develop and verify a thermodynamic model of similar processes. Series of calculations are conducted in a wide temperature range (100–850°C). The verification on high-temperature experiments is performed and the forecast of SO$_2$ behavior is given for the conditions similar to subsurface geological formations.

The technique of experiments is described in detail in the paper [*Li, et al.,* 2010]. Experiments were carried out under the double quartz capsules. Total pressure of (SO$_2$+O$_2$) gases was created by

decomposition of potassium peroxodisulfate ($K_2S_2O_8$) during its heating above 100°C. In addition, in experiments without excess of oxygen the open small capsule with certain amount of elementary sulfur was placed into external capsule. Reaction products have been analyzed by XRD (MSU, Department of Crystallography, STOE Stadi MP and DRON UM-1) and X-ray spectral microanalysis (GEOHI RAS, CAMECA SX100). It is shown that interaction of SO_2 and silicates leads to sulfur transition from gas phase to solid; sulfates of alkaline and alkali-earth metals (Na, Ca, Mg) are formed, aluminum remains in (alumino)silicates (fig. 1).
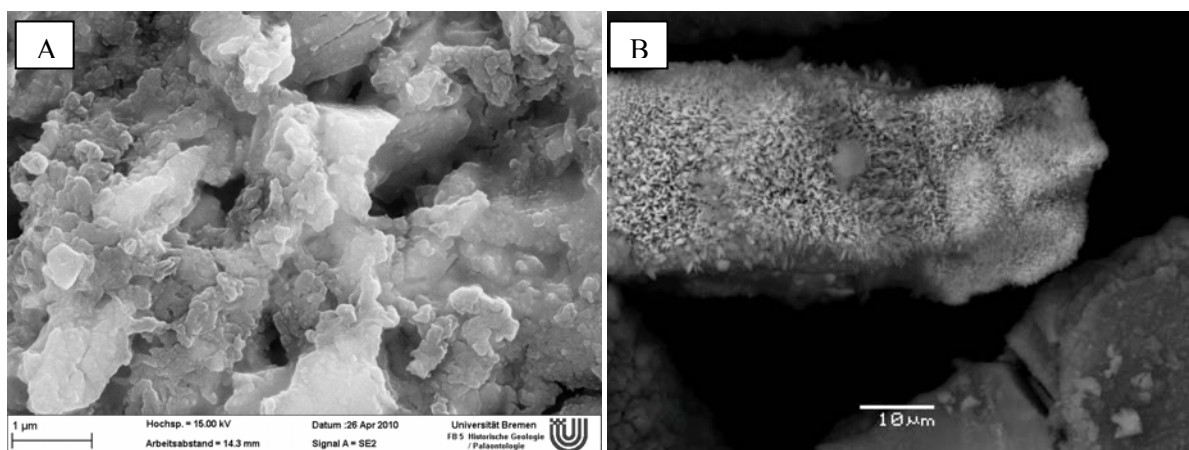

Fig. 1. SEM micrograph image of A – $CaSO_4$ formed on basalt grain; B – Morphology of $MgSO_4$ crystals growing on olivine grain (products of experiment at 650°C, electron image)

The factors influencing on completeness of SO_2 linkage were investigated (such as chemical composition of initial solid phase, particles size and T). Fig. 2 shows that the system approaches steady state with time and, most likely, rock saturation by sulfates is reached.
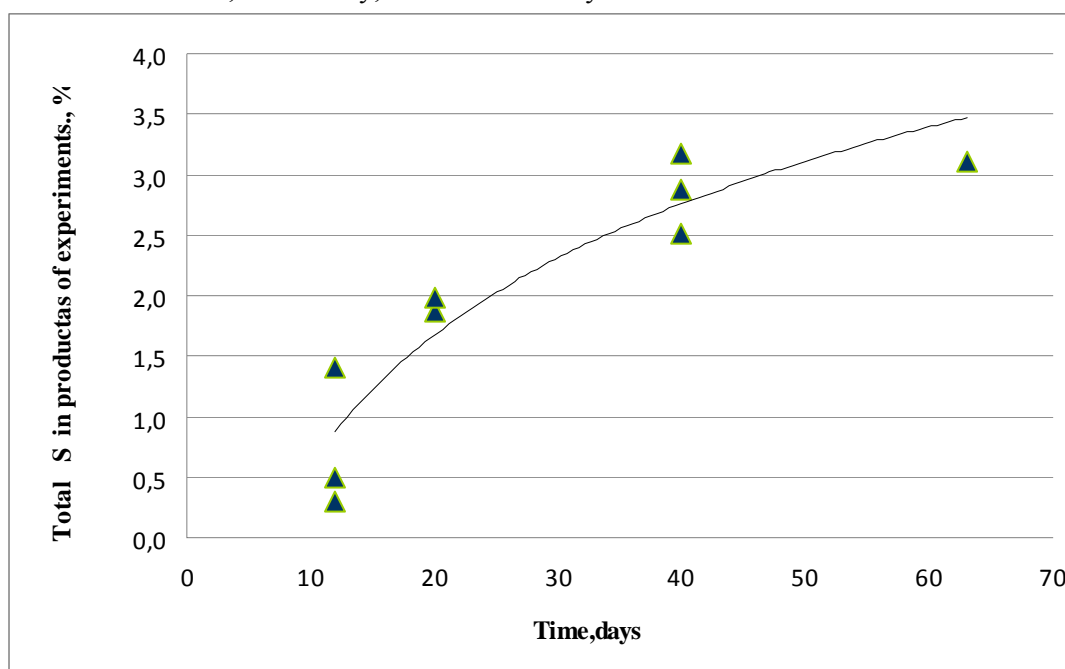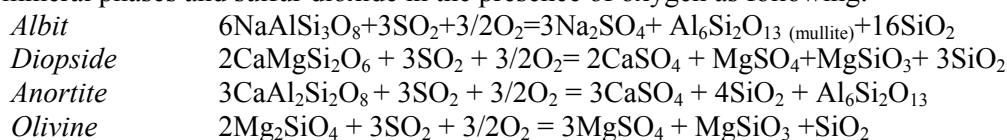

Fig. 2. Sulfur concentration in products of experiments as a function of time (basalt at 650°C). Different symbols specify method used for S-detection

According to data received, it was possible to presume reactions of interaction between monomineral phases and sulfur dioxide in the presence of oxygen as following:

Albit $6NaAlSi_3O_8 + 3SO_2 + 3/2O_2 = 3Na_2SO_4 + Al_6Si_2O_{13 \text{ (mullite)}} + 16SiO_2$

Diopside $2CaMgSi_2O_6 + 3SO_2 + 3/2O_2 = 2CaSO_4 + MgSO_4 + MgSiO_3 + 3SiO_2$

Anortite $3CaAl_2Si_2O_8 + 3SO_2 + 3/2O_2 = 3CaSO_4 + 4SiO_2 + Al_6Si_2O_{13}$

Olivine $2Mg_2SiO_4 + 3SO_2 + 3/2O_2 = 3MgSO_4 + MgSiO_3 + SiO_2$

Our thermodynamic model is developed by means of HCh software package. Calculations have been carried out for a wide range of temperatures (100–850°C), pressure (1–1000 bar) and fluid/rock ratio (from 0 to 12.5 kg (200 mol) SO$_2$ per 1 kg of rock). Model was constructed for system basalt–SO$_2$–O$_2$±S$_2$] (SO$_2$:O$_2$:S$_2$ = 2:1:1) and for system basalt–SO$_2$–O$_2$±S$_2$–H$_2$O] for ultimate imitation of natural conditions. Comparison of mineral compositions received in experiments and in modeling shows agreement of mineral associations of the studied systems. It proves high quality of the developed model.

According to modeling general scheme of basalt transformation during interaction with (SO$_2$+O$_2$) gas mix has appeared approximately identical in all studied temperature range (fig. 3). In calculations without any addition of a gas phase initial basalt is presented by following mineral association: plagioclase (57 mol. %, minals: anortite+albite+microcline) + diopside (17 mol. %) + olivine (20 mol. %, minals: forsterite+fayalite) + magnetite (6 mol. %) + pyrrhotite (0.2 mol. %). During interaction with gas phase firstly olivine is used, then the diopside is replaced with "enstatite + anhydrite". Addition of 1.8–2.2 mol of (SO$_2$+O$_2$) on 100 g of rock leads to replacement of anortite with association "anhydrite + quartz + sillimanite/andalusite/disthene". Sodium and potassium plagioclases are replaced with "quartz + sillimanite/andalusite/disthene" + Na and K sulfates" at addition of 4.5–8 mol of (SO$_2$+O$_2$). In the same range enstataite is replaced with quartz and magnesium sulfate.
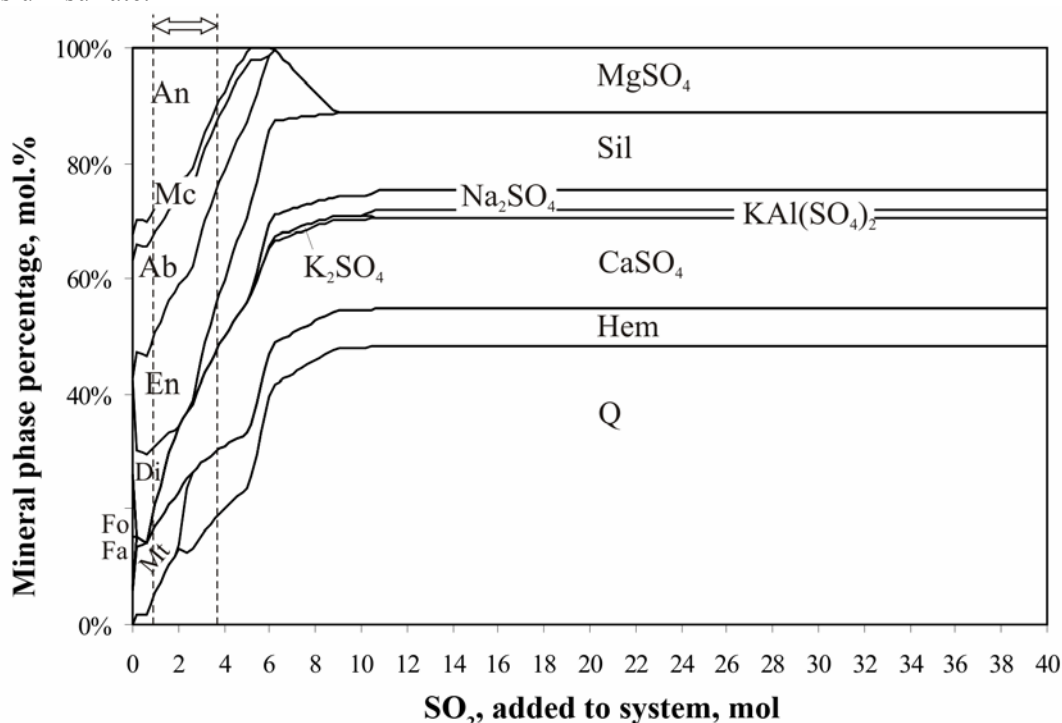

Fig. 3. Results of thermodynamic calculations in system [basalt - SO$_2$ - O$_2$]. T=850°C, P = 3 bar. Weight of initial rock is 100 g

Stabilization of mineral composition in interaction products is reached with different fluid additives at different temperatures (from 11 mol at 850°C to 22–24 mol at 500–100°C). The received ultimate association includes "quartz + hematite + silicates Al + sulfates". It corresponds to mineral composition typical for natural secondary quartzites (besides phases well soluble in water).

Unlike results of calculations in oxidizing conditions, in system basalt–SO$_2$–O$_2$–S$_2$ transformation of initial mineral composition has smaller scales (fig. 4). Formation of secondary sulfates occurs only at temperatures lower 700°C, although the temperature sequence of sulfate appearance remains: anhydrite (700°C) + Na, K and Mg sulfates (500, 400 and 450°C accordingly) + Fe (II) sulfate (350°C) + Al sulfate (200°C). At all fluid/rock ratios and temperatures (above 200°C) pyrrhotite or pyrite are steady. At temperature 200°C and large amount of fluid in system elementary sulfur appears as compound of steady association.

Similar researches can be used as a tool for reconstruction of some natural metamorphic and hydrothermal processes.
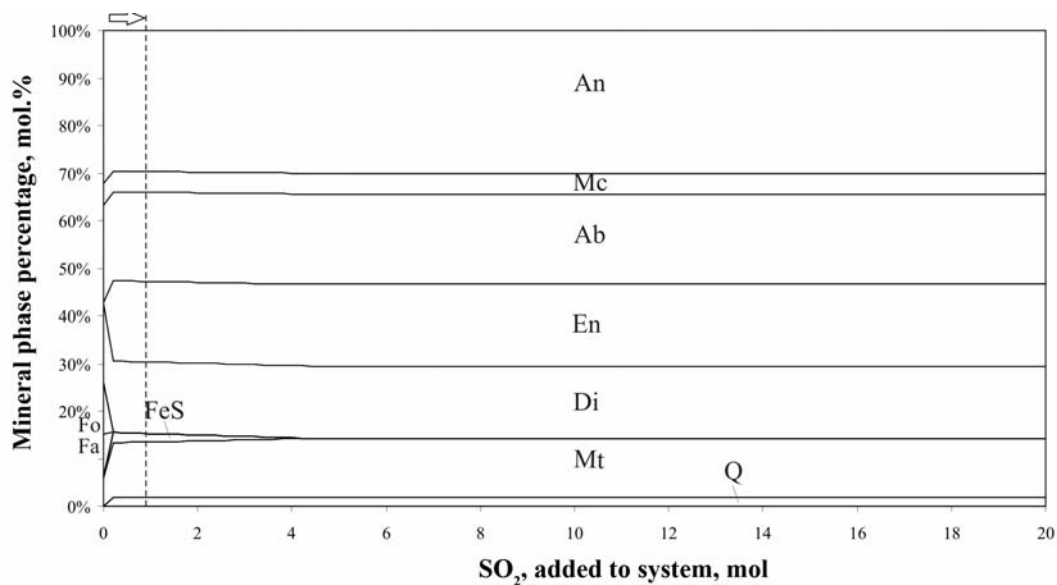
Fig. 4. Results of thermodynamic calculations in system [basalt - SO$_2$ - O$_2$ - S$_2$]. T=850ºC, P = 3 bar. Weight of initial rock is 100 g

Our research draws the following conclusions:

• Interaction between SO$_2$ and silicates at temperature range 450 to 850ºC with formation of (Na, K, Ca, Mg, Fe, Al) sulfates is experimentally confirmed.

• The reaction mechanisms for pure minerals exposed to SO$_2$ are suggested.

• Thermodynamic model of SO$_2$ interaction with silicates is developed and verified; it correctly reproduces results of experiments at temperature range 450 to 850ºC in studied systems.

• Distinctions of the mineral associations formed at the conditions with excess/lack of O$_2$ in the system are shown. SO$_2$ linkage occurs more effectively with excess of O$_2$ in system and sulfates form even at high T; whereas with lack of oxygen in system formation of sulfates is complicated and sulfur binds in the form of iron sulfides.

• Type of change in mineral association during interaction between sulphurous gas and basalt is identical in principle in a wide temperature range; this interaction leads to formation of (Na, K, Ca, Mg) sulfates, quartz and hematite in high-temperature area (T=700–850ºC), and also Al and Fe sulfates at temperature decrease (to 650ºC).

• According to results of calculations, the capacity of basalts concerning SO$_2$ linkage increases with temperature decrease.

• The buffer effect is observed before disappearance of basalt primary minerals, after this quantity of SO$_2$ in gas phase increases indefinitely.

References

Fegley, B. (2003), Venus, *Treatise on Geochemistry. Volume 1: Meteorites, Comets, and Planets.* Eds. H.D. Holland, K.K. Turekian. Elsevier.

Fegley, B., A. H. Treiman (1992), Chemistry of atmosphere-surface interactions on Venus and Mars, *Venus and Mars: Atmospheres, Ionospheres, and Solar Wind Interactions. Geophysical Monograph 66,* Am. Geophysical Union, Washington, pp.7–71.

Goldberg, D. S., T. Takahashi, A. L. Slagle (2008), Carbon dioxide sequestration in deep-sea basalt, *Proceedings of the National Academy of Sciences of USA. Vol.105(29),* pp.9920–9925.

Johnson, M. L., D. S. Burnett (1993), SO$_2$-rock interaction on Io - Reaction under highly oxidizing conditions. *J. Geophys. Res., vol. 98,* N E1, pp. 1223–1230.

Kargel, J. S., P. Delmelle, D. B. Nash (1999), Volcanogenic Sulfur on Earth and Io: Composition and Spectroscopy, *Icarus, vol. 142,* Issue 1, pp. 249–280.

Li, E. Yu, D. A. Chareev, S. N. Shilobreeva, D. V. Grichuk, O.A. Tyutyunnik (2010), Experimental Study of Sulfur Dioxide Interaction with Silicates and Aluminosilicates at Temperatures of 650 and 850°C, *Geochemistry International, vol. 48*, No. 10, pp. 1039–1046.

Palandri, J. L., R. J. Rosenbauer, Y. K. Kharaka (2005), Ferric iron in sediments as a novel CO$_2$ mineral trap - CO$_2$-SO$_2$ reaction with hematite, *Appl. Geochem., vol. 20,* N 11, pp. 2038–2048.

Xu, T., J. A. Apps, K. Pruess, H. Yamamoto (2007), Numerical modeling of injection and mineral trapping of CO$_2$ with H$_2$S and SO$_2$ in a sandstone formation, *Chem. Geol., v. 242,* N 3, pp.319–346.