Modeling of multicomponent C-H-O-S-silicate melt interactions

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The behavior of volatile components in magmas is crucial for understanding magmatic and volcanic process from the deep regions of magma generation and storage to the shallow regions of magma eruption and emplacement. Water, carbon dioxide, and sulfur compounds are the main volatile components in natural magmas, generally comprising more than 99% of the volcanic gases released before, during, and after eruption. Multicomponent modeling of the equilibrium between a 4-component H_2O – CO_2 – SO_2 – H_2S gas phase and a 13-component silicate liquid made of ten major oxides plus dissolved H_2O, CO_2, and S shows that feedback relations are established between redox state and volatile solubility. Therefore, oxidation state (e.g. fO_2), must be considered as a major control variable of the partition of volatiles between gas and liquid phases, together with pressure, composition and temperature. The model we have developed performs calculations involving homogeneous reactions in the gas phase and heterogeneous gas – liquid saturation modeling by joining two different but approaches based on classical Gibbs thermodynamics and the Toop-Samis polymeric treatment. Sulfur is assumed to be present in two different oxidation states in the gas (sulfur dioxide and hydrogen sulfide) and liquid (sulfide and sulfate ions) phase. Sulfur-bearing solid phases and Fe-O-S immiscible liquid are not accounted for in the modeling. Within the framework of the Toop-Samis polymeric approach, the thermodynamic model also accounts for the role of pressure and dissolved water content on iron speciation. In particular, water is treated as an amphoteric oxide in the Lux-Flood sense, originating two ionic species, OH^- and H^+. By defining appropriate redox buffers, the model allows to explore the effect of the redox state on the shape of the saturation surface, highlighting the non-linear trends shown by liquid and gas compositions upon pressure decrease. The largest compositional differences are shown by sulfur species, however, the concentrations of water and carbon dioxide in the two phases at equilibrium also show non-negligible dependence on the adopted redox conditions. Therefore, the characterization of the oxidation state in depressurizing magmas on the basis of deviations from solid buffers (usually NNO or QFM) may not be appropriate. Finally, it is shown that our amphoteric treatment of water speciation within the Toop-Samis polymeric approach is consistent with some recent NMR findings (Xue and Kanzaki, 2004) and also with the IR data on water speciation at T > Tg, therefore providing an independent check of the model capability to account for melt reactivity.