

Minerals influence hydrothermal chemistry of amines

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Minerals can play a critical role in organic carbon and nitrogen transformations in hydrothermal environments. Amines, which contain both nitrogen and carbon atoms, are of great interests to hydrothermal geochemistry and deep-sea biology research, in large part due to their involvement in biological metabolism, such as in the form of amino acids and proteins, and also to their participation in the deep nitrogen cycle and potential contribution to the origin of life. Although there have been experimental studies on hydrothermal reaction of amines, very few have considered the impact of minerals on their reactivity in geological systems. In this study we investigated the chemistry of a group of aromatic and aliphatic amines, including aniline, benzylamine, cyclohexylamine, and cyclohexanemethylamine, under a hydrothermal condition of 250 °C and 40 bar. In the absence of minerals, these amine compounds showed quite different hydrothermal reactivity, with a reaction conversion from less than 5% in 96 h up to more than 45% in 2 h. We observed that alcohols (R-OH) and secondary amines (R-NH-R) were formed as major products during early reaction times, which suggest a nucleophilic substitution reaction mechanism for amines. Product distribution analysis also suggests that the stability of carbocation intermediates and steric effects could be important factors that determine the reaction pathways of amines. In the presence of minerals, we found that, while oxide minerals such as hematite, magnetite, and corundum had no significant effect on the hydrothermal reactions of amines, brucite and gibbsite were able to accelerate the decomposition of amines, in particular to cyclohexylamine and cyclohexanemethylamine. Hydrothermal experiments at different pH also showed that the non-aromatic amines were more readily reacted under acidic or basic conditions than in pure water. Our results suggest that, in the studied system, mineral-promoted amine hydrothermal reactions could be mainly attributed to the change of pH by mineral dissolution, rather than bond-activation catalysis on mineral surfaces. It also highlights the need to consider the roles of minerals in changing dissolved species and solution chemistry, which can influence organic carbon and nitrogen transformations during hydrothermal geochemical processes.