

Anomalous S isotope fractionations during reactions with an organic surface: II. Investigations on natural and experimental systems

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Recent investigations of multiple S-isotope ratios in natural rocks have revealed that not all Archean sedimentary rocks possess anomalous S isotope fractionations (ASIF); the ASIF is referred to a sample when its $\Delta^{33}\text{S}$ value falls outside of $0\pm 0.2\text{‰}$ and $\delta^{33}\text{S}/\delta^{34}\text{S}$ value outside of 0.51 ± 0.01 . The following geochemical characteristics are recognized in sedimentary rocks with ASIF signatures: (a) high organic-C contents ($>1\text{ wt}\%$); (b) highly matured (altered) kerogen (H/C ratios <0.1); (c) abundance of carbonates with unusually low $\delta^{13}\text{C}$ values ($<-8\text{‰}$); and (d) strong hydrothermal alteration signatures (e.g., enrichment of Zn and Cu). In contrast, sedimentary rocks with no/little ASIF signatures lack one or more above characteristics. These characteristics suggest that the ASIF signatures in some Archean sedimentary rocks were created by reactions between organic-rich sediments and sulfate-rich solutions under hydrothermal temperatures. To evaluate the validity of this suggestion, we have conducted laboratory experiments using solid amino acids, solid sulfate, and water at $T = 150\text{--}220^\circ\text{C}$.

Important observations on the experimental system are: (i) reduction of sulfate to sulfide occurred at T as low as 150°C within several days; (ii) the products (H_2S and organically-bound S compounds) possess positive $\Delta^{33}\text{S}$ values, ranging from $+0.2$ to $+2.1\text{‰}$, while the residual sulfates possess slightly negative $\Delta^{33}\text{S}$ values; (iii) the largest ASIF signature was found on a product of the highest-temperature experiment ($T = 220^\circ\text{C}$); and (iv) the solid products include water-insoluble black organic compounds with Raman spectra similar to that of kerogen.

The observations of geochemical and isotopic characteristics in natural and experimental samples are consistent with the results from our theoretical investigations (Otake *et al.*, Part I), which suggest that the anomalous S isotope fractionations in sedimentary rocks were created by surface reactions involving organic matter, minerals and S-bearing aqueous solutions at elevated temperatures, rather than by atmospheric photochemical reactions.

Synthesis and characterization of the high-pressure phases NH_4 -hollandite, NH_4 -wadeite, NH_4 -cymrite and NH_4 -phengite

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Ammonium in eclogite facies metasediments is mainly bound in micas, where concentrations may reach a few thousand ppm. This study will show that NH_4 can also be stored in high-pressure potassium silicates via structural exchange of NH_4^+ for K^+ . Possibly this provides an important mechanism for nitrogen and hydrogen transport into the Earth's mantle during deep subduction.

The ammonium analogues of the high-pressure potassium silicate phases K-hollandite, K-wadeite, K-cymrite, and phengite were synthesized in the system $(\text{NH}_4)_2\text{O}(\text{--MgO--Al}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O})$ using multi-anvil and piston-cylinder equipments. Syntheses resulted in NH_4 -hollandite [$\text{NH}_4\text{AlSi}_3\text{O}_8$] at 12.3 GPa, 700°C ; NH_4 -wadeite [$(\text{NH}_4)_2\text{Si}_4\text{O}_9$] at 10 GPa, 700°C ; NH_4 -cymrite [$\text{NH}_4(\text{Mg}_{0.5}\text{Al}_{1.5})(\text{Al}_{0.5}\text{Si}_{3.5})\text{O}_{10}(\text{OH})_2$] at 4 GPa, 700°C . Cell parameters of the new NH_4 -phases were determined by powder XRD with Rietveld refinements to $a = 9.4234(9)\text{ \AA}$, $c = 2.7244(3)\text{ \AA}$, $V = 241.93(5)\text{ \AA}^3$ (NH_4 -hollandite); $a = 6.726(1)\text{ \AA}$, $c = 9.502(3)\text{ \AA}$, $V = 372.3(1)\text{ \AA}^3$ (NH_4 -wadeite); $a = 5.3595(3)\text{ \AA}$, $c = 7.835(1)\text{ \AA}$, $V = 194.93(5)\text{ \AA}^3$ (NH_4 -cymrite). NH_4 -phengite consisted of a mixture of $1M$, $2M_1$, $2M_2$, $3T$, and $2Or$ polytypes. The most abundant polytype $2M_1$ had the cell dimensions $a = 5.2195(9)\text{ \AA}$, $b = 9.049(3)\text{ \AA}$, $c = 20.414(8)\text{ \AA}$, $\beta = 95.65(3)^\circ$, $V = 959.5(5)\text{ \AA}^3$. All unit cell volumes are enlarged compared to the potassium analogues. Substitution of NH_4^+ for K^+ does not cause changes in space group or symmetry. The ammonium incorporation was confirmed by the appearance of NH_4 -vibration modes ν_4 and ν_3 together with overtones and combination modes in the FTIR-spectra occurring in the wavenumber range of $1397\text{--}1459\text{ cm}^{-1}$ and $3223\text{--}3333\text{ cm}^{-1}$.