Carbon and chlorine isotope fractionation during degradation of trichloroethene by metals

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Granular iron has been used in permeable reactive barriers to treat groundwater contaminated with chlorinated ethenes. In addition to iron, other metals or bi-metals such as Zn and Ni-Fe have been found to be effective in the dechlorination reactions. However, the pathways of chlorinated ethene reaction with metals are not fully understood. The compound-specific carbon isotope technique has been used as a tool to delineate degradation of chlorinated ethenes by iron, and substantial isotope fractionation was observed during the reaction. In this study, we combined carbon isotope with chlorine isotope analysis to examine the reactions between trichloroethene (TCE) and different metals, and to derive additional information on reaction pathways.

In a series of batch experiments, TCE was reacted with granular iron, electrolytic iron, nickle-plated iron, and zinc, and sampled at different times. Granular iron from two different suppliers (Connelly and Peerless) was used. Ni-plated Connelly iron was prepared using an electroless plating method. Electrolytical iron and zinc were from Fisher Scientific and BDH, respectively. In each sample, 10 mg/L TCE solution and a w/s ratio of 5 was used. Complete mixing was provided during reaction.

Under the given experimental conditions, carbon isotope enrichment factors of -15.7 and -7.7‰ were measured for Connelly and Peerless iron, respectively. An enrichment factor of -12.5‰ was obtained for Ni-plated Connelly iron, and -20.2‰ for electrolytic iron. The strongest ^{13}C enrichment was associated with Zn, with an enrichment factor of -31.3‰. Substantial chlorine isotope enrichment was also determined, with enrichment factor ranging between -6.4‰ (zinc) and -1.8‰ (Peerless iron). Overall, the chlorine isotope enrichment factor correlated positively with carbon isotope enrichment factor. However, a constant chlorine enrichment factor of -4.3±0.1‰ was observed among Connelly, Ni-plated iron, and electrolytic iron. The overall positive correlation between carbon and chlorine isotope fractionation and the deviation of Connelly and Ni-plated iron from this correlation is likely controlled by the reductive dechlorination process.

Volatiles in mantle minerals: A xenolith study, Eastern China

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Volatiles in nominally anhydrous mantle minerals have long been thought to reside primarily in fluid inclusions. Abundances of volatiles in olivine (Olv), orthopyroxene (Opx) and clinopyroxene (Cpx) from in lherzolite and pyroxenite xenoliths in Cenozoic basalts from eastern China were investigated by combined techniques of grain-size reduction, ameliorative vacuum stepwise heating, mass spectroscopy and infrared spectra measurements, and show that significant amounts of volatiles in these minerals in fact reside in structural defects and vacancies.

Early-stage and late-stage two types of fluid inclusions can be readily identified based on differences in shape, size, distribution and homogenization temperature (HT). Volatiles from different crushing size of Olv, Opx and Cpx separates have been released at three temperature intervals: 400-600°C, 600-1000°C and 1000-1200°C. The total volatile content increases with decreasing crushing size at a given temperature interval. The volatile release peak at 300-600°C disappears in crushing size (0.03mm) close to the size of late-stage fluid inclusions (10-200 μm). The volatile release peak at 1000-1200°C shifts towards small crushing size (0.06-0.03mm). The FTIR absorbance peaks of structural OH^- in Olv and Opx have been reduced only after degassing at 1200°C.

Progressively crushing breaks larger size of fluid inclusions and releases volatiles accordingly, but volatiles stored in defects and vacancies of crystal structures are still retained. Ameliorative vacuum stepwise heating technique can effectively separate volatiles with different occurrence modes for analysis. Early-stage fluid inclusions are decrepitated at a temperature range (600-1000°C) similar to HT (861-1074°C), whereas late-stage fluid inclusions are released at lower temperature range (300-600°C) due to their large sizes, irregular shapes and micro-cracks developed along inclusion walls. Volatiles in mineral structural defects and vacancies are released at higher heating temperatures (1000-1200°C) close to mineral formation temperatures (987-1296°C), and are more abundant than volatiles hosted in fluid inclusions. This has important implications for mantle volatile in the storage, distribution and recycling.

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