Geochemical interactions between nitroaromatic (TNT) and nitramine (RDX and HMX) explosives and sediments

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Training with artillery, mortars, hand grenades and small arms containing nitroaromatic (e.g., TNT) and nitramine (e.g., RDX and HMX) explosives is common at military training installations worldwide. Adsorption and transformation reactions of explosives are sensitive to the composition and geochemical conditions in the soils and sediments onto which they are deposited. Thus the geochemical relationships between training range sediments and explosives affect range sustainability, environmental stewardship and site remediation options. Our work addressed fundamental relationships between soil and water geochemistry and explosives degradation through two laboratory experiments.

First, we quantified the breakdown of TNT, RDX and HMX in surface waters containing different concentrations of sediment and dissolved organic carbon. Samples spiked with 10 different explosives and explosives breakdown products were sampled over 85 days and the explosives and breakdown products were measured. We found that the presence of either dissolved organic carbon or fresh mineral surfaces promoted the breakdown of nitroaromatics TNT, 1,3,5-trinitrobenzene and tetryl. RDX and HMX concentrations remained stable in all samples as expected. Concentrations of all explosives phases remained constant in 18Mohm-cm control water throughout the exposure period suggesting that either an organic substrate or a mineral surface is required to facilitate explosives transformation or breakdown.

In a second aspect of the study we investigated the interaction between explosives and freshly fractured mineral surfaces to assess the effects of detonation shock on the interactions between explosives species and sediments. Three different surface sediment samples were crushed with a 50,000 psi steel plate to simulate blast fracturing. Uncrushed “pristine” sediments were sieved using size fractions similar to the crushed samples. Column and batch experiments using waters spiked with TNT, HMX and RDX were applied toward investigating the reactive transport of explosives through the crushed versus pristine sediments. Grain surface morphology was examined by scanning electron microscopy. TNT in some of the columns comprised of fractured sediment showed greater retardation compared to the columns with pristine sediment suggesting that TNT is adsorbed or preferentially transformed on fresh mineral surfaces.

Electrolyte-promoted demineralization of biogenic, vitreous, and crystalline silica: A density functional investigation

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The dissolution of amorphous and crystalline varieties of SiO_2 is an integral part of the global biogeochemical cycle of silicon. Nanoparticulate biogenic silica produced by marine phytoplankton and terrestrial plants are of particular interest because their enhanced reactivity and abundance make them important sources and sinks of dissolved silicon in natural environments. Low concentrations of major solutes have been shown to enhance the rate of silica dissolution by up to a hundred times. Recent experimental results on Q_3-terminated (100) surfaces of quartz, show that the presence of dissolved electrolytes triggers a crossover in the dominant dissolution mechanism from defect assisted dissolution and simple step retreat, to nucleation of vacancy islands. However, the underlying reaction mechanism remains poorly understood (Dove *et al*., 2005).

The specific effects of group II metal cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) on the energetics of Si-O bond hydrolysis have been investigated with density functional methods (B3LYP) and a relatively large neutral silica cluster ($H_8Si_6O1_6$). Reactant, product, and transition states for Q_3 to Q_2 hydrolysis in the presence and absence of the afore-mentioned cations have been determined with all electron (6-31G(d)) and effective core potential (SDDALL) Gaussian basis sets. The free energy of activation for Q_3 to Q_2 Si-O bond hydrolysis was determined to be approximately 5 kJ/mol lower for Ca^{2+} than Mg^{2+} at the 6-31G(d) level. Similar calculations for Ca^{2+}, Sr^{2+} and Ba^{2+} using the SDDALL basis set yielded similar molecular geometries to the all-electron results, and free energies of activation for Sr^{2+} and Ba^{2+} that are ~10 kJ/mol and ~15 kJ/mol lower than for Ca^{2+} respectively. These results are consistent with experimental results which show that these cations increase the maximum rate of silica dissolution in the order $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$. Although these calculations successfully reproduce the relative rates observed in the presence of these cations, they also predict that the rate of Si-O bond hydrolysis should be faster in the absence of electrolyte, which is contrary to experiment. To address this issue, supplemental calculations are being performed to determine how the incorporation of surface charge into the model will affect the energy landscape and mechanism of Si-O bond hydrolysis.

References

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