The effects of sulfide and sulfate ions on degradation kinetics of chlorinated organics by nanoscale zero valent iron

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A promising technology for the clean-up of aquifers contaminated by toxic chlorinated organic compounds is the sub-surface injection of nanoparticles of zero valent iron (NZVI) into the contaminated zones to enable rapid, *in situ* destruction of chlorinated compounds to non-toxic end products via surface-mediated electron transfer and hydrogenation reactions. However, iron oxide shells form readily on the surface of the NZVI which may reduce its reactivity over time. Although several studies have examined the reactivity of NZVI to chlorination aliphatic pollutants, there is limited knowledge on the effects of natural groundwater ions on the surface chemistry and reactivity of NZVI to target pollutants. In this study we show that sulfide and sulfate ions, which are ubiquitous in groundwater environments, may significantly alter the reactivity of NZVI.

Sulfide and sulfate ions readily react with NZVI in solution to form various iron sulfide precipitates on the NZVI surface. An FeS coating NZVI enhances the ability of the NZVI to degrade chlorinated organic compounds due to the creation of a conductive outer layer that efficiently transfers electrons from the electron rich core of the zero valent iron nanoparticle. Our studies show that the reactivity of the NZVI-FeS was distinct from the reactivity of pure FeS. Rapid dechlorination of trichloroethylene (TCE) was observed particularly at lower concentrations of sulfide (~ 2 mM). The first order TCE degradation rate constant increased from 0.013 hr^{-1} for NZVI only to 0.432 hr^{-1} NZVI reacted with sulfide. The surface morphology and chemistry of NZVI reacted with sulfide and sulfate were studied using TEM-EDX and X-ray photoelectron spectroscopy (XPS), and these techniques confirmed the presence of FeS at the surface and provided data on the spatial distribution of FeS. Particle size measurements by nanoparticle tracking analysis showed no observable change in the average hydrodynamic diameter of bare NZVI and NZVI reacted with sulfide and sulfate. Thus increases in reactive surface area cannot be attributed to the increase in reactivity. Rather, the increased efficiency of electron transfer through a thin FeS outer layer on the NZVI enhances NZVI reactivity.

Textural and compositional zoning of plagioclase as archive of magmatic evolution: The Mt. Etna case study

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Textural and compositional features of plagioclase represent an useful tool to investigate magma chamber processes and changes in physical-chemical conditions of the shallow feeding system. Notwithstanding a coherent and univocal description and classification of plagioclase textural features is still lacking, as well as their link to magmatic processes. The study of more than 130 thin sections from Mt. Etna recent eruptions (2001, 2002-2003, 2004-2005 and 2006) offer a unique opportunity to fill this gap. Classification was developed taking into account different portion of the crystals, rather than simply label a single crystal. This allows to recognize different types of core (euhedral and rounded) and rims (dusty or with melt inclusion alignment) divided by oscillatory zoned overgrowth. Thermobarometric and crystal-melt equilibrium equations have been used to estimate the oxygen fugacity in magmas [1] and the amount of dissolved water content using the hygrometers of [2]. These data were introduced in the MELT's modelling to estimate the plagioclase stability field and to calculate theoretic composition at distinct water content, thus relating each crystal portion to growth or dissolution events occurring at specific P-T-fO_2 conditions and water contents. Results suggest a rather continuous plumbing system, ruling out the hypothesis of significant magma chambers in the Etnean plumbing system. Such system is persistently filled by magmas with quite similar major element composition but different dissolved H_2O, with the initial H_2O content constraining the depth at which plagioclase crystallizes. A small number of phenocrysts nucleate at 14 km whereas most plagioclase nucleates between 7 and 4 km of depth. At this depth, mixing occur between variably H_2O-enriched magmas, causing dusty textures in more albitic plagioclase. On the other hand, volatile loss due to fast ascent decompression promotes undercooling and crystal growth enhancing melt inclusions entrapment at crystal rims.

[1] France *et al.* (2010) *J. Volcanol. Geotherm. Res.* **189**, 340-346. [2] Lange *et al.* (2009) Am. Mineral. **94**, 494-506.

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