Redox interactions of Technetium with Fe(II) mineral phases

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Iron minerals influence the redox behaviour and mobility of metals in the environment, including the radioactive element technetium. Here, we have investigated several environmentally relevant reduced iron minerals with the potential to control the biogeochemistry of technetium in environmental media. Technetium is highly mobile in its oxidized form pertechnetate ($Tc(VII)O_4^-$), however, when it is reduced to Tc(IV) it immobilizes via precipitation or sorption. Pertechnetate was added to samples of both biogenic and abiotically synthesized Fe(II) mineral phases (magnetite, vivianite, siderite, and an amorphous Fe(II) phase). The pertechnetate was reduced and immobilized on all of the Fe(II) mineral phases as hydrous TcO_2 like phases. Samples of the reduced iron mineral phases were exposed to oxidizing conditions, including exposure to air and inoculation with a consortium of nitrate-reducing Fe(II)-oxidizing bacteria. The nitrate-dependent oxidation of vivianite, magnetite, or siderite by the consortium was minimal, although it was able to oxidize the amorphous Fe(II)-phase. X-ray absorption spectroscopy (XAS) of Tc in the samples identified mostly Tc(IV) in both reduced and reoxidized samples although XAS analysis of iron in magnetite and the amorphous Fe(II) phase indicated structural changes in the samples following oxidation. This study highlights the utility of studying specific Tc-mineral interactions, to better understand the biogeochemistry of Tc behavior in complex environmental media.

Phosphorus zonation as a record of olivine crystallization history

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Rapid diffusion of divalent cations through olivine at magmatic temperatures can result in relaxation of their zoning profiles and a loss of information regarding early crystallization history. Recent studies [1-3] show that zoning of P (and often associated Al and Cr) is ubiquitous in igneous olivines from a range of rock types, even in crystals homogenized with respect to divalent cations. We present results of 1-atm controlled cooling rate experiments (5-15°C/hr; QFM) that crystallized olivine from a natural Hawaiian basalt to which olivine was added (liquidus = 1287°C) and a P-free but otherwise compositionally identical synthetic analog. Experiments were either initially superheated to 1300°C for 3 h (leading to destruction of olivine nuclei) or held at subliquidus conditions for 3 h (1280°C; resulting in ~5% olivine nuclei), followed by linear cooling, and then quenching at 1150°C.

Our experiments replicate zoning features (i.e., sector and oscillatory zoning) seen in natural olivines. Individual olivines from each experiment lie on generally well defined trends in Al-Cr-P space that depend on the details of the experiment; however different sectors within a single crystal define distinct parallel trends. Al and Cr are positively correlated and are generally positively correlated with P in P-bearing runs suggesting connections between their modes of incorporation into olivine. Although Al and Cr zoning are spatially correlated with P zoning in some natural olivines and in olivines from the P-bearing experiments, the presence of P is not a prerequisite for zoning of Al and Cr as such zoning also occurs in olivines from the P-free runs. There are differences in some of the details of the P-Al-Cr systematics between olivines grown in initially superheated experiments and those from subliquidus experiments and natural samples. These differences plus the lack of a strong correlation of the results with cooling rate suggest that (1) crystal growth rate is the dominant factor in the development of zonation of these elements in igneous olivine, and (2) that P-Cr-Al zoning probably largely reflects local processes occurring at the crystal-melt interface. Our results also demonstrate that observed oscillatory zoning in magmatic olivines can form in magmas undergoing relatively simple cooling histories and that variable olivine growth rates can occur for such magmas.

[1] Milman-Barris *et al.* (2008) *CMP*. [2] McCanta *et al.* (2008) *LPSC* abs.# 1807. [3] Beckett *et al.* (2008) *LPSC* abs.# 1726.