

Iron corrosion product identification using micro-Raman spectroscopy

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Introduction

The corrosion of iron metal in aqueous systems results in the formation of a variety of iron bearing mineral phases. Many of these phases are highly redox sensitive, making their study by *in-vacuo* techniques difficult and potentially fraught with artefacts. Raman spectroscopy is a powerful technique that can be used to analyse environmental interfaces *in-situ* and we have used it to examine corrosion product formation.

Permeable reactive barriers containing zero-valent iron have been shown to be a viable technology for the remediation of contaminated groundwaters. Although contaminant-iron interactions have been fairly well studied, the changes that occur in the chemistry of the iron surface over time have not received as much attention. Here we describe *in-situ* Raman results obtained from column experiments conducted to examine the effects of various inorganic species and organic contaminants on iron interfacial composition.

Experimental

In-situ Raman spectroscopic measurements were obtained using a Renishaw 1000 Raman microscope system. This instrument consists of an Olympus microscope, a single spectrograph fitted with holographic notch filters, and a thermoelectric cooled charge coupled device (CCD) detector. An objective lens with 50x magnification provided spatial resolution of 2 μm^2 and a focal depth of 26 μm .

Results and Discussion

Upon contact with chlorinated hydrocarbon contaminants for a period of 308 days, the appearance of Raman bands at 425 and 504 cm^{-1} indicate the presence of the highly redox active species carbonate green rust and a band at 669 cm^{-1} that corresponds to magnetite. After 921 days, however, the bands for green rust have disappeared leaving Raman bands at 382 and 669 cm^{-1} , corresponding to the species goethite and magnetite.

In addition to temporal variations, interfacial corrosion product identity was found to be a function of solution composition and spatial distance along a laboratory column. These alterations indicate that the precipitates formed at the iron-water interface are both spatially and temporally heterogeneous. This result may partially explain observed variations in iron reactivity towards contaminant species.

This presentation will address the use of *in-situ* Raman spectroscopy for the analysis of the interfacial composition of a corroding surface. Additionally, this presentation will examine the use of *in-situ* Raman spectroscopy for the study of other surface-water interfacial systems where redox active species are present.

Paleozoic upper mantle of the southern frame of the Siberian platform: Structure and composition

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Abundant deep-seated xenoliths in lamprophyre dikes of the Western Sangilen provide information about composition, structure and evolution of the Paleozoic lithospheric mantle of the southern frame of the Siberian Platform. The mesostasis of camptonites and biotite and amphibole megacrysts have been analyzed with the Ar-Ar method and yielded a plateau age of 441.3 \pm 1.1 Ma (Izokh et al., 2002).

The camptonite dikes contain a lot of mineral megacrysts and phenocrysts as well as lherzolite, websterite and gabbro xenoliths. According to mineral composition the lherzolite nodules can be divided into primitive, depleted and enriched varieties. In turn, the depleted xenoliths vary from strongly to weakly depleted.

The HREE, Sr and Y contents in the clinopyroxenes from primitive spinel lherzolites are comparable with those in typical primitive mantle peridotites ($\text{Yb}_n = 10.2\text{-}13.8$), which have moderate HREE enrichment and minor depletion in LREE, Th, U and Nb. The La/Yb ratios in the clinopyroxenes vary insignificantly within a range of 0.44 to 0.97. All clinopyroxenes have small negative Zr-Hf-Ti anomalies. The HREE contents in clinopyroxenes from weakly depleted lherzolites are slightly lower than in those from primitive lherzolites ranging from 9.6 to 12.8. The REE distribution patterns are almost flat in the MREE and HREE regions and gradually slope down from Nd to La. La/Yb ratios in the clinopyroxenes are significantly lower ($\text{La/Yb} = 0.12\text{-}0.17$) than in the previous group. Likewise the clinopyroxenes from primitive lherzolites the clinopyroxenes of this group have small negative Zr-Hf-Ti anomalies.

The REE patterns in clinopyroxene from strongly depleted lherzolites are almost flat gradually sloping down from Yb to La. The HREE contents range from 4.6 to 11.7, whereas La/Yb ratios are < 1 (0.06-0.09). The negative Zr-Hf-Ti anomalies are less pronounced.

The chemical and mineralogical data obtained on the lherzolite nodules from Western Sangilen camptonite dikes allowed us to make several conclusion. The upper mantle domain beneath the Western Sangilen at a depth of the spinel facies consist of mainly 'dry' lherzolites varieties. The spinel lherzolites are dominated by depleted varieties (>50%). Mineral equilibria were attained at rather high temperatures of 1040–1190°C. This suggests a high geothermal gradient beneath the Western Sangilen during the capturing of xenoliths.