GSA Data Repository item 2001083: Field, experimental, and mass spectrometry techniques and data (Supplement to Geology article "A demonstration of significant abioitc iron isotope fractionation in nature", by T.D. Bullen, A.F. White, C.W. Childs, D.V. Vivit, and M.S. Schulz)

FIELD METHODS

Spring- and stream-water samples were collected in March 1999 from the field site on the western flank of Mt. Ruapehu. Samples were filtered through a 0.1 µm filter and acidified with Teflon-distilled HCl in the field. Chemical analysis revealed that the spring water sample contained less Fe than the sample collected and reported by Childs et al. (1982) for a December 1978 sampling, possibly because of unanticipated ferrihydrite precipitation in the spring vent or sampling vessel. Therefore we used the Fe concentration of the sample collected in December, 1978 as the true spring composition, and calculated percentage of spring water Fe remaining in the stream water based on the Fe/B ratio (assuming conservative behavior for boron). Ferrihydrite samples were collected from the streambed at the time and site of water-sample collection by scraping the fluffy surface material into a collection beaker.

LABORATORY EXPERIMENTS

Batch and "steady-state" ferrihydrite precipitation experiments were conducted by oxidizing ferrous chloride solution in a CO_2-HCO_3^--buffered pH-stat reactor at ~22 ^{o}C. In the batch experiment conducted at pH = 5.9, a research-grade equilibrated gas mixture consisting of 5% CO_2 + 95% air was bubbled through distilled water in a continuously stirred reaction vessel. Once solution pH steadied, the water was titrated to a pH of 6.0 by addition of 1 M $NaHCO_3$. Sufficient $Fe(II)Cl_2$ solution, prepared in a pure N_2 environment, was injected into the reaction vessel to provide a starting solution concentration of 0.7 mM Fe. As Fe precipitated, pH was held

constant by automatic metered additions of 1 M $NaHCO_3$. Incremental samples of solution and suspended ferrihydrite were collected by extracting a small sample of the reactor contents through a 0.45 μm cellulose acetate filter as the amount of Fe(II) in solution decreased from 99% to 15% of the starting concentration.

The steady-state experiments utilized a flow-through design that minimized potential isotopic back reaction between the solid and aqueous phases. The procedure for the steady-state experiments was identical to that for the batch experiment except that (1) gas mixtures consisting of both 5% CO_2 + 95% air and 1% CO_2 + 99% air were used to saturate the distilled water, (2) the water, at a flow rate of ~1 L/h, and $Fe(II)Cl_2$ solution, at a constant flow rate sufficient to provide a starting solution concentration of 0.7 mM Fe were continuously metered into the reaction vessel throughout each experiment, and (3) experiments were carried out over a range of pH from 5.4 to 6.2. Upon reaching the steady-state condition of constant Fe(II)-Fe(III) aqueous concentrations, samples of suspended ferrihydrite and coexisting solution were collected for analysis. Because water and $Fe(II)Cl_2$ solution were each metered into the reaction vessel at the same rates in each experiment, steady-state Fe(II) aqueous concentrations provide a direct comparative measure of the Fe(II) oxidation reaction rate.

Concentrations of aqueous species in the experimental and natural waters were determined by using the speciation code WATEQ4 (Ball and Nordstrom, 1991). Input parameters for the experimental waters included total C (determined by equilibrium with CO_2), Fe(II) (determined by using the ferrozine method), Cl and Na (calculated from quantities added), pH, and estimated pE. Input parameters for the Tongariro waters included total chemistry and pH reported by Childs et al. (1982) and estimated pE.

SAMPLE PREPARATION AND MASS SPECTROMETRY

Fe isotope compositions were measured by using a Finnigan MAT 261 thermal-ionization mass spectrometer (TIMS) and employing a ^{57}Fe-^{58}Fe double-spike amendment to allow for correction of analytically-induced isotope fractionation of the ^{56}Fe/^{54}Fe ratio (Johnson and Beard, 1999; Johnson et al., 1999). The double-spike method is a well-established procedure, and the particular algorithm used here is identical to that described previously for analysis of selenium isotope compositions on the same TIMS instrument (Johnson et al., 1999). The Fe isotope composition used as the initial "best-guess" of the natural composition in the iterative procedure was that reported by Johnson and Beard (1999) for "bulk earth-moon" based on analysis of an array of lunar and terrestrial igneous rocks. The composition of the ^{57}Fe-^{58}Fe double-spike and the consistent ratio of sample:spike were chosen to provide a mixture in which greater than 90% of ^{54}Fe and ^{56}Fe were derived from the sample and greater than 90% of ^{57}Fe and ^{58}Fe were derived from the double spike.

For sample preparation, sufficient volume of water, ferrihydrite (dissolved in 6 N HCl), or pre-dissolved U.S.G.S. standard basalt BIR-1 to provide 1.25 μg Fe was mixed with a fixed amount of ^{57}Fe-^{58}Fe double-spike tracer and evaporated, then treated with H_2O_2 to eradicate organic components and re-dissolved in 6 N HCl. This procedure resulted in consistent sample:spike ratios ($\pm 5\%$) in all measured samples. Fe in each sample was then purified using AG1-X8 anion exchange resin by first loading the sample onto the column in the 6N HCl solution, rinsing the column several times with 6N HCl, and finally stripping the Fe with 0.5N HCl. Prior to loading into the TIMS, purified Fe samples were mixed with a small amount of phosphoric acid, treated again with H_2O_2 and deposited onto single Re filaments in a mixture of colloidal silica and alumina.

Isotopes were measured in blocks consisting of 10 sets of three sequential scans: ^{56}Fe-^{57}Fe-^{58}Fe (simultaneously), ^{54}Fe-^{56}Fe (simultaneously), all on Faraday collectors, and ^{52}Cr on an ion counting device to correct for occasional minor isobaric interference of ^{54}Cr on ^{54}Fe (assuming ^{54}Cr/^{52}Cr = 0.0282; Matzar, 1978). ^{60}Ni was likewise monitored using the ion counter, but rather than make a correction for isobaric interference of ^{58}Ni on ^{58}Fe, block data was rejected if the signal was > 50 cps. Baseline counts were measured prior to and after each block. Individual sample filaments were analyzed until the standard deviation of the accumulated block average of the ^{56}Fe/^{54}Fe ratio was 0.15‰ or better. Total procedural replicate analyses were made for each sample, and all replicates agreed within 0.20‰. All analyses are quoted in standard per mil notation using the Icelandic basalt BIR-1 as the standard; positive values indicate relative enrichment in the heavier isotope.

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TABLE 1. CHEMICAL AND ISOTOPIC DATA FOR FIELD SAMPLES

Sample	Distance (m)	pH	Fe (ppm)	Fe/B (ppm)	$\delta^{56}Fe$ (replicate 1)	$\delta^{56}Fe$ (replicate 2)	$\delta^{56}Fe$, average (std. dev.)
spring	0	5.8	30	15.0			
Ton 1-water	0	6.0	10.2	10.2	-0.66‰	-0.83‰	-0.74‰ (0.12‰)
Ton 1-ferrihydrite	0				+0.18‰	+0.04‰	+0.11‰ (0.10‰)
Ton 5-water	200	6.8	7.9	9.5	-0.85‰	-1.05‰	-0.95‰ (0.14‰)
Ton 5-ferrihydrite	200				-0.22‰	-0.10‰	-0.16‰ (0.08‰)
Ton 6- water	400	7.2	3.6	6.5	-1.28‰	-1.41‰	-1.34‰ (0.09‰)
Ton 6-ferrihydrite	400				-0.34‰	-0.52‰	-0.43‰ (0.13‰)
Ton 7- water	600	7.5	1.1	2.1	-2.06‰	-2.15‰	-2.10‰ (0.06‰)
Ton 7-ferrihydrite	600				-1.04‰	-1.16‰	-1.10‰ (0.08‰)
Ton 8- water	900	7.5	0.2	1.2	-2.29‰	-2.11‰	-2.20‰ (0.13‰)
Ton 8-ferrihydrite	900				-1.48‰	-1.35‰	-1.42‰ (0.09‰)
Ton 9- water	1600	7.6	0.1	0.3	-2.08‰	-2.22‰	-2.15‰ (0.10‰)
Ton 9-ferrihydrite	1600				-2.08‰	-1.96‰	-2.02‰ (0.08‰)

TABLE 2. ISOTOPIC DATA, BATCH FERRIHYDRITE PRECIPITATION

Sample	Gas mixture	pH	Reaction time (hours)	Fe (ppm)	$\delta^{56}Fe$ (replicate 1)	$\delta^{56}Fe$ (replicate 2)	$\delta^{56}Fe$, average (std. dev.)
Initial	5% CO$_2$ 95% air	5.9	0	39.0	-0.51‰	-0.68‰	-0.60‰ (0.12‰)
FE C1 Solution	"	"	0.1	38.6	-0.60‰	-0.71‰	-0.66‰ (0.08‰)
Fe C1 ferrihydrite	"	"	0.1	-	+0.20‰	+0.29‰	+0.24‰ (0.06‰)
Fe C2 Solution	"	"	1.5	30.8	-0.83‰	-1.01‰	-0.92‰ (0.13‰)
Fe C2 Ferrihydrite	"	"	1.5	-	+0.11‰	-0.05‰	+0.03‰ (0.11‰)
Fe C3 Solution	"	"	3.7	29.3	-1.05‰	-1.11‰	-1.08‰ (0.04‰)
Fe C3 Ferrihydrite	"	"	3.7	-	-0.06‰	-0.16‰	-0.11‰ (0.07‰)
Fe C4 Solution	"	"	5.5	23.8	-1.19‰	-1.33‰	-1.26‰ (0.10‰)
Fe C4 Ferrihydrite	"	"	5.5	-	-0.06‰	-0.26‰	-0.16‰ (0.14‰)
Fe C5 Solution	"	"	7.0	16.4	-1.55‰	-1.45‰	-1.50‰ (0.07‰)
Fe C5 Ferrihydrite	"	"	7.0	-	-0.40‰	-0.53‰	-0.47‰ (0.09‰)
Fe C6 Solution	"	"	24.0	5.9	-2.32‰	-2.15‰	-2.24‰ (0.12‰)
Fe C6 Ferrihydrite	"	"	24.0	-	-0.72‰	-0.86‰	-0.79‰ (0.10‰)

TABLE 3. ISOTOPIC DATA, STEADY-STATE FERRIHYDRITE PRECIPITATION

Sample	Gas mixture	pH	Reaction time (hours)	Fe (ppm)	$\delta^{56}Fe$ (replicate 1)	$\delta^{56}Fe$ (replicate 2)	$\delta^{56}Fe$, average (std. dev.)
Initial		all	0	39.0	-0.51‰	-0.68‰	-0.60‰ (0.12‰)
FI-5 Solution	5% CO_2 95% air	5.4	7.0	36.1	-0.56‰	-0.70‰	-0.63‰ (0.10‰)
FI-5 ferrihydrite	"	"	"	-	-0.14‰	-0.26‰	-0.20‰ (0.08‰)
FI-4 Solution	"	5.6	8.3	31.1	-0.73‰	-0.63‰	-0.68‰ (0.07‰)
FI-4 Ferrihydrite	"	"	"	-	-0.06‰	-0.24‰	-0.15‰ (0.13‰)
FI-2 Solution	"	5.8	6.5	28.0	-0.88‰	-0.72‰	-0.80‰ (0.11‰)
FI-2 Ferrihydrite	"	"	"	-	+0.00‰	+0.10‰	+0.05‰ (0.07‰)
FI-8 Solution	"	6.0	6.0	6.6	-1.84‰	-2.04‰	-1.94‰ (0.14‰)
FI-8 Ferrihydrite	"	"	"	-	-0.32‰	-0.44‰	-0.38‰ (0.08‰)
FI-13 Solution	1% CO_2 99% air	5.5	7.0	36.4	-0.54‰	-0.67‰	-0.60‰ (0.09‰)
FI-13 Ferrihydrite	"	"	"	-	+0.28‰	+0.20‰	+0.24‰ (0.05‰)
FI-12 Solution	"	5.7	4.5	33.6	-0.58‰	-0.74‰	-0.66‰ (0.11‰)
FI-12 Ferrihydrite	"	"	"	-	-0.22‰	-0.08‰	-0.15‰ (0.10‰)
FI-14 Solution	"	5.9	8.0	30.8	-0.82‰	-0.71‰	-0.76‰ (0.08‰)
FI-14 Ferrihydrite	"	"	"	-	+0.03‰	-0.13‰	-0.05‰ (0.11‰)
FI-7 Solution	"	6.1	7.5	0.9	-1.39‰	-1.29‰	-1.34‰ (0.07‰)
FI-7 Ferrihydrite	"	"	"	-	-0.60‰	-0.44‰	-0.52‰ (0.11‰)
FI-6 Solution	"	6.2	7.3	0.1	-1.51‰	-1.63‰	-1.57‰ (0.08‰)
FI-6 Ferrihydrite	"	"	"	-	-0.47‰	-0.64‰	-0.55‰ (0.12‰)