



Chemical Interactions of Arsenate, Arsenite, Phosphate and Silicate with Iron (II, III) Hydroxycarbonate Green Rust

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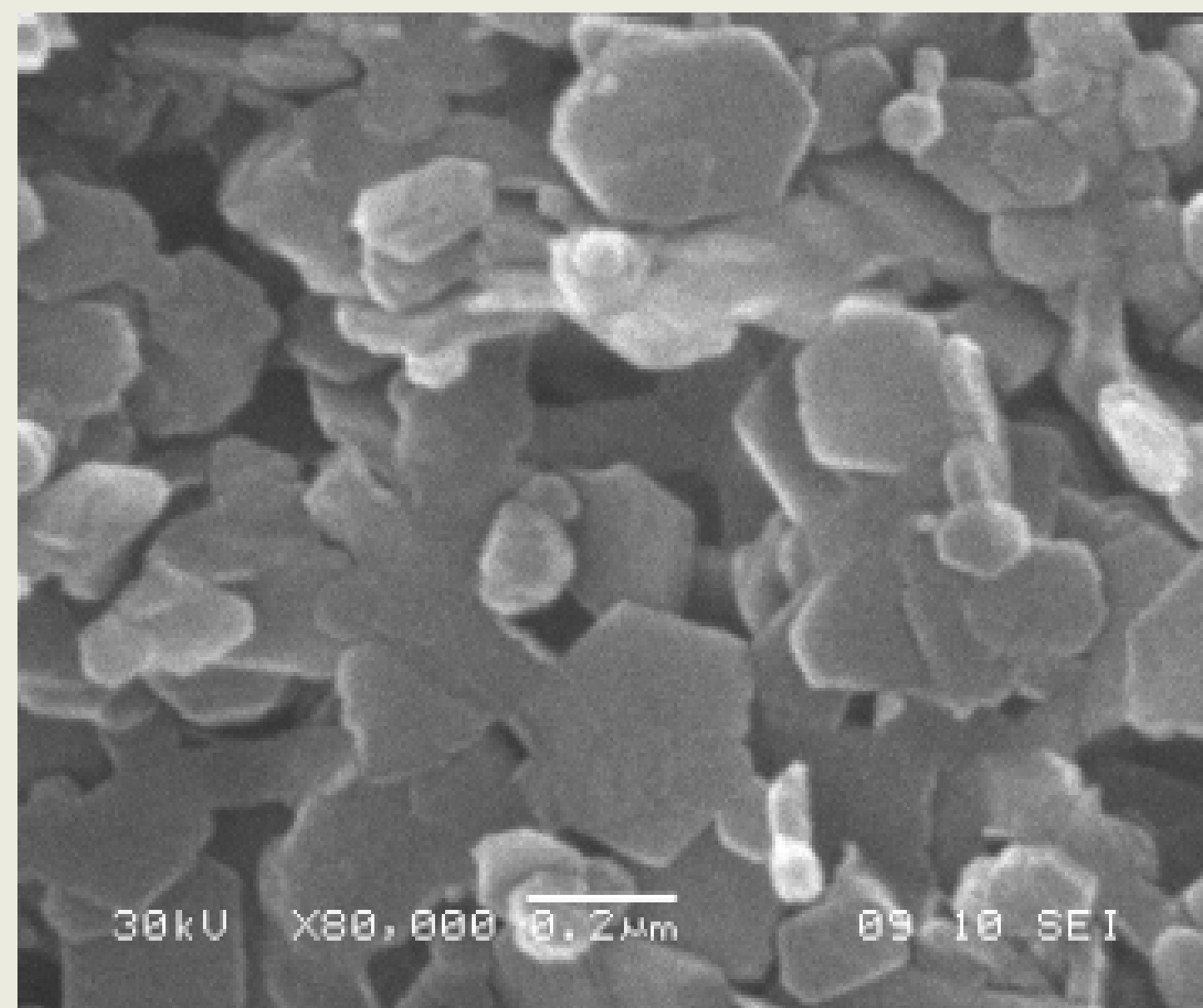


Abstract

We studied chemical interactions between iron(II, III) hydroxycarbonate green rust (CGR) and arsenate, arsenite, phosphate, and silicate using scanning electron microscopy, X-ray diffraction, and wet chemical analysis in a pH range from 7.5 to 10.7. Both arsenate and arsenite sorption increased with increasing time up to 60 days. More arsenite was sorbed at pH 7.5 than at pH 10.4. Arsenite showed much higher sorption than arsenate. Sorbed arsenite (up to 90 g kg⁻¹) was partially oxidized at the surface of CGR. Sorption of the anions seems to stabilize the structure of CGR. The phase transformation temperature of CGR to hematite and at a lesser degree to magnetite was substantially increased due to anion sorption.

Introduction

Granular zerovalent iron has been proposed to be used as a medium in permeable reactive barrier (PRB) to remove arsenic from contaminated groundwater. Iron(II, III) hydroxycarbonate green rust (carbonate green rust, or CGR) is a major corrosion product of zerovalent iron under anaerobic conditions. CGR is also found in certain hydric soils and sediments. It is important to study the chemical interactions of inorganic arsenic species (arsenate and arsenite) and common oxyanions (phosphate and silicate) with this green rust in order to understand the behavior and fate of these anions in groundwater systems. To maximize the effectiveness of iron barriers, it is essential to evaluate the influence of geochemical parameters such as arsenic concentration, pH, and time on the interactions of arsenic with iron corrosion products.



SEM micrograph of synthetic carbonate green rust showing mostly hexagonal platy particles.

Materials and Methods

CGR was synthesized according to a procedure described by Su and Wilkin (2005) by neutralizing ferrous sulfate solution with sodium hydroxide and sodium carbonate or sodium bicarbonate followed by air sparging. The synthetic products were characterized with X-ray diffraction (XRD), thermogravimetric analysis, scanning electron microscopy, X-ray absorption spectroscopy, and wet chemical analysis. Batch arsenic sorption experiments were conducted with arsenate and arsenite in an anaerobic glovebox.

CGR samples of 0.1 g were reacted separately with 36 mL of arsenate or arsenite at 10 mM, phosphate or silicate at 1 and 10 mM for 1, 30, and 60 days in 50-mL centrifuge tubes in an anaerobic glovebox (CGR concentration 2.78 g L⁻¹). Reacted CGR was examined with XRD and compared to CGR without phosphate and silicate.

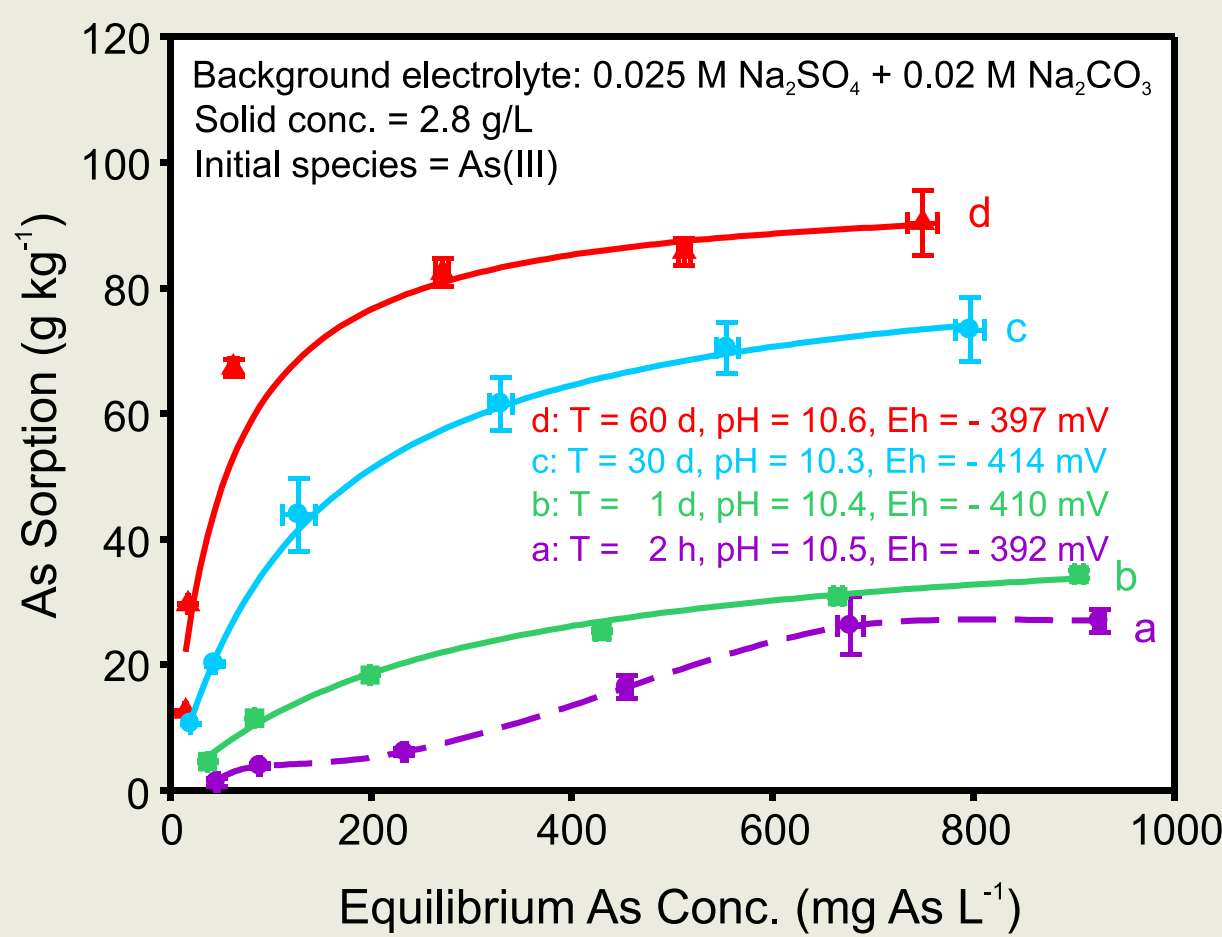
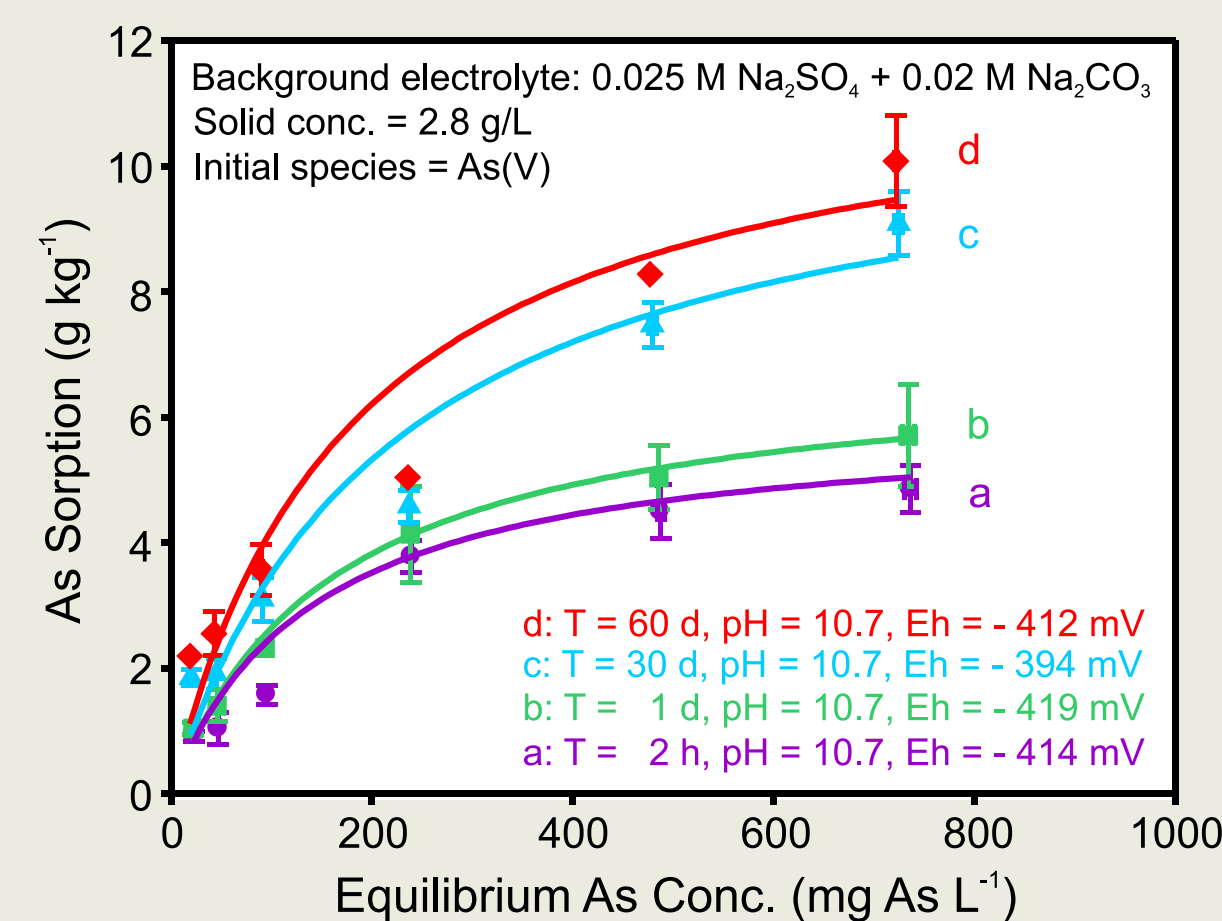
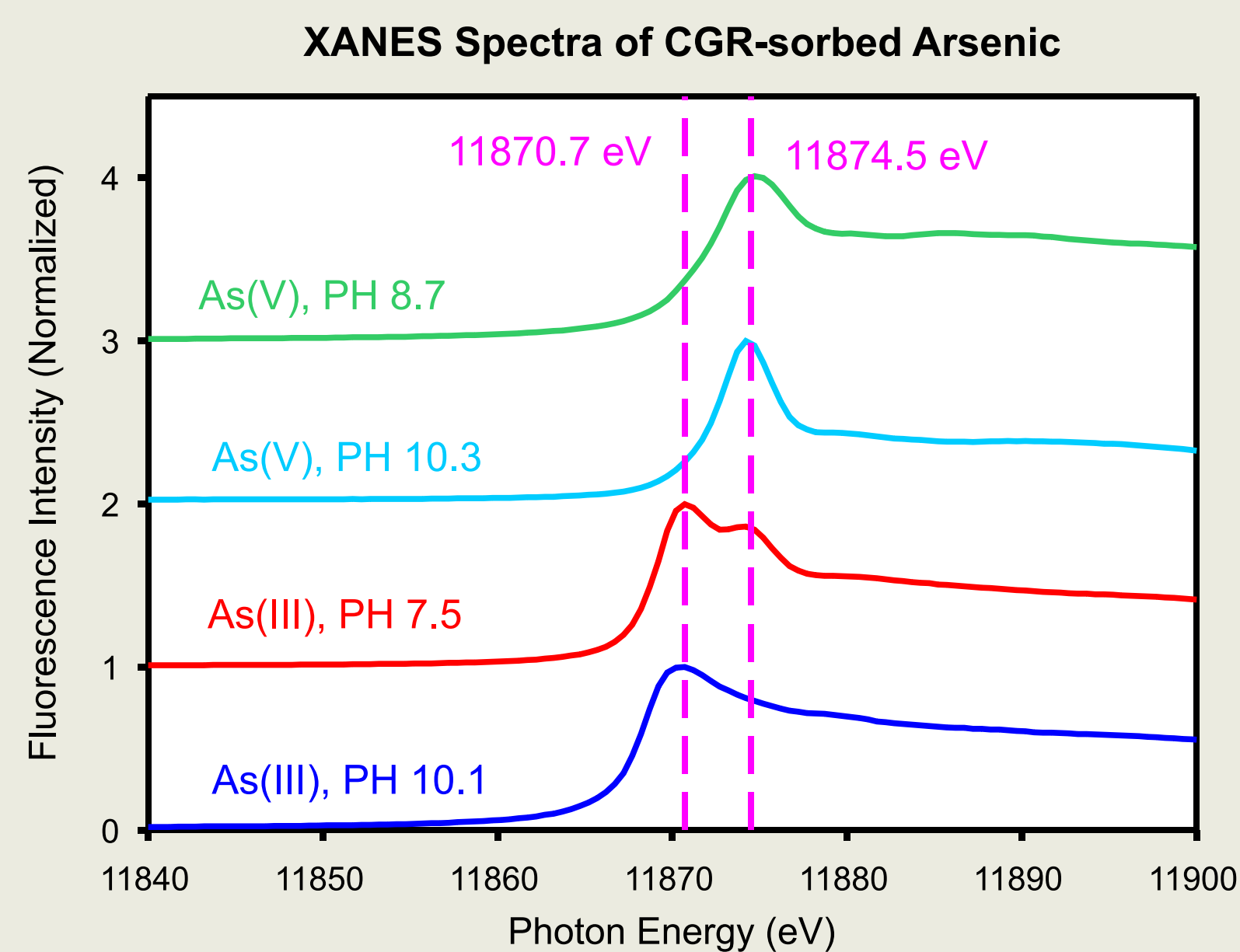


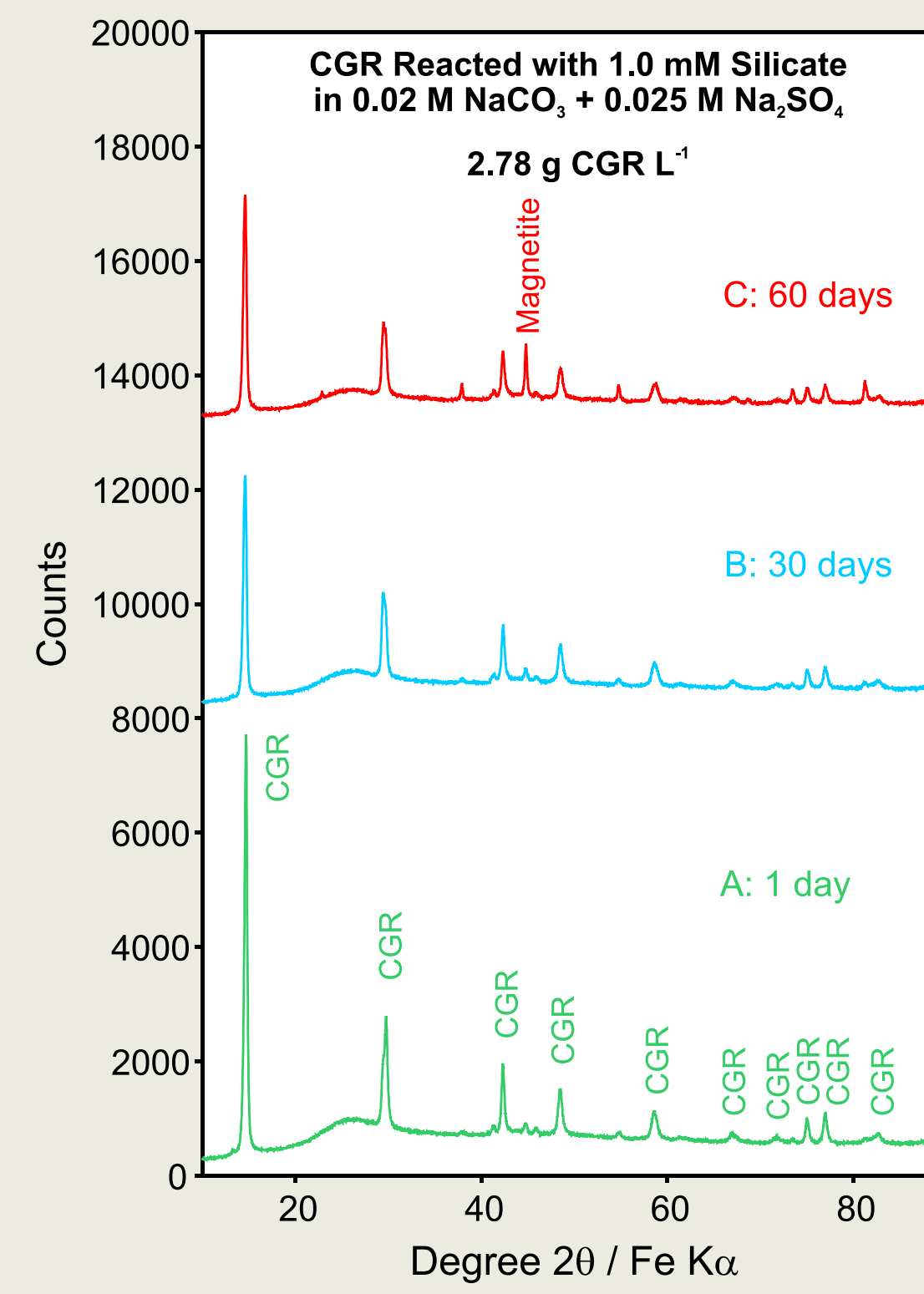
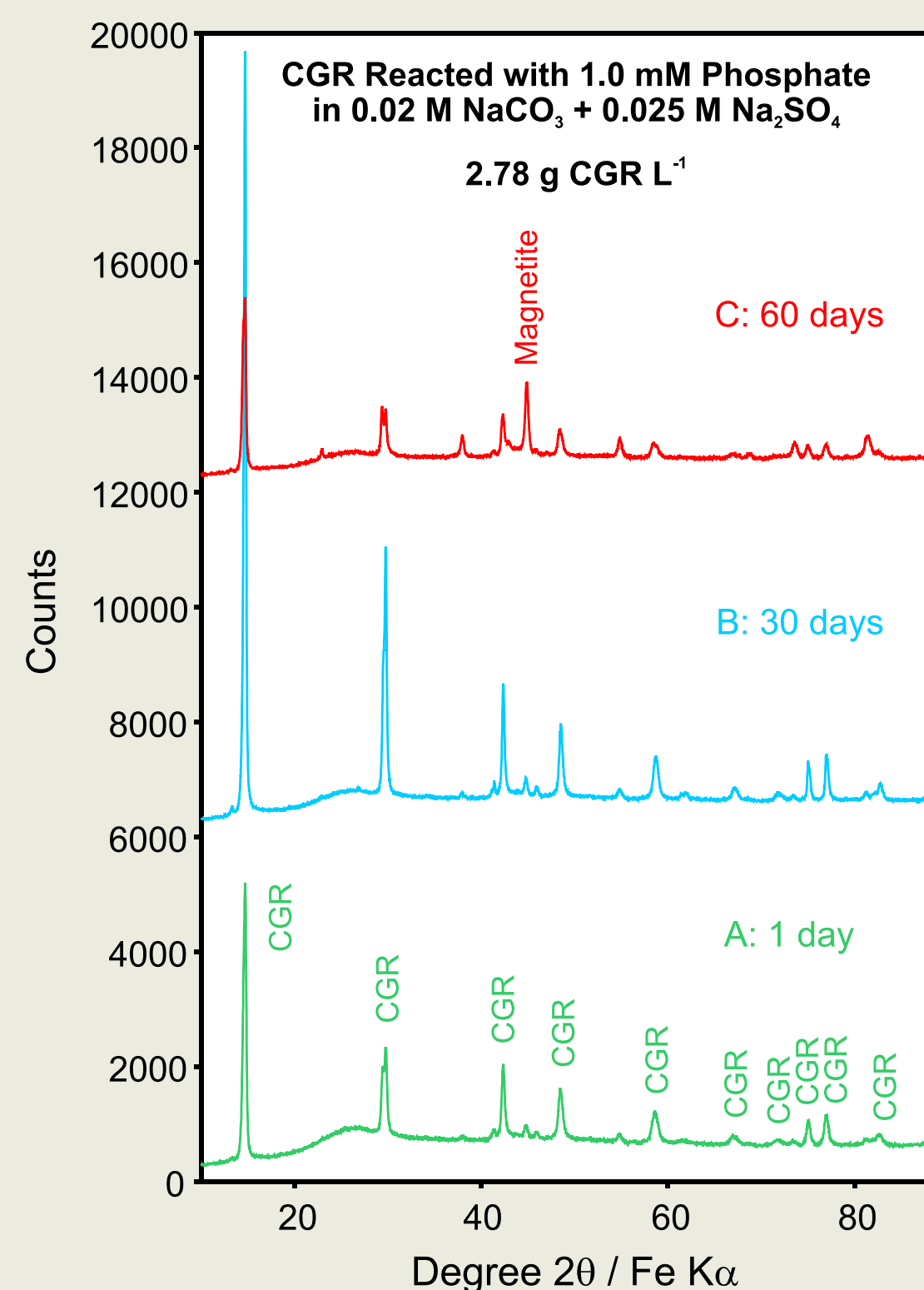
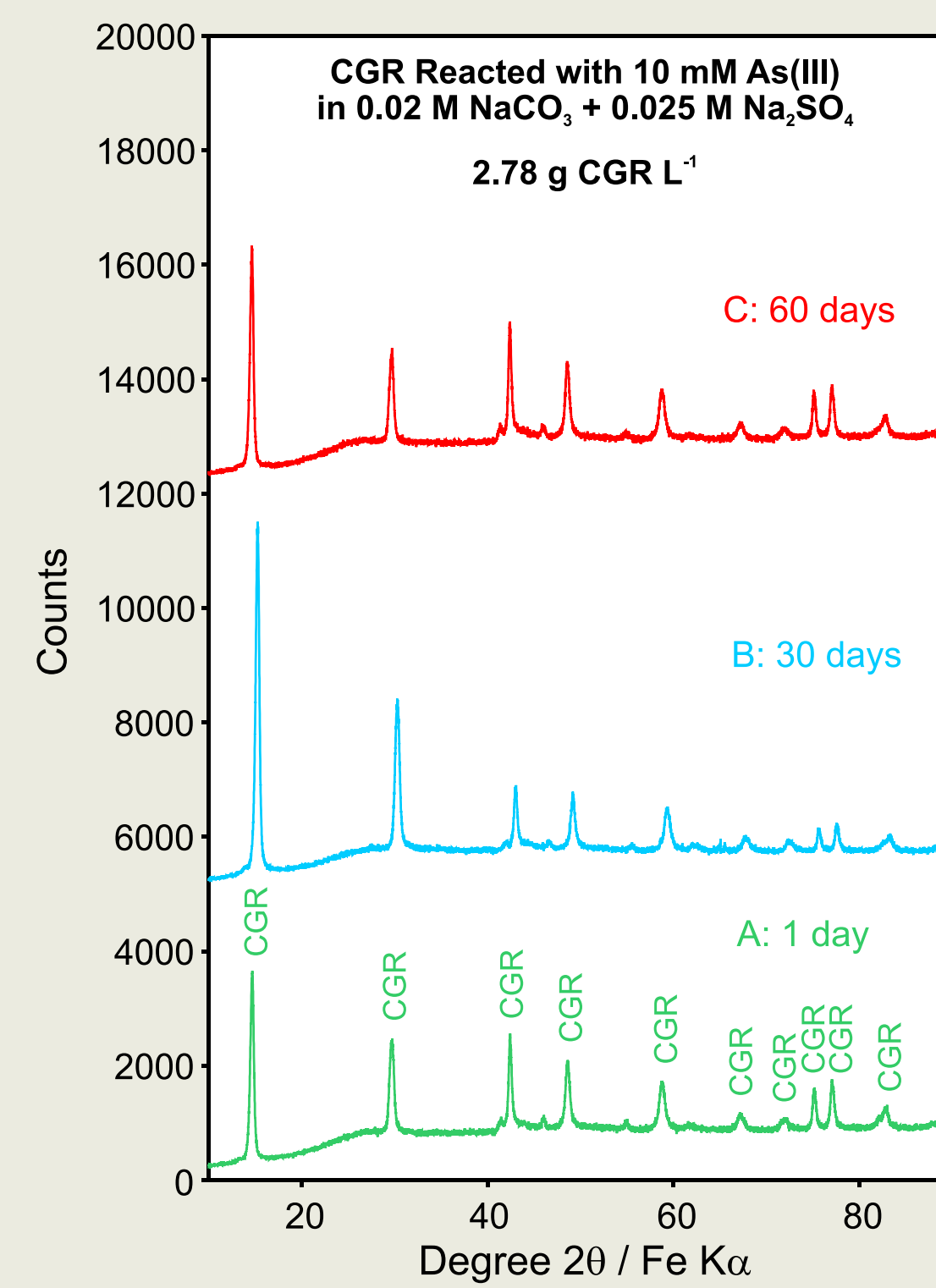
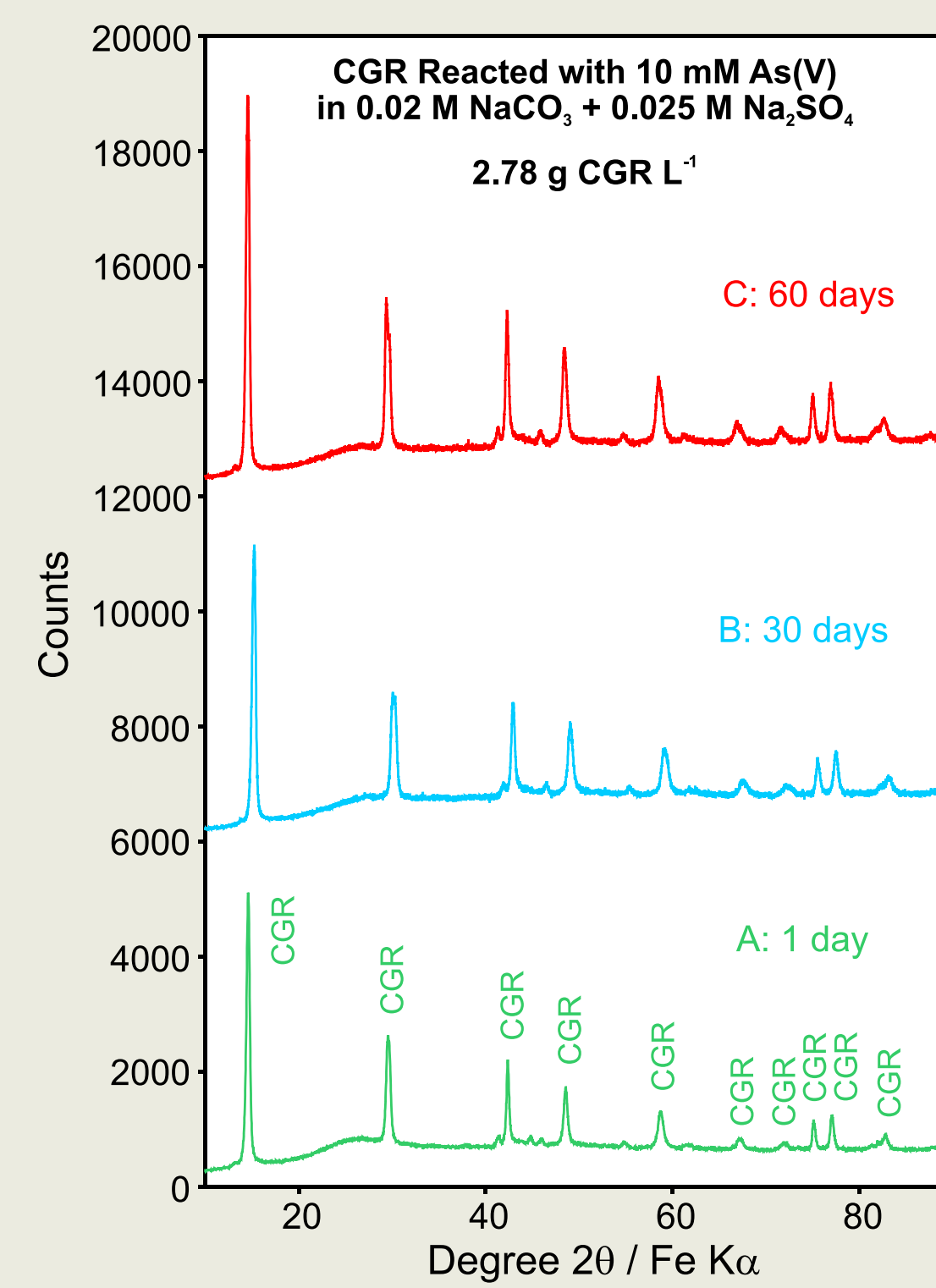
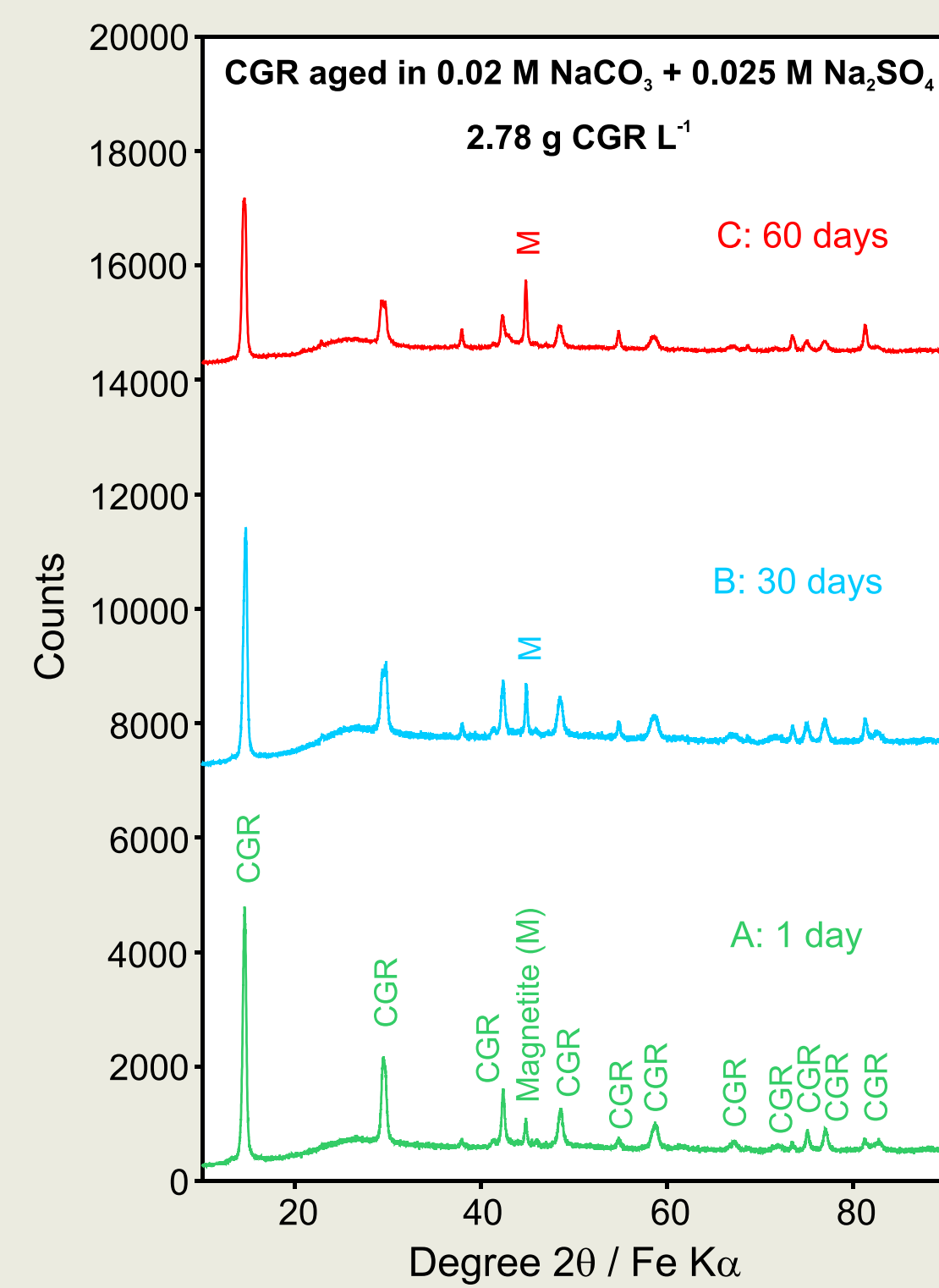
Table 1. Summary of Langmuir Sorption Isotherms for As(V) and As(III) on Carbonate Green Rust.

	Time	pH	Eh (mV)	R ²	K (L mg ⁻¹)	M (mg kg ⁻¹)
As(V)	2 h	10.7 ± 0.1	-414 ± 20	0.919	0.0071 ± 0.0042	6.01 ± 2.28
	1 d	10.7 ± 0.1	-419 ± 16	0.982	0.0062 ± 0.0017	6.91 ± 0.53
	30 d	10.7 ± 0.1	-394 ± 18	0.924	0.0046 ± 0.0005	11.11 ± 0.31
	60 d	10.7 ± 0.1	-419 ± 16	0.921	0.0055 ± 0.0008	11.85 ± 0.40
As(III)	2 h	10.5 ± 0.2	-392 ± 12	0.114	NA	NA
	1 d	10.4 ± 0.2	-410 ± 4	0.982	0.0037 ± 0.0002	43.8 ± 1.2
	30 d	10.3 ± 0.2	-414 ± 23	0.998	0.0071 ± 0.0009	87.2 ± 10.1
	60 d	10.6 ± 0.2	-397 ± 10	0.983	0.0195 ± 0.0069	96.2 ± 13.0
As(III)	1 d	9.3 ± 0.1	-259 ± 25	0.912	0.0058 ± 0.0030	47.9 ± 12.3
	1 d	7.5 ± 0.3	-181 ± 33	0.762	0.0022 ± 0.0002	123 ± 6



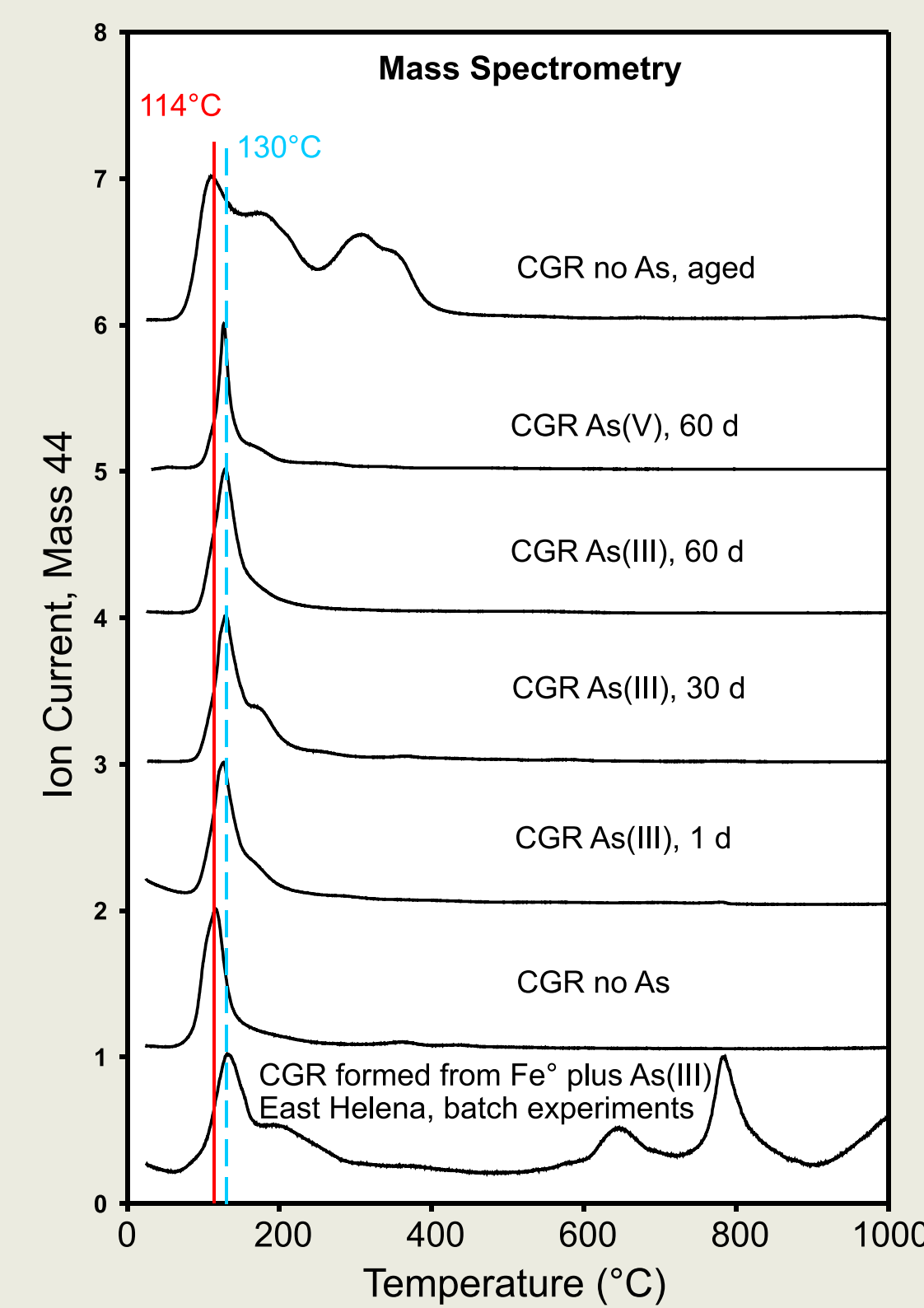
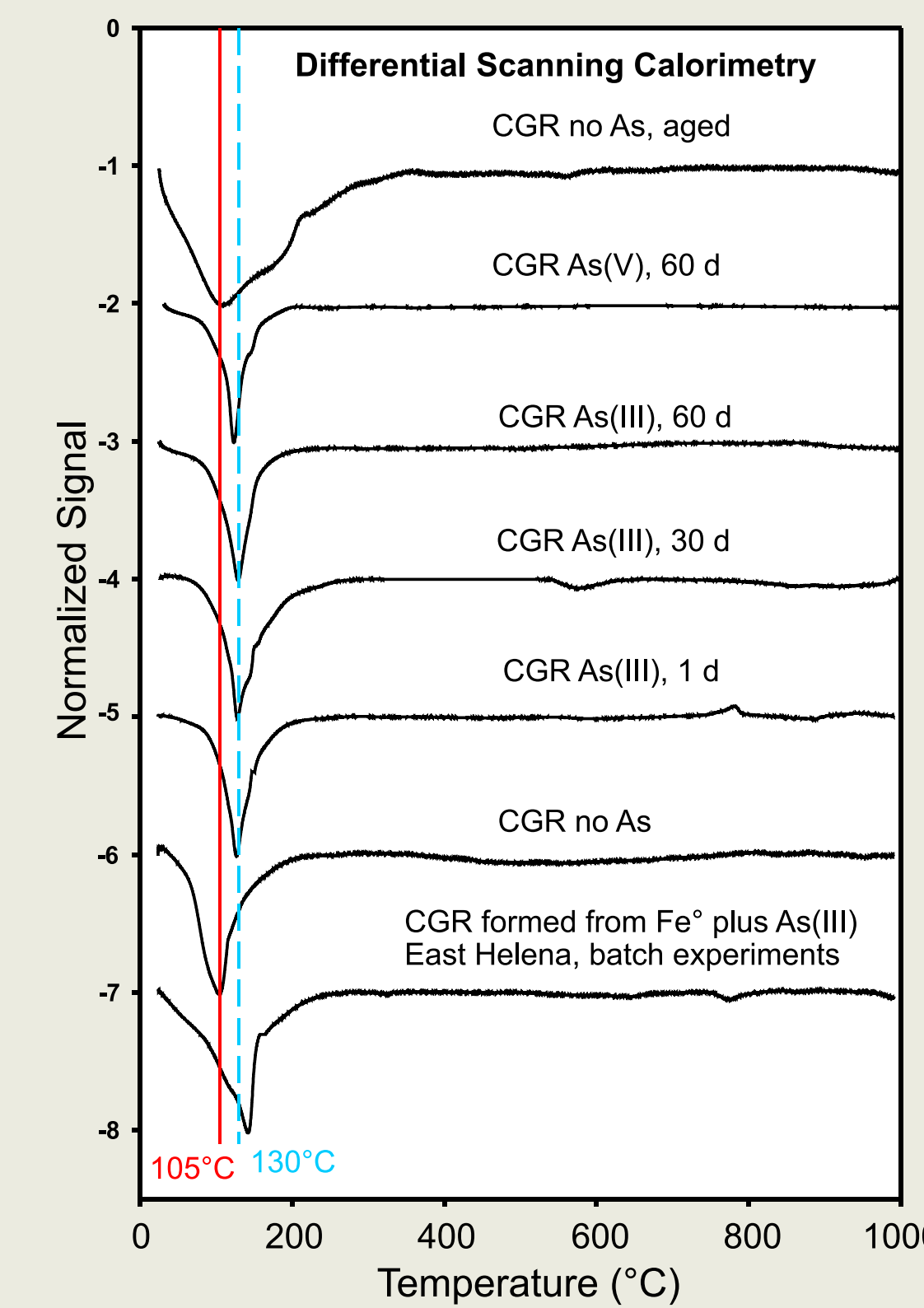
Results and Discussion

Both arsenate and arsenite sorption increased with increasing time up to 60 days. Arsenite showed much higher sorption than arsenate. Adsorbed arsenite (up to 90 mg kg⁻¹) was partially oxidized on solid surface as determined by arsenic speciation analysis of sorbed arsenic extracted with hydrochloric acid. X-ray absorption near edge structure spectroscopy results confirmed partial oxidation of arsenite by CGR.



Phosphate and silicate at 1 mM seem to stabilize the structure of CGR for at least 30 days based on XRD results. Substantial magnetite was formed after 30 days. No magnetite was found when 10 mM phosphate or silicate was used for 60 days.

Differential scanning calorimetric patterns showed one main endothermic peak that ranges from about 110 to 130 °C. Arsenate and arsenite bearing green rusts decomposed at a higher temperature compared to As-free green rust. Arsenic tended to stabilize the green rust structure via stabilization of the surface bonding environment. Examination of the mass spectra data shows that the endothermic decomposition corresponds to the release of H₂O and CO₂ molecules. Green rust that has been allowed to age (without As) or that forms as a consequence of zerovalent iron corrosion shows more complicated thermal behavior due to mineral transformation and formation of other carbonate minerals (siderite, iron hydroxy carbonate, calcite). Combination of thermogravimetric, wet chemical, and solid phase carbonate analyses confirm the green rust stoichiometry.



The laboratory results should have positive implications for field applications of zerovalent iron based PRBs to remediate arsenic in groundwater. Uptake of either arsenate or arsenite by carbonate green rust will likely keep the iron corrosion product stable in the subsurface. Oxidation of sorbed arsenite could be advantageous because arsenate is generally less toxic and less mobile than arsenite in the subsurface. Naturally occurring carbonate green rust may be more common than previously thought and it can be an important sink for arsenic. Further study is needed to evaluate its contribution to natural attenuation of arsenic in the subsurface.

References

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