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To: Meena Sachdeva <sachdeva@lanl.gov>
From: Meena Sachdeva <sachdeva@lanl.gov>
Subject: Fwd: July 12 the e-mail from Tom Johnson

Date: Sat, 12 Jul 2008 16:29:33 -0500
From: Tom Johnson <tmjohnsn@uiuc.edu>
Subject: Re: need advice on report
Cc: Glessner_Justin <jglessne@uiuc.edu>
X-ELNK-AV: 0
X-ELNK-Info: sbv=0; sbrc=.0; sbf=0b; sbw=000;

Jeff,
You're asking questions that we are hoping to answer in the next few years... See below.

Hi Tom and Justin:

I'm trying to wrap up the peer review copy of my report this weekend, but I've managed to get myself confused after reading Izbicki et al., 2008.
I've always treated $\delta^{53}\text{Cr}$ initial as ~ 0 ‰, whether for contamination- or background-derived Cr(VI). Izbicki et al seem to take a different approach and consider that for natural Cr(VI) there can be reduction of Cr(VI) to Cr(III) on the surface of mineral grains following weathering and oxidation, but prior to exchange of Cr(VI) into solution. They seem to take the isotopic composition of this enriched Cr(VI) that goes into solution as $\delta^{53}\text{Cr}$ initial. These authors appear to treat reduction of Cr(VI) from solution under low oxygen conditions separately from reduction on mineral grains.

This is a fairly recent complication. We don't have a lot of data yet, but on the broad scale, it seems that when Cr weathers out of rocks, the Cr(VI) shows up somewhat elevated in $\delta^{53}\text{Cr}$. This is perplexing, as we still think the rock should be about zero. So the ad hoc explanation so far is there must be something happening as the Cr is released that causes a small fractionation. I think the USGS guys have data from other places that suggest this occurs in more places than just the Mojave. In my group, I think we have a few data that point in the same direction.

This is all puzzling to me. If the rock really is zero and it keeps coughing up Cr(VI) that is enriched in heavy isotopes, there must be some growing pool of Cr that is NOT release and is depleted. We haven't looked for it yet- maybe it's clays or ferric oxides.

However, maybe I shouldn't be puzzled. Newly formed Cr(VI) has to make its way from a reducing environment (the Cr bearing minerals mostly contain Fe(II)) to the oxic groundwater. Is it really surprising that some of the Cr(VI) gets re-reduced on the way out? Diffusion would tend to randomly move some Cr(VI) back toward the reducing zones, some out toward the more oxic zones. Does that make sense?

I just finished writing a proposal to look at oxidation processes in the lab. Also, my former student Andre Ellis just came out with data showing a 1 per mil-ish increase in $\delta^{53}\text{Cr}$ as Cr(III) is oxidized to Cr(VI). See attached GSA abstract. Caveat: That result is for DISSOLVED Cr(III) at low-pH. Seems like it would be much harder to have fractionation when a solid is consumed.



My first thought was I should be doing this too, while my second was that I have no idea how I am going to doing that!

I see at least three problems with trying to apply their approach in our setting:

1. We're not always sure in our setting where we are seeing contaminant Cr(VI) versus background Cr(VI), and in many cases it will be a mixture. This would make it difficult to assign different $d_{53}Cr_{initial}$ based on whether Cr(VI) is natural or contamination.

Yes.

2. $d_{53}Cr$ of our known background locations is quite variable, and it is impossible to tell how much of the reduction occurred on mineral grains following initial weathering/oxidation of Cr(III) to Cr(VI) versus how much occurred later and elsewhere along background flow paths.

Yes, one needs more information (e.g., spatial patterns showing changes along flow paths) to nail down the location of reduction. But with the background Cr, do we care where it got reduced?

3. Our groundwater aquifers are primarily oxidizing, so it is likely that much (most?) of our reduction actually occurs on mineral surfaces. I'm assuming that most of our Cr(VI) reduction involves reactions on mineral surfaces containing reduced iron

or involves bacteria that live in microenvironments on those surfaces....

while Cr(VI) is reversibly sorbed to these surfaces. Does this make sense?

Yes, in general I would guess the reducing power of the abundant Fe(II) is somehow behind Cr(VI) reduction.

Do you feel that my approach of considering all sources of Cr(VI) to have $d_{53}Cr_{initial}$ of ~ 0 ‰ is valid if I acknowledge that the calculated ‰Cr reduction could include initial reduction on mineral surfaces before Cr(VI) ever goes into solution in the case of background chromate?

Yes, I think that is a reasonable approach.

Tom, on another note, you had e-mailed me that the current range of fractionation factors was 2.5 - 4.3 ‰, but there is a slightly larger range in the Sikori et al. paper you just sent (1.8-4.7 ‰?).

The low-donor experiment results (the relevant ones) form a single population with best-fit value of 4.1. I attribute the high 4.5 value to random chance- not a statistically significant difference. So I would still

keep 4.3 for max epsilon. But this is a really fine point, so use 4.5 if it fits your sentence better.

Is there something I can use in my report to explain the initial values you sent? I've already done all of my plots and tables based on those earlier values.

Yes, I would use Ronny Schoenberg's recent paper (attached) to say that the rock is probably zero. Then I would explain that, based on Ibicki's very recent paper, we now need to factor in the possibility that some reduction could occur in the Cr(VI) weathering/release process.

I don't have time to think through this rigorously, but it seems to me that you still have what you need for the contaminant chromium. We can still assume it starts near zero. It is true that some of the isotopic variability we measure could be caused by mixing with variable $d^{53}\text{Cr}$ background Cr. But if most much of the Cr in a sample is background Cr, and not contaminant, that's good, right?

We should get in the habit of talking on the phone once each month. Sorry I didn't call several weeks ago, deadlines closed back in on me after those few days of feeling free to catch up. I have a new student getting trained and he might be able to do some experiments or other things related to LANL waters.

I'm off to Goldschmidt tomorrow AM. Should have good email access.

Cheers,
Tom

Take care and thanks!

Jeff

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