## Overview of reaction modeling with The Geochemist's Workbench®

This lab serves to introduce the GWB and the basis swapping technique upon which its programs are founded.

## <u>Demo 1 — The Geochemist's Spreadsheet</u>

**GSS** is a spreadsheet designed for geochemists. The program works with the other software tools in The Geochemist's Workbench. You enter, paste, or drag the analyses for your samples into a **GSS** data sheet.

You can then convert units, create plots and diagrams, mix samples, compare replicate analyses and check standards, calculate speciation and saturation, and more. You can drag samples into the other GWB apps, and drag calculations results from the other apps into **GSS**.

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AI+++	$\nabla$	mg/kg		Þ	0.0	7							
Fe++	<b>\$</b>	mg/kg		Þ	0.0	6	0.02						
Ca++	•	mg/kg		Þ	4.	3	38		1	5			
Mg++	<b>A</b>	mg/kg		Þ	1.	1	10		4.	1			
Na+		mg/kg		Þ	1.	8	20		6.	3			
K+	•	mg/kg		Þ			2.9		2.	3			
HCO3-	Ť	mg/kg		Þ	1	9	113		5	3			
so <sub>4</sub>	*	mg/kg		Þ		3	51		1	1			
CI-		mg/kg		Þ	1.	9	24		7.	3			
F-	X	mg/kg		Þ	0.	2	0.3						
NO3-	*	mg/kg		Þ	0.	1	2.4			1			
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To get started, double click on "RiverWaters.gss":

Analytes and their units are listed in the leftmost columns. Columns to the right hold data for the samples. You add analytes to the datasheet by clicking on the + analyte button, and samples with the + sample button. Exchange rows and columns by selecting Edit  $\rightarrow$  Transpose Data Sheet.

GSS GWB Adv	anced Profession	al - C:\Users\B	rian F\Dropbox (Ac	queous Solutions)\GWBco	urse	es\11-Workshops\Rea	ctive Tr	anspor —	×
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Na <sup>+</sup>	🛂 mg/kg		1.8	3	20		6.3		
K+	ᅌ mg/kg	•			2.9		2.3		
HCO3-	💆 mg/kg	•	19	9 1	113		58		
SO4	💆 mg/kg	•	;	3	51		11		
Cŀ	📮 mg/kg	•	1.9	9	24		7.8		
F-	🖉 mg/kg	•	0.2	2	0.3				
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To convert units, select one or more analytes

then right-click on the unit field and select a new unit under the **Units** pulldown.

To complete the task, select each of the chemical components listed with units of "mg/kg", then click on **Units**  $\rightarrow$  "mmol"  $\rightarrow$  "mmol/kg". When the program prompts



select **Yes**. The analyses for the components you selected should now appear in the new units. If you had selected **No**, the unit designation would have changed, but the numerical values would have remained unaltered.

Why can't TDS (Total Dissolved Solids) be converted to mmol/kg like the chemical components?

Laboratories commonly report analyses in elemental equivalents, such as sulfate as mg/kg of sulfur, or bicarbonate as mg/kg of carbon. To specify such a unit in a **GSS** spreadsheet, choose the "SO<sub>4</sub>--" analyte, for example, right-click the units column, and select **As**  $\rightarrow$  "S" rather than **As**  $\rightarrow$  "SO<sub>4</sub>--".

You can similarly set concentrations in species equivalents, in terms of protonated or deprotonated forms of the species in the spreadsheet, such as bicarbonate as mg/kg of carbon dioxide, or ammonium as mg/kg of ammonia. To specify such a unit, choose the "HCO<sub>3</sub>-" analyte, for example, right-click the units column, and select **As**  $\rightarrow$  "CO<sub>2</sub>(aq)".

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To plot the data, go to **Graphs** and choose from the list of plots and diagrams

The Piper diagram is useful for portraying the major ion composition of a suite of samples. How does the Mississippi River sample differ from the others?



Right-click in various places on the plot—on the samples, labels, and axes—to explore how you can modify its appearance. You can turn sample legends and labels on or off, for example, and change the size, font, or color of text.

**GSS** works with **SpecE8** to quickly perform tasks such as computing mineral saturation or gas fugacity. Go to  $\rightarrow$  **Calculate** and choose from the lists of analytes for the various variable types.

## <u>Demo 2 — Reaction balancing with **Rxn**</u>

To balance a reaction with **Rxn**, first set a species, mineral, etc., to appear on the left side of the reaction. Then, swap the basis to pull in the various species you want to appear in the reaction.

For example, to show the reaction by which  $H_2S(aq)$  oxidizes to sulfate, start **Rxn** and move to the **Basis** pane. Under "balance reaction for", select "???"  $\rightarrow$  **Aqueous...**  $\rightarrow$   $H_2S(aq)$ . Set "temperature" to 25 °C.

The pane should look like this

≓ Rxn GWB Advanced Professional - C:\Users\Brian F	-		×
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Move to the **Results** pane and click **Run**. What chemical reaction does the program give? What is its log *K*?

Now let's balance the corresponding half-cell reaction. Click on the swap button  $\rightleftharpoons$  next to the basis entry for "O2(aq)" and select **Aqueous...**  $\rightarrow$  e-

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Move to the **Results** pane and click **Run**. How has the reaction changed?

To recast the reaction to liberate dihydrogen, once again click on the swap button  $\rightleftharpoons$  next to the basis entry for "O2(aq)" (where e- is currently swapped in) and select **Aqueous...**  $\rightarrow$  H2(aq)

<u>E</u> dit Run	Config <u>V</u> iew	<u>H</u> elp								
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Return to the **Results** pane and click **Run**. How has the reaction changed?

To see more information about the reaction, including the corresponding equilibrium equation and the equilibrium constant at each of the principal temperatures, click the + button

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Basis	Command Results								
+	+ $H2S(aq) + 4 H2O = 2 H+ + SO4 + 4 H2(aq)$								
	Log K at 25 C = -53.0573								

## <u>Demo 3 — Eh-pH diagrams</u>

**Act2** calculates geochemical stability diagrams on activity or fugacity coordinates. To calculate an Eh-pH diagram for selenium, for example, start the program and move to the **Basis** pane:

- 1. Under "diagram species", click on "???" and select "SeO3--". Set activity to 10^-6.
- 2. Under "on axes", for "on x axis" click on "???" and select "H+". Change the unit from "log activity" to "pH". The axis automatically spans from 0 to 14, but you can adjust the range.
- For "on y axis" click on "???" and select "O2(aq)". Click on the swap button 
   *i* next to the basis entry for "O2(aq)" and select Aqueous...→ e–. Change the unit from "log activity" to "Eh".

The pane should look like this:

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	pressure				•	bars 🔻				

Move to the **Plot** pane to view your diagram.

You can copy your plot and paste it into your documents, including Microsoft Word, Excel, and PowerPoint, or Adobe Illustrator. First, select Edit  $\rightarrow$  Copy



then, paste into PowerPoint as an Enhanced Metafile. Ungroup the image to enable editing



Microbes take advantage of the redox disequilibrium found in the natural environment to derive energy. Respiring microbes trap energy released when electrons liberated by an electron donating reaction are taken up by an electron accepting reaction.

The difference  $\Delta Eh$  between the *Eh* for the accepting and donating reactions is a measure in volts or mV of the energy released. The value is given as

$$\Delta Eh = Eh_{acc} - Eh_{don} = -\frac{\Delta G_r}{nF}$$

where *n* is the number of electrons transferred and *F* is the Faraday constant. Reactions with positive *Eh* values release energy.

Basis Medium Co	mmand	Results			
constraints on initial system					
	H2O		1.0	▼ free kg ▼	Soil gas
cc	)2(g) 🛱	HCO3-	0.01	▼ fugacity ▼	
Fe(OH)3	ippd) 🛱	Fe+++	1.0	▼ free cm3 ▼	
	н+ ₽		6.0	r PH → Irc	on minera
	d- ₽		15.0	▼ mg/kg ▼	
	Na+ 🛱		10.0	▼ mg/kg ▼	
C	a++ ₽		15.0	▼ mg/kg ▼	
Μ	g++ 🛱		2.0	▼ mg/kg ▼	
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Double click on file "microbe.sp8". When SpecE8 opens, move to the Basis pane

The input describes the analysis of a hypothetical groundwater, assuming equilibrium with ferric hydroxide and a soil gas in which  $f \text{ CO}_2 = 10^{-2}$ . Note that constraints are provided for the distribution of several elements across differing redox states.

To see why, opening the **Config**  $\rightarrow$  **Redox Couples...** dialog

Redox couples			-		×
$\begin{tabular}{ c c c c c } \hline \hline$	decouple >> decouple all << couple couple all	select with decoupled CH <sub>3</sub> COO <sup>-</sup> /HCO <sub>3</sub> <sup>-</sup> CH <sub>4</sub> (aq)/HCO <sub>3</sub> <sup>-</sup> Fe <sup>+++</sup> /Fe <sup>++</sup> H <sub>2</sub> (aq)/H <sup>+</sup> H5 <sup>-</sup> /SO <sub>4</sub> <sup></sup> NH <sub>4</sub> <sup>+</sup> /NO <sub>3</sub> <sup></sup> NO <sub>2</sub> <sup>-</sup> /NO <sub>3</sub> <sup></sup>	▼ inve	rt selection	
	OK	Apply Ca	ancel	Rese	t

Several redox pairs have been disabled.

Move to the **Results** pane and click **Run**, then **View Results**. In **SpecE8**'s output file, check the Nernst Eh values for the following redox couples:

Redox couple	Eh (mV)
$e^- + \frac{1}{4} O2(aq) + H^+ \leftrightarrow \frac{1}{2} H_2O$	836
$2 e^- + 2 H^+ + NO_3^- \leftrightarrow H_2O + NO_2^-$	481
$8 e^- + 10 H^+ + NO_3^- \leftrightarrow 3 H_2O + NH_4^+$	443
$e^- + Fe^{+++} \leftrightarrow Fe^{++}$	322
$8 e^- + 9 H^+ + SO_4^- \leftrightarrow 4 H_2O + HS^-$	-126
$8 e^- + 9 H^+ + HCO_3^- \leftrightarrow 3 H_2O + CH_4(aq)$	-187
$2 e^- + 2 H^+ \leftrightarrow H_2(aq)$	-199
$8 e^- + 9 H^+ + 2 HCO_3^- \leftrightarrow 4 H_2O + CH_3COO^-$	-230

Which couple is the most energetically favorable as an electron donating reaction? Which is the best at accepting electrons?

For each of the following metabolisms, determine  $\Delta Eh$ . Which metabolisms are favorable for microbes living in contact with this groundwater?

- Oxidation of acetate by ferric iron.
- Oxidation of methane by molecular O<sub>2</sub>.
- Reduction of sulfate by ferrous iron.
- Oxidation of H<sub>2</sub> by nitrate.