Computational Geology 2

Speaking Logarithmically

H.L. Vacher, Department of Geology, University of South Florida, 4202 E. Fowler Ave., Tampa FL 33620

Introduction

If you have ever taken a course in geochemistry you have learned that aqueous geochemists speak differently about numbers than the rest of us. If you have a course in aqueous geochemistry in your future, you will learn that number-language. When you do, you will have a much better understanding of logarithms.

The language that aqueous geochemists use for numbers can be illustrated as follows. The solubility product of calcite is 0.00000000447. This number, as you know, can be expressed in a more friendly way by using scientific notation: $4.47 \times 10^{-9}$. Aqueous geochemists, however, express the number as $10^{-8.35}$. Similarly, instead of saying that the partial pressure of CO$_2$ in the atmosphere is $3.16 \times 10^{-4}$, they say it is $10^{-3.5}$. Although I can't say that I have heard this, it would not surprise me if one of these people would refer to the age of the earth as $10^{9.6}$ yrs or the distance to the moon as $10^{5.6}$ km.

Why do aqueous geochemists speak of numbers this way? The purpose of this column is to explore that question and, in the process, to show how this number-language is related to others that are more familiar.

Logarithms

The numbers used as exponents in expressions such as $10^{9.6}$, $10^{5.6}$ and $10^{-3.5}$ are the *logarithms of the quantities*. That is, specifically, the logarithm of 4.6 billion is 9.6; the logarithm of 380,000 is 5.6; the logarithm of $3.16 \times 10^{-4}$ is $-3.5$. Don't take my word for it; try it on your calculator. Enter 380,000, for example, and press the LOG key; you will get 5.579783597. Now press the 10$^x$ key; you will get 380,000 -- the number you started with. From this it is obvious that taking logs is the opposite of exponentiation; they are inverse functions.

All this should be no surprise; it is what you learned when you learned the definition of a logarithm -- "For a positive number, $N$, the logarithm of $N$ is the power to which some number $b$ [the base] must be raised to give $N$" (J. Dantith and R.D. Nelson, The Penguin Dictionary of Mathematics, Penguin Books, London, 1989, p. 203). In the form of equations:

$$\log_b N = x, \quad \text{if} \quad b^x = N. \quad (1)$$

It is sometimes useful to combine the two equations of (1) into a single equation:

$$b^{\log_b N} = N. \quad (2)$$
Logarithms were defined as exponents by the great Swiss mathematician Leonhard Euler (1707-1783) in a two-volume treatise, *Introductio in analysin infinitorum*. Publication of that book in 1748 brought the then-new mathematics of infinitesimal calculus of Newton (1642-1727) and Leibniz (1646-1716) to a status comparable to that of the well-established geometry and algebra. That was 250 years ago, some fifty years before Hutton's *Theory of the Earth* (1795), the event that we say gave birth to geology as a science.

The realization that logarithms are nothing more than exponents should clear away any mystery about where the Rules of Logarithms come from. For example, when you multiply two power-of-ten numbers together, you add their exponents:

\[
10^a \cdot 10^b = 10^{a+b}; \text{ e.g., } (10^3)(10^2) = 10^5.
\]

When you divide them, you subtract their exponents:

\[
\frac{10^a}{10^b} = 10^{a-b}; \text{ e.g., } \frac{10^3}{10^2} = 10^1.
\]

And when you raise a power-of-ten number to a power again, you multiply the two exponents together:

\[
(10^a)^b = 10^{ab}; \text{ e.g., } (10^3)^2 = 10^6.
\]

So, if you represent the power-of-ten number by its logarithm -- i.e., the exponent in the power-or-ten expression -- then the multiplication of the original numbers is paralleled by the addition of their logarithms; division of the two numbers is paralleled by subtraction of their logarithms; and raising one of them to a power is paralleled by multiplication of its logarithm by the power. Thus results the three rules:

**Rule 1:** \( \log AB = \log A + \log B \),

**Rule 2:** \( \log(A / B) = \log A - \log B \),

**Rule 3:** \( \log A^n = n \log A \).

**Logarithmic notation**

There are many ways of expressing a number. Let's go back to 380,000 – a distance in kilometers to the moon. You can express that number in scientific notation: \(3.8 \times 10^5\). As we have discussed, you can express it by using its logarithm as an exponent (as in Equation 2): \(10^{5.6}\). We will call that logarithmic notation.

But, as you know, there can be other bases for logarithms besides 10.

One base you have certainly encountered is \(e\), the base of natural logarithms. The transcendental number \(e\) has a value of 2.71828 (to six figures), and it was introduced by Euler in his *Introductio*. You can easily determine the natural logarithm of a number by using the LN
key of your calculator; thus \( \ln(380,000) \) is 12.848. This means that another way of expressing 380,000 in logarithmic notation is \( e^{12.848} \).

In addition to the natural base, \( e \), and the "unnatural" base 10, there is an infinitude of other "unnatural" bases that could be used to express numbers logarithmically. These other unnatural bases are rarely used, so when they are used, the base is specifically denoted as a subscript of the log (e.g., \( \log_2 N \) means the base is 2). If the log has no subscript (e.g., \( \log N \)), the understanding is that the base is 10. The decimal or base-10 log is known as the common logarithm. Table 1 includes some other ways of expressing 380,000 using unnatural bases:

<table>
<thead>
<tr>
<th>base</th>
<th>380,000 =</th>
</tr>
</thead>
<tbody>
<tr>
<td>binary</td>
<td>2</td>
</tr>
<tr>
<td>octal</td>
<td>8</td>
</tr>
<tr>
<td>decimal</td>
<td>10</td>
</tr>
<tr>
<td>duodecimal</td>
<td>12</td>
</tr>
<tr>
<td>hexadecimal</td>
<td>16</td>
</tr>
<tr>
<td>sexagesimal</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 1. Alternative logarithmic expressions for 380,000.

All the numbers given as exponents in Table 1 are the logarithms of 380,000 to the various bases.

How can you move from the logarithm of a number in one base to the logarithm of a number in another base? You probably recall that there is a Rule of Logarithms that deals with that question:

Rule 4: \( \log_b N = \frac{\log_a N}{\log_a b} \),

where \( b \) is the "new base", and \( a \) is the "old base". In words, the rule says, "The log in the new base of \( N \) is equal to the log in the old base of \( N \) divided by the log in the old base of the new base. The rule is derived very easily (once you know how to do it). First, take the log in the new base of both sides of Equation 2:

\[ \log_a \left( b^{\log_b N} \right) = \log_a N . \]

Next, apply Rule 3 of logs to the left side:

\[ (\log_a N)(\log_b b) = \log_a N . \]

Then, rearrange to solve for \( \log_b N \), and you get Rule 4. All the exponents in the above listing for the various bases were calculated using this rule. For example \( \log_{16}(380,000) \) is \( \log(380,000) \) divided by \( \log(16) \), or 5.5798/1.2041.

Now let's look at the same conversion problem in terms of logarithmic notation. That is, how does \( 10^{5.5798} \) convert to \( 16^{4.6339} \) (Table 1) in the context of logarithmic notation? This
A question in the form of an equation is:

\[ 380,000 = 10^{5.5798} = (16^x)^{5.5798}, \]

or simply,

\[ 16^x = 10, \]

where \( x \) is the unknown. In other words, what number in the form of \( 16^x \) do you replace 10 with? You find \( x \) easily by taking logs of both sides, and applying Rule 3:

\[ x \log 16 = \log 10 = 1, \]

so \( x = 1 / \log 16 = 0.83048 \).

Then substituting \( 16^{0.83948} \) for 10 in the power-of-ten expression, you get:

\[ 380,000 = (10^{5.5798}) = (16^{0.83948})^{5.5798} = 16^{4.6339}, \]

which gives the answer. Note that this line shows the entire logic of the conversion. It is equivalent to Rule 4.

**Scientific notation**

There is a clear-cut relationship between a number such as 380,000 in logarithmic notation, \( 10^{5.5798} \), and the same number in scientific notation, \( 3.80 \times 10^5 \). The scientific notation isolates the whole number in the exponent that appears in the logarithmic notation. The isolation is by means of Rule 1 (exponents add). Thus:

\[ 380,000 = 10^{5.5798} = 10^{0.5798} \times 10^5 = 3.80 \times 10^5, \]

because \( \log(3.80) \) is 0.5798 (or \( 10^{0.5798} = 3.80 \)). As you can see, the number that controls the coefficient in the scientific notation (i.e., 3.80 here) comes from the fractional part of the exponent of the logarithmic notation. The whole number is the order of magnitude: the part that controls the location of the decimal point of the number when it is written normally (380,000). Similarly, when the coefficient in the number in scientific notation has a single number to the left of the decimal point (3.8), then the exponent of the power-of-ten part gives the order of magnitude of the number (5).

For numbers less than one, such as the solubility product of calcite, \( 10^{-8.35} \), the exponent in the logarithmic notation is invariably negative, because \( \log_b(1) \) is zero, no matter what the base is (i.e., \( b^0 = 1 \)). For such fractional numbers, there is an intermediate step in converting between logarithmic notation and the usual form of scientific notation. Thus:

\[
10^{-8.35} = 10^{-0.35} \times 10^{-8} = 10^{1-0.35-1} \times 10^{-8} = 10^{0.65-1} \times 10^{-8} = 4.47 \times 10^{-9}.
\]
The intermediate step is where the negative fractional exponent is converted to a positive exponent. The purpose of this step is only to make the coefficient of the scientific notation come out in the usual way where there is a nonzero digit to the left of the decimal point. If you were to go directly from $10^{-0.35} \times 10^{-8}$ into scientific notation, you would get $0.447 \times 10^{-8}$, because $10^{-0.35}$ is 0.447. This is simply another manifestation of the fact that the number to the left of the decimal point in the exponent of the logarithmic notation controls only the location of the decimal point in the normal notation (i.e., the order of magnitude).

We use a scientific notation in which the base of the order-of-magnitude part is 10. Clearly, other bases could be used, and they would be worked out in a similar way (Table 2).

<table>
<thead>
<tr>
<th>Base</th>
<th>Logarithmic notation</th>
<th>Intermediate step</th>
<th>Scientific notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>binary</td>
<td>$2^{18.5356}$</td>
<td>$= 2^{0.5356} \times 10^18$</td>
<td>$= 1.45 \times 10^{18}$</td>
</tr>
<tr>
<td>octal</td>
<td>$8^{6.1785}$</td>
<td>$= 8^{0.1785} \times 8^6$</td>
<td>$= 1.45 \times 8^6$</td>
</tr>
<tr>
<td>decimal</td>
<td>$10^{5.5798}$</td>
<td>$= 10^{0.5798} \times 10^5$</td>
<td>$= 3.80 \times 10^5$</td>
</tr>
<tr>
<td>duodecimal</td>
<td>$12^{5.1704}$</td>
<td>$= 12^{0.1704} \times 12^5$</td>
<td>$= 1.53 \times 12^5$</td>
</tr>
<tr>
<td>hexadecimal</td>
<td>$16^{4.6339}$</td>
<td>$= 16^{0.6339} \times 16^4$</td>
<td>$= 5.80 \times 16^4$</td>
</tr>
<tr>
<td>sexagesimal</td>
<td>$60^{3.1380}$</td>
<td>$= 60^{0.1380} \times 60^3$</td>
<td>$= 1.76 \times 60^3$</td>
</tr>
</tbody>
</table>

Table 2. Converting 380,000 from logarithmic notation to scientific notation in each of the bases of Table 1.

To see how the equivalencies of Table 2 work, consider the first one, which involves a binary base for the order of magnitude. The value of $2^{18}$ is 262,144. The result of multiplying 1.45 and 262,144 is 380,000 (to 3 figures).

It is clear from this Table 2 that scientific notation is a partial logarithmic notation. The part of the scientific notation that expresses the order of magnitude is written in logarithmic notation. The coefficient is written in the normal way, non-logarithmically.

**Positional notation**

When logarithms were developed by John Napier (1550-1617), they were eagerly adopted by the computational scientists of the day. Notable among them was Tycho Brahe (1546-1601), whose painstaking study of the celestial bodies provided the data for the landmark inferences of his successor at the Danish Observatory, Johannes Kepler (1571-1630), another great user of logarithms. The reason that logarithms were so enthusiastically welcomed was that Rules 1-3 greatly facilitated the detailed calculations that were necessary for astronomy and navigation. This invention of logarithms was one of the most important breakthroughs for computation up to that time.

Probably the all-time greatest breakthrough for computation – apart from counting and the use of numbers in the first place – was positional notation. To understand (and appreciate) positional notation, consider multiplying 93 by 18, without a calculator. No problem: you can do it easily on a scrap of paper. Now do it using Roman numerals: multiply XCIII by XVIII. There you can see the difference between positional and non-positional notation. In positional notation, there is a string of figures each one of which fills a place, and each place represents an order of magnitude. In this place-value notation, and with a base of 10,
Recalling that
\[(a + b)(c + d) = ac + ad + bc + bd,\]
the result of the multiplication is:
\[
\begin{align*}
(9 \times 10^2) + (72 \times 10^1) + (3 \times 10^1) + (24 \times 10^0) \\
= (16 \times 10^2) + (2 \times 10^1) + (3 \times 10^1) + (2 \times 10^1) + (4 \times 10^0) \\
= (1 \times 10^3) + (6 \times 10^2) + (7 \times 10^1) + (4 \times 10^0) = 1674
\end{align*}
\]

In Roman numerals, the result is MDCLXXIV. How can you possibly get that result except by shifting to some more user-friendly notational scheme?

We use a fully developed, decimal, positional scheme. In this scheme, each of the places is \(10\times\) larger than the one to the right, and these places include those for orders of magnitude less than one (i.e., decimal fractions). In this scheme, we have exactly 10 symbols (0 to 9) with which to fill the places, and these numerals include a symbol for zero, which means "nothing" and can serve as a placeholder where necessary. This scheme, which is so familiar to us, was a monumental achievement and evolved over a long period of time.

Our decimal, positional scheme is commonly referred to as the Hindu-Arabic system. Although the early evolution of this system is poorly recorded, most historians recognize that a decimal, place-value system incorporating a zero became established in India around the 4th to 7th century AD. By the 9th century, the system was in Baghdad, where it was taken up by the Arabs and spread across north Africa to Spain. Particularly important were the writings around 825 of the Moslem scholar, Mohammed ibn-Musa al-Khowarizmi, by many accounts, the most influential mathematician of medieval times. Translated into Latin in the 12th century – probably by an English monk – his book introducing the Hindu-Arabic system starts with Algoritmi dixit ("Al-Khorwarizmi says"), from which the word algorithm, meaning computational process, has come. But the decimal fractions that are now part of the system were not incorporated until 1585 with the work of a Dutch physicist, Simon Stevin (1548-1620), a contemporary of Napier. Indeed the popularity of logarithms played a major role in the adoption of decimal fractions.

The idea of positional notation goes back to at least the ancient Babylonians of 2000 B.C. They used a base of 60. A vestige of this sexagesimal system is our 60 seconds to the minute and 60 minutes to the hour. In a sexagesimal system, the "units" place ranges from 1 to 59; two-place numbers range in magnitude from 60 to 3599 (one less than \(60^2\)); and three-place numbers range from our 3600 to 215,999 (one less than \(60^3\)). Using our decimal notation for the numbers occupying sexagesimal places, the distance to the moon would be represented by

\[
\text{distance to moon} = 1,45,33,20;0
\]

where the commas separate places and the semicolon is a "sexagesimal point" separating whole
numbers on the left from fractional parts to the right. To convince yourself that this succession of four "sexagesimal digits" represents 380,000, multiply out the following expression, which shows in expanded view what the positional system is all about:

\[1,45,33,20; = (1 \times 60^3) + (45 \times 60^2) + (33 \times 60^1) + (20 \times 60^0).\]

Continuing the idea of positional notation using other bases, consider what we might be using if we had evolved to have eight, instead of five, digits on each hand (imagine the musical instruments!). We very well might be using a hexadecimal place-value system instead of our familiar decimal system. In that case, our 380,000 would be expressed as something like (i.e., using decimal numerals for the digits):

distance to the moon = 5,12,12,6,0;0

meaning \[ (5 \times 16^4) + (12 \times 16^3) + (12 \times 16^2) + (6 \times 16^1) + (0 \times 16^0). \]

From these examples, we can see the connection between place-value systems and the logarithmic and scientific-notation systems. With our decimal base, the number 580,000 is a six-figure number, one more than its order of magnitude expressed in scientific notation as \(5.8 \times 10^5\), or fractionally (logarithmically) as \(10^{5.5798}\). With a sexagesimal base, the same number is a four-figure number (to the left of the sexagesimal point), one more than its order of sexagesimal magnitude, \(1.7 \times 60^3\), or fractionally (sexagesimal-logarithmically), \(60^3.1380\).

Geochemical computations

Aqueous geochemists use decimal-logarithmic (i.e., power-of-ten) notation to express equilibrium constants. The key to equilibrium constants is the Law of Mass Action (LMA). Use of the LMA involves multiplication and division of variables that range over many orders of magnitude. Such calculations are made easy if the numbers are expressed logarithmically.

The LMA states a relation amongst the concentrations of the participants in a chemical reaction when that reaction is at equilibrium. The LMA says that the equilibrium condition for a reaction,

\[ \text{reactants} \rightleftharpoons \text{products}, \]

is that the multiplicative product of the activities of the reaction products divided by the multiplicative product of the reactants is equal to a particular number that depends only on temperature (\(T\)) and pressure (\(P\)). The particular number is the equilibrium constant (\(K_{\text{equil}}\)). The concept of activity takes some discussion in geochemistry courses. For our purposes, we will simply say that activity is a variant of concentration that is used for thermodynamic calculations.

As an example of the LMA, consider the reaction stating the dissolution and precipitation of calcite:

\[ \text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}. \]

The LMA says that, at equilibrium, the product of the activities of \(\text{Ca}^{2+}\) and \(\text{CO}_3^{2-}\) divided by the
activity of CaCO$_3$ is equal to a number that depends only on $T$ and $P$. Because the activity of a pure solid is 1, the equilibrium constant in this case is simply the product of the two activities on the right, and so it is called a solubility product. At 25°C and 1 atm pressure, the solubility product of calcite, $K_{\text{calcite}}$, is $10^{-8.48}$, as noted at the beginning of this column. Thus, in one line, the critical information is written

$$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \quad K_{\text{calcite}} = 10^{-8.48} \quad (3)$$

Note that if the reaction were written in reverse order -- so that the ions were on the left and the solid was on the right -- then the ratio given by the LMA would need to be inverted, and the equilibrium constant would be the reciprocal of $10^{-8.48}$. The reciprocal of $10^{-8.48}$ is $10^{8.48}$, because, in terms of logs and Rule 2,

$$\log(1/10^{-8.48}) = \log(1) - \log(10^{-8.48}) = 0 - (-8.48) = 8.48$$

To illustrate the efficacy of logarithmic notation in geochemical calculations, consider the following reaction:

$$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (4)$$

This reaction, more than Equation 3, is the one to consider in natural waters, because HCO$_3^-$ dominates over CO$_3^{2-}$ at normal pH's, and CO$_2$ is commonly involved in the dissolution and precipitation of calcite. This is the equation, for example, that is used to point out that increasing the PCO$_2$ of a solution at equilibrium with calcite will cause more calcite to dissolve, and that decreasing the PCO$_2$ of a solution at equilibrium will drive the precipitation of calcite. The question, then, is: What is the equilibrium constant for the reaction of Equation 4?

The reaction of Equation 4 can be seen to be the sum of four reactions, each with their own equilibrium constants. The first is the dissolution of calcite (equation 3), for which the LMA gives

$$K_{\text{calcite}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-8.48},$$

where the brackets refer to activities. The second is the dissolution of CO$_2$ into the water

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3, \quad K_{\text{CO}_2} = [\text{H}_2\text{CO}_3]/\text{PCO}_2=10^{-1.47}$$

because the activity of a gas is its partial pressure, and the activity of water is 1. The third is the dissociation of carbonic acid:

$$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-, \quad K_{\text{H}_2\text{CO}_3} = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = 10^{-6.35}.$$  

And the fourth is the dissociation of the bicarbonate ion:

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}, \quad K_{\text{HCO}_3} = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] = 10^{-10.33}.$$
To see how these reactions result in Equation 4, it is helpful to arrange them in a list in such a way that the sum of the rows results in the desired reaction. Thus:

\[
\begin{align*}
\text{CaCO}_3 &\rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}, & K_{\text{calcite}} = 10^{-8.48} \\
\text{CO}_2 + \text{H}_2\text{O} &\rightleftharpoons \text{H}_2\text{CO}_3, & K_{\text{CO}_2} = 10^{-1.47} \\
\text{H}_2\text{CO}_3 &\rightleftharpoons \text{H}^+ + \text{HCO}_3^-, & K_{\text{H}_2\text{CO}_3} = 10^{-6.35} \\
\text{CO}_3^{2-} + \text{H}^+ &\rightleftharpoons \text{HCO}_3^-, & 1/K_{\text{HCO}_3} = 10^{+10.33}
\end{align*}
\]

Note that the last reaction has been reversed (and its equilibrium constant inverted). The reaction is reversed so that the \( \text{H}^+ \)'s and the \( \text{CO}_3^{2-} \)'s drop out when you add up the four reactions. The \( \text{H}_2\text{CO}_3 \)'s also drop out in the addition, and so you get the desired reaction, Equation 4.

To get the \( K_{\text{equil}} \) of the reaction of Equation 4, simply multiply all the \( K \)'s of the second column together. The reason that you multiply the \( K \)'s together can be seen if you write out all the LMA's and multiply them together. The result is:

\[
\frac{K_{\text{calcite}} K_{\text{CO}_2} K_{\text{H}_2\text{CO}_3}}{K_{\text{HCO}_3}} = \frac{[\text{Ca}^{2+} [\text{HCO}_3^-]]}{P_{\text{CO}_2}}.
\]

Because the equilibrium constant of the sum of the reactions is obtained by multiplication of the equilibrium constants of the constituent reactions (each written in the appropriate order with respect to numerator and denominator of the LMA's), then all you have to do to get the result is to ADD the exponents of the equilibrium constants expressed logarithmically. Thus

\[
\frac{K_{\text{calcite}} K_{\text{CO}_2} K_{\text{H}_2\text{CO}_3}}{K_{\text{HCO}_3}} = 10^{-8.48-1.47-6.35+10.33},
\]

or \( 10^{-5.97} \). The ease of this last step – addition instead of multiplication – illustrates the advantage of using logarithmic notation for equilibrium constants.

As another example, consider the following problem. If calcite comes into equilibrium with water that is open to atmospheric \( \text{PCO}_2 \) (i.e., \( 10^{-3.5} \) atm), and, assuming there are no ionic species in the water other than \( \text{Ca}^{2+}, \text{H}^+, \text{HCO}_3^-, \text{CO}_3^{2-} \) and \( \text{OH}^- \), it can be shown that the solution will have a pH of 8.4. Under these conditions, what is the activity of \( \text{Ca}^{2+} \)? (This would be the solubility of calcite under these conditions.)

As a first step, arrange the four reactions so that you get a reaction with \( \text{CaCO}_3, \text{Ca}^{2+} \) and \( \text{H}^+ \):

\[
\begin{align*}
\text{CaCO}_3 &\rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}, & K_{\text{calcite}} = 10^{-8.48} \\
\text{CO}_3^{2-} + \text{H}^+ &\rightleftharpoons \text{HCO}_3^-, & 1/K_{\text{HCO}_3} = 10^{+10.33} \\
\text{HCO}_3^- + \text{H}^+ &\rightleftharpoons \text{H}_2\text{CO}_3 & 1/K_{\text{H}_2\text{CO}_3} = 10^{-6.35} \\
\text{H}_2\text{CO}_3 &\rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} & 1/K_{\text{CO}_2} = 10^{-1.47}
\end{align*}
\]

Adding up the column on the left, you get:

\[
\text{CaCO}_3 + 2\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \quad (5)
\]
Multiplying the equilibrium constants of the second column together, you get:

\[
\frac{K_{\text{calcite}}}{K_{HCO_3}K_{H2CO_3}K_{CO_2}} = 10^{-8.48+10.33+6.35+1.47}
\]

or \(10^{-9.67}\), which is the \(K_{\text{equil}}\) for the reaction in Equation (5). Next, write the LMA for the same reaction (Equation 5):

\[
\frac{[Ca^{2+}]P_{CO_2}}{[H^+]^2} = 10^{9.67}.
\]

(The activities for calcite and water do not appear, because they are both equal to 1.) Then rearrange to solve for \([Ca^{2+}]\)

\[
[Ca^{2+}] = \frac{10^{9.67}[H^+]^2}{P_{CO_2}}
\]

Now you can plug in the given values. Recall that pH is \(-\log[H^+]\) so the given pH of 8.4 means that \([H^+] = 10^{-8.4}\). So:

\[
[Ca^{2+}] = \frac{10^{9.67}(10^{-8.4})^2}{10^{-3.5}} = 10^{9.67-16.6+3.5},
\]

or \(10^{-3.6}\), which is the answer in logarithmic notation., In scientific notation, \([Ca^{2+}] = 2.5 \times 10^{-4}\) moles/L.

Note that in both these examples, there were many multiplications and divisions required, but all we did was add and subtract exponents. Given that the numbers were all in logarithmic notation, the calculations could be done easily without a calculator. That’s the point! With logarithms, multiplication becomes addition, and division becomes subtraction.

**Other considerations**

You may have noticed that Napier, the inventor of logarithms, preceded Euler, who presented them as exponents, by more than a hundred years. If logarithms were not exponents in Napier's day, then what were they? Moreover, how could Napier invent natural logarithms if he had no concept of, nor even knew that there was such a thing as, \(e\), which was discovered by Euler? And what is so natural about logarithms with a base of \(e\)? The answers to those questions are related to why graphs involving logarithms – graphs that are widely used in geology and other science books – are so common and so useful. These questions will be taken up in the next column, CG-3, Progressing Geometrically.

**Concluding remarks**

We have considered three types of notation. The one that we use all the time is a
positioned, place-value notation in which each place stands for an order of magnitude. It is a familiar step from this notation to scientific notation in which the order of magnitude of the number is expressed logarithmically, as an exponent of ten. It is only a short step further to express the rest of the number as a fractional order of magnitude, thus resulting in a combined logarithmic expression, including a decimal fraction, as the exponent of ten. Such a logarithmic notation allows users, including aqueous geochemists, to replace multiplications and divisions with additions and subtractions. Such easing of computation is why logarithms were invented in the first place.

Sources and further reading
The historical material in this column is from a terrific resource for teachers: *Historical Topics for the Mathematics Classroom* by the National Council of Teachers of Mathematics (NCTM), 1989 (542 pp., ISBN 0-87353-281-3, $28.00). Written by nearly a hundred authors and edited by a panel of four (John Baumgart et al.), this book includes eight major overviews on the history of a branch of mathematics and 120 capsules with details about particular topics. I drew from the following entries: "The history of numbers and numerals" (B.H. Gundlach, p. 18-36); Babylonian numeration system" (B.D. Vogeli, p. 36-38); "Hindu-Arabic numeration system" (C.V. Benner, p. 46-49); "Origin of zero" (L.C. Merick, Jr., p. 49-50); "Al-Khowarizmi" (D. Schrader, p. 76-77); "The history of computation" (H.T. Davis, p. 87-117); "Decimal fractions" (L. Miller and J. Fey, p.137-139); and "Logarithms" (B.J. Yozwiak, p. 142-145).

Acknowledgments
I am grateful for the memories of geochemistry professors who in trying to teach me geochemistry, taught me logarithms. I thank Carl Steefel for a faculty perspective and Jim Inman for student feedback on an early draft of the original column.