Broecker Brief #8

Long-term Changes in Ocean Chemistry

Reconstructing the concentrations of Mg, Ca, K, Na and SO_4 in past seas poses a difficult challenge. Based on measurements on halite fluid inclusions, and on the magnesium content of both ridge crest calcites and aragonitic corals, it appears that during the last 50 million years the Mg to Ca ratio has risen by roughly a factor of five. Prior to 50 million, this ratio hovered around unity (see Figure 1). Based on fluid inclusions in halite, it can be stated with confidence that the ratio of SO_4 to Ca has undergone a continuous increase over this time period (see Figure 2). Further, 100 million years ago, the concentration of Ca in seawater was larger than that of SO_4. It should be noted that in both cases only the ion ratios are constrained. There is no information about the concentrations of individual ions.

Many years ago, I proposed a way in which the concentration of Ca^{++} might be reconstructed. As summarized in Figure 3, it was based on the uranium content of corals. However, based on discussions with my colleague, Bob Anderson, regarding the validity of the assumption that the uranium content of seawater was proportional to the $CO_3^=$ ion concentration, I put this idea aside.

Then a year ago, Princeton's Anne Gothmann working with Michael Bender and John Higgins found evidence that my $CO_3^=$ ion assumption may have been correct after all. She cites a paper on the chemistry of Mongolian closed basin lakes which documents that their uranium concentrations are proportional to their ΣCO_2 concentrations. One of these lakes has, as does Mono Lake (on which my original case was based) two order of magnitude higher U and ΣCO_2 content than seawater.

Anne Gothmann also made uranium measurements on aragonitic corals ranging back to 60 million years. As shown in Figure 4, she found that over the last 50 million years, the U to Ca ratios has risen by a factor of four. Based on my assumptions, this suggests that the calcium content of seawater dropped by a factor of two over this time period (see Figure 5).

Based on these three pieces of information, it is possible to constrain the changes in concentration for Mg, Ca, (Na+K), and SO_4 over the last 50 million years (see Table 1). Note that in order to maintain charge balance it is necessary to call on a slightly higher (Na^+ + K^+) contribution 50 million years ago.

It must be kept in mind that as each of the three assumptions made regarding the Ca reconstructions is likely no better than ±15 percent, this reconstruction merely shows how a more reliable one might be created.

Table 1. Approximate major ion composition of seawater 50 million years ago.

	Now	Then
	10^{-3} EθU/LIT	
Ca^{+}	+ 20	+40
Mg^{++}	+100	+40
$SO_4^{=}$	– 60	–40
Σ	+ 60	+40
$\Delta Na^{+} + K^{+}$	–	+20
Charge Balance	+ 60	+60

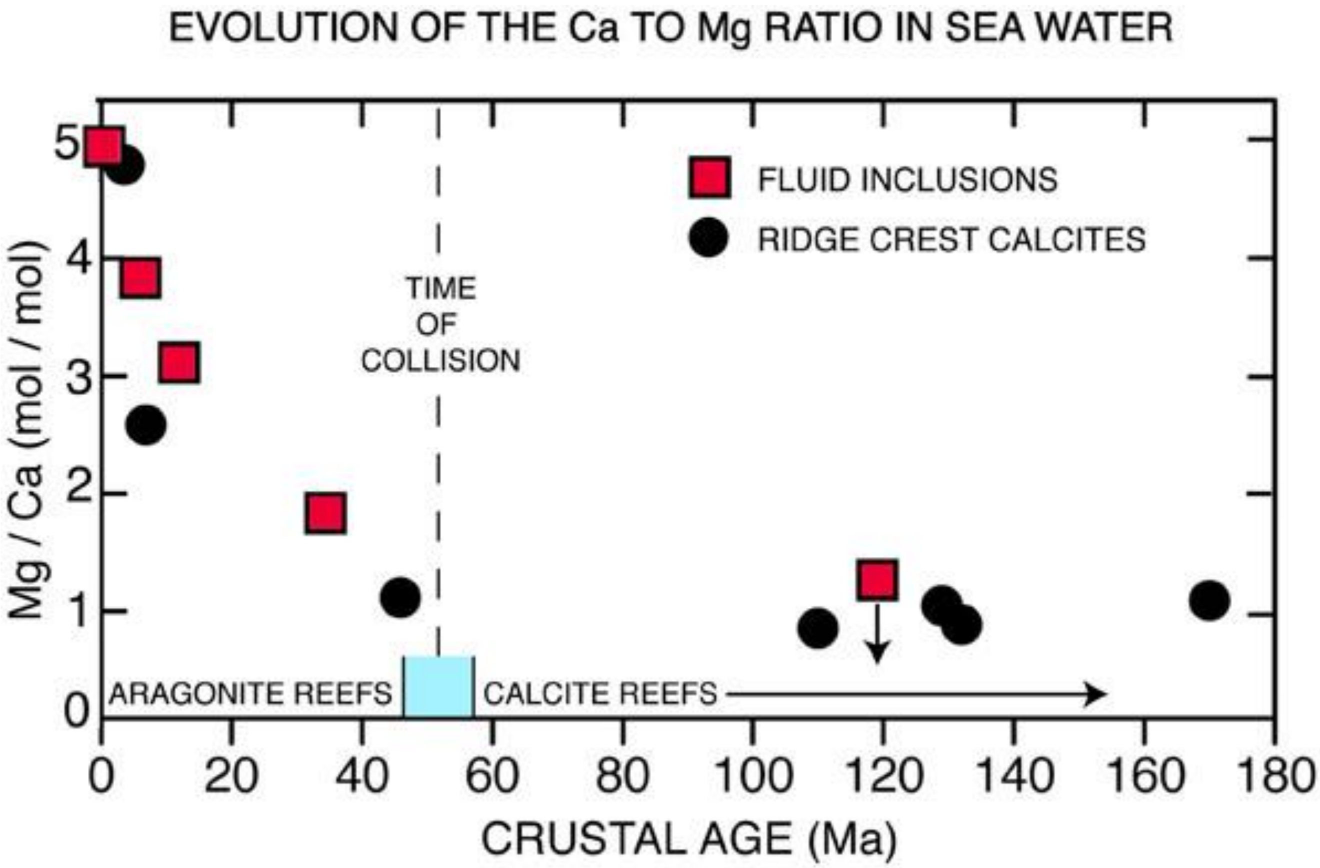

Figure 1. Reconstructions of the ratio of Mg to Ca over the last 180 million years based on measurements of the Mg content of fluid inclusions in halite and on the Mg content of ridge crest calcites. Not shown are Mg contents of aragonitic corals obtained by Anne Gothmann. Although noisy, her record confirms the temporal increase in this ratio.

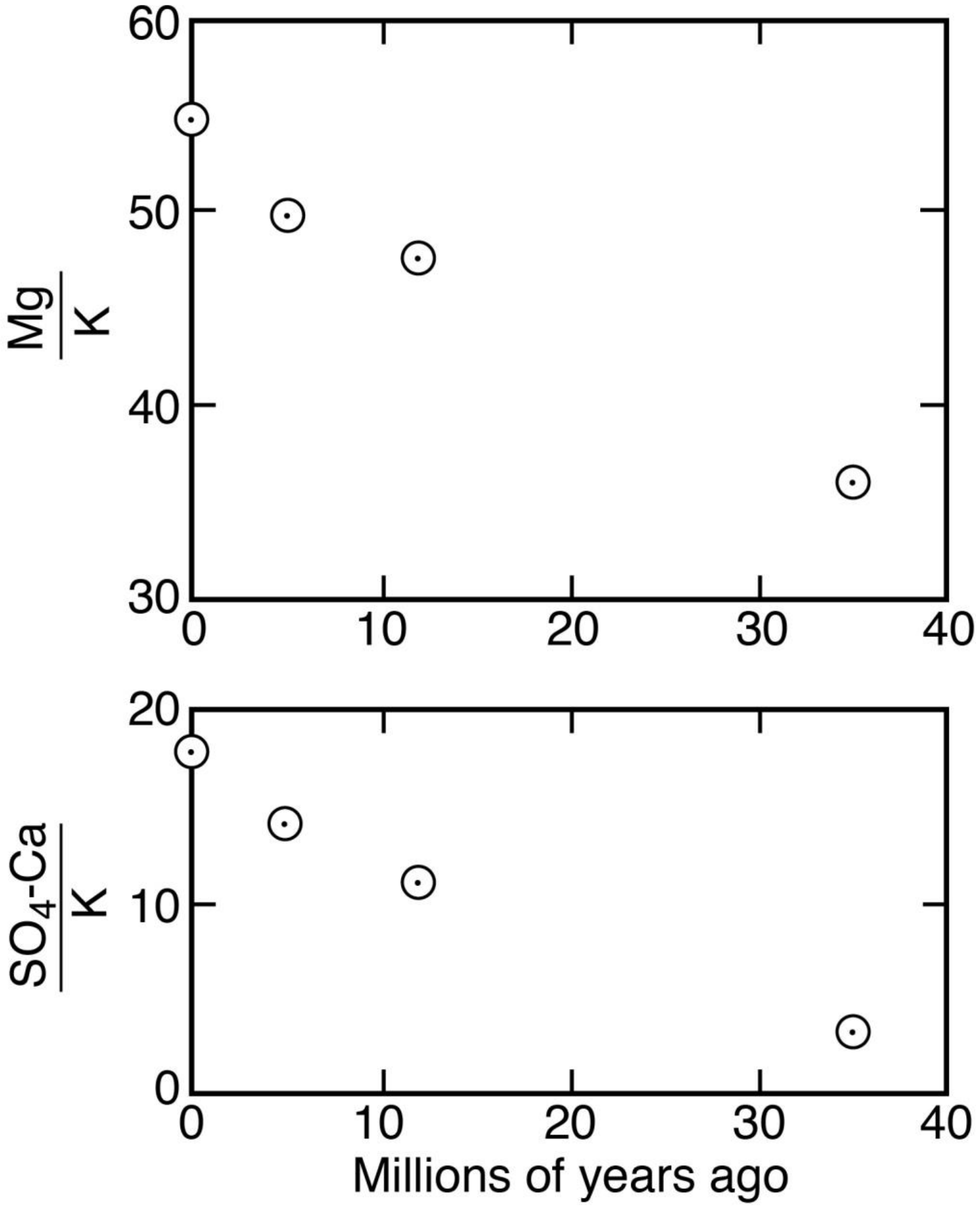

Figure 2. Based on measurements on fluid inclusions trapped in halite, Tim Lowenstein and his colleagues concluded that over the past 36 million years the concentration of Mg increased from 36 to 55 μmol/liter and that the excess of sulfate over calcium decreased from 18 to 3 μmol/liter. Their estimates are based on the assumption that the potassium content of the ocean has remained constant over this time interval.

Not shown here is the additional piece of information that 100 million years ago the amount of calcium exceeded the amount of SO_4. Based on this observation, it can be inferred that 50 million years ago the amounts of calcium and sulfate in the ocean were approximately equal.

Although the assumption that the potassium content in seawater remained constant is certainly open to challenge, the change in Mg content proposed by Lowenstein is broadly consistent with those based on ridge crest calcites and on aragonitic corals.

U METHOD FOR Ca RECONSTRUCTION

ASSUMPTIONS

1) $U/Ca_{CORALS} \cong U/Ca_{SEAWATER}$

2) $U_{SEAWATER} \ \alpha \ CO_{3\,SEAWATER}^{=}$

3) $(Ca^{++} \times CO_3^{=})_{SEAWATER} \sim$ CONSTANT

IF SO

$$Ca_{SEAWATER} = \sqrt{\frac{1}{\left(\frac{U}{Ca}\right)_{CORAL}}}$$

Figure 3. Broecker’s scheme for reconstructing the calcium content of seawater. Although assumptions 1) and 3) are likely good to ±15 percent, assumption 2) remains open to criticism. The case for it is based on U to ΣCO_2 ratios in closed basin lakes.

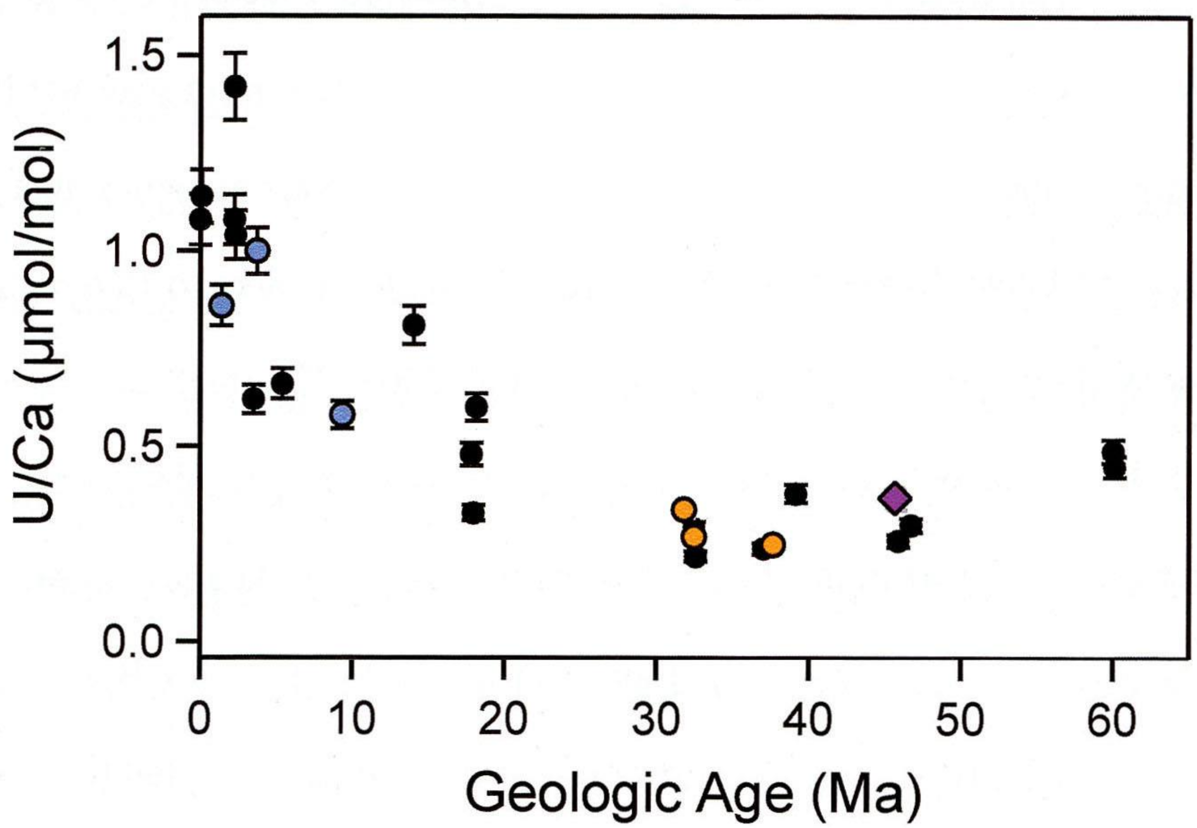

Figure 4. U to Ca ratios measured by Anne Gothmann on aragonitic corals ranging back 60 million years in age. As these corals yield He/U ages close to their geologic ages, their U contents have not been altered by diagenesis.

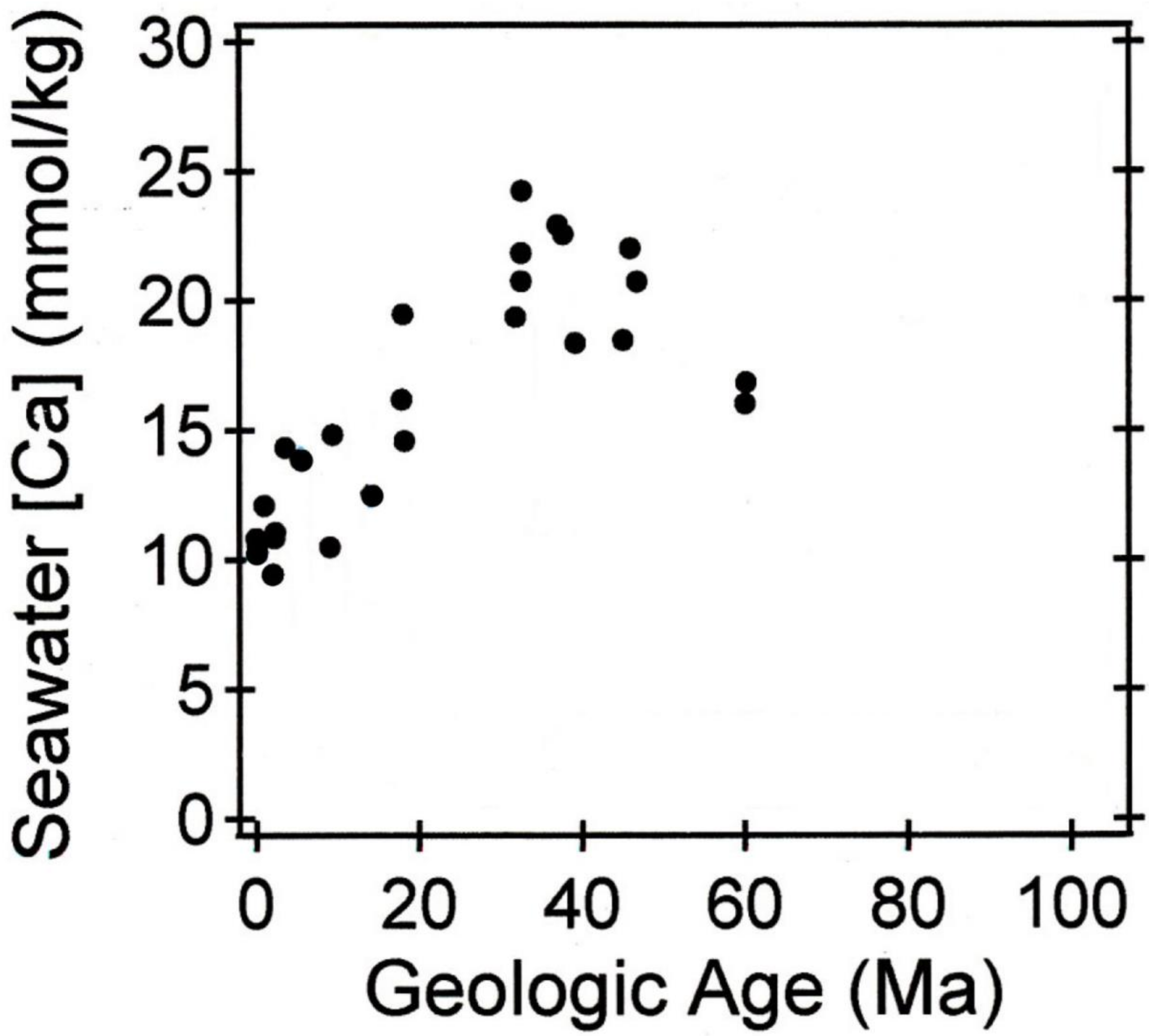

Figure 5. Calcium contents of seawater reconstructed by Anne Gothmann based on the assumptions listed in Figure 3.