Hadean ocean carbonate geochemistry

J. W. Morse — Department of Oceanography, Texas A&M University, College Station, Texas 77843, USA

F. T. Mackenzie — Department of Oceanography, University of Hawaii, Honolulu, Hawaii 96822, USA

Relatively soon (~0.2 Ga) after the Earth formed, it is likely that major oceans appeared in a hot (~100°C) reducing environment where carbon dioxide was probably the dominant atmospheric gas, with P_{CO_2} values reaching perhaps in excess of 10 atm. During the Hadean Eon between 4.3 and 3.8 Ga BP, major changes in the concentration of atmospheric CO_2 and associated temperature changes had a profound influence on the carbonate geochemistry of the Hadean Ocean. Although no rocks are known to have survived prior to the Archaean Eon, it is still possible to calculate approximate values for important seawater parameters during the Hadean Eon based on other sources of information and reasonable assumptions about processes such as weathering reactions.

Our calculations are based on a linear temperature change from 100°C to 70°C and log P_{CO_2} change from 1 to -1.5 over the Hadean Eon. Over this range in temperature and P_{CO_2}, the influence of T is relatively small, but changes in P_{CO_2} result in large compositional variations in the carbonate chemistry of Hadean seawater. In the early Hadean, seawater pH was probably about $5.8 \pm$~0.2, DIC may have reached close to 130 mM, and alkalinity was perhaps close to 30 mM. By the late Hadean, seawater pH probably had changed to close to neutral (~6.8), and DIC and alkalinity were closer to present-day values. Even large uncertainties in $Na^+ + Cl^-$, K^+ and Mg^{2+} concentrations produce relatively small uncertainties in our calculated values for the carbonic acid system. However, larger uncertainties result from reasonable ranges for Ca^{2+} concentrations and the saturation state of Hadean seawater with respect to calcite.

Our calculations support the hypothesis that a carbonate chemistry of seawater roughly similar to that of modern oceans could have been acquired very early in Earth history. If seawater composition were buffered by reactions involving carbonates and silicates, then the composition of late Hadean-early Archaean seawater was not vastly different from that of today. Thus, by the conclusion of the Hadean Eon, if not before, environmental conditions at the Earth's surface, including temperature and seawater composition, were sufficiently equable for the evolution of life, including the Archaebacteria: the extreme halophiles and thermophiles and methanogens. Contrary to the hypothesis of an early Na-bicarbonate ocean, our calculations suggest the possibility that the early oceans of Earth were a NaCl-dominated aqueous solution, with somewhat higher DIC and alkalinity concentrations, higher saturation state, and the possibility of lower calcium concentrations. The time course of approach of Hadean seawater to a carbonate composition closer to that of today is difficult to predict. It is distinctly possible that the concentration of calcium in seawater did not reach levels like that of modern seawater until the late Precambrian and thus constrained the timing of the 'Big Bang' of organic evolution, the emergence of the shelled invertebrates at the beginning of the Phanerozoic.