



GEOLOGY

Seafloor hydrothermal systems control long-term changes in seawater $[\text{Li}^+]$: Evidence from fluid inclusions

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Secular variations in the major ion chemistry and isotopic composition of seawater on multimillion-year time scales are well documented, but the causes of these changes are debated. Fluid inclusions in marine halite indicate that the Li concentration in seawater $[\text{Li}^+]_{\text{sw}}$ declined sevenfold over the past 150 million years (Ma) from $\sim 184 \mu\text{mol/kg H}_2\text{O}$ at 150 Ma ago to $27 \mu\text{mol/kg H}_2\text{O}$ today. Modeling of the lithium geochemical cycle shows that the decrease in $[\text{Li}^+]_{\text{sw}}$ was controlled chiefly by long-term decreases in ocean crust production rates and mid-ocean ridge and ridge flank hydrothermal fluxes without requiring changes in continental weathering fluxes. The decrease in $[\text{Li}^+]_{\text{sw}}$ parallels the 150 Ma increase in seawater $\text{Mg}^{2+}/\text{Ca}^{2+}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, and the change from calcite to aragonite seas, KCl to MgSO_4 evaporites, and greenhouse to icehouse climates, all of which point to the importance of plate tectonic activity in regulating the composition of Earth's hydrosphere and atmosphere.

INTRODUCTION

The major ion (Mg^{2+} , Ca^{2+} , Na^+ , K^+ , SO_4^{2-} , Cl^- , HCO_3^-) (1) and isotopic composition (i.e., $\delta^7\text{Li}$, $^{87}\text{Sr}/^{86}\text{Sr}$) (2, 3) of seawater have varied in the Phanerozoic Era. Systematic changes in the Mg^{2+} , Ca^{2+} , and SO_4^{2-} concentrations in Phanerozoic seawater regulate the alternating MgSO_4 and KCl mineralogies of marine potash evaporites (4). Variations in the Mg^{2+} and Ca^{2+} concentrations may have influenced the evolution of marine shell-building organisms, including dominant reef-builders and skeletal algae, because the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of seawater controls which carbonate, calcite, or aragonite precipitates during so-called calcite seas and aragonite seas (5). The $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio of seawater from the Jurassic to the present closely matches the marine $^{87}\text{Sr}/^{86}\text{Sr}$ curve, and both show a sharp rise in the Cenozoic similar to that exhibited by the marine lithium isotope ($\delta^7\text{Li}$) record from 60 to 0 million years (Ma) ago (Fig. 1) (3, 6, 7). Long-term changes in the major ion chemistry of seawater broadly correlate with variations in atmospheric CO_2 and icehouse-greenhouse climate, suggesting links to the carbon cycle (8).

Long-term variations in seawater composition are now well documented, but there is disagreement over which input or output fluxes were responsible for those changes. Proposed controls of temporal changes in seawater chemistry include variations in the rates of (i) ocean crust production and mid-ocean ridge (MOR) hydrothermal discharge (4), (ii) river flux (RFV) and terrestrial weathering intensity (9), (iii) deposition of marine carbonates and dolomitization (10), (iv) low-temperature, off-axis alteration of oceanic crust (AOC) (11), and (v) formation of marine authigenic aluminosilicate clays (MAAC) (12). AOC and MAAC together can be considered reverse weathering (3).

Recent advances in laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) now allow quantitative

measurement of minor and trace elements in fluid inclusions in halite, including lithium (Li^+) (13). Li^+ , a trace element in seawater, is particularly useful for understanding the drivers of long-term changes in seawater chemistry. It is a conservative element not incorporated to any significant degree in minerals precipitated from evaporating seawater, such as calcite, aragonite, gypsum, or halite (fig. S1). Li^+ is entirely derived from terrestrial silicate mineral weathering and seafloor-basalt interactions with hydrothermal fluids at MORs, and its concentration in seawater is not significantly influenced by biological processes or precipitation of carbonates (3). Li^+ today is supplied to the oceans by MOR hydrothermal fluids ($F_{\text{MOR}} = 13.7 \pm 2.8 \times 10^6 \text{ mol/year}$, $58 \pm 12\%$ of global input flux) and rivers ($F_{\text{RFV}} = 9.9 \times 10^6 \text{ mol/year}$, $\sim 42\%$) (14, 15). $[\text{Li}^+]$ in MOR hydrothermal fluids are three orders of magnitude higher than rivers (457 ± 66 versus $0.265 \mu\text{mol/kg}$ of H_2O , here termed μmolal) and $\sim 17 \pm 3$ times that of seawater ($27 \mu\text{molal}$) (15–17). Small fluctuations in ocean crust production rates and hydrothermal fluxes could therefore change seawater Li^+ ($[\text{Li}^+]_{\text{sw}}$). Li^+ is removed from seawater during low-temperature (off-axis) AOC ($F_{\text{AOC}} = 2$ to $21 \times 10^6 \text{ mol/year}$) (18, 19) and MAAC formation ($F_{\text{MAAC}} = 11$ to $20 \times 10^6 \text{ mol/year}$) (3, 20).

Recent records of $\delta^7\text{Li}_{\text{sw}}$ in Cenozoic seawater from foraminifera (3) and brachiopods (21) show an increase of ~ 8 to 9% over the past 60 Ma, which is thought to be due to (i) increased tectonic uplift that increased continental clay mineral formation (3), (ii) increased diagenetic reactions of marine clays (20), (iii) increased land surface reactivity and erosion (22), (iv) increased Li isotopic fractionation between seawater and oceanic crust (18), and (v) decreased continental soil formation (23). Modeling and interpretation of the Cenozoic $\delta^7\text{Li}_{\text{sw}}$ record, however, are based on the assumption that the $[\text{Li}^+]_{\text{sw}}$ has been roughly constant (3, 18, 22, 23). Li and West (20) tested 12 model scenarios to explain the Cenozoic $\delta^7\text{Li}_{\text{sw}}$ record and suggested that knowledge of $[\text{Li}^+]$ in ancient seawater would help distinguish the major controls responsible for changes in the global Li cycle. Here, we show from measurements of fluid inclusions in marine halite that $[\text{Li}^+]_{\text{sw}}$ in Jurassic and Cretaceous seawater was up to seven times greater than in modern seawater. Such variations are not included in any

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Seafloor Spreading Centers Hydrothermal Systems Benchmark Papers In Geology Number 56

Carroll L. Hoyt



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Seafloor Spreading Centers Peter A. Rona, Robert P. Lowell, 1980 **Hydrothermal Processes at Seafloor**

Spreading Centers Peter A. Rona, Kurt Boström, Lucien Laubier, Kenneth L. Smith, 2013-11-21 During the past ten years evidence has developed to indicate that seawater convects through oceanic crust driven by heat derived from creation of lithosphere at the Earth encircling oceanic ridge rift system of seafloor spreading centers This has stimulated multiple lines of research with profound implications for the earth and life sciences The lines of research comprise the role of hydrothermal convection at seafloor spreading centers in the Earth's thermal regime by cooling of newly formed lithosphere oceanic crust and upper mantle in global geochemical cycles and mass balances of certain elements by chemical exchange between circulating seawater and basaltic rocks of oceanic crust in the concentration of metallic mineral deposits by ore forming processes and in adaptation of biological communities based on a previously unrecognized form of chemosynthesis The first workshop devoted to interdisciplinary consideration of this field was organized by a committee consisting of the co editors of this volume under the auspices of a NATO Advanced Research Institute ARI held 5-8 April 1982 at the Department of Earth Sciences of Cambridge University in England This volume is a product of that workshop The papers were written by members of a pioneering research community of marine geologists geophysicists geochemists and biologists whose work is at the stage of initial description and interpretation of hydrothermal and associated phenomena at seafloor spreading centers

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The Sea

Floor Eugen Seibold, Wolfgang H. Berger, 1996-02-06 The Sea Floor deals with the most important results achieved in Marine Geology over the last three decades Relevant geophysical geochemical sedimentological and paleontological methods are shortly described They should allow the reader to comment on new results about plate tectonics marine sedimentation from the coasts to the deep sea climatological aspects paleoceanology and the use of the sea floor The text tries to transmit to the reader the excitement of marine geological research both aboard and in modern laboratories Basic mineralogical geochemical biological and other relevant data and a detailed list of books and symposia are given in an Appendix The third corrected and revised edition contains an enlarged and updated list of references and some new figures

Principles of

Sedimentology and Stratigraphy Sam Boggs, 1995 Aimed at advanced undergraduates but suitable also for graduate students and professionals it covers processes of sedimentation describes the characteristics of sedimentary rocks formed in major sedimentary environments and discusses the fundamental principles of stratigraphy and basin analysis including recent developments in the important fields of magnetostratigraphy seismic stratigraphy sequence stratigraphy isotope

stratigraphy and sea level analysis The book presents divergent views on controversial topics and is extensively referenced and up to date thus encouraging students to refer to recently published literature **The Publishers' Trade List Annual** ,1983 Metallic Minerals on the Deep Seabed G. A. Gross,C. R. McLeod,1987 Technology developed in recent years has made it possible to explore mineral occurrences on the deep seabed that are analogous to many mineral deposits mined on land This paper reviews the main types of occurrences on the deep seabed their geological setting in relation to major geological features and their proximity to land areas Brief notes on the mineral occurrences describe their type and depositional environment A world map shows islands and continents areas 370 km from land major tectonic features the distribution of manganese nodules and crusts various types of metalliferous sediments and crusts and areas where hydrothermal processes are now or have been active on the seafloor **Proceedings of the Ocean Drilling Program** Ocean Drilling Program,1985 Vol 174AX bound with Proceedings of the Ocean Drilling Program Scientific results Vol 174A

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