

Hydrothermal Chemistry/ Reverse Weathering

Marine Chemistry Seminar

- **1974** Drever, The Sea Chapter 10: The Magnesium Problem
- **1979** Edmonds et al., Ridge Crest Hydrothermal Activity and the Balances of Major and Minor Elements in the Ocean
- **1994** Mottl & Wheat, Hydrothermal Circulation through mid-ocean ridge-flanks
- **1995** Vinnik et al., Recent deformations of the deep continental root beneath southern Africa
- **1995** Michalopoulos & Aller, Rapid Clay Mineral Formation in Amazon Delta Sediments

What is the Magnesium Problem?

Drever

“...the known processes by which Mg is removed do not appear to be quantitatively sufficient to balance the known input.”

Oceanographers make the assumption that the ocean operates at a steady state.

The problem: Where is the residual Mg ending up?

The Magnesium Problem:

Processes Magnesium is not involved in

- Major clay mineral transformations (i.e. Kaolinite → Chlorite)
- Interlayer transformations
- Transformations of amorphous material
- Conversion of gibbsite to chlorite
- Mg-silicate precipitation (minor occurrences)

The Magnesium Problem:

Where the Magnesium is definitely going

Table of Mg^{2+} Removal from
the Oceans removed due to
copyright restrictions.

The Magnesium Problem:

Where the Magnesium might be going

- Modern day pH is anomalously high
 - There is currently less Mg incorporated into brucite than in the geologic past
- The Mg^{2+} sink is localized
 - keep looking
- Model sediments are atypical
 - Other sediments in other places *might* react with seawater to remove Mg^{2+}
- Igneous rocks react with Mg^{2+} below the seafloor to form chlorite
 - Rxn must occur at depth since basalts leach Mg^{2+} to seawater

2: Ridge Crest Hydrothermal Activity

Edmond et al.

- 4 hot spring fields sampled on the 'crest' of a spreading ridge
- Low-temperature (3-13 °C) dilution trends are extrapolated out to high temperatures
- He derived heat flow measurements used to calculate elemental fluxes
- “The object is to establish orders of magnitude relative to fluvial input”

Ridge Crest Hydrothermal Activity

Table of the alkalies removed due to copyright restrictions.

Ridge Crest Hydrothermal Activity

Table depicting that anions; bromide and borate are invariant.

Ridge Crest Hydrothermal Activity

Table depicting that the alkaline earths; strontium is invariant.

Hydrothermal removal of Mg is 45% higher than the river input

Ridge Crest Hydrothermal Activity

Most significant result for today's discussion

- Hydrothermal reactions balance the river input of Mg and SO₄

Graph of magnesium vs. silica removed due to copyright restrictions.

Graph of silica vs. temperature. All vents removed due to copyright restrictions.

Graph of sulphate vs. silica removed due to copyright restrictions.

Ridge Crest Hydrothermal Activity

Variations within hot spring fields

- Differing stages in the evolution of a circulation cell
- Differing substrate compositions (glassy or crystalline)
- Variations in water/rock ratios

Conclusions

Table of charge balance calculations removed due to copyright restrictions.

Conclusions

Table of water/rock ratios removed due to copyright restrictions.

3: Hydrothermal Circulation through mid-ocean ridge flanks: Fluxes of heat and magnetism

Mottl & Wheat

- Improved constraints on Mg budget and the site of Mg removal
- Studied differences between ridge axis, flanks and ocean basin
- Used heat flow budgets, heat flow anomalies, endmember compositions, and sediment porewater profiles
- Speculate as to depth of water/rock interactions (penetration of gabbros or dykes): not necessarily resolved, addressed in one of our other papers..

Hydrothermal circulation and heat flux: Ridge axis

- 10-40% river influx of Mg is removed during high-temperature alteration on axis
- Assumes rock cools only to 350°C and that entire crust be penetrated and a large fraction be altered
- Active advective heat flow regime

Hydrothermal circulation and heat flux: Ridge axis

Graph of % vs. 10^{18} cal/yr removed due to copyright restrictions.

Hydrothermal circulation and heat flux: Ridge flanks

- Most of the heat loss and seawater flux
- Circulating seawater only loses less than 1-2% Mg in order to solve the Mg balance
- Passive and active- advective heat flow regime
- Basement temperature: measured heat flow, sediment thickness, and thermal conductivity
- Chemical compositional changes: sediment porewater profiles
- Basement temperature and chemical flux can be used to calculate global geochemical flux

Hydrothermal circulation and heat flux: Ridge flanks

Graph of mean temperature vs. age province removed due to copyright restrictions.

Graph of mean exit temperature vs. mean upflow velocity removed due to copyright restrictions.

Hydrothermal circulation and heat flux: Ridge flanks

Graph of Mg^{2+} in basement fluid vs. temperature at basement interface removed due to copyright restrictions.

Two heat flow regimes based on basement temperatures

- Cooler one (basement <10 degrees), larger advective component, smaller loss
- Warmer one (basement >45 degrees), smaller advective component, greater loss

4: Evolution of East Pacific Rise hydrothermal fluids following a volcanic eruption

Von Damm et al.

- Measured hydrothermal vents on the East Pacific Rise right after a lava flow
- Variability in chemical composition of vent fluids continues for duration of a 3 year study

“The unique chemical composition and continued temporal variability on the timescale of years after a volcanic eruption may have a profound influence on the net chemical flux from sea-floor hydrothermal systems.”

Evolution of East Pacific Rise hydrothermal fluids

Table depicting changes in vent chemistry removed due to copyright restrictions.

Changes as small as 10°C in the water/rock equilibration/reaction, or changes of <50 bar could account for the range of the compositional

Changes

1991: First sampling

- H_2S values are high and Cl is low compared to other hydrothermal vent fluids: suggests phase separation, consistent with a shallow heat source
 - Unusual sulfur source to seawater
- Extremely low silica contents reflecting equilibration with mineral phases at shallow depths (shallow heat source)
- Seismic data also consistent with shallow heat source
- Observed fluid composition is the result of a dyke intrusion within upper 200m of crust and subsequent seawater/basalt interactions

Evolution of East Pacific Rise hydrothermal fluids

- Overtime, Si and Cl increase
- Continuing instabilities, cooling of the dyke intrusion, deepening of the reaction zone

5: Rapid Clay Mineral Formation in Amazon Delta Sediments

Michalopoulos & Aller

- “reverse weathering”
 - Hasn't yet gained widespread acceptance due to lack of evidence of *significant* precipitation of such minerals
- On a quest for sufficient direct evidence of such a process

Clay precipitation experiments

- Study of Amazon river sediments
- Inserted membrane covered solid substrates into sediments
 - Kaolinite, quartz sand grains, FeOOH coated sand grains, glass beads
 - Incubated at 28°C, anoxically for 1-3 years in 250-1000mL bottles

Rapid Clay Mineral Formation in Amazon Delta Sediments

- Dissolution of glass beads is symptomatic of silica undersaturation
- Kaolinite disintegrated
- Mineral phase formed on coated and uncoated sand grains

Rapid Clay Mineral Formation in Amazon Delta Sediments

- Calls upon 'indirect' evidence: porewater profiles which agree with material precipitated on the probes
- Conclude that this could provide a sink for up to 10% of the K input and a significant fraction of the F input
- Potentially contributes to silica budget

Summary/Progression of ideas

1. Recognition of missing sink in Mg equation
2. Identification of MOR as likely sink
3. Refinement of nature of MOR sink and estimates of size of sink
4. Recognition of potential variation in sink over short time scales
5. Re-consideration of an additional source within authigenic deposits