Hydrothermal Minerals Record

CO$_2$ Partial Pressures in the Reykjanes Geothermal System, Iceland

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Presentation Overview

• Introduction
• Mineral Assemblage
• Thermodynamic Considerations
• Analytical Methods
• Calculated Results
• Conclusions
Introduction

• Premise:
  - Magmatic CO$_2$ from the mantle released at MAR
  - Seawater penetrates coastal Reykjanes Geothermal System (RGS), reacts with CO$_2$ & basaltic host rock, forming secondary hydrothermal minerals
  - Under specified conditions, the geothermal fluid $P_{CO_2}$ may be calculated as a function of the composition of hydrothermal minerals: epidote & prehnite
  - *Using thermodynamics, mineralogy may record the evolutionary history of CO$_2$ in the geothermal system*
Reykjanes Geothermal System

- High-T geothermal system distribution
- Reykjanes system in SW Iceland where MAR diverges
Mineral Alteration Zones

Assemblage: Epidote-Prehnite-Calcite-Qtz

RN-9, RN-10, RN-17
Observed Mineral Assemblage

- At > 250° C (chl-epi & epi-act):
  - Assemblage: epi-preh-cc-qtz
  - **Epidote** observed in abundance
  - **Zoning Trend**: Fe-rich cores, Al-rich rims
  - **Extreme Fe content**: observed nowhere else in world
Mineral Chemistry

Within RGS **epidote and prehnite** both display compositions with varying degrees of Al and Fe(III) substitution.

Epidote: $\text{Ca}_2\text{Fe}_x\text{Al}_{3-x}\text{Si}_3\text{O}_{12}(\text{OH}), \ x = n_{\text{Fe(III)}}$ substituted for Al

Solid solution end-members: **clinozoisite**: $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$; **epidote**: $\text{Ca}_2\text{Al}_2\text{FeSi}_3\text{O}_{12}(\text{OH})$; **pistacite**: $\text{Ca}_2\text{Fe}_3\text{Si}_3\text{O}_{12}(\text{OH})$

$x_{ps} = n_{\text{Fe}}/(n_{\text{Fe}} + n_{\text{Al}})$, $n_{\text{Fe}}$ and $n_{\text{Al}}$ # atoms per formula unit, % Fe(III) in sites

Prehnite: $\text{Ca}_2\text{Al}_{1-x}\text{Fe}_x(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$, $x = n_{\text{Fe(III)}} = X_{\text{Fe,Preh}}$, #atoms Fe(III) substituted for Al
Mineral Assemblage

\[ \text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH}) + \text{CaCO}_3 + 1.5 \text{SiO}_2 + \text{H}_2\text{O} = 1.5 \text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2 + \text{CO}_2 \]

*Clinozoisite*  *Calcite*  *Quartz*  *Prehnite*
Mineral Assemblage

\[ Ca_2Al_3Si_3O_{12}(OH) + CaCO_3 + 1.5 \text{SiO}_2 + H_2O = 1.5 Ca_2Al_2Si_3O_{10}(OH)_2 + CO_2 \]

*Clinozoisite*  *Calcite*  *Quartz*  *Prehnite*

Equilibrium Constant Reaction:

\[ \log P_{CO_2} = \log K_{T,P} + \log a_{\text{Czo}} - 1.5 \log a_{\text{Preh}} + \log a_{H_2O} \]
Mineral Assemblage

\[
\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}\text{(OH)} + \text{CaCO}_3 + 1.5 \text{SiO}_2 + \text{H}_2\text{O} = 1.5 \text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}\text{(OH)}_2 + \text{CO}_2
\]

*Clinozoisite  Calcite  Quartz  Prehnite*

Equilibrium Constant Reaction:

\[
\log P_{\text{CO}_2} = \log K_{T,P} + \log a_{\text{Czo}} - 1.5 \log a_{\text{Preh}} + \log a_{\text{H}_2\text{O}}
\]

If: K, chemical composition (activity) of epidote and prehnite

Then: May calculate fluid \( P_{\text{CO}_2} \) that formed minerals
Phase Rule Constraints

\[ f = c + 2 - p \]

c: number of chemical components = 7 (NaCl, CaO, Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), SiO\(_2\), H\(_2\)O, CO\(_2\) )
p: number of phases = 5 (calcite, epidote, prehnite, quartz, fluid)
f: variance (independent variables) = 7 + 2 - 5 = 4 (quadra-variant assemblage)

∴ Fix 4 intensive variables (e.g., T, P, \(a_{H2O}\), \(a_{czo}\) and/or \(a_{preh}\)), equilibrium uniquely defined.

- **T & P**: constrained as a function of depth in the drillholes
- **\(a_{H2O}\)**: computed using aqueous species distribution algorithms
- **\(a_{czo}\) and **\(a_{preh}\)**: calculated using chemical composition of samples from drillhole cuttings in RN-9, 10, 17 (use electron microprobe analysis)

\[ \log P_{CO2} = \log K_{T,P} + \log a_{Czo} - 1.5 \log a_{Preh} + \log a_{H2O} \]
Evaluation of Local Equilibrium

Before continuing the investigation, it is important to evaluate the extent to which the *in situ* hydrothermal fluids are in equilibrium with the mineral assemblage...

Thermodynamic activities of aqueous species for geothermal fluids collected at the wellhead (l + s) derived using computer programs (SOLVEQ, WATCH).

<table>
<thead>
<tr>
<th>Well #</th>
<th>RN-19</th>
<th>RN-21</th>
<th>RN-12</th>
<th>RN-23</th>
<th>RN-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (ºC)</td>
<td>275</td>
<td>285</td>
<td>295</td>
<td>300</td>
<td>310</td>
</tr>
<tr>
<td>pH</td>
<td>5.41</td>
<td>5.32</td>
<td>5.39</td>
<td>5.23</td>
<td>5.33</td>
</tr>
<tr>
<td>SiO$_2$(aq)</td>
<td>9.75 × 10$^{-3}$</td>
<td>1.11 × 10$^{-2}$</td>
<td>1.08 × 10$^{-2}$</td>
<td>1.20 × 10$^{-2}$</td>
<td>1.24 × 10$^{-2}$</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>1.76 × 10$^{-6}$</td>
<td>2.08 × 10$^{-6}$</td>
<td>1.92 × 10$^{-6}$</td>
<td>2.98 × 10$^{-6}$</td>
<td>1.13 × 10$^{-6}$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>4.14 × 10$^{-2}$</td>
<td>4.00 × 10$^{-2}$</td>
<td>4.01 × 10$^{-2}$</td>
<td>4.08 × 10$^{-2}$</td>
<td>3.84 × 10$^{-2}$</td>
</tr>
<tr>
<td>Fe$_T$</td>
<td>7.96 × 10$^{-6}$</td>
<td>9.05 × 10$^{-6}$</td>
<td>8.63 × 10$^{-6}$</td>
<td>1.30 × 10$^{-5}$</td>
<td>3.50 × 10$^{-5}$</td>
</tr>
<tr>
<td>$a_{H_2O}$</td>
<td>0.984</td>
<td>0.985</td>
<td>0.986</td>
<td>0.985</td>
<td>0.986</td>
</tr>
<tr>
<td>$P_{CO_2}$ (bar)</td>
<td>1.41</td>
<td>1.50</td>
<td>2.42</td>
<td>1.54</td>
<td>2.34</td>
</tr>
</tbody>
</table>

All concentrations reported in mol/kg solution
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Thermodynamic activities of aqueous species for geothermal fluids collected at the wellhead (l + s) derived using computer programs (SOLVEQ, WATCH).

Quartz Solubility Reaction:
\[ \text{SiO}_2,\text{Quartz} \leftrightarrow \text{SiO}_2,\text{aq} \]
Evaluation of Local Equilibrium

**Calcite Hydrolysis Rxn:**

\[
\text{CaCO}_3 + 2\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2,_{\text{g}}
\]

In EQ (within upper limits of assumed uncertainty)

**Czo Hydrolysis Rxn:**

\[
\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}\text{OH} + 13\text{H}^+ \rightleftharpoons 2\text{Ca}^{2+} + 3\text{Al}^{3+} + 3\text{SiO}_{2,\text{aq}} + 7\text{H}_2\text{O}
\]

In Equilibrium

**Preh Hydrolysis Rxn:**

\[
\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2 + 10\text{H}^+ \rightleftharpoons 2\text{Ca}^{2+} + 2\text{Al}^{3+} + 3\text{SiO}_{2,\text{aq}} + 6\text{H}_2\text{O}
\]

In Equilibrium
Electron microprobe used to determine mineral chemistry (JEOL 733A, 15 kV accelerating potential, 15 nA beam current)

General trend of RGS: epidote crystals Fe(III)-rich cores and Al-rich rims, occasional oscillatory zoning
Compositional Results

**Epidote $X_{ps}$ Range:**
- RN-9: 0.19-0.44
- RN-10: 0.18-0.48
- RN-17: 0.17-0.46

**Prehnite $X_{Fe}$ Range:**
- RN-17: 0.13-0.59

- Demonstrate extreme range of Fe(III)-Al substitution similar to RGS epidotes.
- Scarce, small grain size (~20 µm), few samples
Prehnite Composition

- Sigmoidal regression fit to data set of coexisting epidote and prehnite compositions from active geothermal systems

- Compositional constraints on regression:
  - $X_{ps} = 0$ coexists with $X_{Fe,Prehnite} = 0$
  - $X_{ps} = 0.36$ coexists with $X_{Fe,Preh} = 0.60$ (Fe(III)-richest epidote found in cuttings where prehnite also found)

Can calculate $X_{Fe,Prehnite}$ values for every epidote analysis ($X_{ps} < 0.36$)

**Trends:**

- Calculated & measured prehnite compositions range from $X_{Fe,preh} = 0.05$ to 0.6.
- Calculated & measured compositional range very similar, confident in method
Thermodynamic Considerations

\[
\log P_{CO2} = \log K_{T,P} + \log a_{Czo} - 1.5 \log a_{Preh} + \log a_{H2O}
\]

\[a_{H2O} = 0.985 \text{ (SOLVEQ)}\]

\[a_{Preh} = X_{Al,Prehnite} = 1 - X_{Fe,Prehnite} = 1 - \text{sigmoid regression} = 1 - \left(0.9903/(1 + \exp(-(X_{ps} - 0.3321)/0.0641))\right)\]

\[a_{Czo} = X_{Al,M1} \cdot X_{Al,M3}\]

Determined the distribution of Al (and Fe(III)) in crystallographic sites using measured \(n_{Fe}, n_{Al}\) and a solid solution T-dependent substitution order-disorder model (Bird and Helgeson, 1980)

\[\log K = 57.781 - 22843/T^2 - 4792.99/T + 0.00829T + 0.6864 \times 10^{-6} T^2 - 19.302 \log T\]

Calculated using T-dependent algorithm (Arnorsson et al., 2007)
Calculated $P_{CO2}$

$$\log P_{CO2} = \log K_{T,P} + \log a_{Czo} - 1.5 \log a_{Preh} + \log a_{H2O}$$

Trends:

- At $\leftrightarrow T$, $P_{CO2}$ $\uparrow$ with $\downarrow X_{ps}$
- At $\leftrightarrow X_{ps}$, $P_{CO2}$ $\uparrow$ with $\uparrow T$
  (but to a lesser degree with $\uparrow Fe(III)$ content in epidote)
**Calculated $P_{CO2}$**

\[ \log P_{CO2} = \log K_{T,P} + \log a_{Czo} - 1.5 \log a_{Preh} + \log a_{H2O} \]

**Comparison with *in situ* fluid compositions**

Composition of reservoir liquid derived from speciation analyses of liquid & steam samples collected at the wellhead (275-310° C)

**In situ Values:**
- 1.4 - 4.0 bars

**Calculated:**
- 0.57 to 6.17 bars (Assemblage)
- 1.32 to 6.81 bars (Non-Assemblage)
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If RGS core-rims formed under assemblage equilibrium conditions:

- @ ⇔ T, requires ↑ $P_{CO2}$ with time (rise in CO$_2$ content may record ↑ in # intrusions of dikes/sills and their magmatic degassing during evolution of Reykjanes GS)
- @ ⇔ $P_{CO2}$, requires ↓ T with time (spatial or temporal changes to system)

Calculated $P_{CO2}$

\[
\log P_{CO2} = \log K_{T,P} + \log a_{Czo} - 1.5 \log a_{Preh} + \log a_{H2O}
\]
Agreement Trends

Assemblage

Cuttings at depths where assemblage observed:
- 143 epidote analyses
- **72%** of the computed values of \( P_{\text{CO}_2} \) (0.57 to 6.17 bars) are within \( P_{\text{CO}_2} \) range of collected formation fluids (1.3 to 4.0 bars);

Non-Assemblage

Cuttings at depths where assem. NOT observed:
- Prehnite and/or calcite missing
- 124 epidote analyses
- **58%** of the computed values of \( P_{\text{CO}_2} \) (1.3 to 6.8 bars) are within \( P_{\text{CO}_2} \) range of collected formation fluids (1.3 to 4.0 bars)
Conclusions

• Method for calculating fluid $P_{\text{CO}_2}$ proven quite reliable (72%) when all four index minerals of epidote-prehnite-calcite-quartz assemblage present.

• If only epidote, prehnite and quartz are observed, our method appears to serve as a moderately accurate (58%) predictive proxy for fluid $P_{\text{CO}_2}$ values in the RGS.

• Strong agreement between sampled and predicted fluid compositions provides insight into future abilities to characterize:
  - $P_{\text{CO}_2}$ in active and fossil hydrothermal and low-grade metamorphic environments in mafic lithologies
  - The nature of reactions that involve natural sequestration of $\text{CO}_2$ derived from magmatic degassing
  - The nature of reactions that involved injection of industrial $\text{CO}_2$-rich fluids within hydrothermal environments in basaltic rocks.
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*Thermodynamics reveals that mineralogy records the evolutionary history of $\text{CO}_2$ in the geothermal system*
Thank You

Questions?