Hydrothermal Minerals Record CO_2 Partial Pressures in the Reykjanes Geothermal System, Iceland

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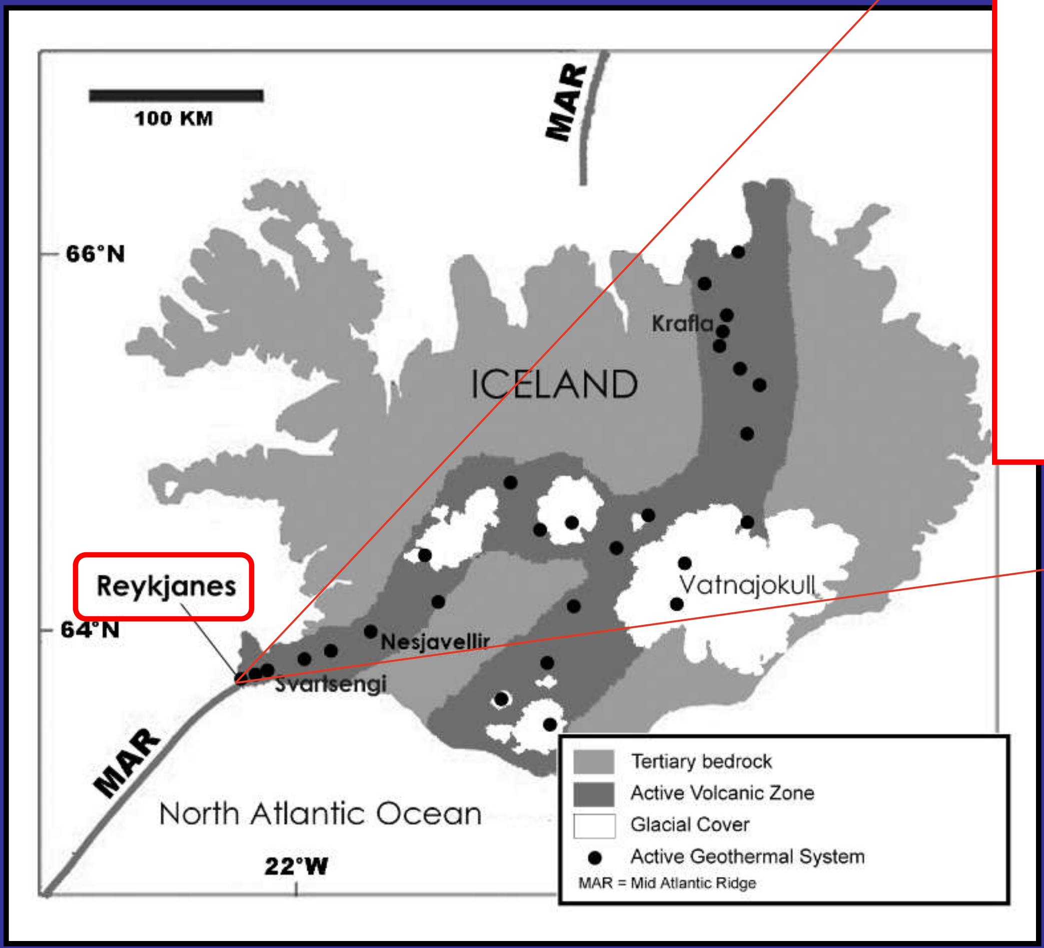
Presentation Overview

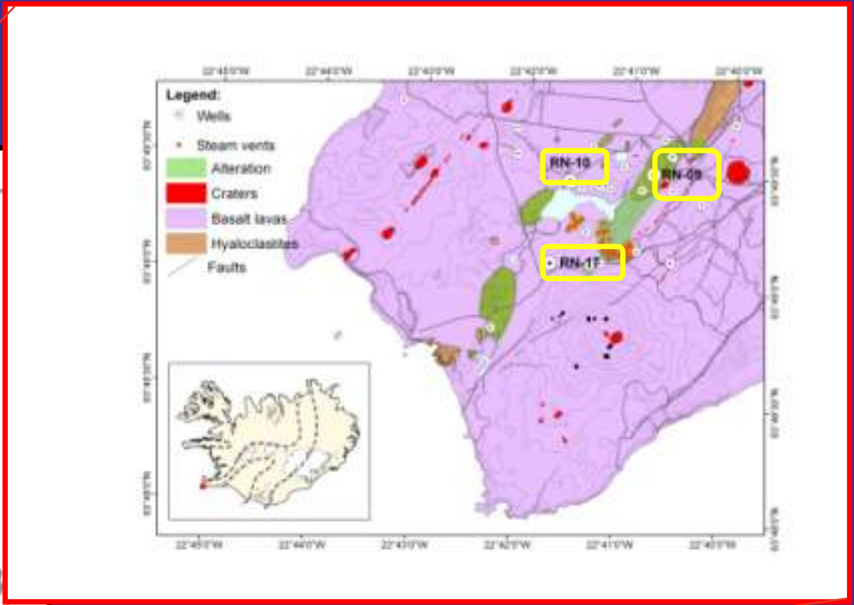
- Introduction
- Mineral Assemblage
- Thermodynamic Considerations
- Analytical Methods
- Calculated Results
- Conclusions

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_{CO2} 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***

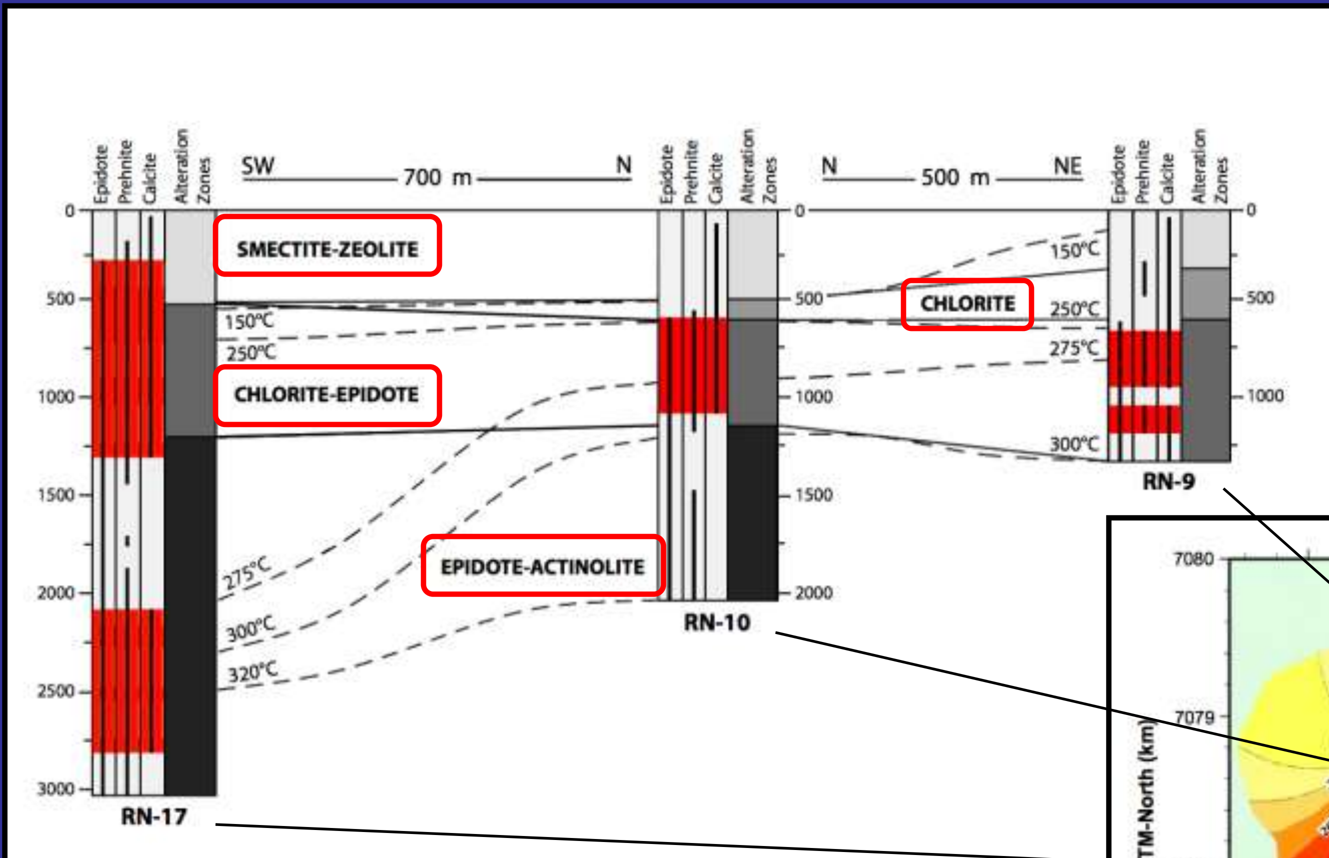
Reykjanes Geothermal System

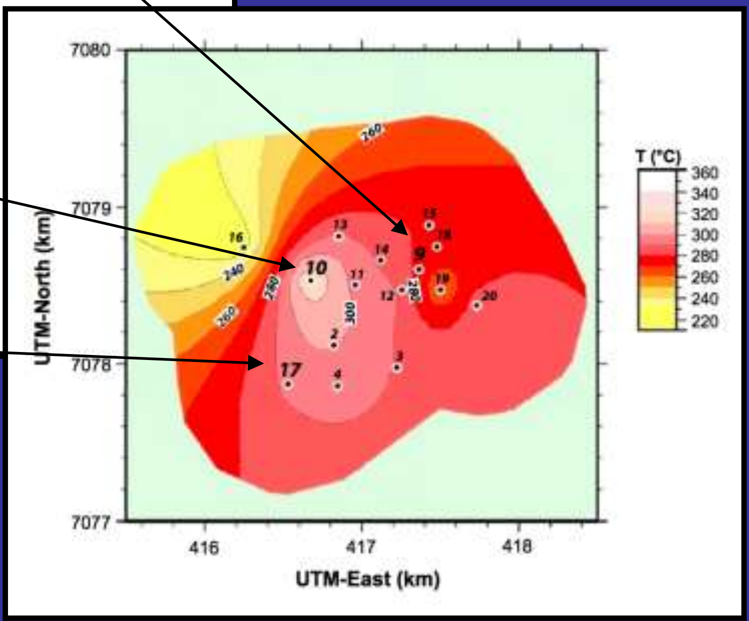




- •High-T geothermal system distribution
- •Reykjanes system in SW Iceland where MAR diverges

Mineral Alteration Zones



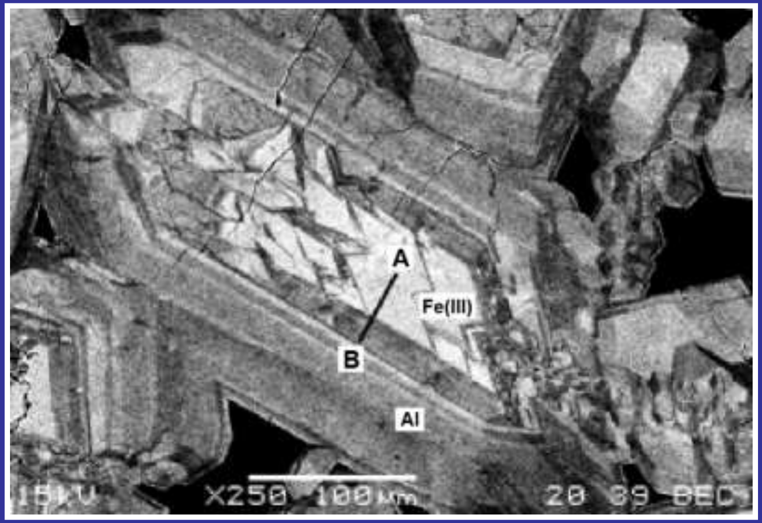


Assemblage: Epidote-Prehnite-Calcite-Qtz

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: $Ca_2Fe_xAl_{3-x}Si_3O_{12}(OH)$, $x = n_{Fe(III)}$ substituted for Al

Solid solution end-members: ***clinozoisite****:* $Ca_2Al_3Si_3O_{12}(OH)$;
epidote: $Ca_2Al_2FeSi_3O_{12}(OH)$; ***pistacite****:* $Ca_2Fe_3Si_3O_{12}(OH)$

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

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Prehnite: $Ca_2Al_{1-x}Fe_x(AlSi_3O_{10})(OH)_2$,
$x = n_{Fe(III)} = X_{Fe,Preh}$, #atoms Fe(III) substituted for Al

QuickTime™ and a decompressor are needed to see this picture.

Mineral Assemblage

$$Ca_2Al_3Si_3O_{12}(OH) + CaCO_3 + 1.5\ SiO_2 + H_2O = 1.5\ Ca_2Al_2Si_3O_{10}(OH)_2 + CO_2$$

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

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Equilibrium Constant Reaction:

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

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

→ Then: **May calculate fluid P_{CO2} that formed minerals**

Phase Rule Constraints

$$\mathbf{f = c + 2 - p}$$

c: number of chemical components = 7 (NaCl, CaO, Al_2O_3, Fe_2O_3, SiO_2, H_2O, 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
- $\mathbf{a_{H2O}}$: computed using aqueous species distribution algorithms
- $\mathbf{a_{czo}}$ **and** $\mathbf{a_{preh}}$: calculated using chemical composition of samples from drillhole cuttings in RN-9, 10, 17 (use electron microprobe analysis)

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

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).

Well #	RN-19	RN-21	RN-12	RN-23	RN-10
T (ºC)	275	285	295	300	310
pH	5.41	5.32	5.39	5.23	5.33
$SiO_{2(aq)}$	$9.75 \bullet 10^{-3}$	$1.11 \bullet 10^{-2}$	$1.08 \bullet 10^{-2}$	$1.20 \bullet 10^{-2}$	$1.24 \bullet 10^{-2}$
Al^{3+}	$1.76 \bullet 10^{-6}$	$2.08 \bullet 10^{-6}$	$1.92 \bullet 10^{-6}$	$2.98 \bullet 10^{-6}$	$1.13 \bullet 10^{-6}$
Ca^{2+}	$4.14 \bullet 10^{-2}$	$4.00 \bullet 10^{-2}$	$4.01 \bullet 10^{-2}$	$4.08 \bullet 10^{-2}$	$3.84 \bullet 10^{-2}$
Fe_T	$7.96 \bullet 10^{-6}$	$9.05 \bullet 10^{-6}$	$8.63 \bullet 10^{-6}$	$1.30 \bullet 10^{-5}$	$3.50 \bullet 10^{-5}$
a_{H2O}	0.984	0.985	0.986	0.985	0.986
P_{CO2} (bar)	1.41	1.50	2.42	1.54	2.34
All concentrations reported in mol/kg solution					

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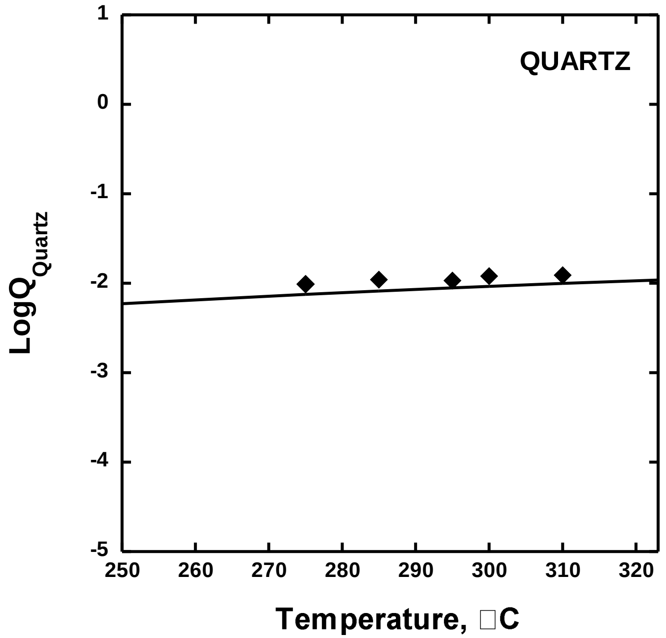
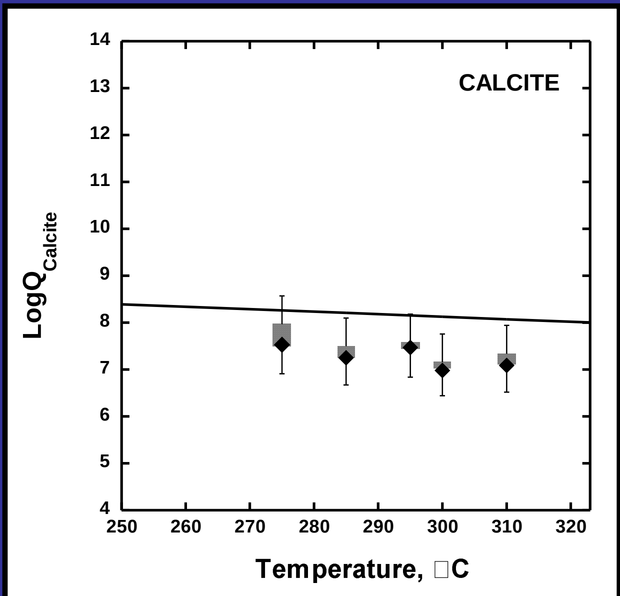
Quartz Solubility Reaction:

$$SiO_{2,Quartz} \Leftrightarrow SiO_{2,aq}$$



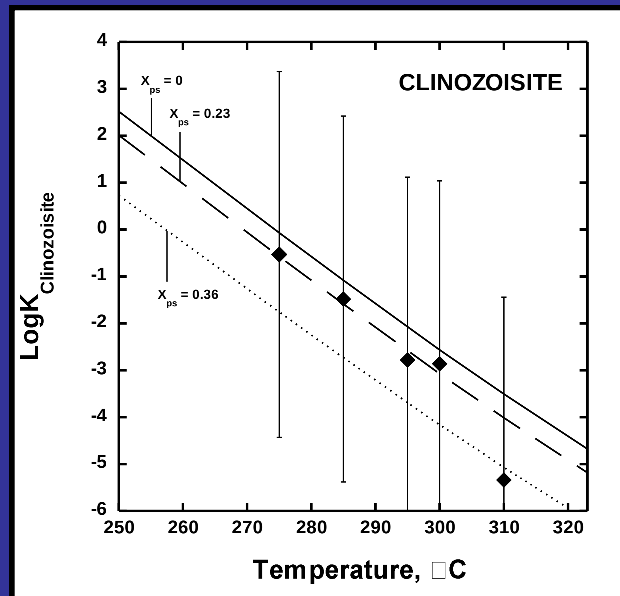
Evaluation of Local Equilibrium



Calcite Hydrolysis Rxn:

$CaCO_3 + 2H^+ \Leftrightarrow$
$Ca^{2+} + H_2O + CO_{2,g}$

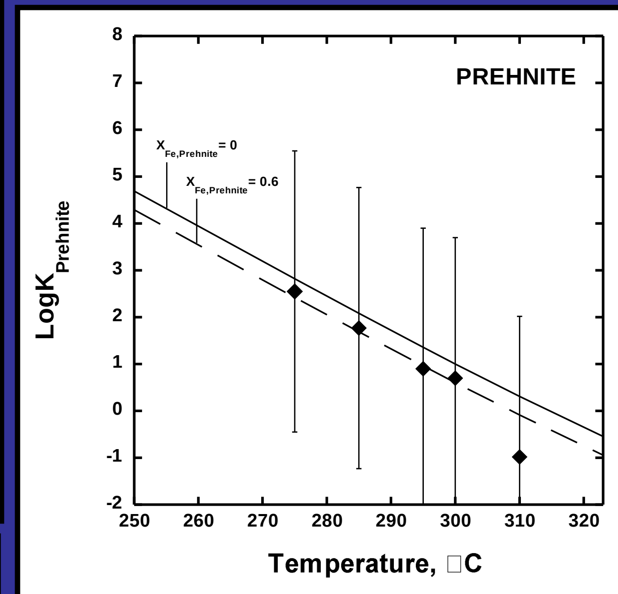
In EQ (within upper limits of assumed uncertainty)



Czo Hydrolysis Rxn:

$Ca_2Al_3Si_3O_{12}OH + 13H^+ \Leftrightarrow$
$2Ca^{2+} + 3Al^{3+} + 3SiO_{2,aq} + 7H_2O$

In Equilibrium

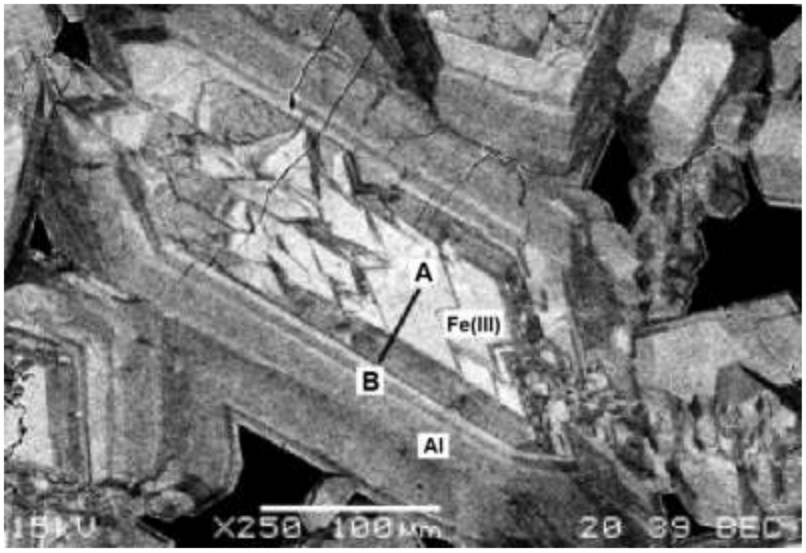


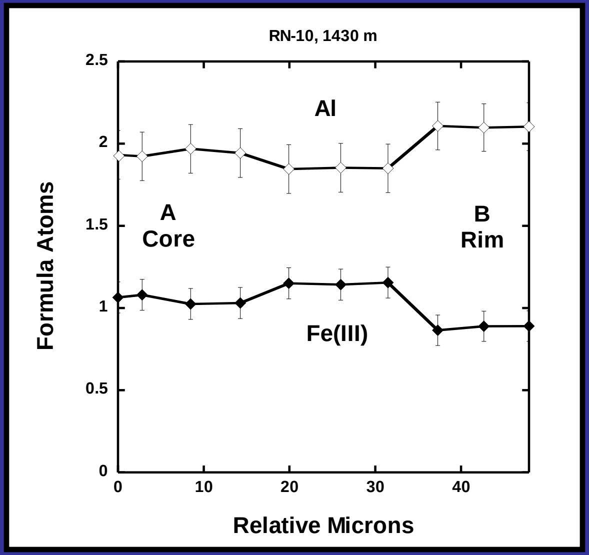
Preh Hydrolysis Rxn:

$Ca_2Al_2Si_3O_{10}(OH)_2 + 10H^+ \Leftrightarrow$
$2Ca^{2+} + 2Al^{3+} + 3SiO_{2,aq} + 6H_2O$

In Equilibrium

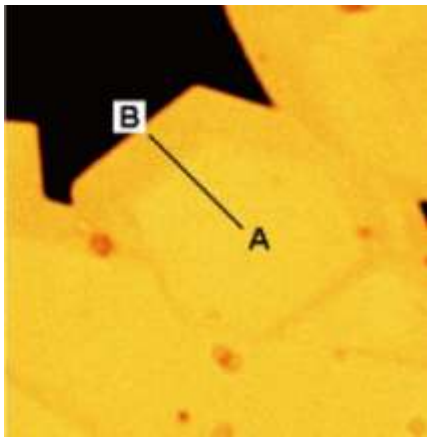
Analytical Procedures

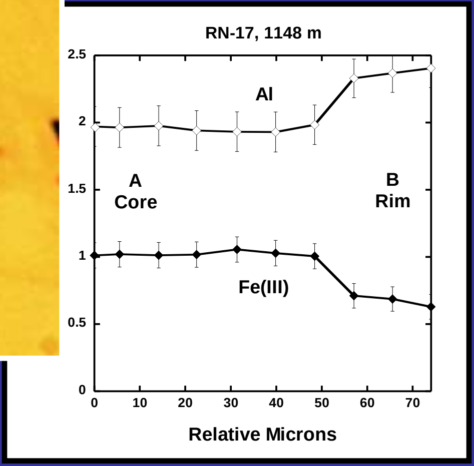




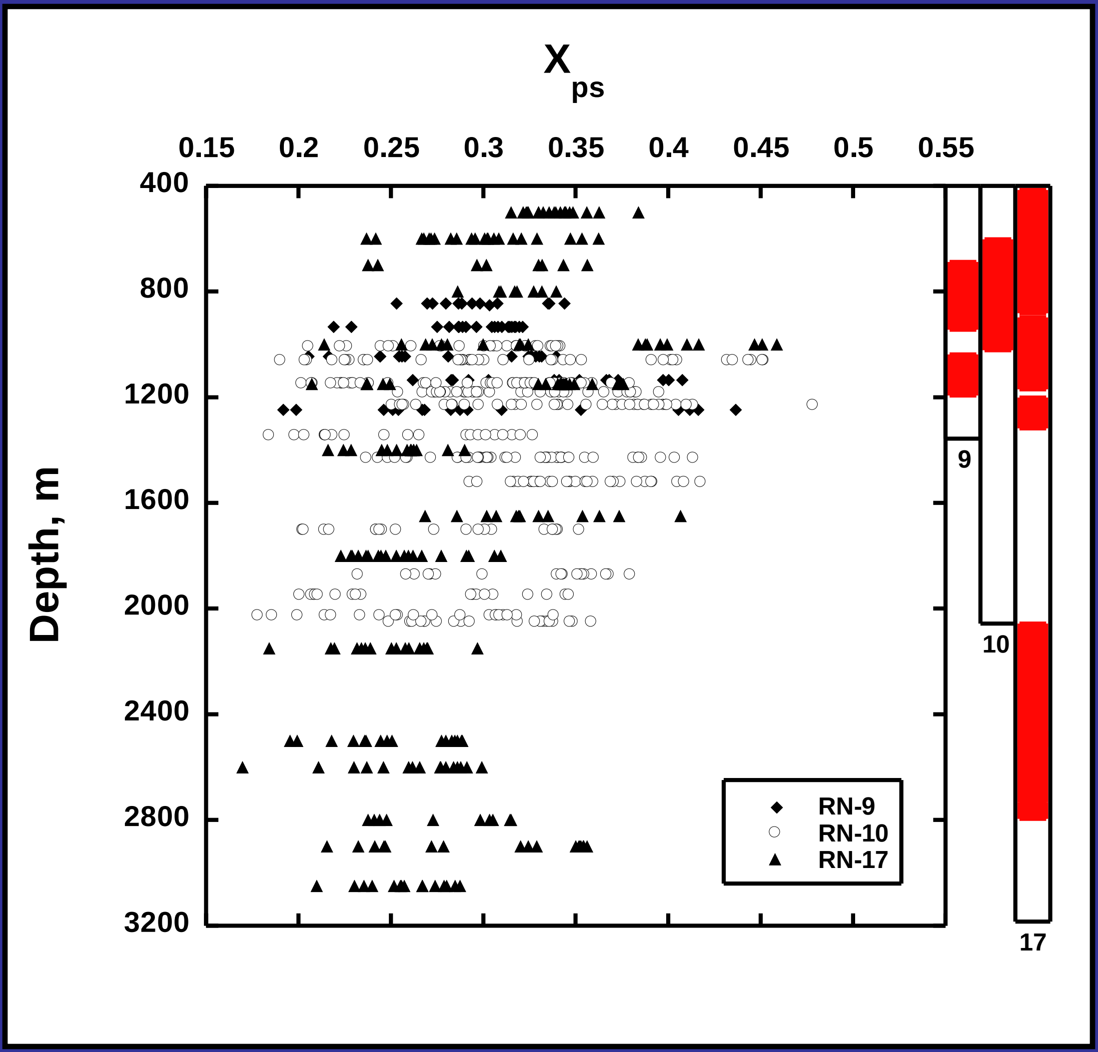
•**Electron microprobe** used to determine mineral chemistry (JEOL 733A, 15 kV accelerating potential, 15 nA beam current)

•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:

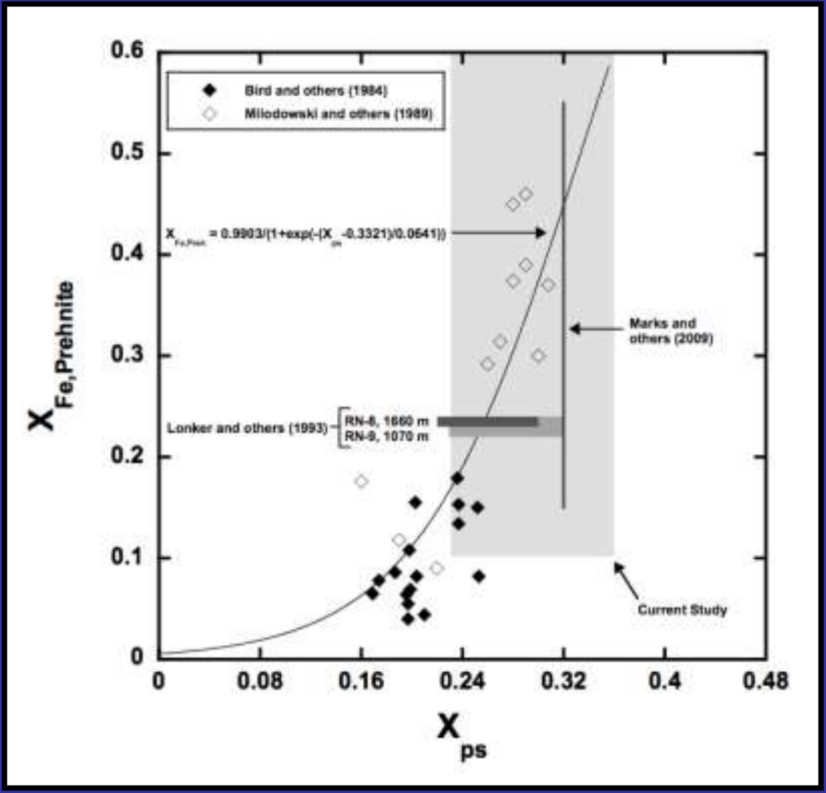
RN-17: 0.13-0.59

- 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

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

$\mathbf{a_{H2O}}$ = 0.985 (SOLVEQ)

$\mathbf{a_{Preh}} = X_{Al,Prehnite} = 1 - X_{Fe,Prehnite}$ = 1 - sigmoid regression =

$1 - (0.9903/(1 + \exp(-(X_{ps} - 0.3321)/0.0641)))$

$\mathbf{a_{Czo}} = X_{Al,M1} \bullet X_{Al,M3}$

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)

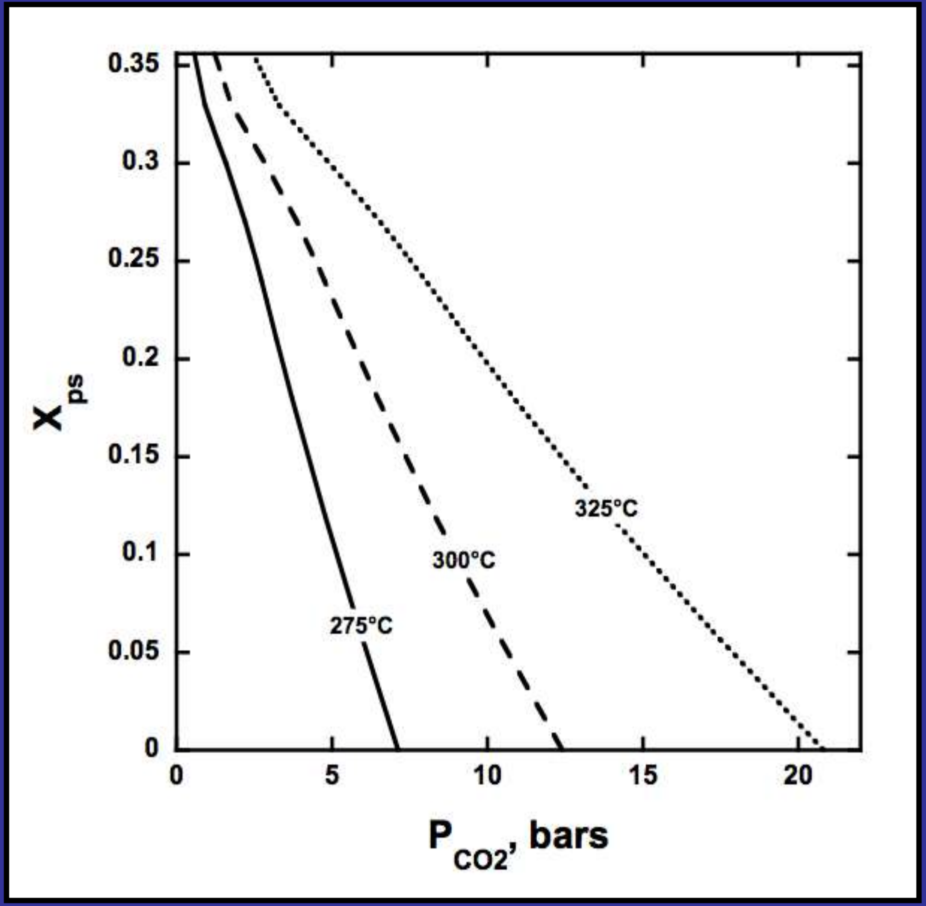
Log K $= 57.781 - 22843/T^2 - 4792.99/T + 0.00829\,T +$

$0.6864x10\text{-}6\,T^2 - 19.302\,\mathrm{LogT}$

Calculated using T-dependent algorithm (Arnorsson et al., 2007)

Calculated P_{CO2}

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

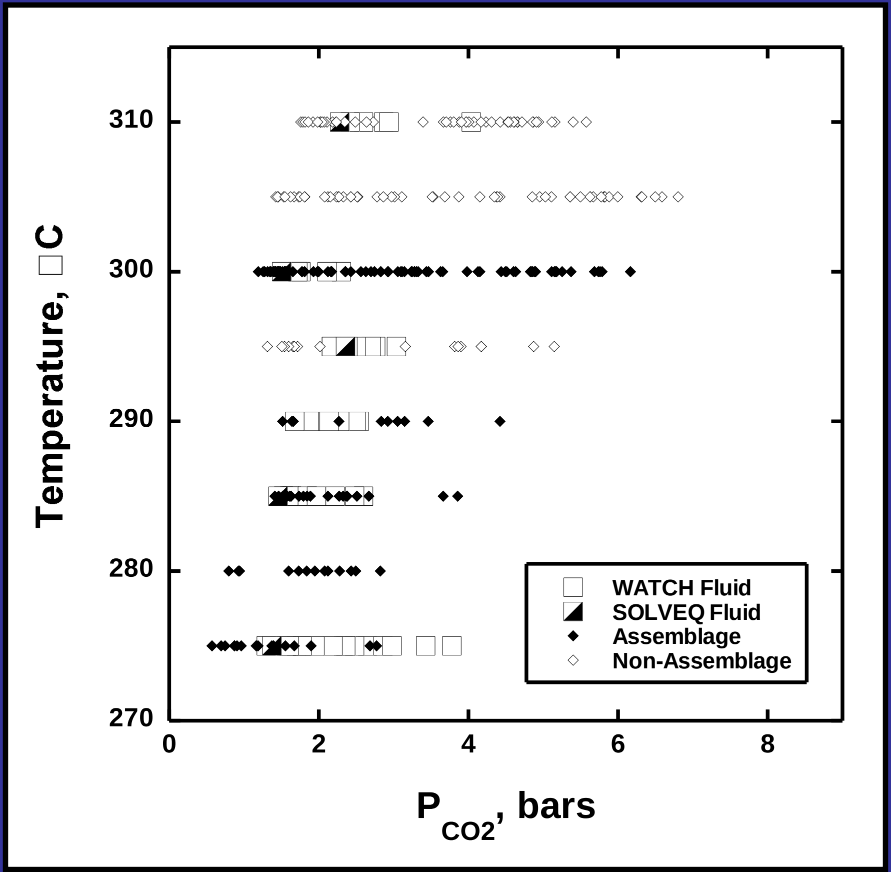


Trends:

- At ⇔ T, P_{CO2} ⇑ with ⇓ X_{ps}
- At ⇔ X_{ps}, P_{CO2} ⇑ with ⇑ T (but to a lesser degree with ⇑ 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-Assemb.)

Calculated P_{CO2}

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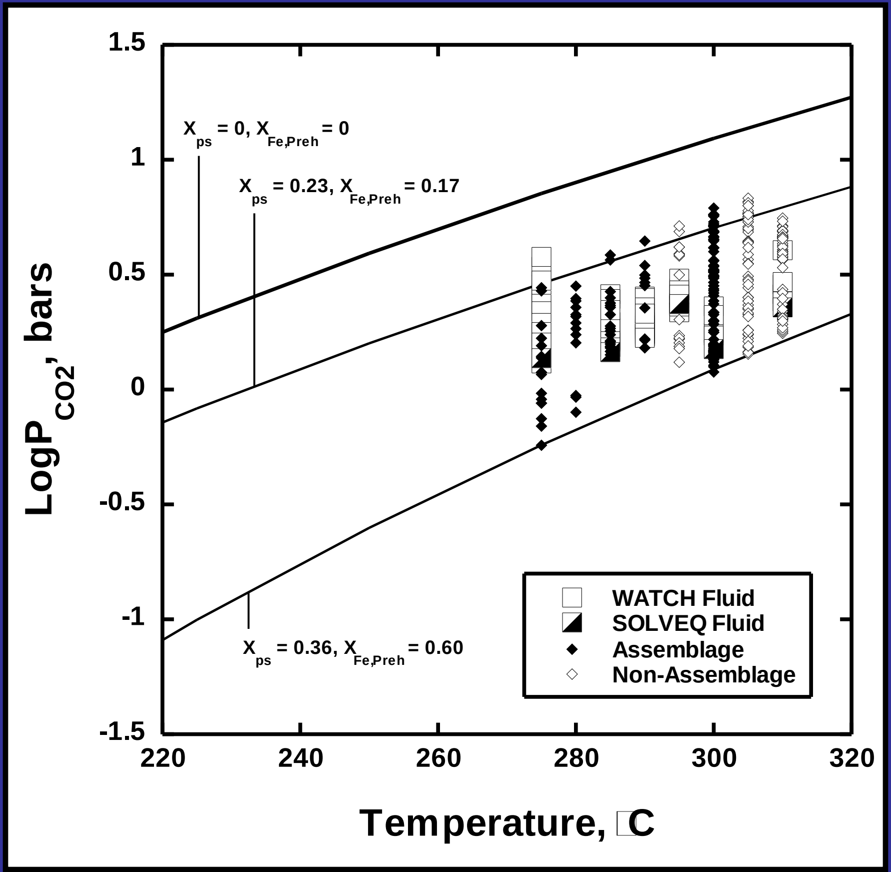

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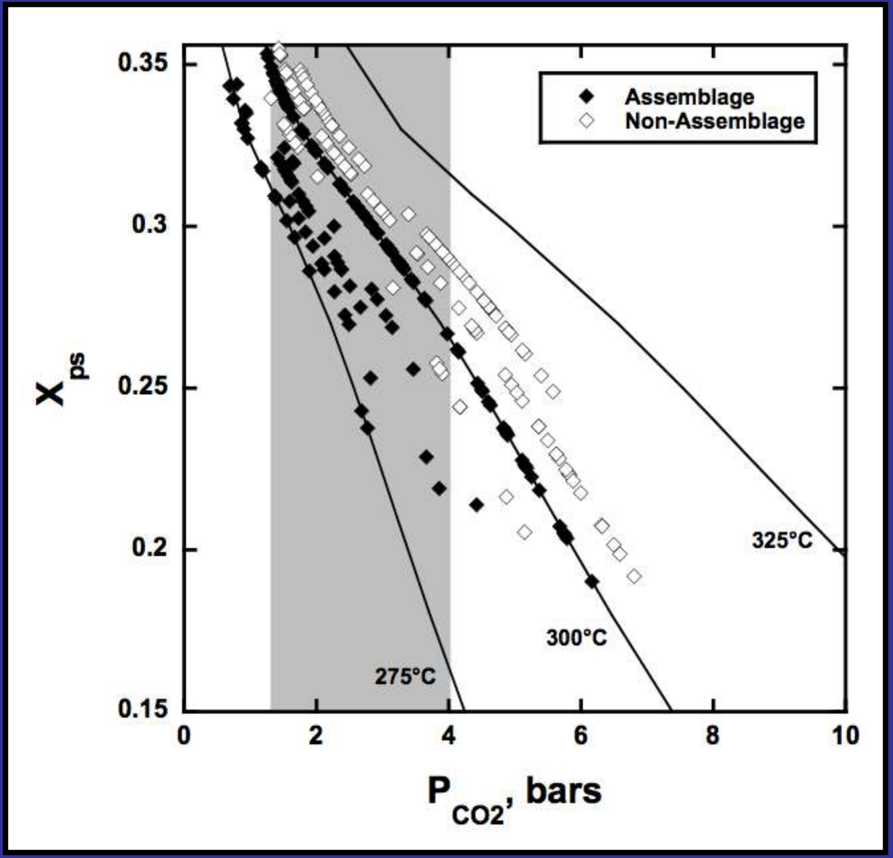


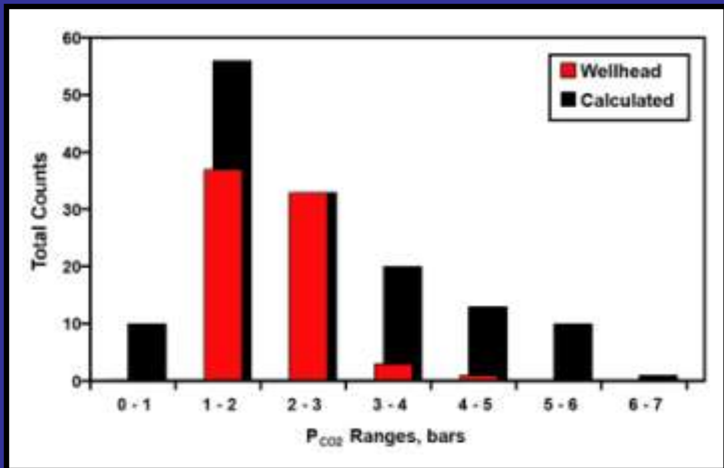
Shaded area: range of *in situ* fluid compositions

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)

Agreement Trends

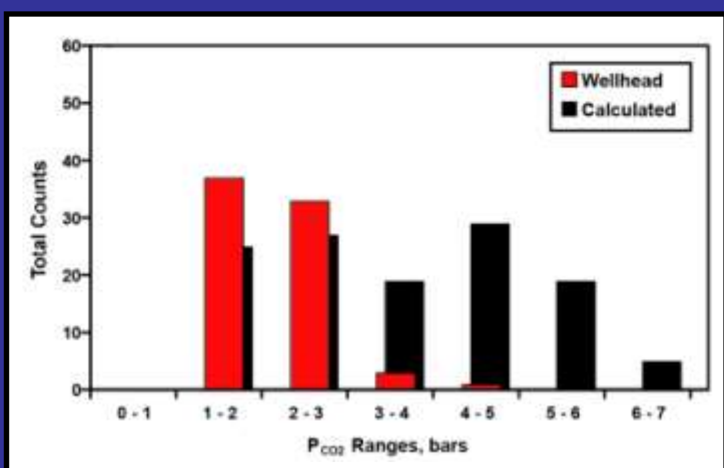
Assemblage



Cuttings at depths where assemblage observed:

- 143 epidote analyses
- **72%** of the computed values of P_{CO2} (0.57 to 6.17 bars) are within P_{CO2} 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_{CO2} (1.3 to 6.8 bars) are within P_{CO2} range of collected formation fluids (1.3 to 4.0 bars)

Conclusions

- **Method for calculating fluid P_{CO2} 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_{CO2} values in the RGS.

- **Strong agreement between sampled and predicted fluid compositions** provides insight into future abilities to characterize:
    - P_{CO2} in **active and fossil hydrothermal** and low-grade metamorphic environments in mafic lithologies
    - The nature of reactions that involve **natural sequestration** of CO_2 derived from magmatic degassing
    - The nature of reactions that involved **injection of industrial** CO_2-rich fluids within hydrothermal environments in basaltic rocks.

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Thermodynamics reveals that mineralogy <u>records</u> the evolutionary history of CO_2 in the geothermal system


Thank You
Questions?