

HYDROTHERMAL CARBONATE GEOCHEMISTRY OF THE NGATAMARIKI SUBSURFACE RESERVOIR, NEW ZEALAND

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ABSTRACT

Geochemical assessment of rocks and fluids enables improved drilling success and geothermal development. Hydrothermal carbonates are potential indicators of hydrothermal fluid source(s), fluid mixing processes and metasomatic/alteration temperatures. Here, we use core samples from the Ngatamariki Geothermal Field located in the Taupo Volcanic Zone, New Zealand, to ascertain the source, migration and temperature history of the hydrothermal fluids via isotopic and thermodynamic geochemistry of the hydrothermal carbonates. Microthermometric analyses and boiling curves demonstrate platy calcite is deposited from a dilute, CO₂-rich steam-heated fluid at 250°C to 270°C and ~3km depth. Calcite stable isotope compositions further reveal that calcite is deposited from both CO₂-rich steam-heated fluids and less evolved magmatic fluids. Calcite δ¹³C values range between -3.0 and -9.7% (V-PDB), similar to the composition of mantle carbon. Calcite δ¹⁸O values range between -17.2 and -29.4% (V-PDB) suggesting calcite within the Ngatamariki reservoir is derived from a variably evolved magmatic fluid with temperatures of formation ranging between ~250 and ~300°C. Together, isotope results suggest that Ngatamariki geothermal fluids have a significant magmatic component. Thermodynamic modeling supports the magmatic origin of Ngatamariki reservoir fluids and provides a means to evaluate the fluid-rock interactions as these fluids migrate from source to surface.

INTRODUCTION

The Ngatamariki Geothermal Field (NGF) in the Taupo Volcanic Zone (TVZ), New Zealand, is a high enthalpy system currently being developed for power generation. A primary objective of geothermal development at NGF is to identify the nature and source of the geothermal fluids and the related chemical and mineralogical interactions of the fluids with the host rock. Core samples obtained from NGF exploration wells (~2-3km depth) provide an opportunity to examine the geothermal and alteration

history of the subsurface reservoir. Specifically, hydrothermal carbonate and quartz, common secondary minerals in geothermal systems, are utilized to examine the boiling, mixing, and dilution processes of the fluid during its ascent through the subsurface. Through coupling isotopic, microthermometric, and mineralogical analyses, we interpret the geochemical origin, migration, and temperature history of the reservoir fluids. Geochemical modeling of the NGF subsurface fluids provides a larger context facilitating interpretation of the geochemical evolution of fluids and mineral formation in the subsurface reservoir.

GEOLOGY

The NGF is located in the Whakamaru caldera complex in the central portion of the TVZ (Figure 1); (Urzua, 2008). Approximately 20km NE of the Taupo township, it is one of 20 high enthalpy geothermal systems within the TVZ (Bignall, 2009).

The surface geology of Ngatamariki is dominated by Quaternary hydrothermal eruption breccias (Urzua 2009). Surface deposits overlaying the NGF form layered sequences of pumice breccias/tuffs, mantled by hydrothermal eruption material, that overlies Orakonui Formation deposits of ignimbrite and pumice breccias. Bedded gravels and related sediments of the Hinuera Formation overlie lacustrine and fluvial sediments (Huka Falls Formation). These lacustrine sediments act as barriers to vertical flow of deep-sourced geothermal fluids due to their high clay content (Bignall, 2009; Urzua, 2009).

Tephra, lithic tuffs, breccias and fluvial sediments constitute the uppermost, shallow sequences of the Ngatamariki stratigraphy. These grade progressively with depth to porphyritic lavas, pumiceous-rhyolite breccias and ignimbrite (Wairakei). At ~300m depth, the Tahorakuri Formation commences and is represented by tuffs and sediments (400-700m), lithic-rich tuff/breccia ignimbrite (200-800m), and

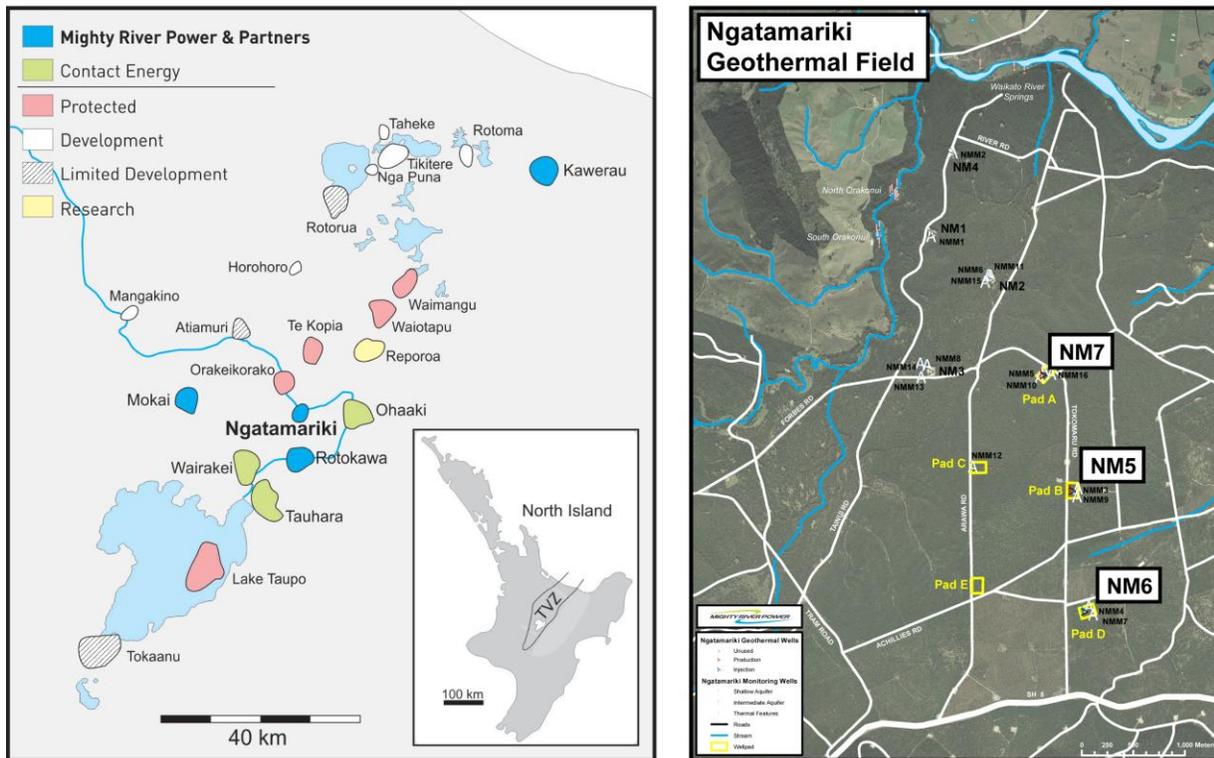


Figure 1: (Left) Geothermal sites located in the Taupo Volcanic Zone on the North Island, New Zealand. (Right) Aerial photograph of the Ngatamariki Geothermal Field with exploration wells NM5, NM6, and NM7 shown. Both images are courtesy of Jeremy O'Brien and Mighty River Power.

andesite lava and breccia (>800m). The Tahorakuri Formation overlays the strongly folded and indurated Torlesse greywacke basement.

Ngatamariki exploration wells have intersected porphyritic andesite lava and associated hydrothermally altered andesitic breccia which have been dated at 1.2 Ma by Arehart et al. (2002). One exploration encountered a diorite pluton (underlying the andesite lava and breccias) and is the first and only pluton identified within the TVZ (Bignall, 2009).

SAMPLING, ANALYSES, AND MODELING

Mineralization and hydrothermal alteration was studied in three NGF wells (NM5, NM6, and NM7; See Figure 1). Samples were chosen based on their primary lithologies and depth within the core to enable a comparison of the hydrothermal alteration assemblages between lithological units as a function of depth. Additionally, mineral textures were noted for collected and analyzed samples (Figure 2; See Atkinson (2010) for more detail).

Fluid Inclusion Microthermometry

Heating and freezing measurements were performed on primary fluid inclusions (4–6 μm in diameter) in secondary quartz from core NM6 (Figure 1). Fluid inclusions were dominantly liquid filled with an accompanying small vapour bubble (i.e., two-phase fluid inclusions). The fluid inclusions were studied in double-polished thick sections (80 μm) using the Linkam THMSG600 heating stage, controlled by Linksys 32 DV software situated at GNS Wairakei Research in Taupo. Heat was incrementally released via a heating coil to the heating stage where the cut sample was sitting. As the heat increased, the vapor bubble decreased in size until it homogenized with the liquid. The temperature at which this occurs was the homogenization temperature (T_h). Freezing temperatures (T_m) were also determined.

Stable Isotope Analyses

The carbon and oxygen isotopic composition of hydrothermal carbonate was measured from powdered carbonate samples (200 μg) from core

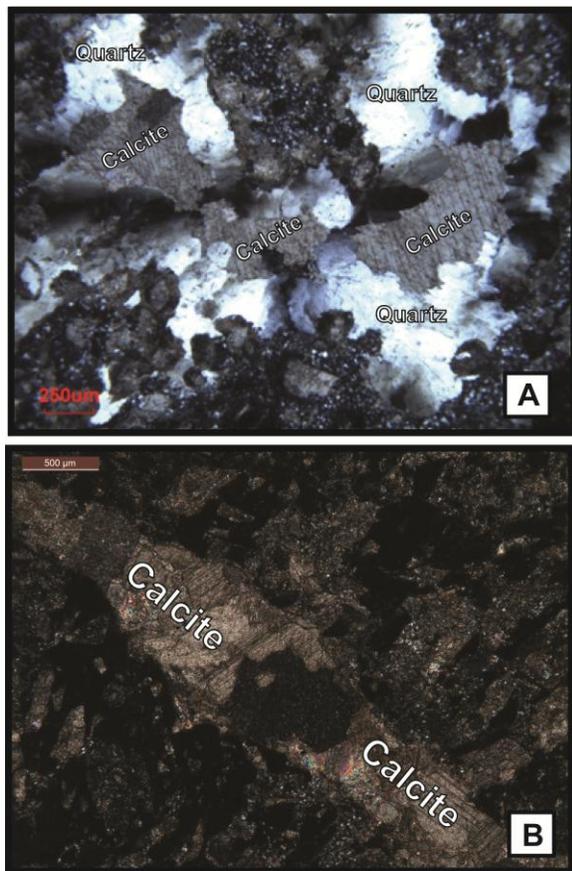


Figure 2: Photomicrographs of A) void-filling secondary calcite surrounded by hydrothermal quartz from ~3 km depth and B) vug-filling secondary calcite from ~4 km depth.

samples. Samples were extracted from veins and vugs using a 400µm diamond drill bit mounted on a Dremel tool. A Thermo Scientific GasBench II connected to a Delta V Plus gas isotope ratio mass spectrometer under continuous flow conditions was used to measure the oxygen and carbon isotopic composition of the carbonate samples. A total of 51 samples representing drillcores NM5, NM6 and NM7 were prepared for stable isotopic analysis. Stable oxygen and carbon isotopic compositions are accurate to <0.10 ‰ based on replicate analysis of NBS-19 and NBS-22 certified reference materials.

Thermodynamic Modeling

Geochemical thermodynamic modeling at elevated P-Ts for geochemical reactions was completed using the program SUPCRT92 (Johnson et al., 1992). Thermodynamic values used for these calculations are from the slop98 database (GEOPIG, 1998, compilation of data from Shock et al. (1997))

RESULTS AND DISCUSSION

Fluid inclusion analyses of secondary quartz and stable isotope analyses of hydrothermal carbonate are summarized in Table 1. Primary lithologies and depth are included. These results provide discussion with regards to geothermal fluid evolution based on fluid inclusion microthermometry, isotopic investigations, and thermodynamic modelling.

Fluid Inclusion Microthermometry

Fluid inclusion analyses in hydrothermal quartz were obtained from core samples from well NM6. On heating, homogenisation temperatures (T_h) are between 256° and 293°C (Table 1). Freezing temperatures (T_m) were between -0.3° to -1.4°C indicating the entrapped liquids have ~1.7 NaCl eq wt % (Table 1).

Twelve primary two-phase liquid-vapor fluid inclusions hosted by vein calcite were also analyzed in the same core (NM6) yielding T_h values between 254.8°C and 299.9°C (Bignall, 2009). Homogenization (T_h), melting (T_m) and calculated salinity measurements after Simmons and Christenson (1994) of the quartz and carbonate fluid inclusions are shown in Figure 3. Quartz fluid inclusion analyses plot congruently with boiling curves determined from carbonate fluid inclusions. These analyses constrain temperatures of the hydrothermal fluids and supports mineral textural data (see Atkinson, 2010) that quartz and calcite are cogenetic.

The change from primary single-phase parent fluid to secondary two-phase CO₂-rich steam-heated fluid occurs where fluid-mineral equilibrium is disrupted due to boiling and mixing as a result of changes in temperature and pressure with depth. At this ‘transition’ stage, boiling of the primary fluid occurs releasing CO₂ and H₂O into the vapor phase, increasing the pH of the fluid, thereby, increasing carbonate saturation. This loss of CO₂ and H₂O from the parent fluid due to boiling is reflected as platy calcite deposition in the Ngatamariki samples at ~3 km depth. These observations indicate that H₂O liquid-vapor saturation temperatures provide the best estimate to constrain P-Ts for geochemical modeling. Alternatively, these observed boiling trends could be related to liberated H₂O, CO₂, and heat resulting from a pulse of magmatic activity.

Stable Isotopes

Stable isotopic analysis of secondary vein minerals provides an opportunity to interpret the hydrothermal conditions present in the NGF subsurface. By independently constraining mineral formation temperatures via fluid inclusion analysis, hydrothermal carbonates enable the interpretation of the fluid composition assuming isotopic equilibrium

Table 1. Summary of NM5, NM6, and NM7 core lithology, depth, calcite isotope and temperature data

Well	Primary Lithology	Depth (m)	Calcite		Water*	Temperature	
			$\delta^{13}\text{C}$ (‰ VPDB)	$\delta^{18}\text{O}$ (‰ VPDB)	$\delta^{18}\text{O}$ (‰ VSMOW)	T_h^{**}	Down-hole [‡]
NM5	Ignimbrite	1,775	-5.92	-25.00	-1.14		277
			-6.27	-25.05	-1.20		
			-5.40	-22.83	1.09		
			-8.00	-25.69	-1.86		
			-9.08	-27.64	-3.87		
NM5	Dacite	2,903	-5.86	-26.72	-2.92		
			-5.16	-18.30	5.76		
NM6		2,686	-6.87	-22.35	0.98		260
			-6.91	-24.90	-1.64		
			-6.60	-26.59	-3.13		
			-6.59	-27.05	-3.86		
			-5.97	-24.45	-1.18		
			-5.45	-24.19	-0.78		
			-7.35	-25.74	-2.51		
			-7.33	-25.63	-2.39		
NM6	Andesite Lava	3,032	-7.07	-25.25	-2.01		260
			-6.70	-25.80	-2.57		
			-7.75	-25.63	-2.39		
			-7.48	-25.64	-2.40		
			-7.42	-22.39	0.95		
			-6.21	-21.26	2.11		
			-7.22	-26.80	-3.60		
			-6.95	-26.32	-3.11		
			-6.81	-26.64	-3.44		
			-6.76	-26.35	-3.14		
NM6	Greywacke Basement	3,395	-6.70	-26.17	-2.95		260
			-6.47	-26.46	-3.25		
			-5.87	-24.24	-0.96		
			-2.95	-20.88	2.50		
			-9.94	-17.17	6.33		
			-9.82	-19.79	3.63		
			-8.36	-26.16	-1.83		
			-7.49	-26.29	-3.04		
			-7.39	-24.77	-1.50		
			-7.25	-27.99	-4.83		
			-7.04	-25.19	-1.94		
			-5.20	-27.86	-4.84		
			-4.58	-26.89	-3.69		
-9.68	-26.20	-2.98					
-8.90	-24.89	-1.63					
-8.71	-26.74	-3.54					
-8.45	-26.00	-2.77					
-8.04	-26.33	-3.12					
NM7	Andesite Breccia	2,179	-5.84	-28.87	-5.04		280
			-6.60	-27.38	-3.50		
			-5.23	-25.62	-1.69		
			-5.66	-25.16	-1.22		
			-6.76	-29.42	-5.61		
			-5.74	-25.87	-1.95		
			-5.85	-26.48	-2.58		
-8.48	-22.62	1.40					

* Calculated using temperature-dependent equilibrium fraction equation for the calcite-water system O'Neil et al (1969).

‡ Downhole temperatures sourced from the GNS Science Consultancy Report 2009/94.

** Homogenization temperatures (T_h) measured from quartz fluid inclusions from selected samples.

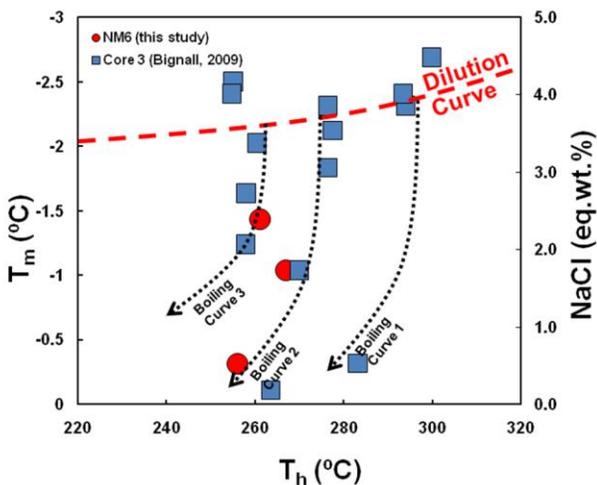


Figure 3: Model boiling curves (dotted) are constructed using fluid inclusion data plotted as a function of the melting temperature (T_m) and homogenisation temperature (T_h). Red circles represent the Ngatamariki samples of this study and the blue squares represent Ngatamariki samples from Bignall (2009). Both sets of data are obtained from samples taken within the same well (NM6) at 3-4 km depth. Primary two-phase fluid inclusions measured in this study are from hydrothermal quartz. Primary two-phase fluid inclusions measured are from hydrothermal calcite (Bignall, 2009). Boiling curves are fitted (line of best fit) to the plotted data and where values fit boiling curves.

was achieved at the time of mineral formation. The integration of these methods may then be used to identify the fluid source of the hydrothermal minerals.

Carbon and oxygen isotope analyses (V-PDB), shown in Table 1, are summarized below:

- 7 samples measured from core NM5: $\delta^{18}\text{O}$ values range from -18.3 to -27.6‰ and $\delta^{13}\text{C}$ values range from -5.2 to -9.1‰;
- 36 samples measured from core NM6: $\delta^{18}\text{O}$ values range from -17.2 to -27.9‰ and $\delta^{13}\text{C}$ values range from -2.9 to -9.9‰;
- 8 samples measured from core NM7: $\delta^{18}\text{O}$ values range from -22.6 to -29.4‰ and $\delta^{13}\text{C}$ values range from -5.2 to -8.5‰.

Figure 4 illustrates the fluid-mixing relationships for the Ngatamariki reservoir using $\delta^{18}\text{O}_{\text{water}}$ and

hydrogen (δD) isotopes, including compositions characteristic of meteoric and magmatic waters, regional rainfall samples (monthly samples collected throughout the North Island in 2010), surface hot springs, geothermal production well fluids, and calculated hydrothermal calcite parent fluids. Calcite parent fluid oxygen isotope compositions were calculated using a temperature-dependent equilibrium fractionation equation (O'Neil et al., 1969) and down-hole reservoir temperatures or fluid inclusion temperatures of homogenization. These calculated $\delta^{18}\text{O}_{\text{water}}$ values are plotted against an assumed hydrogen isotopic composition (i.e. δD) of -41‰ V-SMOW, the average δD value of production well fluids.

Calcite parent fluids plot along a meteoric-magmatic water mixing trend, including several samples that may have formed from a magmatic end-member fluid source. Whether these magmatic fluids are the result of a continual supply or fluid injection pulses is difficult to discern. However, the large range in parent fluid compositions (Figure 4 and Figure 5b), and the inherently dynamic nature of upper crustal magmatic systems, favor the latter.

Vein calcite $\delta^{13}\text{C}$ values are consistent with a predominantly magmatic parent fluid source for the Ngatamariki system. Figure 5a presents calcite $\delta^{13}\text{C}$ plotted against their homogenization temperatures (T_h), in addition to the equilibrium carbon isotope composition of CO_2 present at the time of calcite formation (dashed lines in Figure 5a). As magmatic CO_2 $\delta^{13}\text{C}$ values typically range between -7.5‰ and -5.5‰ V-PDB (Exley et al., 1986), and the isotopic equilibrium fractionation between carbon dioxide and calcite at $\sim 270^\circ\text{C}$ is approximately +1.5‰, the simplest explanation for the observed Ngatamariki calcite $\delta^{13}\text{C}$ values (average = -7.6‰ V-PDB) is formation from a magmatic parent fluid. This interpretation is further strengthened by the fact that there are no significant sources of organic (ca. -25‰) or marine carbonate (ca. 0‰) in the regional stratigraphy. Similar values at Broadlands-Ohaaki and Waiotapu geothermal fields (Simmons and Christenson, 1994), represented by the yellow and green triangles respectively (Figure 5), are shown for comparison.

In summary, hydrothermal carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values provide strong evidence that the Ngatamariki geothermal field includes a significant magmatic water component at depth. Variability in the isotopic compositions of vein carbonate, reservoir fluids, and surface hot springs further indicates that the system is not static. Rather, the fluids present in the Ngatamariki system are variably affected by steam-heating, boiling, degassing, fluid injection and dilution by meteoric water.

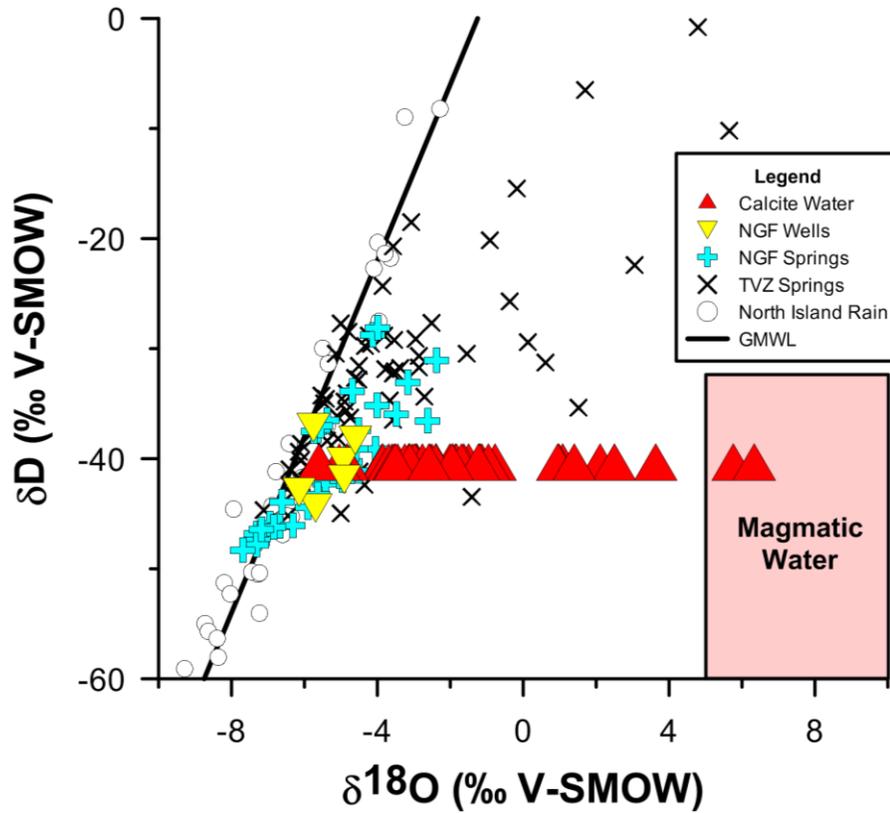


Figure 4: Fluid-mixing graph displaying oxygen ($\delta^{18}O$) and hydrogen (δD) isotope composition of the primary hydrothermal fluid of Ngatamariki carbonate.

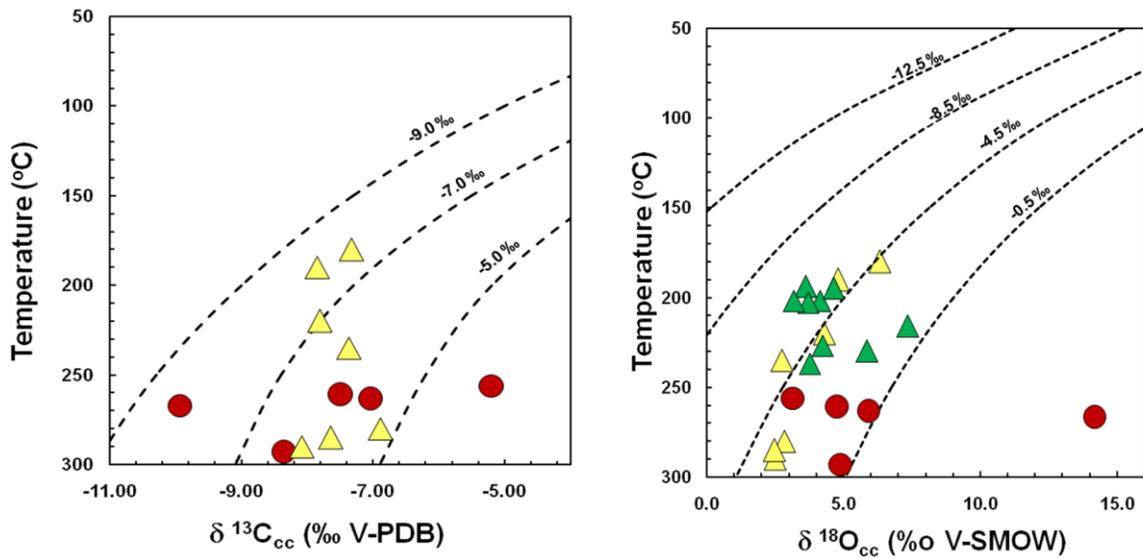


Figure 5: a) $\delta^{13}C$ values versus measured homogenization temperatures and b) $\delta^{18}O$ values versus homogenization temperatures of Ngatamariki calcite (red circles). Dashed curves represent the isotopic composition of CO_2 in equilibrium with calcite (Simmons and Christenson, 1994). Values for Broadlands-Ohaaki (yellow triangles) and Waiotapu (green triangles) geothermal field fluids are included.

Table 2. Selected geothermal well water chemical analyses

	Ngatamariki ¹	Broadlands ²	Waiotapu ³	Reykjanes ⁴
<i>h</i> (kJ/kg) ^a	1,060	1,315	1,279	1,256
<i>T</i> (°C) ^b	260	265	230	267
pH ^c	6.3(20°C)	7.9 (20°C)	7.5 (20°C)	5.2 (22°C)
T-Corrected pH ^d	3.5	5	5	2.3
Equilibrium pH	6	5.9	5.6	5.2
	-----mg kg ⁻¹ -----			
SiO ₂	573	796	450	668
Na	664	975	965	9,903
K	124	232	135	1,314
Mg	0.008	0.01	1.05	1.05
Ca	3.5	3.0	22.5	1,548
Fe				0.33
Al				0.09
CO ₂ ^e	789	191*	780	47
HCO ₃ ⁻	64.1	157	26	
SO ₄	29.5	3.5	48	24
H ₂ S			152	3.4
Cl	997	1,858	1,600	20,534

¹ Ngatamariki Geothermal Field, Taupo Volcanic Zone, well NM6, New Zealand (Corrected to reservoir conditions using quartz geothermometry); (Bignall, 2009)

² Volcanic system in silicic-andesitic rocks, Broadlands, well 8, New Zealand (Simmons and Christenson, 1994)

³ Volcanic system in silicic-andesitic rocks, Waiotapu, well wt4, New Zealand (Hedenquist and Browne, 1989)

⁴ Seawater-supplied geothermal system, Reykjanes, well 15, Iceland (Arnorsson et al., 2007)

^a Discharge enthalpy

^b Approximate well temperature

^c pH/temperature of measurement

^d pH value based on 0.3pH unit decrease per 25°C increase

^e Total carbonate carbon as CO₂

* From Arnorsson et al. (2007)

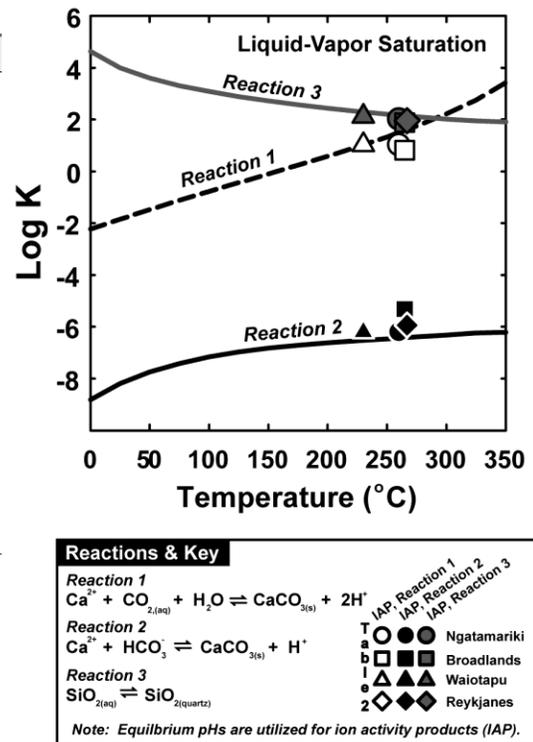


Figure 6: Thermodynamic evaluation of well water fluids (Table 2) with respect to calcite and quartz are shown.

Thermodynamic Modeling

Conditions related to the formation and deposition of hydrothermal calcite and quartz in fluid-dominated reservoirs may be evaluated via direct thermodynamic considerations. Changes in fluid temperature, pH, and ion activities as fluids ascend through the host rock and sediment play a key role in the distribution and deposition of these minerals. The presence of calcite and quartz throughout drill core samples clearly indicate that fluids became equilibrated or oversaturated with respect to these two mineral phases during their upward migration. As noted by microthermometry analyses, fluid inclusion and temperature data support that calcite and quartz were formed at equilibrium. Additionally, H₂O liquid-vapor saturation conditions appear to best characterize the P-T conditions present in the hydrothermal reservoir. To evaluate mineral-solution equilibrium, calcite and quartz equilibrium constants (in terms of log K) for carbonate and quartz reactions were calculated via SUPCRT92 and these values are shown in Figure 6. Additionally, ion activity products (IAPs) calculated from NGF fluids as well as those from other geothermal reservoirs, for comparison, including Broadlands (NZ), Waiotapu (NZ) and Reykjanes (Iceland) from Table 2 are plotted in Figure 6. One assumption for our thermodynamic calculations is that elemental and compound activities are accurate (i.e., samples were properly sampled, prepared and analyzed).

Solution pH measured at the surface does not accurately reflect the pH at depth. pH values garnered at ~20°C provide IAPs (not shown) that are highly oversaturated (except Reykjanes). Temperature corrected pH values (T-Corrected pH as shown in Table 2) result in IAPs (not shown) that are highly undersaturated and do not account for the buffering capacities of the solutions. By adjusting pHs until IAPs for Reactions 1 and 2 (Figure 6) equal log K at their respective temperature, we are able to determine the equilibrium pHs (Table 2) for the well water fluids at depth. Collectively, equilibrium pH values for the geothermal fluids in Table 2 are between 5 and 6 (i.e., between surface and T-corrected pHs). Note that geothermal fluids are in equilibrium with quartz (Reaction 3, Figure 6) where pH is not considered. Overall, these results support that both quartz and calcite formed at or near equilibrium; however, we are not able to discern the evolution of these fluids with respect to time or if mineral formation is related to specific events such as pulses in magmatic activity.

As geothermal fluids ascend to the surface, temperature and pressure decrease resulting in quartz oversaturation and calcite undersaturation. Additionally, H₂O and CO₂ exsolution complicate

evaluating mineral formation and growth in hydrothermal systems. Overall, calcite and quartz formation are generally favorable and fast for a wide variety of scenarios. This continual and potentially punctuated progression of mineral formation means that the porosity of a geothermal system will decrease over time unless: 1) the character of the fluids and/or P-T conditions change and/or 2) the rocks/sediments are mechanically broken. As an example, pulses in magmatic activity may result in conditions related to carbonate and quartz oversaturation; however, the mechanical benefits may potentially outweigh the chemical drawback by mechanically rejuvenating fluid flow pathways. Understanding how these minerals *thermodynamically* and *kinetically* originate, integrate, and evolve from a hydrothermal source to the surface as well as circumventing their formation with fluid reinjection is a major thrust of research at the University of Canterbury.

CONCLUSIONS

Hydrothermal carbonates provide a means to examine the history of geothermal fluids at depth. Isotope geochemistry of carbonates at the NGF highlights that magmatic water has an important role with regards to character and stability of geothermal systems in the TVZ. As CO₂ is liberated from either boiling processes and/or directly from magmatic processes, the ascension of this gas to the surface provides an opportunity to examine real time processes at depth as well as to potentially ‘tease out’ the origin and evolution of CO₂. Coupling hydrothermal carbonate core analyses as shown here with CO₂ ‘soil’ gas measurements collected at the surface provides our next step for geothermal exploration and for improving success in identifying blind geothermal systems at the University of Canterbury and with support from Mighty River Power.

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