FINGERPRINTING THE TEMPERATURE AND FLUID SOURCE OF CALCITE IN GEOTHERMAL SYSTEMS USING CLUMPED ISOTOPES

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ABSTRACT

Geothermal exploration relies on locating sufficient permeability and high temperature. Traditionally, minerals can be used to map the thermal structure of paleo or active geothermal systems via temperature dependent hydrothermal mineral deposition (e.g., smectite→illite-smectite→illite) or methods such as fluid inclusion microthermometry.

Clumped isotopes offer a new way of characterising the temperature and fluid source from which calcite is deposited. This technique is based on the thermodynamic relationship between carbonate mineral growth temperature and the abundance of chemical bonding (“clumping”) between ^{13}C and ^{18}O isotopes (expressed as Δ_{47}) within single carbonate ions. In the gas phase, isotopic exchange between CO_2 molecules and water is continuous (e.g., Eiler, 2007) and so CO_2 gas will record the ambient fluid temperature. When the CO_2 is trapped in a solid mineral phase, the isotope ratio is fixed. Thus, clumped isotopes will record the temperature of crystallisation, enabling the application of clumped isotope paleothermometry to a range of geological problems (e.g., Dale et al., 2010; Huntington et al., 2010; Henkes et al., 2013; MacDonald et al. 2015).

As a geothermal test case in New Zealand, samples from the Kawerau Geothermal Field have been analysed for clumped isotopes. The selected samples have been previously constrained with fluid inclusion and stable isotopes analyses. We present petrography, $\delta^{13}C$ and $\delta^{18}O$, fluid inclusion temperatures, and clumped isotope data to show how clumped isotopes can fingerprint the temperature and fluid source of calcite in geothermal systems.

1. INTRODUCTION

Thermal gradients and permeability, and their change over time are important factors to monitor during the utilisation of a geothermal system. Migration, or cooling of heat sources can occur, and permeability can be modified due to precipitation of secondary minerals. Both of these would influence well targeting for power developments.

Temperature and permeability dependent mineral deposition can be used as an indication of downhole conditions (Browne, 1978), but unless there is clear

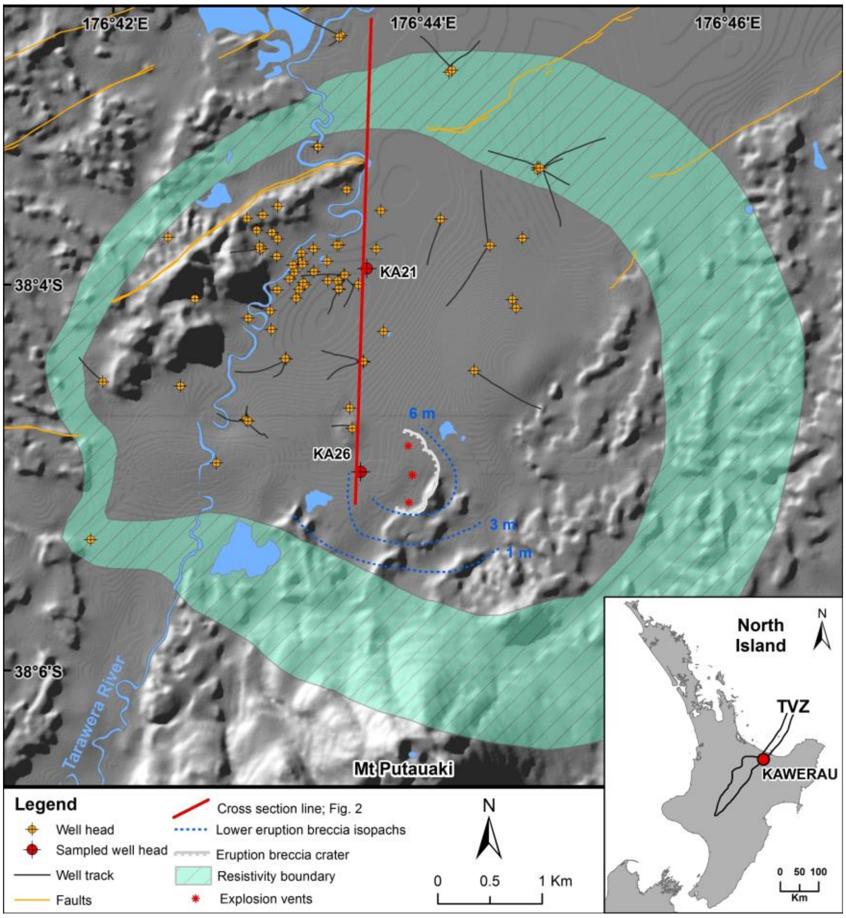

Figure 1: Digital terrain map for the Kawerau area, with locations of wells in the geothermal system. The approximate resistivity boundary zone at about 500 m depth (after Allis, 1997) is shown, along with active faults (Langridge et al., 2016). Inset: locality map for the Taupo Volcanic Zone (TVZ; Wilson et al., 1995).

overprinting of mineral assemblages, changes in temperature can be difficult to determine. A typical example of temperature dependent minerals, is the transition of hydrothermal clays from smectite → illite-smectite (<200ºC) →illite (>220ºC), typically with increasing depth/temperature (Browne, 1978). Analytical techniques such as fluid inclusion microthermometry and stable isotope measurements can give a more accurate idea of temperatures and fluid chemistry at the time of hydrothermal mineral deposition. Although the translation of measured $\delta^{13}C$ and $\delta^{18}O$ into calculated fluid composition requires temperature, which you have to assume from either fluid inclusion temperatures or current well temperatures. Recent advances in stable isotope instrumentation mean it is now possible to measure rare isotopologues and allowed the development of the 'clumped isotope' technique.

Here we present background on the clumped isotope technique and a case study trialing this in the Kawerau Geothermal Field (Fig. 1).

2. CLUMPED ISOTOPES

Clumped isotope palaeothermometry is based on the temperature dependence of bonding between heavy isotopes, e.g. ^{13}C and ^{18}O - in a molecule of CO2. There are numerous arrangements of isotopes of carbon (^{12}C, ^{13}C, ^{14}C) and oxygen (^{16}O, ^{17}O, ^{18}O) (Eiler, 2007) in CO_2 molecules – known as "isotopologues" – but $^{13}C^{18}O^{16}O$ is by far the most abundant (~97%; Huntington et al., 2009) of the isotopologues which has a bond between two heavy isotopes. Therefore, measurement of the abundance of molecules of mass 47 (13+18+16) in a volume of CO_2, enables the temperature at which isotope exchange between molecules last occurred in that CO_2 volume to be calculated. This relationship is independent of pressure.

In a solid carbonate mineral, such as calcite, isotope exchange was last possible at the point of crystallisation, therefore the abundance of mass 47 CO_2 in calcite will 'lock in' the temperature of crystallisation. CO_2 is regenerated from calcite by acid digestion in phosphoric acid – a standard procedure for isotopic analysis of solid carbonate (McCrea, 1950). The produced CO_2 is purified by well-established procedures (e.g., Huntington et al., 2009; Dennis & Schrag, 2010; Dale et al., 2014). Measurement of CO_2 molecular masses is made on a modified Thermo MAT253 mass spectrometer focussed on masses 44 through 49. From this, the deviation in abundance of mass 47 CO_2 of the analyte from the thermodynamically-derived expected abundance of mass 47 in a volume of CO_2 with a random arrangement of bonds can be calculated (e.g., Eiler & Schauble, 2004; Wang et al., 2004; Schauble et al., 2006; Huntington et al., 2009; Dennis et al., 2011). This deviation, expressed as Δ_{47} (measured in permil, ‰) is derived from isotopic ratios referenced to a gas of nominally known isotopic composition (Huntington et al., 2009).

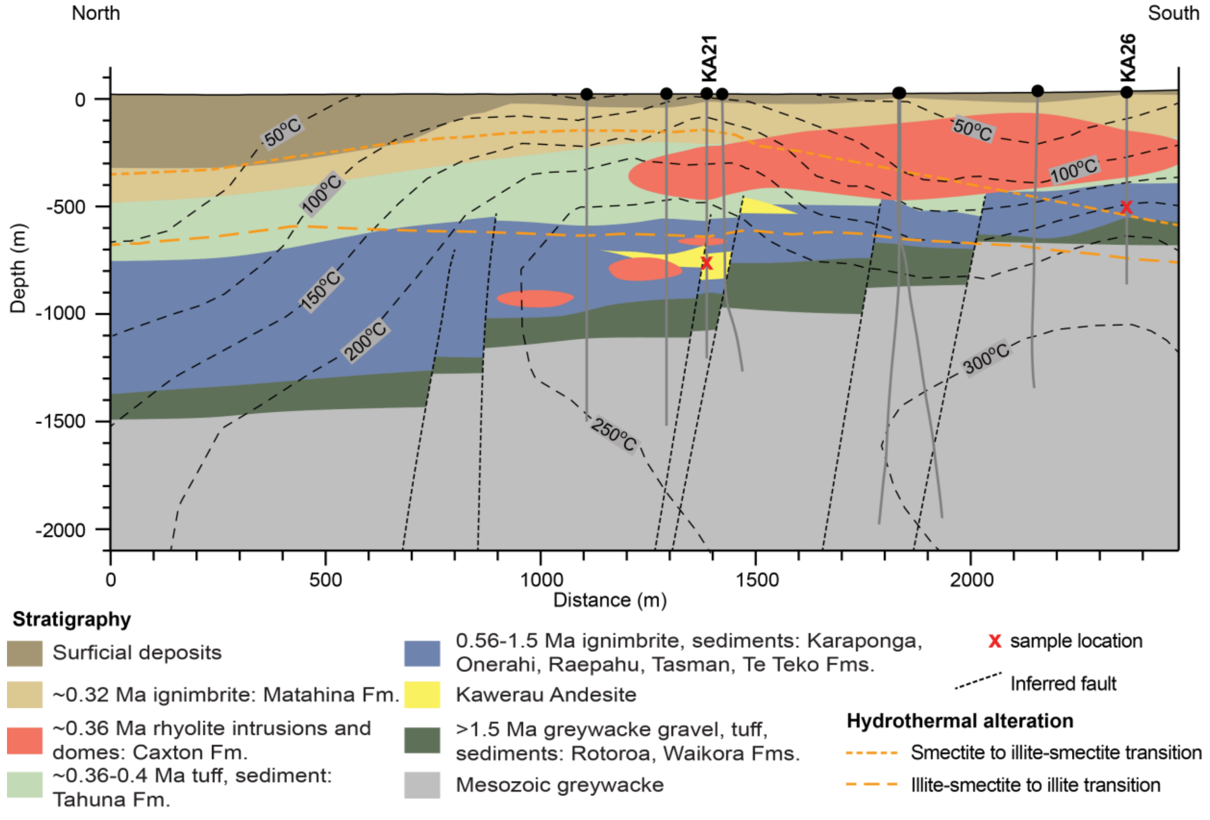

Figure 2: Simplified geological cross section along the line in Fig. 1 showing lithological units overlain by key hydrothermal alteration minerals and alteration assemblages and temperature isotherms. First appearance isograds represent the current geothermal hydrothermal alteration mineralogy, along with crystallisation of calcite and epidote throughout the field. Clay occurrences with depth are based on oriented clay separated x-ray diffraction analysis.

Standard correction procedures for acid fractionation of carbonate ions, mass spectrometer non-linearity and individual laboratory protocols enable Δ_{47} values to be reported in a universal reference frame (Dennis et al., 2011). An empirically derived calibration is required to convert Δ_{47} values to temperature. This involves measuring Δ_{47} in carbonates grown at different temperatures under controlled conditions. In low temperature biogenic carbonates, there is still considerable debate over the reliability and potential species-specificity of calibration curves (e.g., Tripati et al., 2010; Thiagarajan et al., 2011; Zaarur et al., 2011; Grauel et al., 2013; Henkes et al., 2013). However, for the high-temperature inorganic carbonates in geothermal systems, we have the benefit of the recent experimentally-derived calibration curve of Kluge et al. (2015) which goes up to 250 °C, in the range of temperatures expected for geothermal fluids.

A potential complication for high temperature carbonates (>100 °C) is the possibility of post-precipitation solid-state reordering of the bonds between the atoms in the carbonate lattice. Experimental work has suggested that ambient temperatures of >100 °C for millions of years leads to solid-state diffusion of the isotopic bonding which is the basis for the palaeothermometer (e.g., Henkes et al., 2014). If this bond reordering occurs, temperatures of geologically-meaningful events may be overprinted. The higher the ambient temperature, the less time is required to initiate bond reordering. However, given the likely rapidity of precipitation of fracture-filling calcite in geothermal systems, and its relatively recent timing in active geothermal systems, this bond reordering should not be an issue in the geothermal systems of interest.

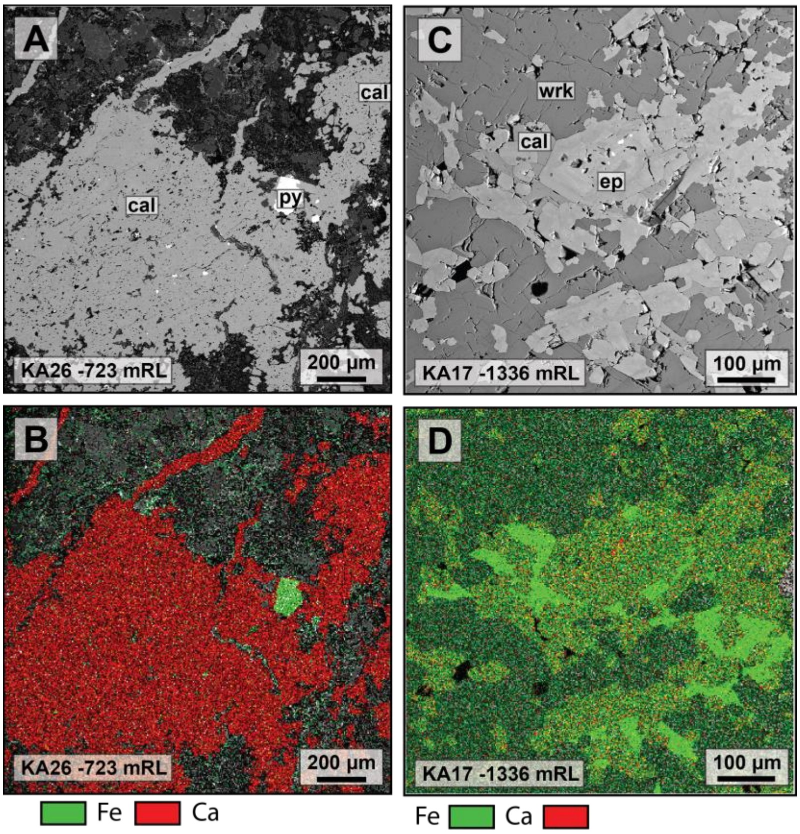

Figure 3: (A) Well KA26, -723 mRL; electron backscatter images of calcite hydrofracture vein fill cutting greywacke with accessory pyrite (py); (B) Well KA26, -723 mRL; element map highlighting mineral distribution. (C) Well KA17, -1336 mRL; (A) electron backscatter images of a vein cutting greywacke with intergrown wairakite (wrk), epidote (ep), calcite (cal) and adularia (ad); (D) Well KA17, -1336 mRL; element map highlighting mineral distribution.

3. KAWERAU GEOTHERMAL FIELD: CASE STUDY

The Kawerau Geothermal Field (Fig. 1) is the most northeasterly of high-temperature (>200 °C) geothermal systems in the Taupo Volcanic Zone (TVZ, New Zealand). The reservoir rocks consist of a ~1 km thick pile of lava, pyroclastic rocks and sediments, with fluid circulating through faulted Mesozoic basement greywacke (Fig. 2). Correlation by petrographic observations and U-Pb age determinations provide estimates of crystallisation and eruption ages (Milicich et al., 2013a) that allow depositional histories of rocks hosting the geothermal system to be reconstructed (Milicich et al., 2013b). Due to the well constrained geological framework hosting the hydrothermal system, thermal and chemical evolution of the hydrothermal system can be linked to specific periods of magmatic activity (Milicich et al., in prep).

Three distinct alteration assemblages can be identified (Absar and Blattner, 1985), from oldest to youngest: 1) wairakite – prehnite, 2) massive calcite (Fig. 3A,B) and 3) present-day calcite – epidote (Fig. 3C,D). All would have been in equilibrium with near neutral chloride fluids and varying CO_2 concentrations. The calcite associated with these assemblages has been analysed by fluid inclusion microthermometry, stable isotope analysis, and scanning electron microscopy and electron dispersive spectroscopy (Milicich et al., in prep), providing an opportunity to assess the accuracy of clumped isotope analysis in a high-temperature geothermal environment.

For clumped isotope analysis, a sample was selected from the massive calcite assemblage (KA26, -518 mRL) and the calcite – epidote assemblage (KA21; -733 mRL). These two assemblages are inferred to be associated with the modern system, though at two different stages. The modern system was initiated at ~16 ka, with hydrothermal eruptions linked to shallow intrusion of magma at the onset of activity that gave rise to the Putauaki andesite cone. Associated with this was a pulse of magmatic CO_2, resulting in large scale deposition of hydrothermal calcite enriched in ^{18}O. Meteoric water-dominated fluids subsequently overwhelmed the magmatic fluids associated with this ^{18}O-rich signature, and reflects a change to the present-day fluid from which the calcite-epidote assemblage precipitated.

The location of the selected calcite samples in relation to the stratigraphy and current isotherms is presented in Figure 2. The analytical data for these two samples is collated in Table 1, with the full data in Milicich et al (in prep).

Table 1: Analysis of Kawerau hydrothermal calcite.

Well	Depth	Depth	$\delta^{18}O_{VSMOW}$	Fluid inclusions (°C)		$\delta^{18}O_{H2O}$	$\delta^{18}O_{VSMOW}$	Clumped	$\delta^{18}O_{H2O}$	Alteration
	mD	mRL	(‰)	T_h range (n)	T_m range	(‰)	(‰)	isotopes (°C)	(‰)	event
KA21	759	-733	3.63	275 to 342 (26)	-0.3 to -0.5	3.2 to 6.8	3.6	335±6	6.4±0.3	Massive calcite
KA26	540	-518	8.41	240 to 293 (10)	-0.2 to -0.8	5.7 to 9.0	8.4	353±62	12.1±2.6	Calcite - epidote

Depth: mD = measured depth in meters; mRL = depth relative to sea level in meters. Temperature range (±10°C) from primary fluid inclusion data. Fluid inclusion temperatures and clumped isotope temperatures were used to calculate $\delta^{18}O_{H2O}$ in equilibrium with Kawerau hydrothermal calcite (Kim & O'Neil et al., 1997).

3.1 Fluid inclusion microthermometry

Fluid inclusions were analysed per the fluid inclusion assemblage (FIA) approach of Goldstein and Reynolds (1994). The two calcite samples were a platy, bladed form. The inclusions mimic the basal pinacoid form and lie coplanar within their host crystal, indicating that the inclusions are primary in origin (Simmons and Christenson, 1994). Thermal profiles in geothermal wells are limited by the boiling point for depth (BPD) curve (Grant and Bixley, 2011) appropriate to the relevant fluid composition (i.e., reflecting the salinity and gas content). Due to this limitation, fluids in inclusions often follow the BPD conditions at the time of entrapment, and this is the case the two samples analysed here (Fig. 4). Disequilibrium is most apparent in secondary inclusions (Fig. 4), with the most likely causes to be boiling and/or mixing with marginal waters (Reed and Spycher, 1984, Hedenquist and Browne, 1989, Hedenquist, 1990). Primary fluid inclusion homogenisation temperatures are close to the BPD curve for a 3.7 wt.% CO_2 fluid and interpreted natural state temperature (Fig. 4), and indicate a general thermal stability since the fluid inclusions were formed.

An exception to thermal stability is a high–temperature FIA (relative to BPD curves) recorded in platy calcite from both KA21 and KA26 (Fig. 5). In KA21 at -733 mRL the mean T_h value for the high-temperature FIA is 326 °C and in KA26 at -518 mRL it is 270 °C. The anomalous FIA are likely due to a transient perturbation in the system, and clearly does not relate to current conditions. Possibilities for this perturbation could be a fault rupture allowing a pulse of hot, deep fluid, shallower into the reservoir or represent boiling related to the depressurisation. Alternatively, the heat pulse could be related to intrusion of magma at depth. As platy calcite is inferred to form in boiling conditions as two-phase fluids exsolve CO_2 (Simmons and Christenson, 1994), the higher temperature FIA are likely to reflect variation in temperature during the boiling process.

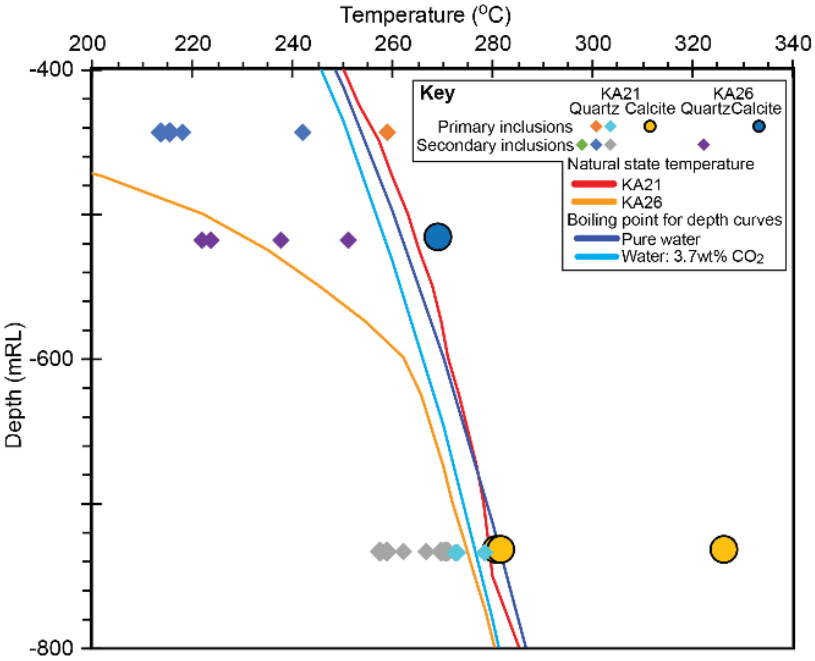

Figure 4: Fluid inclusion results from KA21 and KA26. Each data point represents the mean T_h of a FIA.

3.2 Stable isotopes

Calcite $\delta^{18}O$ values are 3.6 ‰ for KA21 and 8.4 ‰ for KA26. Using the range of temperatures from primary fluid inclusions, the isotopic values of the fluids in equilibrium with the hydrothermal calcite have been calculated using the fractionation factors from O'Neil et al. (1969). The fluid in equilibrium with calcite has oxygen isotope values between -2.8 to -0.9 ‰ for KA21 and 0.7 to 2.6 ‰ for KA26.

The sample from KA26 highlights an enrichment of ^{18}O, inferred to reflect magma degassing and primary neutralisation (Giggenbach, 1981) related to the initiation and growth of the Putauaki magmatic system. The heavy $\delta^{18}O$ values are associated with the massive calcite event and inferred to be deposited during a large hydrofracturing event (Christenson, 1987).

3.3 Clumped isotopes

Calcite $\delta^{18}O$ SMOW values obtained on the same volume of calcite used for the clumped isotope measurements were 3.6 ‰ for KA21 and 8.4 ‰ for KA26. Temperature of precipitation of calcite measure by clumped isotope analysis is 335±6 °C for KA21 -733 mRL and 353±62 °C for KA26 -518 mRL.

Using the range of temperatures indicated by clumped isotopes, the isotopic values of the fluids in equilibrium with the hydrothermal calcite have been calculated using the fractionation factors from Kim and

O'Neil (1997). The fluid in equilibrium with calcite has oxygen isotope values of 6.4±0.3‰ for KA21 and 12.1±2.6‰ for KA26 (Table 1).

3.4 Case study discussion

We have a mixed result from this pilot study. The KA21 -733 mRL clumped isotope temperature fits well with the observed high-temperature FIA, 335 ºC vs 326 ºC respectively. This would indicate that the high-temperature indicated by the FIA reflects either hotter reservoir temperatures at some point in the past, or a transient temperature fluctuation. The fluid inclusion measurement for this sample is precise (±6 °C), and relative to indications from fluid inclusion temperature, accurate.

The KA26 -518 mRL clumped isotope temperature of 353 ºC is much hotter than any temperatures observed in fluid inclusion measurements (highest was 293 ºC). Given the lower precision of this measurement (±62 °C), there is still an overlap of the clumped isotope temperature with the highest of the fluid inclusion measurements.

Another possibility is there was decrepitation of many of the fluid inclusions during measurement of the KA26 sample. This occurred as heating measurements were taken over 300 °C, which could mean that a higher temperature fluid inclusion assemblage was missed.

4. SUMMARY

The clumped isotope technique allows an independent method of assessing temperature of precipitation and chemistry of geothermal fluids. While much work on this technique has addressed the potential for palaeoclimate studies, the application of clumped isotope geochemistry at higher temperatures has been less studied. Kluge et al., (2015) have shown that calcite precipitation from solutions up to 250 °C, under equilibrium conditions, results in clumped isotope distributions consistent with thermodynamic predictions based on temperature. While this a limited pilot study, there appears to be potential in application of this technique in the high-temperature geothermal setting. Future work would widen this study to a number of geothermal areas well constrained by previous fluid inclusion and stable isotope studies. Further investigations will assess how robust this technique is at temperatures >200 °C.

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