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TAKING THE TEMPERATURE OF HYDROTHERMAL ORE DEPOSITS USING CLUMPED ISOTOPE THERMOMETRY

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Abstract

Better tools are needed to map the thermal structure of ore deposits. Here, carbonate clumped isotope thermometry is applied for the first time in epithermal, skarn, and carbonate-hosted deposits to identify the conditions involved in metal transport and deposition. Clumped isotope temperature calibrations were tested by measurement of carbonates from three geothermal fields in the Taupo volcanic zone, New Zealand, that record growth temperatures between 130° and 310°C. Results for modern Taupo volcanic zone calcites were paired with known fluid $\delta^{18}O$ values and these indicate precipitation in equilibrium with produced geothermal waters. Measurements carried out at the Waihi low sulfidation deposit in New Zealand, the Antamina polymetallic skarn in Peru, and the Mount Isa sediment hosted Pb-Zn and Cu deposit in Queensland, Australia, demonstrate that clumped isotope values are sensitive to temperature gradients defined using other methods. At Waihi, an andesite-hosted deposit, temperature controls the majority of variation in carbonate mineral $\delta^{18}O$. At Mount Isa, ~300° to 400°C temperatures were recorded in a 1.5 Ga orebody, which are consistent with fluid inclusion values, highlighting the longevity of clumped isotope archives in dolomite minerals. Collectively, these results demonstrate the potential for clumped isotopes to delineate the heat footprint around deposits that contain carbonates, and to more effectively disentangle magmatic and meteoric fluid $\delta^{18}O$ signals.

Introduction

Advection in the upper crust derives from fluid circulation in hydrothermal systems, which are associated with magmatic intrusions and the formation of hydrothermal ore deposits. In ore-forming systems, hydrothermal solutions attain metals at depth, then rise through buoyancy to deposit economic minerals where pressure and temperature decrease (e.g., epithermal), or in response to fluid-rock interaction (e.g., skarn). Accurate reconstructions of fluid temperature in hydrothermal systems are applied to delineate thermal gradients, which drive metal uptake, transport, and deposition. The resulting understanding of thermal structure, exemplified in Figure 1, underpins development of ore deposit models used in mineral exploration programs (e.g., Heinrich et al., 1996; Ferry and Gerdes, 1998).

There are shortcomings to virtually all techniques that are applied to reconstruct temperature in ore deposits. The interpretation of fluid inclusion homogenization thermometry (T_h) is complicated in cases in which inclusions are absent or are not primary (e.g., many epithermal deposits, Carlin-type sediment hosted Au), and accurate temperature interpretations of fluid inclusions require definition of the pressure (i.e., depth) of formation (Roedder, 1984). Although demonstrably useful, mineral pair isotope thermometers often reflect neither the conditions of crystallization nor closure temperature, and require the assumption that mineral phases precipitate in equilibrium, which is often difficult to prove (e.g., Giletti, 1986).

Carbonate clumped isotope thermometry, which quantifies the thermodynamically dependent abundance of ^{13}C-^{18}O bonds, expressed as Δ_{47}, has the potential to accurately determine the temperature at which hydrothermal carbonates

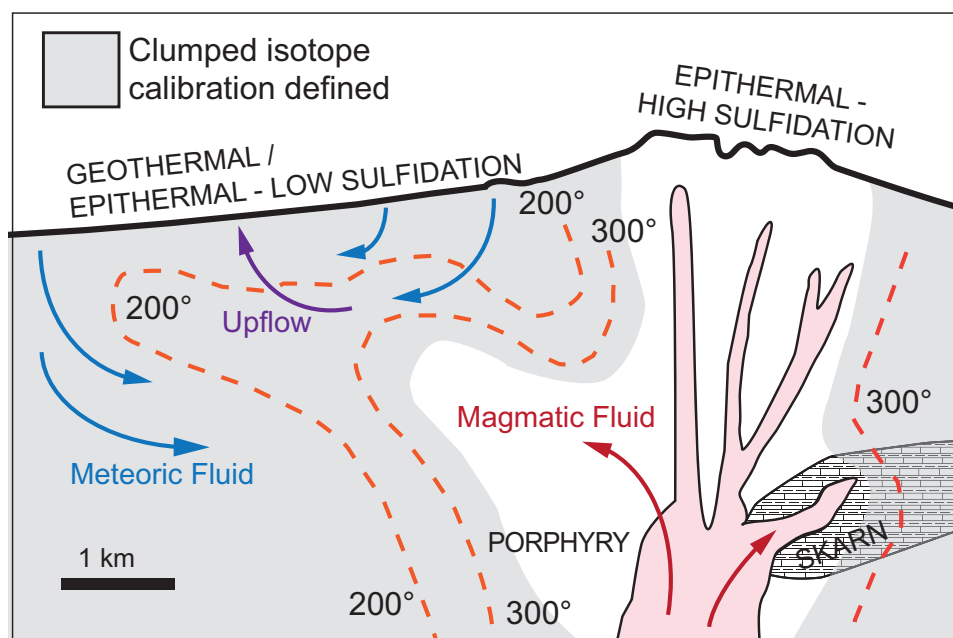† Corresponding author: e-mail, johnmering@gmail.com

Fig. 1. Schematic of convective fluid flow based upon the porphyry- and vein-controlled Au-Ag deposit model presented in Hedenquist and Lowenstern (1994). Hydrothermal mineral deposits occur near hot zones, and temperature decreases significantly, moving away from orebodies to reflect the local geotherm. Epithermal (e.g., Waihi) and geothermal (e.g., Taupo volcanic zone) systems occur at temperatures below 300°C, while porphyry deposits occur at greater depths, in association with intrusions. Skarns (e.g., Antamina) develop where magma intrudes carbonate host rock. Recent developments in clumped isotope methodology extend the range of calibrations up to 350°C, which is suitable for hydrothermal ore deposit investigations.

form. With this approach, analyses may be carried out on a single carbonate mineral without constraints on the oxygen isotope signature of mineralizing fluid (e.g., Eiler, 2007; Huntington et al., 2011). Clumped isotopes consequently have the potential to separate the effects of temperature and $\delta^{18}O_{water}$ on $\delta^{18}O_{mineral}$ composition, and more precisely characterize the range of aqueous fluids involved in ore genesis (Dennis et al., 2018). Within deposits, $\delta^{18}O$ inputs range from –20 to as high as 0‰ Vienna Standard Mean Ocean Water (VSMOW) for meteoric waters, while basinal brines and primary magmatic water range from 5 to 10‰ VSMOW, and metamorphic waters are enriched up to 30‰ VSMOW (e.g., Giggenbach, 1992; Kesler et al., 1997).

Over the last decade, clumped isotopes have been applied extensively to sedimentary and biogenic carbonates to address paleoclimate and paleoceanographic questions (Eiler, 2011; Douglas et al., 2014), and to reconstruct uplift histories (e.g., Huntington et al., 2010; Lechler et al., 2013). In the subsurface, clumped isotopes have been utilized to understand diagenesis (e.g., Dennis and Schrag, 2010), and to describe the movement of fluids through fault zones (e.g., Bergman et al., 2013; Luetkemeyer et al., 2016). Recent work has taken up the challenge of assessing the application potential for Δ_{47} to reliably elucidate temperatures in hydrothermal environments (e.g., Lloyd et al., 2017; Lu et al., 2017; Honlet et al., 2018). New carbonate growth experiments have expanded lab calibration datasets to between 250° (Kluge et al., 2015) and 350°C (Bonifacie et al., 2017). In Mississippi Valley-type (MVT) deposits clumped isotopes have been used to identify fluid source at temperatures between 40° and 100°C (Dennis et al., 2018).

In this study, carbonate clumped isotope thermometry (Δ_{47}) is applied in modern geothermal fields, representative of low sulfidation mineralization, and a range of ancient ore-forming settings. Measurements were carried out on scaling and ejecta calcite samples from geothermal wells at the Broadlands-Ohaaki, Ngatamariki, and Wairakei fields, within the Taupo volcanic zone. The geothermal calcites measured have established formation temperatures between 130° and 310°C, based on T_h results and direct measurements of well fluid (Fig. 2). The Taupo volcanic zone serves as a world-class laboratory for understanding metal transport in hydrothermal environments, with high fluxes of Au, Ag, Cu, Pb, Te, and Zn reported in geothermal fields (Rowland and Simmons, 2012; Simmons et al., 2016). Measurements were also carried out on vein and propylitic calcite at Waihi, a giant low sulfidation deposit (~8 Moz Au, 40 Moz Ag historic production), which formed during the upper Miocene within the Coromandel volcanic arc, North Island, New Zealand (e.g., Brathwaite and Faure, 2002; Christie et al., 2007) and in two ore deposits where temperatures of mineralization exceed 300°C. These high-temperature case studies include the Antamina Cu-Zn polymetallic skarn (561 Mt Cu), Western Cordillera, Peru (Escalante et al., 2010), which formed ~10 Ma, and Mount Isa, a 1.5 Ga globally significant sediment-hosted base metal deposit (Pb-Zn-Ag and Cu) in northwest Queensland, Australia (Heinrich et al., 1989; Hannan et al., 1993). Sites are described in more detail online, in Appendix 1.

Methods

Modern geothermal samples were analyzed from wells with known temperature and hydrologic conditions (Simmons and
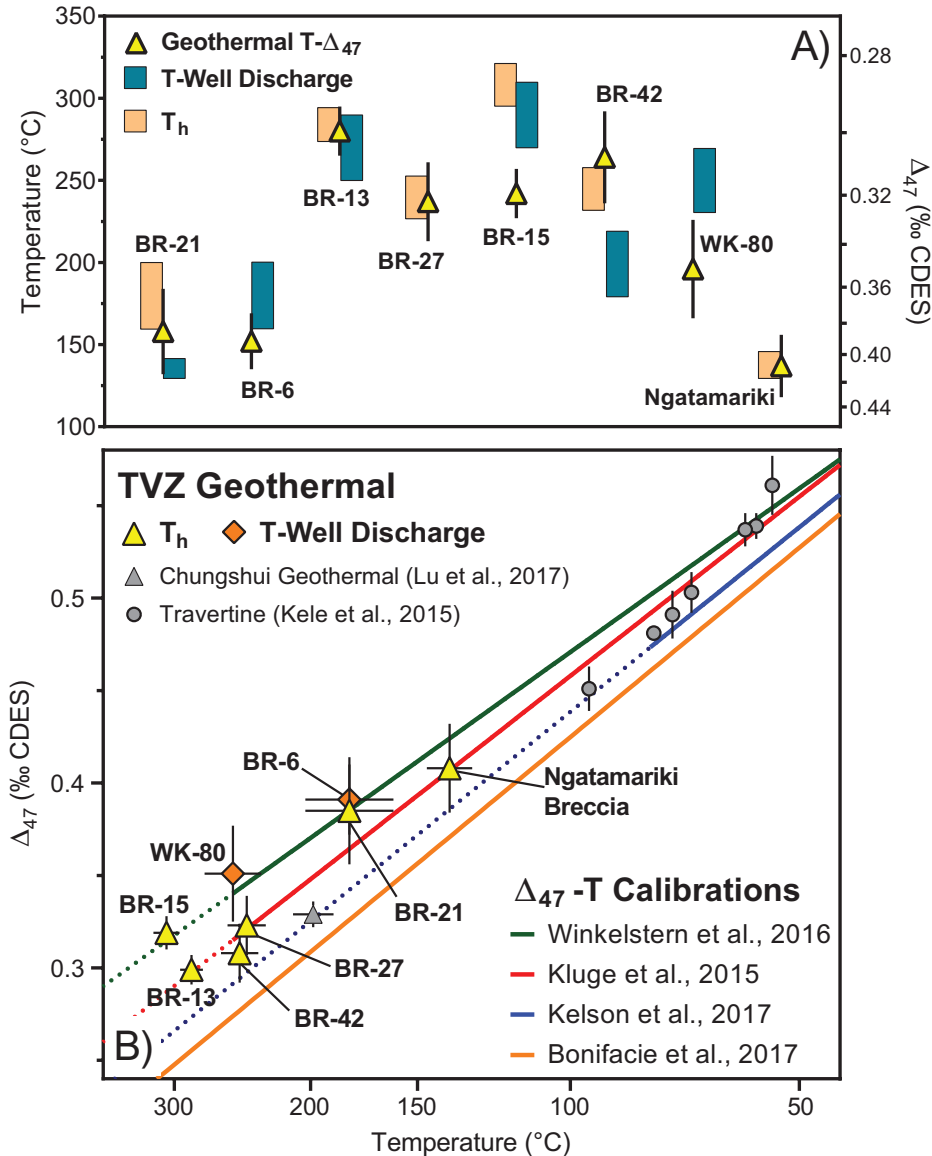
Fig. 2. A. Geothermal sample clumped isotope results compared to temperature constraints from T_h and well fluid discharge measurements. Samples are sourced from three geothermal fields: Wairakei (WK-80), Broadlands-Ohaaki (BR-6, 13, 15, 21, 27, 42), and Ngatamariki (breccia). Discharge temperatures that are below clumped isotope and fluid inclusion constraints for carbonates, reflect diminishing enthalpy over the lifecycle of the geothermal field. B. Taupo volcanic zone (TVZ) geothermal calcite growth temperatures plotted against clumped isotope values (Δ_{47}). For comparison, four calibration relationships are shown along with previously reported results for seven modern hot spring travertines (Kele et al., 2015) and a geothermal calcite (Lu et al., 2017). For calibrations, solid lines indicate the temperature range bounded by samples, while dashed lines are extrapolations.

Christenson, 1994; Christenson et al., 2002; Simpson et al., 2014). Samples from Waihi, Antamina, and Mount Isa were collected within alteration haloes near orebodies. Carbonate was extracted from veins using a microdrill, operated at low speed. Calcite scale samples from geothermal wells were powdered using an agate mortar and pestle. Samples containing 6 to 8 mg of calcite or dolomite were reacted in a 90°C phosphoric acid bath, cryogenically purified on a custom built vacuum line, and analyzed on a Thermo MAT 253 isotope ratio mass spectrometer (IRMS) at the University of Washington following methodology described in Burgener et al. (2016) and Schauer et al. (2016). Carbonate and CO_2 gas standards were analyzed daily.

Carbonate $\delta^{13}C$ values are referenced to Vienna Pee Dee Belemnite (VPDB), and $\delta^{18}O$ measurements of carbonate, and calculated aqueous fluid values, are reported relative to VSMOW (Coplen, 1988). Clumped isotope values (Δ_{47}) are normalized to the Absolute Reference Frame (Dennis et al., 2011), also known as the carbon dioxide equilibrium scale (CDES).

The CDES-corrected Δ_{47} values are converted to temperature using the Kluge et al. (2015) relationship recalculated using Brand et al. (2010) ^{17}O correction parameters. This is the only high-temperature (constrained between 25° and 250°C) carbonate calibration that we can confirm is appropriate for our samples based on agreement of Δ_{47} values for

multiple carbonate standards (ETH-1, ETH-2, ETH-3 and ETH-4; Bernasconi et al., 2018) analyzed at the University of Washington and at the Imperial College London laboratory in which the Kluge et al. (2015) calibration data were produced. The Kluge et al. (2015) relationship also agrees with the University of Washington calibration of Kelson et al. (2017) in the temperature range for which the latter is constrained (4°–85°C). Uncertainties of Δ_{47} results are reported to 1 standard error (1 s.e.) of the average of a set of replicate measurements. Mount Isa samples, which were run as single replicates, are reported with an estimated uncertainty based upon the long-term 1 s.e. for a high-temperature carbonate standard (ETH-1) analyzed at the University of Washington. The calculated $\delta^{18}O$ values of aqueous fluid associated with calcite precipitation are reported using the fractionation factor (α) presented in Kim and O'Neil (1997), while $\delta^{18}O$ fluid values for dolomite at Mount Isa are reported using the relationship presented in Horita (2014).

Results

Isotope results, temperatures, and calculated $\delta^{18}O$ fluid values are presented in Figures 2 through 4 and in the online Tables (Appendix 2). Clumped isotope values for modern Taupo volcanic zone geothermal calcites (scale and ejecta), with known formation temperatures between 130° and 310°C, range from 0.408 ± 0.024 (Ngatamariki) to 0.299 ± 0.008‰ CDES (BR-13-866); these overlap with established thermometer calibrations, as shown in Figure 2. Applying the Kluge et al. (2015) calibration, Taupo volcanic zone geothermal calcite clumped isotope temperatures are between $137^{+20°}_{-17}$ and $280^{+17°}_{-15}$C (Fig. 2). Fluid $\delta^{18}O$ values calculated from carbonate oxygen isotopic values and clumped isotope temperatures range from –4.6 to 2.5‰ VSMOW (Figs. 3, 4).

Vein and replacement calcite at Waihi record Δ_{47} values between 0.373 ± 0.045 and 0.536 ± 0.014‰ CDES. The calibrated temperatures for calcite veins near the principal Martha orebody are between $160^{+13°}_{-12}$ and $170^{+58°}_{-41}$C, while clumped isotope temperatures of propylitic carbonate from this area are $116^{+10°}_{-9}$ to $174^{+34°}_{-28}$C (Figs. 3–4). Veins ~1 km northwest of the orebody record cooler Δ_{47} temperatures of $58^{+7°}_{-6}$ to $124^{+22°}_{-19}$C. Calculated fluid $\delta^{18}O$ values range from –3.9 to –9.8‰ VSMOW.

Samples measured at Antamina include a marble at the skarn contact with a Δ_{47} value of 0.283 ± 0.027‰ CDES, and six carbonate replacement deposit (CRD) sulfide-bearing veins, collected ~300 m to 2 km from the intrusion, with values ranging from 0.361 ± 0.034 to 0.423 ± 0.044‰ CDES (Figs. 3, 4). Vein samples formed from cooler fluids outside the thermal front, at temperatures of $125^{+39°}_{-30}$ to $183^{+46°}_{-35}$C (Fig. 3). The marble (2PAG172) records an apparent equilibrium clumped isotope temperature of $317^{+82°}_{-58}$C, while retaining a sedimentary carbonate $\delta^{18}O$ value of 24.3‰ VSMOW. The marble temperature reflects reordering of ^{13}C-^{18}O bonds during cooling from higher peak metamorphic temperatures associated with the intrusion (e.g., Dennis and Schrag, 2010; Lloyd et al., 2017).

Dolomite vein samples from the northern and southern ends of the Cu orebodies at Mount Isa record Δ_{47} values of 0.291 ± 0.012 to 0.257 ± 0.012‰ CDES, corresponding with temperatures between $297^{+29°}_{-25}$ and $397^{+48°}_{-40}$C (Figs. 3, 4). Notably, the T-Δ_{47} record at Mount Isa overlaps previously determined temperature estimates for the orebody (~250°–350 °C) from fluid inclusion homogenization and quartz-chlorite $\delta^{18}O$ thermometry (Heinrich et al., 1989; Hannan et al., 1993). We therefore interpret the record at Mount Isa to reflect the temperature of Cu mineralization, postpeak metamorphism, rather than apparent equilibrium temperatures reflective of the vein cooling history. These results suggest that preservation of high-temperature clumped isotope signals is possible over long (1.5 Ga) timescales.

Discussion

Carbonate clumped isotope thermometry enables more sensitive mapping of thermal signatures around orebodies, at
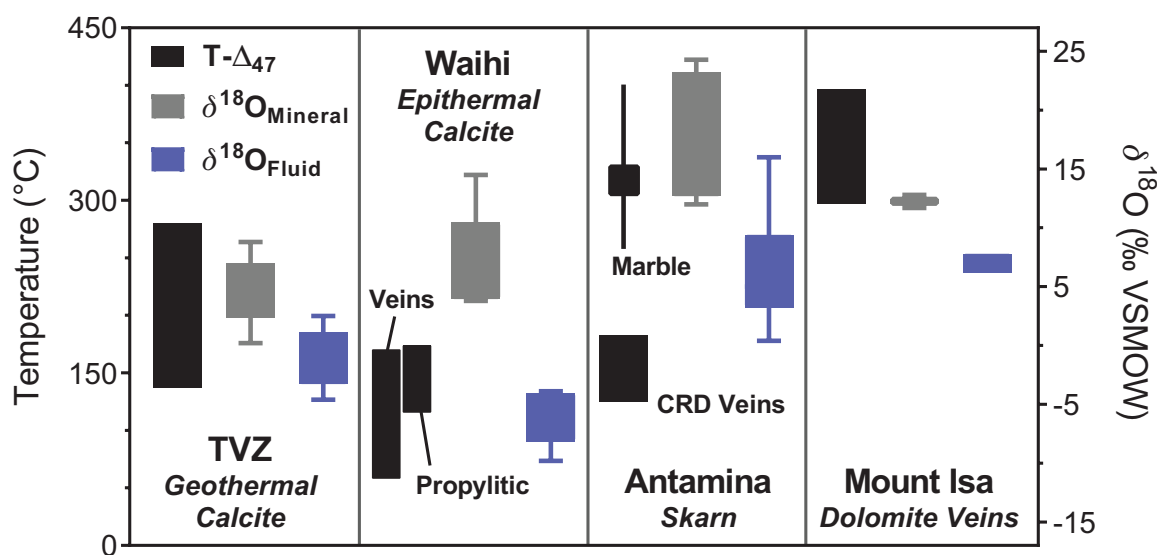

Fig. 3. Results for Taupo volcanic zone (TVZ) geothermal fields and three ore deposits assessed. Clumped isotope temperatures, reconstructed using the Kluge et al. (2015) calibration, were combined with mineral $\delta^{18}O$ values to reconstruct the $\delta^{18}O$ signatures of aqueous fluid.
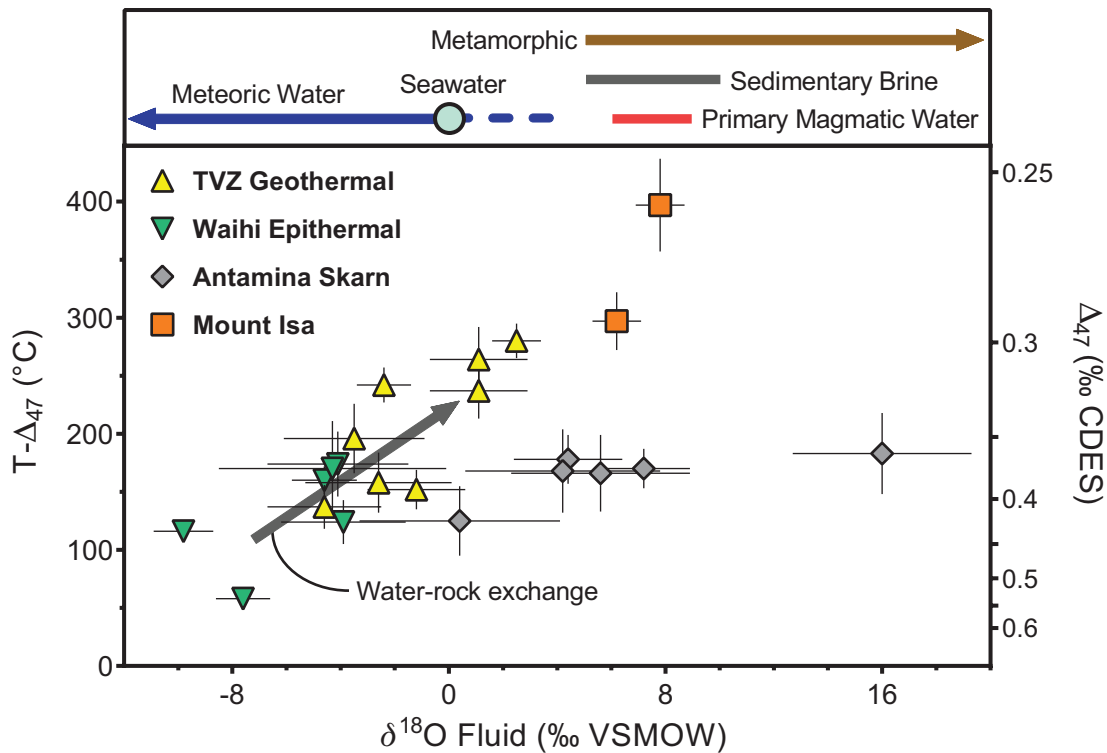
Fig. 4. Calculated fluid $\delta^{18}O$ plotted against calibrated temperatures (left vertical axis) and Δ_{47} values (right vertical axis) for geothermal and ore deposit samples. The apparent enrichment of aqueous fluid $\delta^{18}O$ observed for geothermal samples forming above 200°C is consistent with limited modification of meteoric water by exchange with host rock. Temperatures were calibrated using the Kluge et al. (2015) relationship. The $\delta^{18}O$ values of aqueous fluids were determined using fractionation factors for calcite-water (Kim and O'Neil, 1997) and dolomite-water (Horita, 2014). The isotope value ranges for terrestrial fluids reservoirs are from Giggenbach (1992) and Kesler et al. (1997). TVZ = Taupo volcanic zone.

temperatures up to 350°C (Fig. 1). The temperatures calculated using the Kluge et al. (2015) calibration are most consistent with direct temperature and fluid inclusion homogenization measurements for the set of modern Taupo volcanic zone geothermal carbonates (Fig. 2). The geothermal results indicate that clumped isotope signatures reflect equilibrium conditions (Appendix 1), such that temperatures and mineral $\delta^{18}O$ can be combined to reconstruct fluid history in ore deposits (Figs. 3, 4). The calculated fluid $\delta^{18}O$ for Taupo volcanic zone carbonates (–4.6 to 2.5‰ VSMOW) indicates moderate enrichment in ^{18}O for several high-temperature samples relative to local groundwater (–4.5‰ VSMOW), implicating fluid-rock reaction and/or some minor input of magmatic water in deep fluids (Simmons and Christenson, 1994; Dempsey et al., 2012).

Small offsets between well discharge fluid temperature, T_h, and T-Δ_{47} in geothermal samples are not unexpected (Fig. 2). Prior work at Broadlands-Ohaaki indicates that fluid inclusion homogenization measurements vary by ~20°C within individual calcite crystals (Simmons and Christenson, 1994). Direct measurements of fluid temperature that postdate carbonate growth may be lower than clumped isotope and T_h values (samples Br-21, Br-42), reflecting loss of enthalpy over the production life cycle of the well field. Notably, one deep scale sample from Broadlands-Ohaaki (BR-15-1655) exhibited a clumped isotope temperature of 242°C, which is below mean values indicated by well fluid (290°C) and T_h (308°C).

A statistical correction based on lab-specific empirical observations of samples that were partially equilibrated with water during purification yields an adjusted clumped isotope temperature of 308°C for this sample. The agreement of the adjusted clumped isotope temperature and fluid inclusion temperature supports the idea that modification of ^{13}C-^{18}O ordering during CO_2 sample preparation may explain the discrepancy. Monitoring for partial reset of Δ_{47}, to reflect lower apparent temperatures caused by exchange with H_2O during sample preparation, is critical for reducing uncertainty and obtaining accurate results.

Although the choice of temperature calibration (e.g., Kluge et al., 2015, vs. Bonifacie et al., 2017) and fractionation factor (e.g., Kim and O'Neil, 1997, vs. Horita, 2014) affect interpretation of absolute temperature (Fig. 2), and calculated fluid $\delta^{18}O$ (Figs. 3, 4), the methodology used in this study is sufficient to identify thermal gradients and fluid sources at the deposit scale (Fig. 4), regardless of calibration used (Fig. 2). In settings where magmatic, meteoric, and metamorphic fluids are variably mixed (e.g., porphyries and skarns), Δ_{47} enables more accurate quantification of input from these reservoirs (Fig. 4). This is in line with recent work, in which T-Δ_{47} was applied to quantify fluid flux from deep sedimentary basins in MVT deposits in England (Dennis et al., 2018). In addition to isotope fingerprinting of fluids, clumped isotope thermometry unlocks new potential for single mineral barometry, wherein temperatures are combined with fluid inclusion

homogenization results to define pressure (i.e., depth) within deposits (Honlet et al., 2018).

In epithermal deposits, clumped isotopes enable differentiation between carbonate forming near hotter upflow conduits, which convey metal-rich fluids, and lower temperature peripheral veins where metals typically accumulate at subeconomic concentrations. Notably, temperature, calculated from Δ_{47}, exerts strong control upon calcite $\delta^{18}O$ in the Waihi epithermal samples investigated here. Calcite $\delta^{18}O$ compositions span a range of ~11‰ VSMOW, while the calculated oxygen isotope value of fluid is less variable, ranging between –3.9 and –4.6‰ VSMOW for four samples, while two samples indicate more negative fluid values between –7.6 and –9.8‰ VSMOW (Fig. 4). With control upon the $\delta^{18}O$-Δ_{47} relationship at Waihi, $\delta^{18}O_{carbonate}$ can then be used as a geothermometer to vector towards hotter upwelling zones. Applying this approach to a larger suite of samples, for which only $\delta^{18}O$ is known, in part overcomes the lengthy sample processing time (2–3 hours per replicate analysis) imposed by the methodology used in this study. Compared with other thermometry tools, including clay mineral relationships, which are relatively insensitive to temperature variations across deposits, the outlined approach should allow for more precise temperature reconstructions in epithermal and geothermal environments.

Future Directions

Recent analytical developments have significant promise in terms of reducing time, sample size, error, and operational costs, making clumped isotope thermometry more accessible for ore deposit studies. The newly developed Long Integration Dual Inlet (LIDI) approach lowers sample mass requirements and enables more analyses, providing the means to better overcome analytical uncertainties stemming from measuring fewer (3–5) replicates (Müller et al., 2017). Using the LIDI method, aliquots of ~100 μg of carbonate are measured in 45 minute cycles (Müller et al., 2017). Issues associated with partial reset of clumped isotope temperatures, due to equilibration with water during sample preparation, can be overcome by implementing advanced cryogen-free techniques for purification of CO_2 (e.g., Sakai et al., 2017). Recently developed infrared absorption spectrometers also provide an alternative platform for clumped isotope analyses (Nelson, 2016; Sakai et al., 2017). In addition to lower hardware cost, laser instruments may eliminate issues associated with contamination imparted by sulfur, hydrocarbon, and chlorocarbon compounds, which frequently occur in hydrothermal carbonates, and interfere with measurement of $^{47}CO_2$. However, comparative studies using laser spectroscopy to measure carbonate clumped isotopes are yet to occur.

Conclusions

The results presented here demonstrate that clumped isotope thermometry can be used to better evaluate characteristics of ore deposit genesis, with respect to temperature, fluid source, and depth. This will prove especially useful in carbonate-hosted ore settings (e.g., skarns, Mount Isa, and Carlin-type Au), where temperature, hydrology, and the overall balance of magmatic and meteoric fluid are unclear. In epithermal deposits, Δ_{47} represents a new vector to hot upflow zones, where boiling drives deposition of Au, Ag, and other metals. With analytical improvements, clumped isotopes have the potential to become a powerful exploration tool in settings where carbonate minerals are present. Given the demand for clumped isotope capability in academic venues, and growing interest in the mining and geothermal sectors, we anticipate development of less expensive and more precise measurement platforms over the coming years.

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