GEOTHERMAL SYSTEMS AND EPITHERMAL DEPOSITS OF NEW ZEALAND: A FLUID CHEMISTRY COMPARISON

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Keywords: *Geothermal systems, TVZ, fluid chemistry, epithermal Au-Ag deposits, Hauraki Goldfield, fluid inclusions, LA-ICP-MS, Laser Raman, Synchrotron FTIR.*

ABSTRACT

Geothermal systems are considered the modern analogs of epithermal deposits. In the North Island of New Zealand there are approximately 23 geothermal systems within the Taupo Volcanic Zone (TVZ) and approximately 50 epithermal Au-Ag deposits in the Hauraki Goldfield. The chemistry of fluids in geothermal systems can be directly measured, whereas those for epithermal deposits are only preserved in fluid inclusions; here the fluids from each are compared. Deep reservoir chloride waters from TVZ geothermal systems typically have ≤1,500 ppm Na, but based on laser ablation-inductively coupled plasma-mass spectrometric analyses fluids trapped in epithermal quartz and sphalerite inclusions have up to ~15,600 ppm and 35,300 ppm Na, respectively. Both geothermal fluids and most inclusions in epithermal quartz have Na > K > Ca, although inclusions in sphalerite have enriched Ca that can exceed K. Concentrations of Sb and As in quartz hosted inclusions are 2 to 3 orders of magnitude greater than in geothermal waters (Sb up to 987 ppm vs 2 ppm and As up to 486 ppm vs 4.8 ppm). Most inclusions have Sb > As, whereas geothermal waters have As > Sb. The main gas in geothermal fluids is CO_2, and its concentration can exceed that of dissolved salts in some systems. Laser Raman and limited Synchrotron Fourier Transform Infrared (FTIR) microscopy suggest low amounts of CO_2 within fluid inclusions, but the amount cannot be quantified. Overall, the liquid trapped in epithermal fluid inclusions is more saline and has greater concentrations of Na, K, Ca, Sb and As than TVZ chloride waters. Fluids at the Tui deposit are the most saline, and likely consist of exchanged meteoric waters that include a significant magmatic fluid component. Based on these results it appears that chloride waters in TVZ geothermal systems differ in composition from those trapped in epithermal fluid inclusions of the Hauraki Goldfield, and that the latter are interpreted to have a variable to significant magmatic fluid component.

1. INTRODUCTION

Geothermal systems have long been considered the modern analogs of epithermal deposits with the connection proposed in the early part of the 20th Century (e.g. Lindgren, 1933). Geothermal systems consist of a deeply circulating (>5 km), rising convective column of water under hydrostatic to hydrodynamic pressures. Convection is inferred to be driven by magmatic heat and various thermal features including hot springs, geysers, thermally heated ground and fumaroles may be present at the surface (Henley and Ellis, 1983). Epithermal deposits form within hydrothermal systems that have alteration mineralogy, Au-Ag and base metal ore minerals that generally form at <2km depth and <300°C, and are envisioned to have formed within the 'shallow' portion of a geothermal system (e.g., Simmons et al., 2005). Many of the concepts surrounding mineralisation processes in epithermal deposits have been elucidated from precious metals precipitating in geothermal systems where they can be directly linked to fluids of known composition, temperature and pressure (Krupp and Seward, 1987, Brown, 1986, Simmons and Brown, 2007). The composition of the fluids in geothermal systems is well established from direct measurement (e.g., Henley and Hedenquist, 1986), however the fluids involved in the formation of epithermal deposits are only preserved in fluid inclusions; minute cavities (<5 to rarely >100 microns in maximum dimension) that have trapped minuscule aliquots of liquid and sometimes gas (e.g., Bodnar et al., 1985). Advances in micro-analytical techniques with the development of laser-ablation inductively coupled mass spectrometry (LA-ICP-MS) now permit the determination of trapped fluid composition for individual fluid inclusions (e.g., Günther et al., 1998; Heinrich et al., 2003). In this paper, comparisons are made between the fluid chemistry of reservoir chloride waters in geothermal systems of the Taupo Volcanic Zone and the chemistry of fluids trapped in fluid inclusions in epithermal deposits of the nearby Hauraki Goldfield.

2. GEOLOGIC SETTING

Geothermal systems of the TVZ and epithermal deposits of the Hauraki Goldfield within the Coromandel Volcanic Zone (CVZ) are both associated with convergence along the Pacific-Australian plate boundary (Skinner, 1986; Wilson et al., 1995; Wilson et al., 2009; Mortimer et al., 2010). The TVZ is the continental tip of the largely oceanic Kermadec-Tonga arc system formed due to NW-dipping subduction of the Pacific Plate since 2 Ma. Volcanism in the TVZ rifted arc extends ~250 km from White Island to Ruapehu with the northern and southern segments dominated by cone-building eruptions of andesite, whereas the central segment is dominated by explosive caldera-forming eruptions of rhyolite (Wilson et al., 1995). Most geothermal systems are hosted by thick sequences of rhyolite tuffs and pyroclastics with lesser rhyolite and andesite flows that unconformably overly Mesozoic meta-sediments. Deep drilling at Ngatamariki has also intersected shallow intrusions (<2 km depth) of diorite, microdiorite and tonalite (Chambefort et al., 2014). The geothermal systems have large and deep (>5 km) convection cells of meteoric water that are inferred to

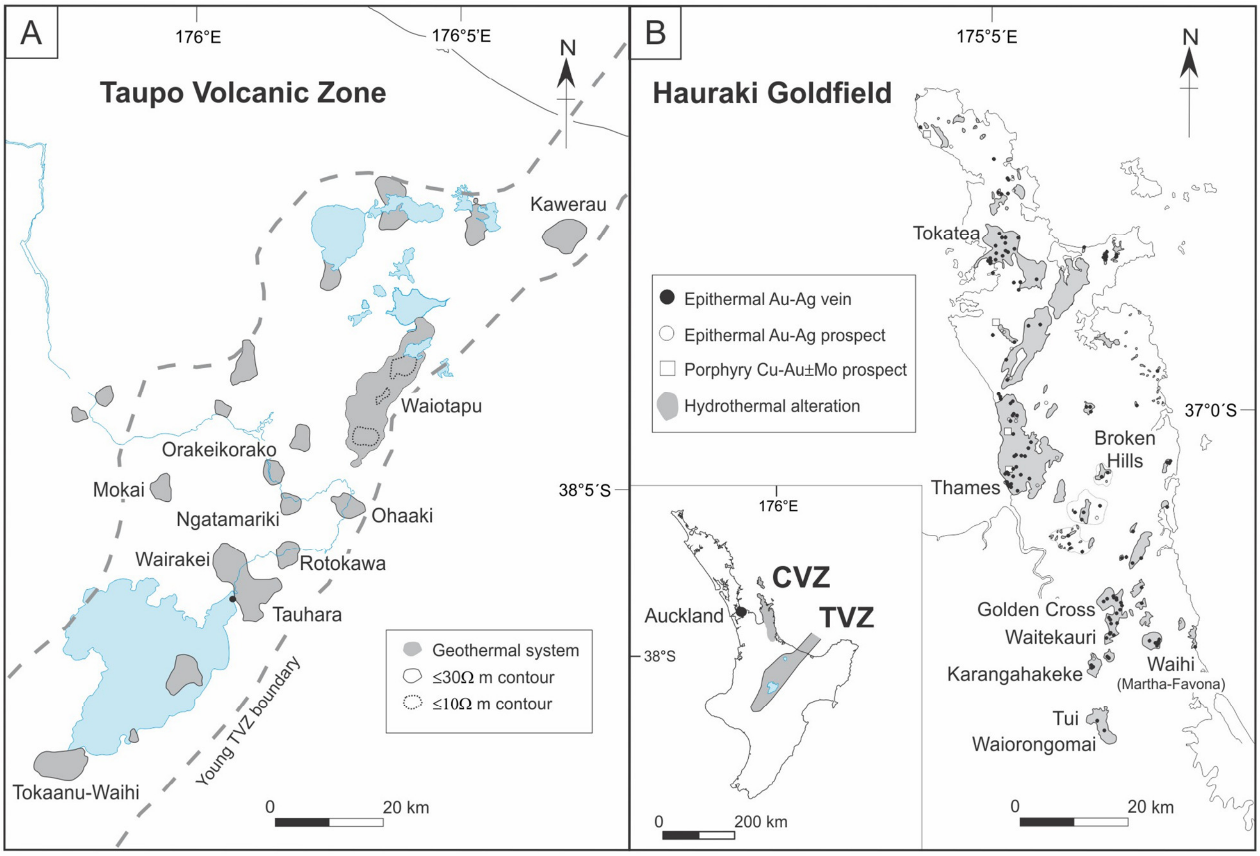

Figure 1: A) Geothermal systems of the Taupo Volcanic Zone (TVZ) and B) Epithermal Au-Ag deposits of the Hauraki Goldfield, Coromandel volcanic zone (CVZ), shown at the same scale. Insert shows location of each in the North Island, of New Zealand. The boundaries for TVZ geothermal systems are based on the less than 30 ohm-meter (m) apparent resistivity contour that broadly defines the upper 300 to 600 m of the geothermal reservoir (Bibby et al., 1995; Stagpoole and Bibby, 1998). Hydrothermal alteration halos surrounding epithermal veins are broadly based on a combination of alteration mapping and aeromagnetic data (Christie at al., 2001; Stagpoole et al., 2001; Morrell et al., 2011).

be heated by magmatic intrusions and modified by fluid-mineral interactions and the incorporation of magmatic gases (Henley and Ellis 1983; Giggenbach, 1997). Geothermal reservoirs occur below 600 m depth and have near neutral pH chloride waters with up to 0.23 weight % dissolved salts and variable gas concentrations of up to 3.5 weight % CO_2 (Henley and Ellis, 1983). In some systems the gas content exceeds that of dissolved salts (Giggenbach, 1995). Precious metals are present in some surface springs and as well scales at Rotokawa, Waiotapu, Ohaaki, and Kawerau (Krupp and Seward, 1987; Brown, 1986; Simmons and Brown, 2007).

The CVZ lies at the continental tip of the extinct NNE-trending Colville Ridge, and extends ~200 km from Great Barrier to Te Puke with the oblique NNW trend of the Coromandel Peninsula related to pre-existing basement structures (Skinner, 1986). The CVZ consists of ~18 to 3.8 Ma andesite and dacite flows, breccias and tuffs that form a series of stratovolcanoes and these rocks inter-finger with ~12 to 1.95 Ma rhyolite tuffs and flows related to several caldera complexes (Booden et al., 2012). The ages of volcanic rocks become younger southward and eastward with andesite dominant in the west and rhyolite in the east. Both andesite and rhyolite overlie Mesozoic meta-sediments and are locally intruded by subvolcanic dikes and a quartz diorite to granodiorite pluton (Skinner, 1986). Gold and silver production from quartz veins in epithermal deposits exceeds 11.5 M oz Au and 75.7 M oz Ag. More than 97% of this production is from veins hosted in andesite and dacite, although these rocks represent only 61% of those exposed (Christie et al., 2007). Significant Au producers include the Waihi (Martha + Favona), Karangahake and Golden Cross deposits, with Zn and Pb recovered from the Tui deposit. Mineralisation is zoned with Au-Ag at shallow to intermediate depths with base metals appearing and becoming more abundant at greater depths (>700 m). Not all veins have minable Au and Ag with those at Tokatea and Waiorongomai mostly barren with the exception of minor mineralisation in associated splay veins (Christie et al., 2007). ^{40}Ar/^{39}Ar dates of vein adularia in the deposits range from 16.3 Ma in the north to 2 Ma in the south, and most of the deposits in the southern Hauraki Goldfield formed between 6.9 to 6.0 Ma (Mauk et al., 2011).

The composition of liquid trapped in fluid inclusions discussed here are for the Tokatea, Broken Hills, Waitekauri, Karangahake, Waihi, Tui, and Waiorongomai deposits (Fig. 1). Microthermometric measurements of two-phase liquid-rich inclusions in quartz, platy calcite, sphalerite and amethyst from these deposits are summarised in Table 1. Fluid inclusions in quartz collectively have a homogenisation temperature (T_h) range of 181° to 298°C and final ice melting temperature (T_m) range of 0.0° to -4.0°C corresponding to apparent salinities of up to 6.5 weight % NaCl equivalent (Bodnar, 1993). Inclusions in sphalerite from the Waihi and Tui deposit are more saline with those from the latter, having up to 11.9 weight % NaCl equivalent. Collectively these deposits formed between ~200 to ~1,400 m below the paleowater table (Strmic Palinkas et al., 2014; Simpson et al., 2015).

Table 1: Summary fluid inclusion microthermometric results for epithermal deposits of the Hauraki Goldfield.

Deposit / mineral	T_h (ºC) range / *median*	T_m (ºC) range	Salinity wt. % NaCl
Tokatea[1]			
Quartz	186 to 267 *(238)*	-0.3 to -0.6	0.53 to 1.05
Amethyst	175 to 280 *(222)*	-0.4 to -1.3	0.70 to 2.24
Broken Hills[2]			
Quartz	186 to 249 *(222)*	0.0 to -0.2	0.00 to 0.35
Waitekauri[3]			
Quartz	210 to 265 *(241)*	0.0 to -0.7	0.00 to 1.22
Karangahake[3]			
Quartz	187 to 287 *(234)*	0.0 to -2.3	0.00 to 3.87
Waihi[3,4]			
Quartz	181 to 280 *(233)*	0.0 to -3.0	0.00 to 4.96
Sphalerite	229 to 285 *(249)*	-2.5 to -5.4	4.18 to 8.41
Calcite (platy)	229 to 294 *(252)*	0.0 to -2.8	0.00 to 4.65
Amethyst	215 to 242 *(225)*	-1.6 to -2.4	2.74 to 4.03
Tui[5]			
Quartz	249 to 291 *(275)*	0.0 to -4.0	0.00 to 6.45
Sphalerite	240 to 287 *(269)*	-2.6 to -8.2	4.34 to 11.9
Waiorongomai[1,6]			
Quartz	198 to 298 *(248)*	0.0 to -2.0	0.00 to 3.39
Sphalerite	232 to 263 *(244)*	-0.4 to -0.6	0.70 to 1.05

[1]Simpson et al., 2010a; [2]Simpson et al., 2010b; [3]Simpson et al., 2015; [4]Strmic Palinkas et al., 2014, [5]Strmic Palinkas et al., 2013; [6]Simpson et al., 2012.

3. FLUID COMPOSITIONS

3.1 Geothermal systems

Table 2 lists the deep reservoir chloride water compositions (mainly of well discharges) for selected geothermal systems of the TVZ. Typically, the near neutral pH reservoir chloride waters contain 500 to 2,300 ppm Cl, and 150 to 1,275 ppm Na (e.g. Henley and Hedenquist, 1986). Greater concentrations of 3,219 ppm Cl and 1,910 ppm Na have been measured for chloride springs at Tokaanu-Waihi, but based on isotopic studies (δD and $\delta^{18}O$) these spring waters are enriched due to steam loss (Robinson and Sheppard, 1986). The pre-boiled fluid is estimated to have a lower Cl content of ~2,400 ppm. Overall, deep reservoir chloride waters have less than 2,300 ppm Cl and ~1,500 ppm Na. The reservoir geothermal fluids have successively lesser amounts of Na, K and Ca. Limited down well sampling of reservoir waters for metalloids and precious metals in six geothermal systems determined ppb concentrations of As, Sb, Au and Ag (Table 2; Simmons and Brown, 2007). Concentrations of Sb range from 0.001 to 1.20 ppm, As from 0.01 to 4.86 ppm, Au from <0.1 to 23 ppb and Ag from 8.4 to 2,400 ppb. Concentrations of As are consistently greater than those for Sb.

The reservoir chloride waters can also have variable concentrations of dissolved gases, dominated by CO_2, that can exceed the concentration of salts (Hedenquist and Henley, 1985). Chloride waters at Wairakei have low concentrations of CO_2 (~0.04 wt. %), whereas those at Ohaaki have higher concentrations (~2.2 wt. %).

3.2 Epithermal deposits

Table 3 lists the summary compositional ranges of liquid trapped in fluid inclusions for seven epithermal deposits of the Hauraki Goldfield determined by LA-ICP-MS. Details on the instrument and technique are outlined in Simpson et al. (2015). LA-ICP-MS is able to detect most cations but cannot quantify Cl due to its high detection limit. Furthermore, the size (i.e. volume of contained liquid) and salinity of trapped liquid influences the detection limits and elements detected. Typically for small (<10 micron) and low salinity (<0.5 wt. % NaCl) inclusions, Na and Sb were the only elements detected, although it was possible to detect K, Ca, Li, Al, Ba, Rb, Sr, and As in more saline (>0.5 wt. % NaCl) inclusions. Some of these elements could also be detected in low salinity inclusions of larger size (>40 microns) because of the greater volume of contained liquid.

The Na content of quartz- hosted fluid inclusions ranges from the limit of detection to 15,616 ppm (Simpson et al., 2015) with greater concentrations in sphalerite of up to 35,300 ppm (Strmic Palinkas et al., 2013). Limited data for inclusions in quartz from Broken Hills, which is the only rhyolite-hosted deposit examined here, generally have the lowest Na content and a maximum concentration of 994 ppm (Simpson et al, 2010b). Inclusions from all deposits commonly have successively lower concentrations of Na, K and Ca. However, inclusions in sphalerite from both Tui and Waihi, as well as most in quartz also from the Tui deposit, have Ca concentrations that can equal or exceed those of K (Strmic Palinkas et al., 2013; 2014).

Antimony is the second most common element detected in fluid inclusions after Na. This metalloid is commonly incorporated into the host quartz and amethyst, thus its absolute concentration in some inclusions is less well constrained since the contribution from the host cannot be separated from that within the inclusion. However, for inclusions in quartz or amethyst with no Sb in the host, this element ranges from 15.7 to 987 ppm (Simpson et al., 2015). Arsenic is also present in a lesser number of inclusions at lower concentrations, ranging from <2.1 to 486 ppm. Similar concentrations of both elements occur in sphalerite with 2.7 to 965 ppm Sb and 6.5 to 109 ppm As (Strmic Palinkas et al., 2013; 2014). By contrast, Sb was detected in very few inclusions in platy calcite, but As is present in ~50 % of those analysed. These have lower concentrations of 0.1 to 1.1 ppm Sb and 0.2 to 23.4 ppm As (Strmic Palinkas et al., 2014). In general, the fluids in quartz and sphalerite have Sb > As, whereas in platy calcite As > Sb. The precious metals Au and Ag are both below the detection limit of 1.5 and 4.5 ppm, respectively (Simpson et al., 2015).

Limited LA-ICP-MS analyses of multiple fluid inclusion generations within an individual crystal reveal different suites of elements and concentrations for some generations. For example, fluid inclusions in a quartz crystal from the Colonist Loop vein at Waiorongomai has two fluid inclusion assemblages with similar salinity and Na, K, Rb, Ba, Li ± Sb concentrations, although the slightly lower salinity assemblage also contains Ca and As. While some variability in element concentration can potentially be attributed to boiling (resulting in element concentration) or mixing (resulting in dilution), the presence or absence of some elements (i.e. Ca) suggests the trapping of fluids with different bulk compositions (Simpson et al., 2012).

Table 2. Representative compositions of reservoir chloride waters in geothermal systems of the Taupo Volcanic Zone.

Geothermal system	Well	T (°C)	CO_2 (mmol / mol)	Cl (ppm)	Na (ppm)	K (ppm)	Ca (ppm)	As (ppm)	Sb (ppm)	Au (ppb)	Ag (ppb)
Kawerau[1,2]	KA8	275º	4,275	1,019	687	121	0.8	-	-	-	-
	KA25	260º	-	-	154	-	-	4.86	0.54	2.1	31.5
Mokai[1,2]	MK3	300º	636	2,273	900	293	10	-	-	-	-
	MK6	322º	-	-	970	308	-	3.9	1.20	0.6	250
Ngatamariki[2,3]	NM3	280º	-	1,574	884	208	3.7	-	-	-	-
	NM4	195º	-	-	483	36	-	0.47	0.03	<0.1	8.4
Ohaaki[2,4]	BR25	290º	12,250	1,429	895	189	1.4	-	-	-	-
	BR47	290º	-	-	525	98	-	1.54	0.36	0.3	2.7
Orakei Korako[1]	OK2	265º	-	546	550	54	<1.0	-	-	-	-
Rotokawa[2,5]	RK3	285º	-	1,947	1,165	146	51.8	-	-	-	-
	RK5	320º	-	-	339	96	-	1.4	0.18	23	2,400
Waiotapu[6]	WT4	225º	780	1,600	965	135	22.5	-	-	-	-
Wairakei[1,2]	WK27	250º	348	1,543	926	154	11.8	-	-	-	-
	WK212	255º	-	-	960	168	-	2.9	0.04	0.3	14.1
	TH1	260º	475	2,222	1,275	223	14.0	-	-	-	-
Tokaanu-Waihi[7]	Pool #5	100º	-	3,219	1,910	174	43	-	-	-	-

Note: all data recalculated to total discharge composition, - = not analysed. [1]Henley and Hedenquist, 1986; [2]Simmons and Brown, 2007; [3]O'Brien, 2010, [4]Hedenquist, 1990; [5]Hedenquist et al., 1988; [6]Hedenquist and Browne, 1989, [7]Robinson and Sheppard (1986).

Table 3. Summary of fluid inclusion LA-ICP-MS analyses for epithermal deposits of the Haruaki Goldfield.

Deposit	Mineral		T_h (°C)	NaCl wt. %	Na (ppm)	K (ppm)	Ca (ppm)	As (ppm)	Sb* (ppm)	Au (ppm)	Ag (ppm)
Tokatea[1]	Quartz	Min	228º	0.53	2,448	67	32	15.3	171.8	-	-
		Max	267º	1.05	3,581	513	100	40.3	508.5	-	-
	Amethyst	Min	175º	0.70	1,645	134	15	7.1	49.1	-	-
		Max	280º	2.41	6,688	1,289	428	324.0	3,759.6	-	-
Broken Hills[2]	Quartz	Min	186º	0.00	234	39	9	3.8	0.8	-	-
		Max	249º	0.35	994	381	127	30.0	425.4	-	-
Waitekauri[3]	Quartz	Min	210º	0.18	320	56	2	3.3	156	-	-
		Max	265º	1.05	3,699	819	389	36.9	439	-	-
Karangahake[3]	Quartz	Min	187º	0.70	263	214	45	60.0	66.2	-	-
		Max	287º	2.24	10,165	1,375	626	406.0	2,167	-	-
Waihi (Martha)[3,4]	Quartz	Min	187º	0.00	464	16	3	1.7	0.6	-	-
		Max	280º	4.96	15,616	3,804	1,990	637.3	4,250.0	-	-
	Sphalerite	Min	229º	4.18	10,899	1,863	1,040	6.5	6.3	-	-
		Max	285º	8.41	25,785	6,276	6,625	90.6	965	-	-
	Calcite (platy)	Min	229º	0.0	239	47.6	nd	0.2	0.1	-	-
		Max	294º	4.65	10,833	3,970	nd	23.4	1.1	-	-
	Amethyst	Min	215º	2.74	524	123	178	6.4	42.5	-	-
		Max	242º	4.03	12,370	3,694	1,842	486.0	2,281.0	-	-
Tui[5]	Quartz	Min	257º	0.18	149	66	34	4.2	1.5	-	-
		Max	291º	5.71	15,000	3,950	3,340	210.0	591	-	-
	Sphalerite	Min	241º	4.65	10,300	2,410	1,760	22.0	2.7	-	-
		Max	276º	11.93	35,300	10,500	7,620	109.0	469.0	-	-
Waiorongomai[1,6]	Quartz	Min	195º	0.18	404	30	245	2.1	0.9	-	-
		Max	298º	3.23	9,200	4,170	577	167.0	466.0	-	-
	Sphalerite	Min	232º	0.88	1,991	427	148	-	45.8	-	-
		Max	263º	1.05	33,166	454	251	-	217.0	-	-

Note: collective minimum and maximum values for all inclusions measured. - = below limit of detection, nd = not determined, since element forms the host mineral. *Sb values include those in which this element occurs both in the trapped liquid and the host. [1]Simpson et al., 2010a; [2]Simpson et al., 2010b; [3]Simpson et al., 2015; [4]Strmic Palinkas et al., 2014, [5]Strmic Palinkas et al., 2013; [6]Simpson et al., 2012.

The gas concentration of the fluid inclusions cannot be determined by LA-ICP-MS (Simpson et al., 2015), but has been investigated by both Laser Raman and by Synchrotron Fourier Transform Infrared (FTIR) spectroscopy (Nieuwoudt et al., 2014). Fluid inclusions from all seven deposits listed in table 1 have been analysed by Laser Raman with CO_2 detected in rare liquid-rich inclusions in sphalerite from the Tui deposit (Strmic Palinkas et al., 2013). It was also detected in a single separate generation of vapour-rich inclusions in quartz from the Karangahake deposit (Simpson et al., 2015). Initial analyses using the more sensitive FTIR spectrometry for fluid inclusions from the Karangahake, Waiorongomai and Broken Hills deposits, revealed CO_2 in some inclusions from Karangahake and Waiorongomai, but many inclusions did not contain CO_2. (Nieuwoudt et al., 2014). No CO_2 was detected in quartz-hosted fluid inclusions from the Broken Hills deposit. Based on limited analyses, CO_2 was detected in inclusions with T_m values of -1.0° to -3.3°C, but was not detected in those with T_m values of -0.1° to -1.2°. The absolute concentration of CO_2 within the inclusions could not be determined from either technique.

4. DISCUSSION

The compositions of fluid inclusions within epithermal veins have been calculated from LA-ICP-MS using Na concentrations deduced from T_m values as an internal standard (Günther et al., 1998; Heinrich et al., 2003; Allan et al., 2005). This assumes that T_m is only due to salts, however, it can also be due to CO_2. Because no CO_2 clathrate ($CO_2 \cdot 5.75\ H_2O$) was seen on freezing, the maximum concentration of CO_2 possible is 3.55 weight %, corresponding to a T_m of -1.48°C (Hedenquist and Henley, 1985). Approximately 89% of inclusions in quartz and 60% of those in calcite have measured T_m values greater than -1.5°C, whereas all those in sphalerite have T_m values cooler than -1.5°C. Laser Raman analyses have only detected CO_2 in rare liquid-rich inclusions in sphalerite from the Tui deposit (Strmic Palinkas et al., 2013), and Synchrotron FTIR analyses revealed CO_2 in some liquid-rich inclusions in quartz from the Karangahake and Waiorongomai deposits (Nieuwoudt et al., 2014). Previous bulk gas chromatography of inclusions in quartz and amethyst from the Waihi deposit have determined low concentrations of 0.05 to 0.24 weight % CO_2 that would contribute only -0.1°C to T_m (Brathwaite and Faure, 2002). Taken together, based on Laser Raman and limited FTIR spectroscopy, plus bulk gas chromatographic analyses, CO_2 occurs in low concentrations or is absent in inclusions. The strong LA-ICP-MS transient signal for many inclusions during ablation further suggests that the main source of the freezing point depression is dissolved salts.

Notwithstanding the difficulty in precise CO_2 quantification, the amount in inclusions appears to be low to inconsequential, quartz-hosted fluid inclusions contain up to 6.5 weight % NaCl and Na content of up to 15,616 ppm, both of which are significantly greater than the measured upper limit of 0.23 weight % NaCl equivalent and ~1,500 ppm Na for chloride waters from TVZ geothermal systems. Fluids trapped in sphalerite are more saline with up to 11.9 weight % NaCl and 35,300 ppm Na (Tui deposit). Even after subtracting the maximum amount of CO_2 (3.5 wt. %), inclusions in sphalerite still contain up to 10.1 weight % NaCl. Only inclusions from the rhyolite-hosted Broken Hills deposit with 0.35 weight % NaCl and 994 ppm Na have identical salinity to TVZ geothermal fluids.

Reservoir chloride waters in TVZ geothermal systems have successively lesser amounts of K and Ca relative to Na, which has similarly been determined for quartz-hosted epithermal deposit inclusions. Because Na/K ratios are controlled by temperature dependent fluid-rock interactions, it has been possible to use the Na/K geothermometer to calculate the 'parent' fluid temperature for the epithermal deposit fluids. For example, the 'parent' fluid temperature calculated from Na/K geothermometer for the Waihi, Karanagahake and Tui deposits is 295°, 287°, and 303°C, respectively (Strmic Palinkas et al., 2013, 2014; Simpson et al., 2015). However, the concentration of Ca in the trapped liquid of epithermal inclusions is more variable. Geothermal chloride waters have Ca/Na ratios of 0.001 to 0.044 (as calculated from the representative analyses of table 2) and those for the liquid trapped in epithermal quartz inclusions average 0.04 to 0.080 (range 0.001 to 0.215). By contrast, inclusions in sphalerite and most in quartz from the Tui deposit have Ca/Na ratio range of 0.181 to 0.516 and 0.206 to 0.224, respectively (Strmic Palinkas et al., 2013). Those in sphalerite from Waihi are more variable ranging from 0.349 to 1.375 (ave. 0.763). The source of this enriched Ca is unclear; as discussed below, it could be from the host rock or from magma.

Most of the deposits except for Broken Hills are in andesite which could be the source of Ca, although since Ca enrichment is mainly associated with sphalerite (Tui and Waihi) and rarely quartz (Tui), a local source is more probable. Alternatively, Ca could be sourced from a magmatic fluid. The composition of magmatic fluids has been inferred from a combination of measured volcanic gas discharges (e.g. Giggenbach, 1997) and various fluid inclusion analyses of inclusions from porphyry deposits (e.g. Audétat et al., 2008). The initial magmatic fluid exsolved from the melt at depth is single-phase and consists of an intermediate salinity fluid with 2 to 13 weight % NaCl equivalent. Depressurisation results in immiscibility and the generation of a low-salinity vapour (~1 wt. % NaCl) and a dense hypersaline liquid (>21 to 50 wt. % NaCl; e.g. Heinrich, 2007). There are few LA-ICP-MS data that report Ca concentrations due to polyatomic interference and also because this element is typically below the detection limit (e.g. Rusk et al., 2004; Audétat et al., 2008). Analyses of fluid inclusions at the El Teniente porphyry Cu-Mo deposit, Chile indicate that the initial magmatic fluid with intermediate salinity fluid (12.2 to 13.0 wt. % NaCl) had a Ca/Na ratio of 0.058 to 0.352. Two generations of hypersaline fluid inclusions (37 to 48 and 49 to >60 wt. % NaCl) have a Ca/Na ratio of 0.141 to 0.171 and 0.048 to 0.101 (Klemm et al., 2007). Both the intermediate salinity and one of the hypersaline generations have Ca/Na ratios that overlap with those in Hauraki Goldfield sphalerite.

Antimony and As are present in geothermal chloride waters and in epithermal deposit fluid inclusions. Concentrations of Sb and As in quartz hosted fluid inclusions range up to 987 and 486 ppm (Simpson et al., 2015), respectively, and are 2 to 3 orders of magnitude greater than those measured for geothermal waters, which have up to 1.2 ppm Sb and 4.86 ppm As (Simmons and Brown, 2007). Fluids trapped in platy calcite have more comparable concentrations with up to 1.1 ppm Sb and 23.4 ppm As; however few inclusions in platy calcite contain measurable concentrations of Sb (Strmic Palinkas et al., 2013). Most inclusions in quartz and sphalerite have Sb > As concentrations. In contrast, geothermal chloride waters have As > Sb concentrations, although chloride waters at the Ngawha geothermal system in Northland have Sb > As (Brown and Simmons, 2003). Ngawha presumably has a mafic rather than a felsic heat source and it is possible, though unproven, that different magmas could provide different proportions of these elements. However, this does not explain Sb > As concentrations in quartz and As > Sb concentrations in platy calcite at the Waihi deposit which instead suggests a more localised control. The poor correlation between Na and either Sb or As in the fluid inclusions suggests that Sb and As are transported as neutral hydroxyl complexes of $Sb(OH)_3$ and $As(OH)_3$ (Pokrovski et al., 2002; Zotov et al., 2003). Furthermore, Sb is variably concentrated in quartz and amethyst in optically indistinguishable bands, which may represent episodic deposition of Sb nanoparticles during changes in temperature and/or S activity.

In the geothermal systems, Au and Ag (Table 2) are present in chloride waters at the ppb level (Simmons and Brown, 2007). Both these precious metals are below the detection limit (ppm level) in fluid inclusions, but this does not preclude their presence at the ppb level. The fluid inclusions analysed in epithermal quartz occur in concordant comb bands or later prismatic crystals that are not coeval with ore minerals, which occur with extremely fine-grained quartz that in many places formed from recrystallised amorphous silica. Even though inclusions have been measured in quartz deposited before and after mineralisation, it cannot be said with certainty that the fluids responsible for Au-Ag deposition are the same. In contrast, primary fluid inclusions (i.e. those trapped during the formation of the host mineral) in sphalerite contain mineralising fluid.

Overall, the liquid trapped in fluid inclusions from the epithermal deposits of the Hauraki Goldfield are generally more saline (up to an order of magnitude greater) and have greater Sb and As concentrations (by 2 to 3 orders of magnitude) than chloride waters from TVZ geothermal systems. Inclusions in sphalerite from the Tui Zn-Pb deposit (~1.4 km depth) and sphalerite from the Waihi deposit (~0.5 km depth) are the most saline and their greater salinity especially for the former is likely due to the incursion and incorporation of a significant magmatic fluid component. Inclusions from the other deposits with lower salinity, but still greater than those for TVZ geothermal systems, likely also include a magmatic fluid contribution, which may be critical for transporting metals to the ore deposit sites. Sulphur isotope values from the epithermal deposits indicates that sulphur is primarily magmatic, which also supports a magmatic contribution to epithermal ore bodies (Christie et al., 2007; Strmic Palinkas et al., 2013).

5. CONCLUSION

Comparison of reservoir chloride waters for TVZ geothermal systems with epithermal fluid inclusions of the Hauraki Goldfield shows that the latter are generally more saline and have significantly greater amounts of Sb and As. There are also differences in the amount of Ca. These relationships suggest that chloride waters present in TVZ geothermal system differ in composition from the liquid in epithermal fluid inclusions of the Hauraki Goldfield, which are interpreted to contain a variable to significant magmatic fluid component. Magmatic fluids likely play a key role in transporting the metals that form epithermal deposits.

ACKNOWLEDGEMENTS

Financial support to write this paper was provided by the GNS Science core-funded Geothermal Resources of New Zealand research program. The epithermal deposit fluid inclusion work summarised here is from cited studies, and was funded by the New Zealand Ministry of Business, Innovation, and Employment, New Zealand Synchrotron Group Limited, Newmont Waihi Operations, and New Talisman Gold Mines Limited. Newmont Waihi Operations and New Talisman Gold Mines Limited are also thanked for access to their deposits, and for permission to publish. Many thanks to Luca Fedele and Charles Farley for data collection at Virginia Tech. We thank Isabelle Chambefort and Peter Vikre for careful and insightful reviews.

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