Te Puia Springs, Gisborne, past and present fluids

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ABSTRACT

Currently, the Te Puia hot springs discharge up to 71-77°C CH_4-rich Na-Ca-Cl fluids with Cl concentrations of 5100-9800 mg/kg, gas:water ratio of 0.1, and an estimated annual water flowrate of ~2.85 x 10^5 m^3/a. Fluid inclusions in calcite veins from sinter mounds adjacent to hot springs yield homogenization temperatures (median: 80°C) and salinity (8300 mg/kg Cl), similar to present-day surface discharge measurements suggesting that spring temperatures and Cl contents have been relatively constant since the hot springs appeared, probably ≤140k years ago. However, gas ratios in fluid inclusions deviate from present-day measurements. In particular, fluid inclusions contain higher relative concentrations of CO_2 and H_2S and lower relative concentrations of hydrocarbons. Within the hydrocarbon fraction, fluid inclusion gas contains higher concentrations of C2+ alkanes, as compared to vent gases, and detectable benzene. This suggests some temporal variability in volatile composition, while temperatures and TDS remained relatively unchanged.

1. INTRODUCTION

1.1 Study area

The Te Puia springs are in Ngati-Porou land, located 101 km north of Gisbone city. Well before the "discovery" by Europeans in the 19th century, the hot springs, especially a large hot muddy pool called "Hiroama", had been used for centuries by Maori for rheumatism, sciatica, and other complaints (Cowan, 1926), including most likely for iodine-deficiency related diseases and as an antiseptic because of the high iodine content of the waters and for dermatological disorders from the high sulfur content. As in several key hot springs on the North Island (Riley and Enting, 1994), the Te Puia hot springs were a meeting place for peaceful healing for Maori of various tribes (Impact Consulting Ltd., 2018). Partially as a consequence of the hot springs, the Te Puia Springs hospital was first established in 1907 (https://teara.govt.nz) and continues to this day as the Te Whare Hauroa o Ngati Porou, the only Maori-owned and -run hospital in the world (www.nph.org.nz). Previously, natural gas from the springs was used for cooking and heating (https://teara.govt.nz), but at present, the gas traps and gas storage tanks have not been used, with domestically-used gas now reliant on commercially available LPG in gas bottles.

Compared to the hot springs at Taupo, the Waikato, and Auckland, the Te Puia springs were at the backwaters of the late 19th to mid-20th century "Great Spa of the South Seas" (Rockel, 1986) mainly because of poor roadways (https://teara.govt.nz) and lack of government support for development. Nevertheless, because of Te Puia hot springs' unusual water composition (high chloride, iodine, and dissolved H_2S) and the presence of natural gas, aqueous fluids were chemically analysed since 1881 (Colonial Museum and Laboratory, 1882) and gases since 1920 (Dominion Laboratory, 1921), primarily for their baleonology and later, for their use as energy sources (e.g., Glover, 1968; McLernon, 1978).

The objective of this study is to find out if fluids and temperatures at Te Puia have changed since the late 19th century, based on a sampling of the vents/springs, and before the area was uplifted from the sea, based on fluid inclusions.

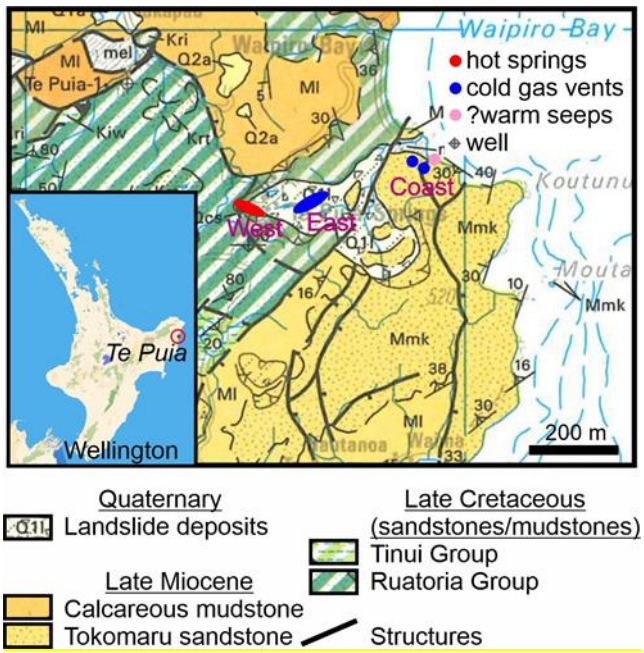


Figure 1: Geological map (Mazengarb and Speden, 2000) and the general location of hot springs, warm seeps and cold gas vents at Te Puia springs and its environs. Inset shows the general location of the study area.

2. GEOLOGY

Tectonically, the Te Puia springs are located on the subaerial accretionary prism of the Hikurangi subduction zone in eastern North Island, where 99.6% of the springs are cold. It is adduced from measurements (Reyes et al., submitted) that the presence of hot springs in crust of low surface heat flow (Allis et al., 1998) is due to ascent rates of hot waters from depth estimated to be 15 to 50x faster than cold springs. As shown in Fig. 1, there are three sets of springs at Te Puia: Te Puia West, where the hot springs are concentrated, Te Puia East discharging cold methane-rich gas, and gas vents and 22-25°C warm seeps near the Waipiro Bay coast to the northeast. The Te Puia West hot springs (Fig. 1) are distributed over an area of about 0.07 km^2, trending NW-SE following a contact fault between Late Cretaceous sandstones and mudstones and Quaternary landslide deposits. All the Te Puia East methane-rich gases (Ross, 1967) vent out from Quaternary landslide

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deposits (Fig. 1). The few coastal gas vents and warm seeps discharge from Late Miocene sandstone sedimentary beds or along a NNW-SSE trending fault. Shallow boreholes up to ~120 m deep were drilled at Te Puia West to search for high natural gas flow rates (Macpherson, 1945). The nearest deep petroleum well to the hot springs Te Puia-1, 400 m northwest. of the hot springs, has an estimated BHT (bottom hole temperature) of 80ºC at 2043 m depth (Reyes, 2007). About ~2.85 x 10^5 m^3/a water with a gas:water ratio of 0.1 emanates from Te Puia West (this study). Figure 2 shows the distribution of hot springs, cold gas vents, calcite sinter/vein deposits/mounds, and the location of samples for the fluid inclusion study.

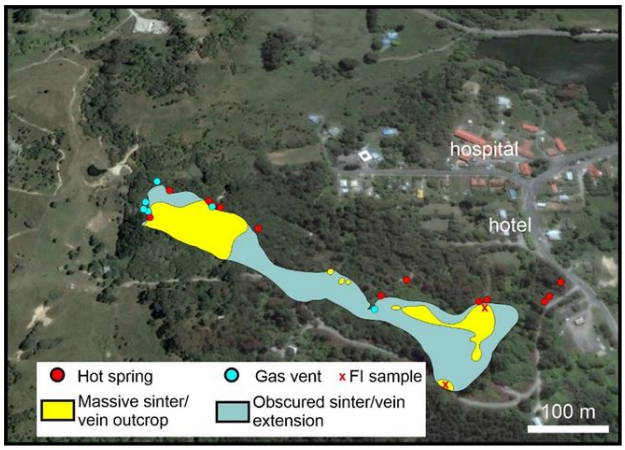


Figure 2: Distribution of hot springs, gas vents, and calcareous sinter at Te Puia West based on Macpherson (1945), Glover (1968), Reyes field notes (1996-2021). "x" is the sampling site for fluid inclusion study.

3. PRESENT FLUID DISCHARGE COMPOSITIONS AND TEMPERATURES

3.1 Aqueous fluid- general composition and origins

The Te Puia hot springs discharge 45-77ºC (Impact Consulting Ltd, 2018) Na-Ca-Cl aqueous solutions with Cl concentrations varying from about 5200- 9800 mg/kg (median: 8100 mg/kg), I at 14-22 mg/kg (median: 17 mg/kg) , Br at 20-32 mg/kg (28 mg/kg), B at 11-66 mg/kg (median: 69 mg/kg), HCO_3 at 42-315 mg/kg (median: 125 mg/kg) and dissolved H_2S at 0.5-39 mg/kg (median: 24 mg/kg) (Colonial Laboratory, 1881, 1893, 1907; Glover, 1968; Reyes, 2010, unpublished results). The unusually high concentration of dissolved H_2S at Te Puia is reflected in the common occurrence of elemental and amorphous sulfur in the hot springs.

The Te Puia aqueous fluids have a Br/Cl ratio similar to seawater (Fig. 3A), with the increase in I/Br ratios from about 0.3 to 0.75 due to either degradation of kerogen in the rock or mixing with clay water of dehydration derived from the transformation of smectite to illitic clays at depth. The ternary diagram Cl-HCO_3-B shows that most of the Te Puia hot spring waters contain 40-60% seawater and >25% water of clay water of dehydration with respect to meteoric water (Fig. 3B).

3.2 Aqueous fluid temperature estimates

Figure 4A shows two sets of convergence for aluminosilicate mineral saturation curves using REACT (Bethke and Yeakel, 2015): at 70-78ºC near the spring discharge temperature, in equilibrium with chalcedony, and at 130ºC at near-equilibrium with quartz. The convergence of non-silicates such as dolomite, aragonite, barite, and dawsonite with fluids at 70-78ºC is consistent with carbonate and sulphate precipitates in the springs (Reyes et al., 2010). The Na-K temperatures at depth (Fig. 4B) are similar to the range of temperatures, from 70 to 130ºC, based on REACT.

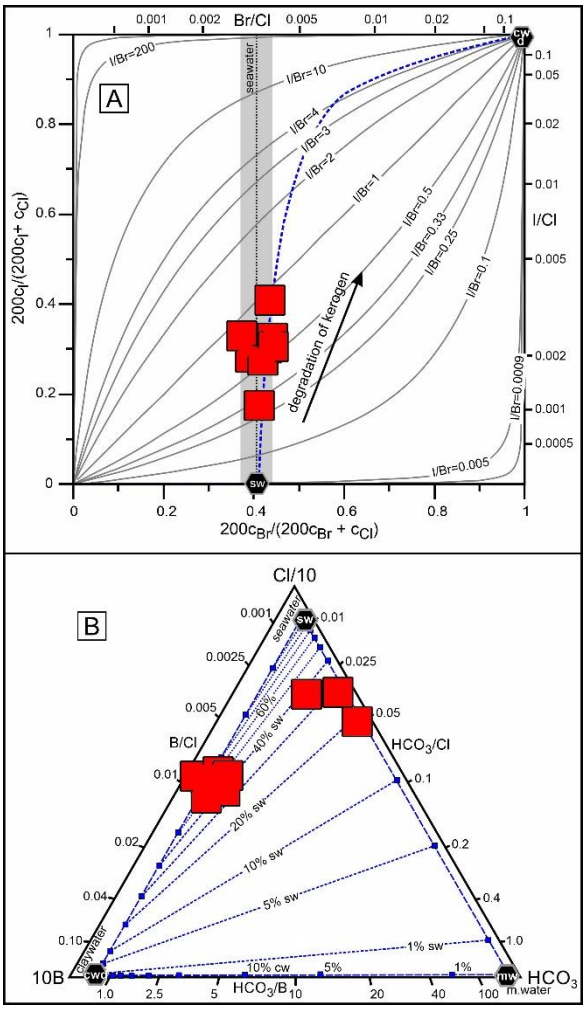


Figure 3: [A] Cross plot of $200C_{Br}/(200C_{Br}+C_{Cl})$ vs. $200C_I/(200C_I+C_{Cl})$ and showing curves for I/Br; [B] relative Cl, HCO_3, and B contents of Te Puia hot springs aqueous fluids. End members include sw: seawater, cwd: water of clay dehydration seawater, and m. water: meteoric water. Water of clay dehydration is expelled when smectite transforms to illitic clays during diagenesis at >100ºC (e.g., Volker and Stipp, 2015).

3.3 General gas compositions

The Te Puia West and East gases are dominated by CH_4 (median: 94%; C1, methane) and C_2H_6 (median: 3.5%; C2, ethane) with minor C_3H_6 (median: 0.73%; C3, propane), CO_2 (median: 0.4%), C_4H_{10} (median: 0.14%; C4, butane) and C_5H_{12} (median: 0.03%; C5, pentane). The isotopic $d^{13}C$ (-34 to -42.6‰ VPDP) and dD (-145 to -182‰ VSMOW) compositions of CH_4 gas in the hot spring discharges cluster within the region of oil-associated thermogenic gas, generated at depth from source rock at >75ºC.

The R/R_A, the ratio of mantle (^{3}He) to crustal helium (^{4}He) in the sample relative to R_A which is the ratio in air (1.4 x 10-6, Ozima and Podosek, 2002), at Te Puia is significant at 1.82-

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1.89 or about 23% mantle gas suggesting that structures in the area are open or permeable to mantle gas.

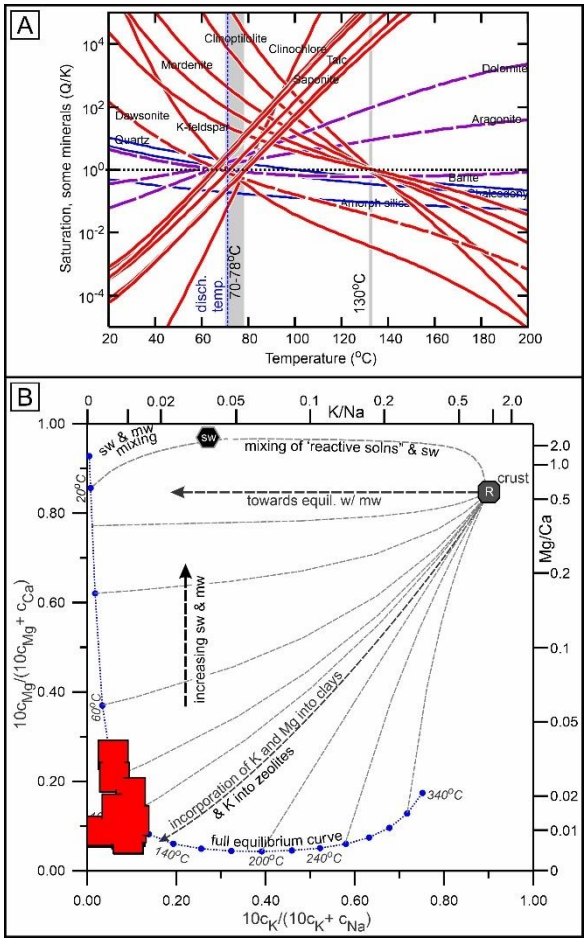


Figure 4: [A] Estimated temperatures of equilibration of aluminosilicate minerals at the discharge temperature and at depth using REACT (Bethke and Yeakel, 2015) at Te Puia hot spring. Also included are silica polymorphs, carbonate and sulphate minerals; [B] cross plot of log[10c_K/(10c_K + c_{Na})] vs log[10c_{Mg}/(10c_{Mg} + c_{Ca})] plot from Giggenbach (1991) with full equilibrium curve recalculated for low-enthalpy waters (Reyes et al, 2010).

3.4 Gas temperatures

As shown in Fig. 5, CH_4 and CO_2 gases at Te Puia East and West appear to be generated at depth with no contributions from marsh gas (mhg), air-saturated water (asw) or air (a). The CH_4-CO_2 temperatures (Giggenbach, 1997) at Te Puia East are lower (80-95°C) than at Te Puia West (95-135°C). Other geothermometers such as CO_2/Ar and H_2/Ar (Giggenbach, 1991) confirm deep crustal temperatures as high as120-125°C at Te Puia West.

4. FLUID INCLUSIONS

4.1 Sample location

Calcite samples were collected from two fossil hydrocarbon seep carbonate mounds in 1995 and 1999, as shown in Fig. 2. Mounds consist of siltstone/sandstone crosscut by numerous veins of calcite with widths of about 1-6cm. Geochemical analysis of these mounds shows 70% $CaCO_3$, and the rest are SiO_2, Al_2O_3, and others (Macpherson, 1945), consistent with the presence of sandstone and siltstone fragments.

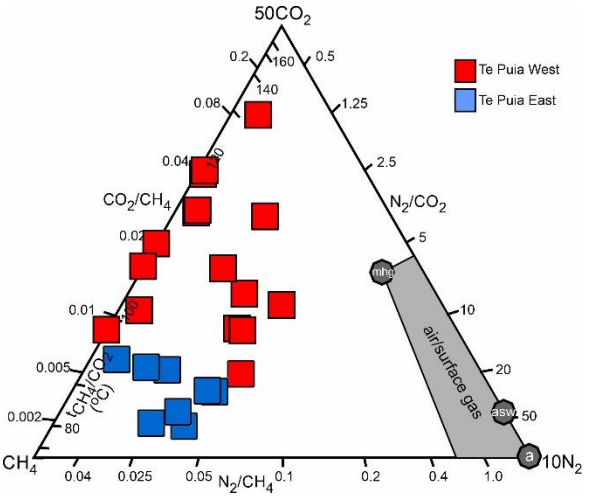


Figure 5: Ternary diagram comparing the relative CO_2, N_2 (corrected for air), and CH_4 compositions of discharges from Te Puia West and East vents/springs. The CH_4/CO_2 temperatures on the left side are from Giggenbach (1997). mhg: marsh gas, asw: air-saturated gas, a: air.

4.2 Homogenization and freezing point depression temperatures

Fluid inclusions were analyzed under plain- and UV-light with a Leitz polarizing microscope. Homogenization and freezing point depression temperatures were measured using a Fluid Inc heating-freezing stage, calibrated at 0.0°C (pure water and ice bath) and -56.6°C (0.75% mole H_2O + 0.25% mole CO_2).

No oil or kerogen was detected under UV-light. Primary fluid inclusions occur as large vacuoles, up to 125mm in diameter, and clusters along crystal overgrowths varying from <1 to 10mm in diameter. Gas bubbles comprise ≤10% of the vacuoles. Secondary or pseudosecondary fluid inclusions along healed fractures crosscut or cut across primary overgrowth fluid inclusions.

Fluid inclusions homogenize to the liquid phase at 78-87°C with a median at 80°C (n= 31). About 65% of the fluid inclusions contain clathrates that appear to dissociate at +0.4 to +9.1°C, suggesting a high concentration of either CH_4 or CO_2 (Roedder, 1984) dissolved in water. Fluid inclusions containing only saline waters exhibit ice melting at -0.4 to -0.9°C, with a median value of -0.76°C. This is equivalent to a salinity of 1.38 weight% NaCl (Bodnar, 1993) or 8360 mg/kg Cl. However, the presence of undetected dissolved gas may affect the freezing point depression temperature and hence the apparent aqueous fluid salinity (Hedenquist and Henley, 1985). Unusual inclusions are common, showing two to four phases: a vapor bubble and several immiscible liquids that respond to freezing and heating. These inclusions probably contain mixtures of CH_4, other hydrocarbon gases, CO_2, and saline aqueous solutions (Pironon and Barres, 1990), as indicated below.

4.3 Gas compositions

Volatiles in bulk calcite crystals from Te Puia were released by automated mechanical crushing and analyzed in a vacuum using quadrupole mass spectrometry. The volatiles in the Te Puia hot spring sinter fluid inclusions include water, alkanes with carbon numbers from C1 (methane, CH_4) to C9 (e.g., nonane, C_9H_{20}), water-soluble aromatic hydrocarbons—most notably benzene, H_2S, and inorganic gases such as H_2, He,

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and CO_2. The alkane hydrocarbon fraction consists of 69-72% CH_4 (C1, methane), 20-25% C_2H_6 (C2, ethane), 2.5-4.0% C_3H_8 (C3, propane) and 0.34-0.48% C4+ (butane and heavier molecular weights; Fluid Inclusion Technologies, 2014). Much of the volatile fraction is dominated by water and CO_2. H_2S concentrations are relatively high.

Ratios	Fluid Inclusions	Vent discharges
H_2S/CO_2	0.009	0.0037
H_2S/C1	0.6	0.0001
C1/CO_2	0.015	51.2
He/H_2	0.001	7.3
C1/C2	3.2	27.2
C1/C3	23.4	128.5
C1/C4	67.8	674
C1/C5+	174	1432
C2/C3	7.2	4.4

Table 1: Gas ratios in fluid inclusions and vent discharges. C1= methane, C2= ethane, C3= propane, C4= butane, C5+= pentane including hydrocarbons with heavier molecular weights.

5. DISCUSSION AND CONCLUSIONS

From the 19th to early 21st centuries, the spring temperatures, aqueous solute ratios (Figs. 3A and B, 4B), and gas ratios (Fig. 5) at Te Puia West have not drastically varied as compared to those recorded in the fluid inclusion data. The main changes in the vent chemistry only occur when a higher volume of meteoric water or shallow gases are expelled when the area is more tectonically active (Reyes et al., submitted). The relative concentrations of CO_2, C_2H_6 and CH_4 (Fig. 6A), CH_4, C_3H_8, and C_2H_6 (Fig. 6B) and $10C_{C2+}/(10C_{C2+}+C_{CH4})$ vs $10C_{H2S}/(10C_{H2S}+C_{CH4})$ (Fig. 7) illustrate the difference between the relative gas contents of fluid inclusions and present-day gas vent gases. Specifically, the inclusion gases are more enriched in CO_2 relative to hydrocarbons and less enriched in methane relative to ethane and propane. They are also significantly more enriched in H_2S relative to methane, and ethane relative to methane.

Discrepancies between vent and inclusion gases may, in part, be related to the nature of the analysis (the exsolved gas in the case of the vent discharge and the entire gas-water system in the case of the fluid inclusions). A comparison of gas solubilities with water (Lide, 2000) shows that gases with higher solubilities in water tend to be higher in fluid inclusions than less soluble gases. Hence the ratios H_2S/CO_2, H_2S/CH_4, and C2/C3 are higher in the fluid inclusions than in the vent discharges, but the ratios of C1 with CO_2, C2, C3, C4, and C5+ are considerably higher in gas from surface vents (Table 1). A second, perhaps more likely, conclusion is that compositions of gases changed over geologic time. In fact, some present-day variability in vent chemistry is observed in Figure 6, and these variability trends can be extrapolated to paleofluid chemistries represented by fluid inclusions.

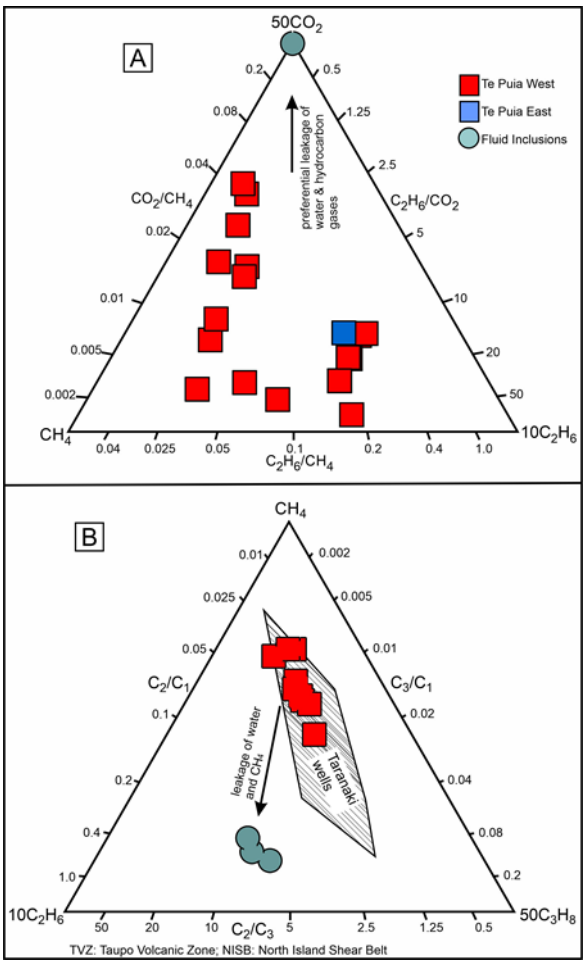


Figure 6: Ternary diagrams showing the relative compositions of [A] CO_2, C_2H_6 and CH_4 and [B] CH_4, C_3H_8 and C_2H_6 in spring/vent discharges and fluid inclusions.

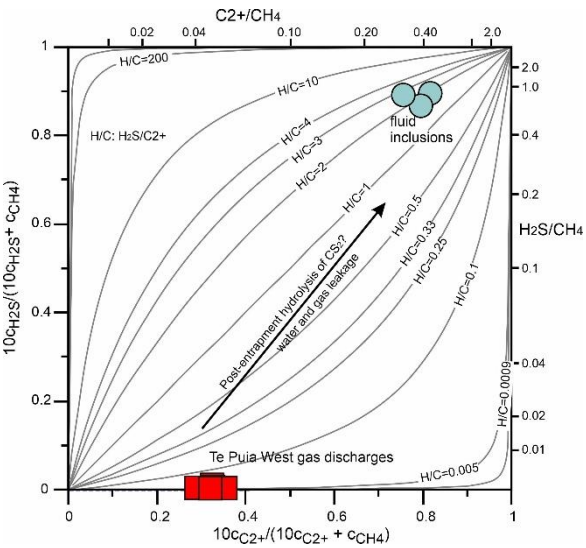


Figure 7: Cross plot of $10C_{C2+}/(10C_{C2+}+C_{CH4})$ vs $10C_{H2S}/(10C_{H2S}+C_{CH4})$ comparing gas discharges from vents and fluid inclusions.

As noted above, the homogenization temperatures and salinities of the Te Puia fluid inclusions are comparable to present-day discharges from the vents and appear similar to present-day conditions. Thus, since the emergence of the

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springs along the Hikurangi Margin, estimated to be about 140,000 years ago (Reyes et al, submitted) or 124,000 years (Berryman, 1988), the temperatures and bulk salinities of the fluids expelled by the springs have generally remained constant. However, gas compositions have varied.

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