VARIATIONS IN CHEMICAL AND ISOTOPIC COMPOSITIONS OF MINERAL SPRING SYSTEMS IN SOUTH ISLAND, NEW ZEALAND

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SUMMARY – There are about 60 mineral springs in the South island, about 42 of which are thermal. Thermal discharges range from 16.7°C to 66°C with the highest temperatures found in springs along the northern half of the Alpine Fault Zone. Estimated maximum subsurface temperatures range from <60°C in Canterbury and the FAFZ to >250°C in the NAFZ and Taeieri basin near Dunedin. Discharge temperatures in the NAFZ springs are lower than in the MFS but the calculated subsurface temperatures are higher due to differences in permeability, degree of conductive heating and possibly depth of fluid source. The highest HCO_3/Cl ratios are confined in springs located along the MFS. In contrast spring waters along the NAFZ and FAFZ, with lower HCO_3/Cl ratios, are farther away from the equilibrium line, suggesting differences in permeability, meteoric water throughput, storage and circulation among the MFS NAFZ and FAFZ and to a certain extent, reflecting (1) variations in water-rock interaction in the fluids circulating through the faults and (2) changes in bedrock composition. Along the Alpine Fault Zone meteoric waters gain solutes from interaction with fault comminuted rock, contributions from the subducted slabs in the NE and SW of the South Island and metamorphic fluids at depth. Anomalous heat along the Alpine Fault Zone is generally believed to be due to rapid uplift and exhumation. Hot waters at depth in the Taieri basin however, are probably due to heat generated from hot mantle at depth.

1. INTRODUCTION

Mineral waters discharging from springs or shallow boreholes contain at least 250 mg/kg total dissolved solids and may be thermal or cold. In this study overtly thermal waters have temperatures at least 4°C above the mean annual ambient air temperature which varies from about 10°C in South Island to 16°C in North Island. However similar to thermal springs, cold mineral springs provide insight into processes in the crust and, in some regions of New Zealand, have geothermally-viable temperatures at depth, blurring the difference between geothermally-significant and -insignificant water discharges based simply on discharge temperatures.

The objective of this paper is to discuss the spatial distribution of mineral springs in South Island, variations in thermal fluid flow, estimated subsurface temperatures and variations in fluid chemical and isotopic compositions along the active deformation front, (Alpine Fault Zone) and in relatively more passive regions such as Canterbury and Dunedin.

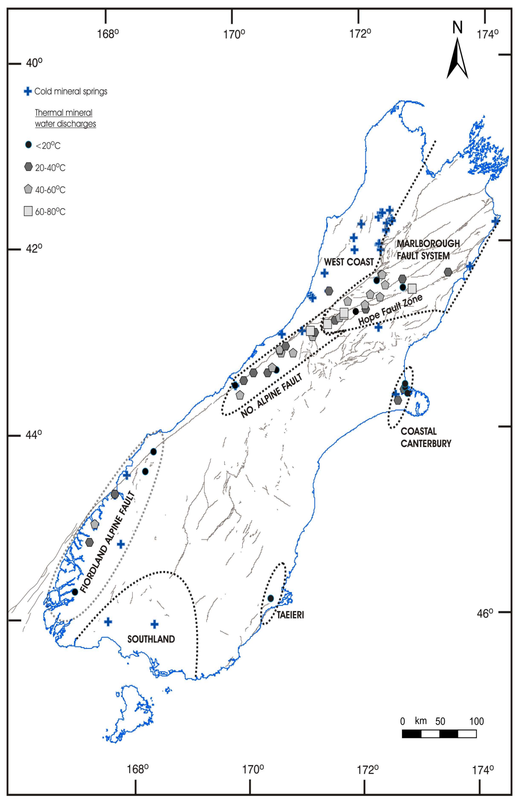

Figure 1- Distribution of nonthermal and thermal mineral fluid discharges in seven regions of South Island. Active faults are shown as light grey lines (data from www.gns.cri.nz). The extension of the Alpine Fault west of Fiordland is from Barnes et al (2001).

2. DISTRIBUTION OF SPRINGS

There are at least 60 mineral spring systems in South Island, nearly 70% of which are thermal. Warm mineral waters are also discharged from wells in Christchurch, the West Coast and near Dunedin. Thermal mineral waters occur in 6 tectono-geographic regions in South Island including (1) coastal Canterbury Plains adjacent to Banks Peninsula, (2) northern Taieri Basin near Dunedin, (3) Marlborough Fault Zone (MFS), (4) northern Alpine Fault Zone (NAFZ), (5) Fiordland Alpine Fault Zone (FAFZ), (6) West Coast (northwestern half of the South Island west of the

Alpine fault), and (7) Southland (Figure 1). A few hydrocarbon wells in Southland have thermal gradients >30°C/km (Reyes, 2007) but no mineral waters were collected during this survey. Methane-rich gases were, however, sampled from gas seeps at Ohai and Hindley Burn derived from buried coal (Lyon and Giggenbach, 1990).

Mineral springs often emerge along the edges of, or in rivers but a few trickle through swamp as in Motukarara in Christchurch, discharge under the sea as in Anchorage Cove or seep along the intertidal region of beaches in Lyttelton harbour or Kaikoura.

At present only two of the spring systems, Maruia and Hanmer, have been commercially developed, using the 54-55°C hot waters mainly for swimming pools and heat exchangers. Except for Maruia, Hanmer, Kotuku, Sylvia Flats in the Lewis River and coastal Canterbury, most of the hot springs are located in areas at least 2 km walk from the road and hence are seldom used except by trampers or hunters.

3. GEOLOGICAL SETTING

South Island is dominated by the oblique collision of the Pacific and Australian plates, marked by the 850 km long dextral strike slip Alpine Fault where dextral displacement of 480 km has been accommodated since the Miocene (Wellman, 1953; Sutherland and Norris, 1995; Barnes et al, 2005). The Alpine fault acts as a hinge between two subduction zones of opposite polarity, the west-dipping Hikurangi subduction zone in the NE and the east-dipping Fiordland subduction zone in the SW (Waschbusch et al, 1998).

In this paper the Northern Alpine Fault Zone (NAFZ) and Fiordland Alpine Fault Zone (FAFZ) are located along the Alpine Fault *sensu strictu*, from Inchbonnie to the SW. The NAFZ corresponds to the 3rd section of Berryman et al (1992) between Inchbonnie and Haast and the FAFZ includes the 4th section of Berryman et al (1992) and extends from Cascade river, near Jackson Bay, to the SW (Figure 1).

Along the Alpine Fault Zone the frequency of seismic events changes from NE to SW. Seismic activity is high in the NE and SW ends of South Island where the Pacific plate in the NE is subducted under the Australian plates and the Australian plate in the SW is subducted beneath the Pacific plate. Where continent to continent collision is paramount along the Alpine fault Zone, seismicity is relatively low but the exhumation rate, conductive heat flow and displacement rates are highest along the deformation front (Wellman, 1979; Berryman et al, 1992; Allis and Shi, 1995; Kohler and Phillips, 2003).

The northwestern section of the Alpine Fault splays into four major fault zones of the Marlborough Fault System (MFS) including Wairau, Awatere, Clarence and Hope (Browne, 1992). Transcurrent motion along the four major fault zones accommodates nearly all plate motion (Eberhart-Phillips and Reyners, 1997; Wilson et al, 2004). The rates of displacement in the four faults generally increases from NW to SE (Phillips and Reyners, 1997) at 3-5 mm/a on the Wairau (Berryman et al, 1992), 6-8 mm/a on the Awatere, 4-8 mm/a on the Clarence and 18-35 mm/a along the Hope (Bourne et al, 1998; Eusden et al, 1999). In the last 150 years, large historical earthquakes have been recorded on the Awatere and Hope faults (Bourne et al, 1998) Most of the rocks exposed on the Marlborough Fault System are Torlesse greywacke and inferences from seismic tomography indicate that this rock extends down to mid crust (Eberhart-Philips and Reyners, 1992; Wilson et al, 2004).

The Torlesse greywackes and argillites on the east of the Southern Alps grade into the Haast schist, of increasing metamorphic grade, towards the west. The increase in metamorphic grade from chlorite to biotite, to garnet, to oligoclase and finally K-feldspar, is mainly related to uplift and exhumation along the Alpine fault and, in part, to localised shear heating (Grapes, 1995).

On the continental crust of the Pacific plate in eastern South Island, intraplate volcanism was widespread with the latest eruptive products on the surface dated 5.8 Ma in Banks Peninsula and 10 Ma in Dunedin (Sewell and Weaver, 1989). Early to middle Tertiary volcanism was probably related to a mildly extensional regime following the opening of the Tasman Sea (Sewell and Weaver, 1989).

Thermal springs in Fiordland are located in a region where the Median Batholith, Western Fiordland Orthogneiss (Mortimer et al, 1999) and dunite (Landis and Coombs, 1967) are exposed on the surface.

4. TEMPERATURES AND SOURCES OF HEAT

The highest discharge temperatures were measured in springs of the MFS and NAFZ, ranging from 38 to 66°C with the other regions having lower discharge temperatures of nearly 17°C to 22°C (Figure 1, Table 1). The lowest thermal spring discharge temperature is 16.7°C in the Cascade Terraces in Fiordland ,within the FAFZ. The highest is 66°C in Julia Hut spring along the Taipo River near the junction between the the Hope fault of the MFS and the NAFZ. Discharge temperatures of up to 80°C have been reported below about 9 m of seawater in Anchorage Cove in Fiordland and as high as 71°C

Regions	Thermal discharges	Discharge T (°C)	Flow Rate (L/min)	Water Type	Major Gases[1]	% Mantle Volatiles[1]	Subsurface T (°C)	Thermal Water Flow (L/a)	Thermal Energy (TJ)
1. Coastal Canterbury Plains	4 springs, 4 wells	19-30	2-6	$Na\text{-}HCO_3\text{-}Cl$, $Na\text{-}HCO_3$	N_2, CH_4	nd	60-135	1×10^7	1
2 Northern Taeieri Basin	1 well	20	nd	$Na\text{-}HCO_3$	CO_2	83	310	?	?
3.Marlborough Fault System	17 springs	38-66	<1 - 150	$Na\text{-}HCO_3$ Na-Cl	CH_4- N_2	10.9	100-185	11×10^7	26
4. Northern Alpine Fault Zone	12 springs	40-63	<1-?100	$Na\text{-}HCO_3$	CO_2, N_2	8.1	120-300	6×10^7	4.3
5. Fiordland Alpine Fault Zone	6 springs	17-25	<1-51	$Na\text{-}HCO_3$ Na-Cl	CH_4	48.4	35-135	4×10^7	3.3
6. West Coast	1 well	22	190	Na-Cl	CO_2, CH_4	45.0	225	10×10^7	9
7. Southland	1 well	nd	nd	nd	CH_4	0.8	nd	nd	nd

Table 1. General characteristics of the spring regions in South Island. Data from this study except for [1] Giggenbach et al, 1993. Values for annual thermal water flow and thermal energy are minima.

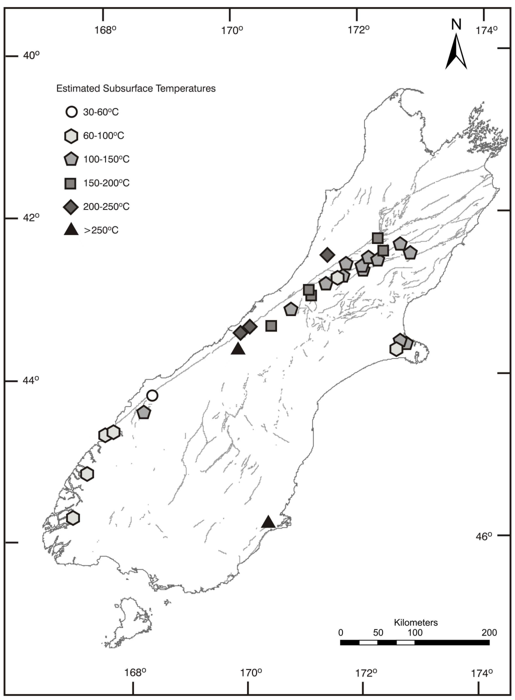

Figure 2 – Maximum estimated subsurface temperatures in South Island spring systems.

in the spring in Taipo River spring (Mongillo and Clelland, 1980). However, Anchorage Cove could not be accessed during this survey and the temperature measured in Taipo River spring was only 66°C in 2005.

The maximum estimated subsurface temperatures, are highest, at ≥300°C, in the Taieri Basin near Dunedin and in Copland, the southernmost spring of the NAFZ. The West Coast, based only on one discharge in Kotuku, has a maximum estimated subsurface temperature of 225°C, higher than in the MFS at 100-185°C and coastal Canterbury plains and FAFZ at 35 to 135°C (Table 1, Figure 2).

The latest active volcanism exposed on the surface in the Dunedin region, was about 10 Ma ago (Sewell and Weaver, 1989). However gases from a well in the Taieri Basin, Dunedin, located in a region of high heat flow (Allis et al, 1998) have an isotopic He signature R/R_A of 6.64 indicating entrainment of about 83% of mantle volatiles (Giggenbach et al, 1993). Seismic studies show a low velocity crust coinciding with a highly reflective region indicating the presence of hot mantle at depth (Godfrey et al, 2001). Hence, the high subsurface fluid temperature (this study) and high heat flow (Allis et al, 1998) in the Taieri basin is probably from heat just reaching the surface due to emplacement of hot mantle at depth, 10 My ago. In contrast, the close correspondence between topographic gradient and maximum subsurface temperatures of <150°C coupled with meteoric water isotopic signatures in the coastal Canterbury Plains and most of the FAFZ springs indicate that deep influx of groundwater, driven by topographic relief, redistributes heat. One gassy spring in the FAFZ has a He isotopic composition indicating nearly 50% entrainment of mantle volatiles in the gases. In contrast to the Dunedin region, Fiordland is essentially at the leading edge of a young subduction zone (Eberhart-Phillips and Reyners, 2001) where the continental crust is thicker (Kohler and Phillips (2003), the heat flow low (Allis et al, 1998) and the mantle is 80 km deep (Eberhart-Phillips and Reyners, 2001). Hence no heat from the mantle is being conducted to the surface yet; although through seismic pumping, mantle gases are released through the Alpine Fault (Giggenbach et al, 1993).

Subsurface temperatures generally increase from the MFS to the NAFZ yet the surface discharge temperatures are generally higher in the MFS. This apparent ambiguity may be caused by differences in permeability among the faults which, in turn, may affect the inflow of cold groundwater, the upflow from depth of heated equilibrated fluids and the speed of circulation of solutions. The MFS is probably more permeable than the NAFZ, being a region where 80 to 100% of plate motion between the Australian and Pacific plates is being accommodated (Eberhart-Phillips and Reyners, 1997). It is possible that, due to high permeability, the MFS faults accept massive inflow of groundwater from the surface but, at the same time, also allow relatively rapid circulation of heated groundwater back to the surface such that less heat is conducted away from the rising hot solutions to the confining rock. In contrast the recirculation of solutions in the NAFZ may be more circuitous, the fault zone less permeable or the fluid source deeper resulting to dispersion of temperatures of the rising solutions to the rock by conduction. Hence the discharge temperatures are lower in the NAFZ springs than in the MFS but the calculated subsurface temperatures are higher.

The West Coast Kotuku well discharging 22°C highly saline formation waters with Cl of 46,720 mg/kg, 2.4x that of seawater, (this study) is located in a region of high heat flow at 84-99 mW/m^2 (Townend, 1999). The high subsurface temperatures in the CO_2-rich highly saline formation waters in the West Coast may be affected by its proximity to the Alpine Fault Zone and its high salinity. Saline formation waters are heated and equilibrated with the rock to 225°C at depth, rise slowly through relatively impermeable structures, lose heat to the rock by conduction at shallower depths, resulting to low discharge temperature of 22°C.

5. FLOWRATES AND THERMAL ENERGY

The estimated minimum volume of overtly thermal waters discharged in the South Island

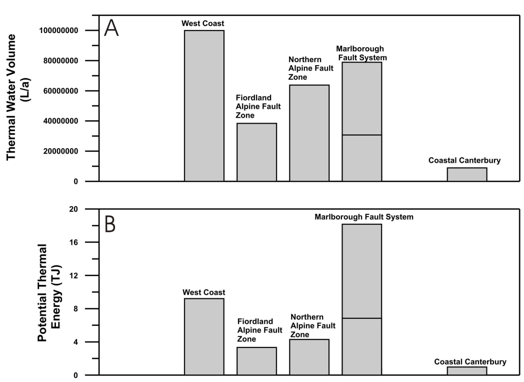

Figure 3- Minimum annual thermal water flow rate (L/a) and thermal energy (TJ) estimates in 5 regions of South Island. No data are available for Taieri Basin and Southland.

range from 1 x 10^7L/a in coastal Canterbury to 10 x 10^7 L/a in the West Coast and 11 x 10^7 L/a in the MFS. The data for the West Coast may be skewed because this is based on water flowing from a well, not springs. In general, thermal water released in the MFS is nearly 2x that of the NAFZ and nearly 3x the FAFZ (Figure 3A) suggesting that the MFS is probably more permeable than the Alpine fault Zone to its SW.

The potential minimum annual surface thermal energy of the spring systems in the South Island ranges from about 1 TJ in coastal Canterbury to a high of 26 TJ in the MFS. In the MFS most of the energy, at 18.2 TJ, comes from Maruia spring located in the Awatere Fault, with about 6.8 TJ from springs located along the Hope Fault and its subsidiaries (Hope Fault zone) and 0.8 TJ from the Clarence Fault springs.

6. CHEMICAL AND ISOTOPIC COMPOSITIONS OF SOLUTIONS

As shown in Figure 4, the springs in South Island discharge Cl, Cl-HCO_3 and HCO_3 waters, with 80% of the springs having HCO_3/Cl ratios of >1. The springs with high sulfate concentrations in Figure 4 (from Barnes et al, 1978) appear to be contaminated. These samples were probably not preserved in air-tight bottles and filtered within 24-36 hours resulting to oxidation of H_2S.

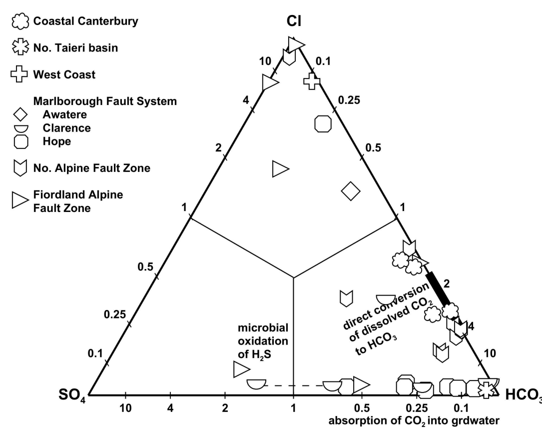

Figure 4- Relative Cl, HCO_3 and SO_4 concentrations of South island spring solutions.

Thermal springs along the Alpine Fault Zone often have microbially formed sulfur threads that tend to oxidise quickly when sampled.

Among the South Island springs, those with the highest HCO_3/Cl ratios are located along the MFS, within the Hope Fault zone. Despite the high HCO_3/Cl ratios, the MFS spring waters are in near equilibrium with the rock as shown in Figure 5. In contrast spring waters along the NAFZ and FAFZ, with lower HCO_3/Cl ratios, are farther away from the equilibrium line, suggesting differences in permeability and meteoric water throughput, storage and circulation between the MFS and AFZ and to a certain extent, reflecting

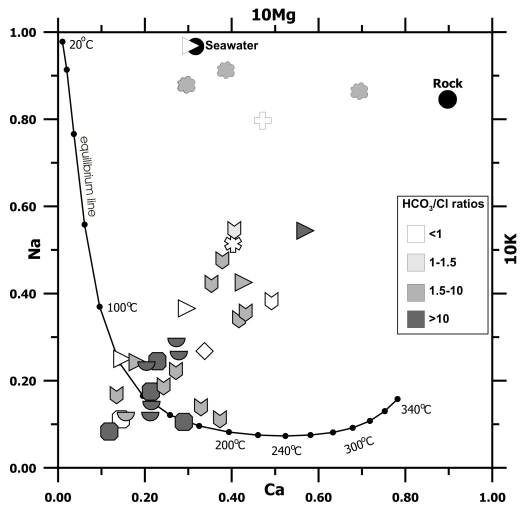

Figure 5- The relative Na-K and Ca-Mg concentrations of South Island springs plotted on a Giggenbach diagram, showing that most of the high HCO_3/Cl springs in the Alpine Fault Zone from the MFS to the NAFZ and FAFZ have nearly attained equilibrium with the rock formation whilst the high HCO_3/Cl waters in Canterbury have apparently not reacted long enough with the rock to approach the equilibrium line. Symbols are the same as in Figure 4.

variations in the degree of water-rock interaction in fluids circulating through the faults, changes in bedrock composition and probably differences in dissolved CO_2 concentrations in the waters. The MFS springs emanate mainly from greywacke and argillite, the NAFZ springs from increasing metamorphic grades of schist and the FAFZ springs from orthogneiss and dunite. The approach to near equilibrium of HCO_3/Cl waters in Alpine Fault Zone springs is probably due to the large surface area-to-volume ratios presented by fault comminuted rock along the fault where reactivity between water and rock would be faster.

Along the Alpine Fault Zone the B/Li and B/Cl ratios of spring waters decrease as the bedrock changes from greywacke and argillite to higher grades of schist and the F/B ratios of the waters approach greywacke compositions. Most of the spring waters have F/Cl ratios approaching that of greywacke except Copland, Hanmer and Irene Valley springs with ratios of 0.001 to 0.003, that may be affected by metamorphic waters. The Cs/Rb ratio is about 1 for all the NAFZ springs and the Maruia springs in the Awatere fault, but in other springs, the ratio approaches that of the crust. All the spring waters issuing from the Alpine Fault Zone are meteoric except for slightly enriched ^{18}O values at Hanmer and Taipo River springs which may be from clay dehydration waters from the subducted slab. There seem to be other chemical signatures of subducted water in Hanmer springs, the northeasternmost thermal spring along the Hope Fault zone as indicated by relatively high concentrations of B, Ba, Cl, Br, Na and ratios of Na/Cl, B/Li and F/B approaching that of seawater. Similarly most of the FAFZ thermal springs, located where the Australian plate subducts under the Pacific plate, have high Br and Ba concentrations and Na/Cl, F/B and B/Li ratios approaching that of seawater.

According the Barnes et al, the ^{13}C-DIC in several springs in the MFS and NAFZ are derived from organic C and the solution of calcite with possible magmatic/mantle C expelled from the two southernmost thermal springs in the NAFZ (Barnes et al, 1978). However the He isotopic ratio in the latter indicates a predominantly crustal origin, probably metamorphic in origin rather than magmatic (Giggenbach et al, 1993).

Waters in coastal Canterbury and the Taieri Basin are meteoric in origin whilst the West Coast thermal discharge is formation water.

7. CONCLUSIONS

Except for the formation waters in the West Coast the spring discharges in most regions of the South Island are of meteoric in origin. Along the Alpine Fault Zone meteoric waters gain solutes from interaction with fault comminuted rock, contributions from the subducted slabs in the NE and SW of the South Island and metamorphic fluids at depth. Waters on the east and west side of the Alpine Fault are heated at depth to 100°C to as high as nearly 300°C. Anomalous heat along the Alpine Fault Zone is generally believed to be due to rapid uplift and exhumation (e.g., Allis et al, 1979). Hot waters at depth in the Taieri basin however, is probably due to heat generated from hot mantle at depth.

ACKNOWLEDGMENTS

Water samples were chemically analysed at GNS-Wairakei and isotopic compositions of waters measured at Iso-Trace, Dunedin.

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