Evaluation of critical elements in geothermal systems of the Taupo Volcanic Zone, New Zealand

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Keywords: critical elements, geochemistry, fluids, minerals, Taupo Volcanic Zone, New Zealand

ABSTRACT

To assess the potential for the Taupo Volcanic Zone (TVZ) geothermal systems to produce critical elements, fluid discharges from hot springs and wells, fresh and altered volcanic rocks, volcanic ash leachates and precipitates from geothermal wells and springs were chemically evaluated, and in the case of solid materials, also petrographically analysed. Assuming a median water output of 340m^3/h for a typical TVZ geothermal system with a ~3:7 ratio for gas and aqueous fluids, elements with the highest concentrations (>100kg/a) in aqueous fluids, from lowest to highest, include Mo, Sb, Sr, W, Al, Cs, Rb, As, Li, Ca, B, Si and Na. Although only ~1-75 kg/a of Au, Ga, Tl, Ag and Ge are produced in the discharge fluids, their high market price warrants further study. With high market prices, the TVZ geothermal fluids may be an alternative source for Cs and Rb, which occur in high concentrations. Amongst gases of economic interest in the TVZ are CO_2 mainly for food processing, C_2H_6 and He. Without considering costs of mining, production and research, cut-off concentrations for mining elements, and current technological capabilities to extract elements from aqueous solutions or silica precipitates, fluids from one producing TVZ geothermal system contains ~NZ$850M/a worth of elements or ~NZ$19.5B/a for 23 active hydrothermal systems. However, as attested by studies of metal and non-metal deposition in geothermal installations and ore mineral deposits, specific conditions are required to induce precipitation or enable fluid-extraction of specific elements including, among others, changes in fluid flow rates, redox conditions, temperature and pressure, phase separation and fluid mixing. Thus, despite the presence of a wide range of critical elements in the TVZ fluids, only a few can be economically and technologically extracted at present.

1. INTRODUCTION

The terms “critical” or “endangered” elements refer to supply risks (https://www.acs.org/) of economically significant natural elements of which there are ~90 (https://www.euchems.eu/euchems-periodic-table). Supply risk, as pointed out by the European Chemical Society, is worsened for elements sourced from regions of conflict (Fig. 1). Based on 2021 consumption levels, 12 elements from He to Ta are deemed to be under serious threat in the next 100 years (Fig. 1). Another 12 are under rising threat and 19 are of limited availability and at future risk to supply from increasing use in rechargeable batteries for smart phones and green energy devices e.g., electric or hybrid vehicles and wind turbines (Fig. 1), solar panels, aircraft engines, thermal imaging devices, GPS equipment, defense equipment and others (e.g., Geology.com). Supply is plentiful for more than 35 elements. Carbon in the form of gases such as CO_2 and CH_4 is generally plentiful although there is a shortage of CO_2 for food processing in New Zealand. Carbon in the form of oil and natural gas is under serious threat as known subterranean supplies diminish and because some of the most productive oil fields are located in regions of political unrest. There are various remediation procedures to decrease the supply risk of elements e.g., recycling, substitution of critical elements with more abundant materials, devising new ways of manufacturing equipment with an intent to recycle, finding new methods or revamping old methods to extract elements from unconventional sources more economically such as seawater (e.g., https://pubs.usgs.gov/periodicals/mcs2022), geothermal fluids, precipitates and altered rock, metal scrap, biological sources and others. A number of studies aver, however, that mineral resources in the earth’s crust are by no means depleted (Kesler and Wilkenson, 2008; Henckens, 2021), with the search for new resources improved by modern geophysical exploration methods (e.g., Best, 2015) and the supply extended by exploitation of resources with lower concentrations.

The focus of this study is the Taupo Volcanic Zone (TVZ) where numerous studies demonstrate the propensity for precious, base, alkaline and alkaline earth metals and non-metals to be precipitated on the surface, in hot springs and geothermal installations (e.g., Liversidge, 1878; Weissberg, 1969; Weissberg et al, 1979; Hedenquist and Henley, 1985; Brown, 1986; Krupp and Seward, 1987; Reyes et al, 2002; Brown and Simmons, 2003; Pope et al, 2005; Wilson et al, 2009; Rowland and Simmons, 2012; Pope and Brown, 2014), deposited in subsurface rock formations (e.g., Ewers and Keays, 1977; Weissberg et al, 1979; Simmons and Browne, 2000) and entrained as solutes in discharge fluids (e.g., Hirner et al, 1998; Wood, 2003). As pointed out by Simmons et al (2016) and Hirner et al (1998), most chemical elements precipitate in the well and rock formations resulting to very low concentrations in surface fluid discharges. Hence, to evaluate the flux of chemical elements in geothermal systems (Simmons and Brown, 2007) downhole well samples have been analyzed by various workers (e.g., Simmons et al, 2016).

The objectives of this paper are to: (1) examine the various elements inherent in the rock, produced by volcanic activity and enhanced by water-rock interaction and other factors and (2) evaluate the mass (kg) of elements that can potentially be extracted from fluids in high-temperature geothermal systems of the TVZ.

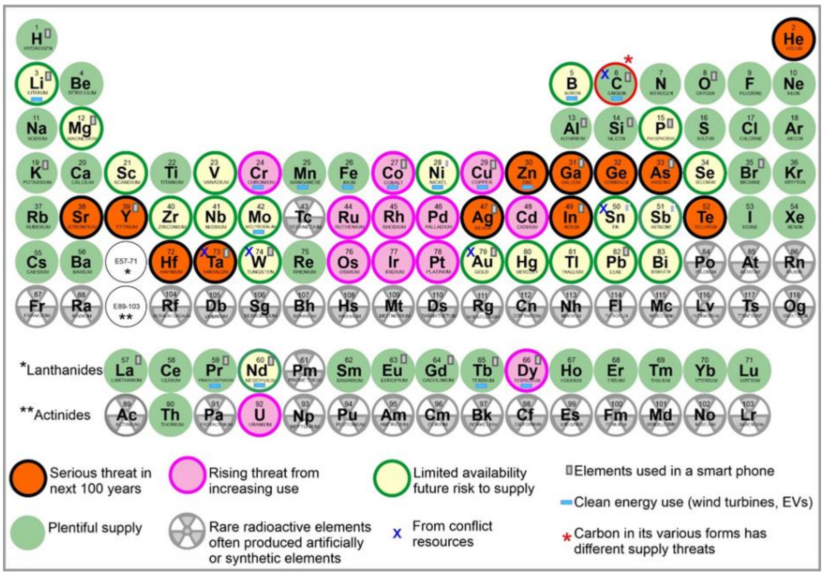

Figure 1: Periodic table showing "critical elements" according to 2021 consumption levels based on the American Chemical Society (https://www.acs.org/) and European Chemical Society (EuChemS; https://www.euchems.eu/euchems-periodic-table).

2. GEOLOGICAL SETTING, HEAT AND MASS FLOWS AND GENERAL FLUID COMPOSITIONS

The Taupo Volcanic Zone is a back arc rift developed from the oblique convergence of the Australian and Pacific plates along the Hikurangi margin east of the North Island (e.g., Cole, 1990, Acocella et al, 2003). The region is the locus of unusually voluminous rhyolite volcanism in the last 1.6 Ma and andesitic magmatism since 2.0 Ma with the volume of erupted rhyolites an order of magnitude higher than andesites (Wilson et al, 1995). There are at least 23 active hydrothermal systems (Fig. 2) with an estimated heat output of 4.2 GWt expelling at least 10^8 m^3/a (10^{11}kg/a) of aqueous fluids (Bibby et al, 1995). Estimated mass flows in kg/a are shown in Fig. 2 and have a median value of 3 x 10^6 m^3/a (340 m^3/h). Six to eight of these systems are utilized for power production with an installed net capacity of more than 940 MWe (www.nzgeothermal.org.nz; www.thinkgeoenergy.com).

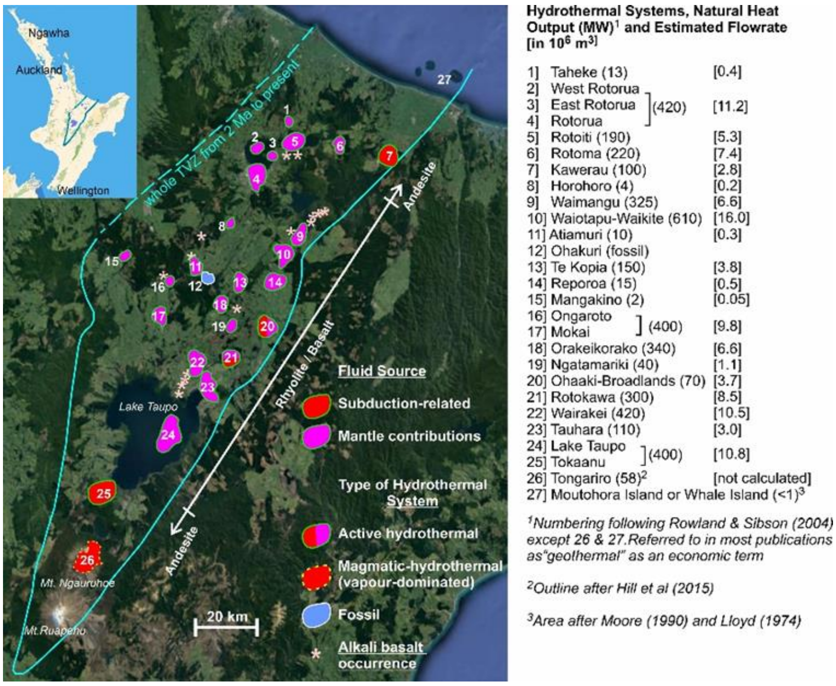

Figure 2: Outline of the TVZ from 2.0 Ma to present, distribution of hydrothermal/geothermal systems, volcanic rock types, natural heat output and general fluid compositions. Inset shows the location of the TVZ in the North Island.

Figure 2 shows the outline of the TVZ from 2.0 Ma to present (Wilson et al, 1995), distribution of hydrothermal/geothermal systems (Bibby et al, 1995; Hill et al, 2015; Lloyd, 1974; Moore, 1990) and natural heat output (Bibby et al, 1995; Walsh et al, 1998). The Moutohora Island heat output (0.3 MW) is based on an area of 0.11 km^2 covered by thermal manifestations (Lloyd, 1974; Moore, 1990) and assumes similar conditions as Kawerau. Rhyolite is the dominant magma erupted in the last 2.0 Ma of the TVZ (Wilson et al, 1995) with alkali basalts extruded in the central part and andesites occurring only in the northernmost and southernmost regions (Rowland and Sibson, 2004). Estimated mass flowrates for each hydrothermal system (Fig. 2), in this study, assumes that the heat output is related to the liquid's enthalpy at depth based on the Giggenbach (1991) CH_4-CO_2 geothermometer. The total mass flow in the TVZ is estimated at ~120M m^3/a and a heat flow of ~4600 MW.

Except for magmatic-hydrothermal systems at Tongariro (26) and White Island (outside map view) all other geothermal/hydrothermal systems in the TVZ are liquid-dominated (Giggenbach, 1995 and 1996). Two geochemically distinct source fluids were identified by Giggenbach (1995): subduction-related usually associated with andesitic volcanism, and rift-type associated with rhyolites and high-alumina basalts. Subduction-related or arc-type hydrothermal fluids, confined in the eastern side of the TVZ, are characterized by high CO_2 contents (1.6 $\pm$ 0.5 mmol/mol), CO_2/Cl mole ratio (3.9 $\pm$ 1.5), $CO_2/^3He$, N_2/Ar, B/Cl (0.06), Li/Cs (12) with a magmatic component of 14 $\pm$ 5%. In contrast rift-type fluids, expelled from the majority geothermal systems, are characterized by lower CO_2 (0.12 $\pm$ 0.05 mmol/mol), CO_2/Cl mole ratio (0.14 $\pm$ 0.1), $CO_2/^3He$, N_2/Ar, B/Cl (0.02), Li/Cs (7) and magmatic input (6 $\pm$ 2%). However, median Cl contents from well discharges are higher in rift-type (~1000 mg/kg) than in arc-type (~600 mg/kg) fluids. About 100M m^3/a of aqueous fluids are expelled from rift-type in contrast to arc-type systems at ~14M m^3/a. The total heat output of rift-type systems is ~4064 MW where CH_4-CO_2 temperatures are highest (>300°C), ~8x that of arc-type systems

3. RESULTS

3.1 Critical elements in melt inclusions, fresh and altered rock

An idealized cross-section of a typical TVZ hydrothermal system (Fig. 3A) shows two major lithologies: the Mesozoic greywacke basement at depth overlain by igneous rocks consisting of extrusives, volcaniclastics (rhyolite, minor andesite and alkali basalt) and intrusives (e.g., Wyering et al, 2014). Sedimentary beds at shallower depths e.g., Huka Falls and Onerahi Formations with tuffaceous intercalations (e.g., Wood, 1994; Wyering et al, 2014) are grouped under volcaniclastics due to similarities in chemical compositions (this study).

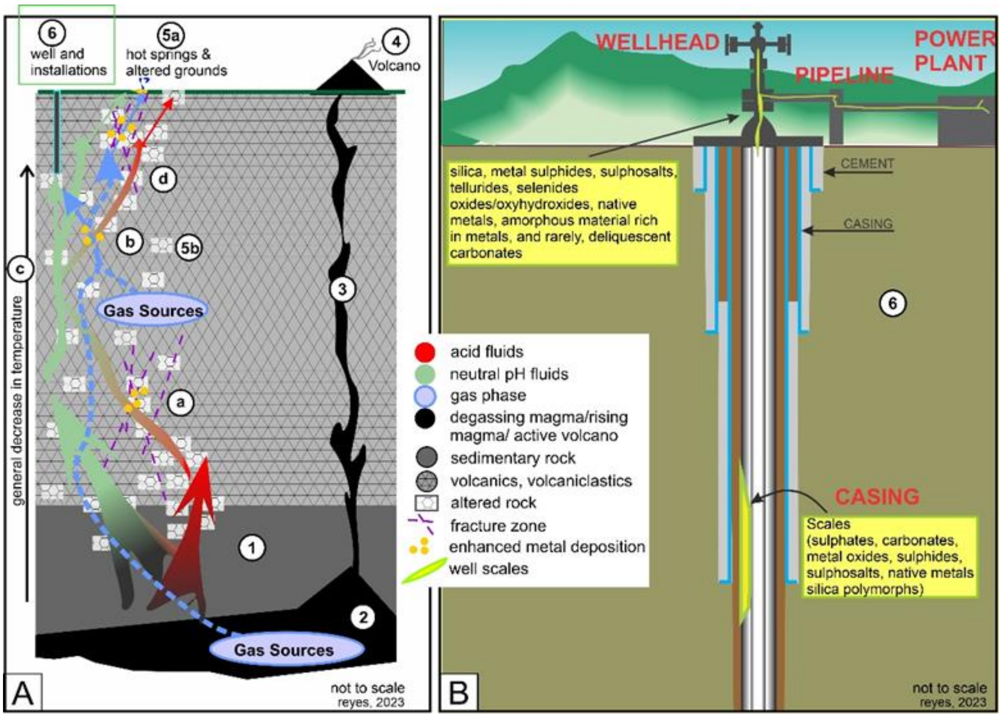

Figure 3: [A] Diagram showing major sources of critical elements in the TVZ marked by numbers and some sites of enhanced metal deposition in the rock formation (a, b, c and d), discussed in the text. Number 6 is shown in detail in [B] main sites and compositions of mineral deposition in a typical TVZ geothermal well and its surface installations (this study).

3.1.1 Greywacke

Apart from Au, B, As, Bi and S which are 2x to 4x more concentrated in the Mesozoic greywacke (1 in Fig. 3A; Ewers, 1977; this study), concentrations of other elements are either similar or less than in the earth's crust. However, hot water-rock interaction experiments showed that volatile species such as As, Sb, Se and S are extracted from greywacke in significant amounts (Ewers, 1977).

3.1.2 Volcanics

Numbers 2 to 4 in Fig. 3A illustrate the sources of elements in volcanic fluids, represented by melt inclusions (Fig. 4A; Reyes et al, 2012, Johnson et al, 2013) and ash leachates and materials adhering on ash during explosive volcanic eruptions e.g., Ruapehu in 1995-1996 (this study; Fig. 4B) and in the rock (Ewart et al, 1968; this study; Fig. 4C). Rhyolitic melt inclusions contain higher concentrations of Cl and B than andesitic ones, reminiscent of rift- and subduction-type geothermal discharge fluids. Melt inclusions show that rhyolitic and andesitic magmatic fluids contain Fe, Ti, Co, Cu, V, Cr, Zn and Ni in various proportions but Mo, Hg, Pb and As appear to have a stronger affinity for rhyolite melt; and Ge for andesite.

Figure 4B (4 in Fig. 3A) illustrates the volume of materials introduced to the surface by ash falls although this example includes materials expelled from the Ruapehu Crater Lake (this study). For a small eruptive episode of 0.04 km^3 of ash for the 1995-1996 eruption of the andesitic Ruapehu volcano (Cronin et al, 1998), $\geq$1 kg each of Tl, Ag, Cd, Se, Cr, As, Li, Co, Ni, Pb, Cu, Zn, Mn, B and Fe together with F, Cl, and SO_4 are expelled in less than a year.

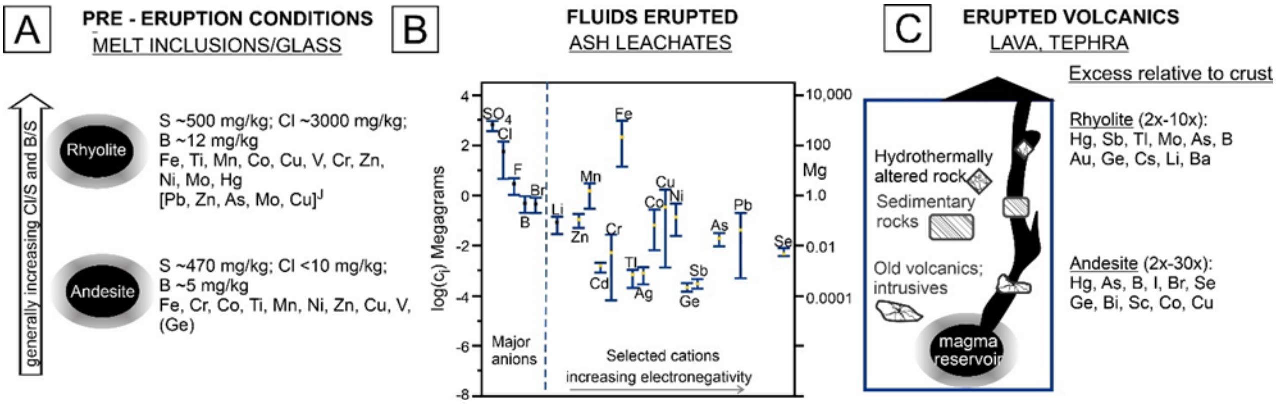

Figure 4: Volcanic sources of elements as indicated by occurrences in[A] melt inclusions and glass of rhyolite and andesite, [B] ash leachates exemplified by expelled material adhering on Ruapehu ash fall during the 1995-1996 eruption, and [C] volcanic rock compositions showing elements >2x more concentrated than the mean crustal abundance. J in [A] is data from Johnson et al (2013).

A comparison of median chemical compositions shows enrichment in Hg, As, B, and Ge in both the TVZ rhyolite and andesite eruptives (Fig. 4C) relative to normal crustal abundances (e.g., Bowen 1979). Antimony, Tl, Mo, Au, Cs, Li and Ba abundances are specifically more enhanced in rhyolite and I, Br, Se, Bi, Sc, Co and Cu in andesites, relative to the earth's crust (this study). However, as shown in Fig. 4C, entrainment and interaction with old materials such as volcanic/intrusives, sedimentary rocks and hydrothermally altered rocks (e.g., Graham and Hackett, 1987) may contribute to trace and minor chemical compositions of volcanic rocks.

Intense alteration of rhyolite on the surface, in hot springs, enhances concentrations of volatile elements by 2x to >1000x including Tl, Hg, Sb and As with most of the other elements enhanced by 2x to 200x relative to fresh rhyolite e.g., Cu, Zn, Sr, Ga, and Au (Fig. 5A; this study). Compared to fresh rhyolite, moderately chloritized and silicified rhyolite altered at 270^{o}C at depth is enriched in Cu, V, Cr, P, Mn, Ti, Mg, Ca and Fe by 2x-50x (Fig. 5B).

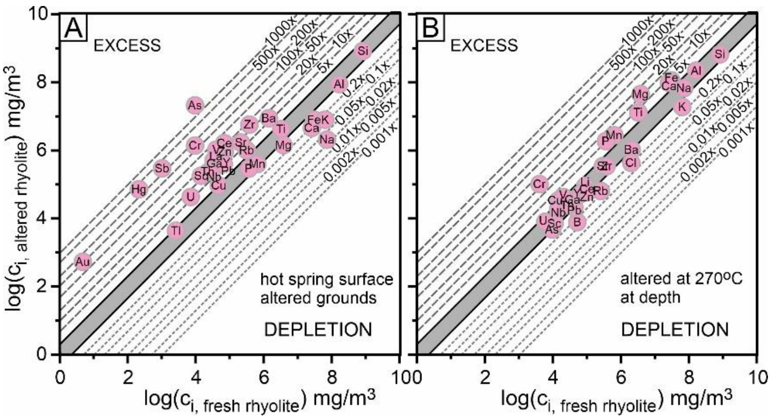

Figure 5: [A] Enhancement of elements in altered rhyolite in hot spring altered grounds and [B] rhyolite at depth moderately altered at 270^{o}C relative to fresh rhyolite (this study). Grey region is typical TVZ rhyolite composition from Ewart et al (1968).

Figure 3A shows some of the processes that enhance element deposition in the TVZ including (a) fluid mixing and neutralization of acid fluids, (b) phase separation and changes in redox conditions, (c) changes in temperature and pressure with depth or caused by hydrothermal brecciation and (d) water-rock interaction and rock dissolution.

3.1.3 Mineralogy and precipitates

At least 24 minerals have been identified as precipitates in hot springs, well casings and well surface installations in the TVZ (Figs. 3B and 6A) containing Fe, As, S, Cu, Sb, Zn, Ag, Te, Pb, Ag and Au (e.g., Weissberg, 1969; Ewers and Keays, 1977; Brown, 1986; Krupp and Seward, 1987; Reyes et al, 2002; Pope et al, 2005; Simmons et al, 2016; this study). The main mineral deposited in wells, well surface installations (Fig. 3B) and hot springs is silica, a "sponge" (Fig. 6B) for a number of elements in discharge aqueous fluids including Li, B, Cr, Ni, Cu, Zn, As, Ag, Hg, Sb, Au, Rb and Cs (Brown, 1986; Reyes et al, 2002; Reyes, 2017). Other substrates to which elements preferentially adhere to include biogenic material for Hg, Ge, As, Sb and Te (Hirner et al, 1998) and possibly pyrite and fahlore (e.g., Makovicky and Karup-Moller, 2017), commonly-occurring minerals in the TVZ. Other abundant elements are found in hot spring silica sinters and rock formations at depth (Fig. 6C) including rare earths (e.g., Wood, 2003) and adhering on ash from volcanic eruptions (Fig. 6D).

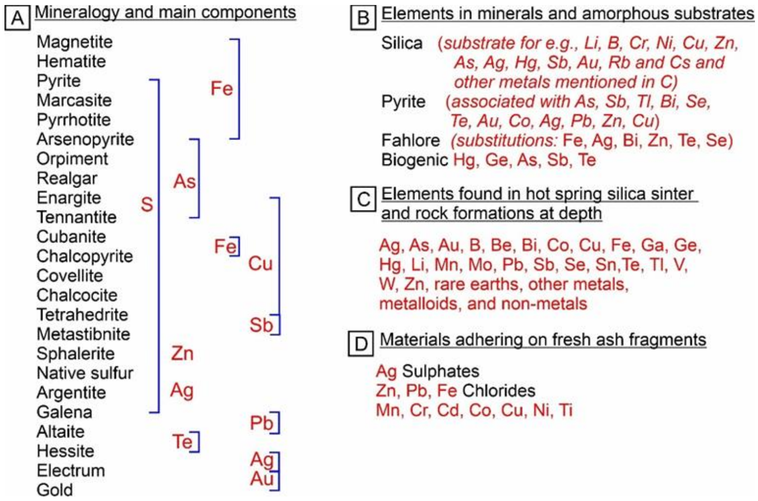

Figure 6: [A] Minerals deposited as spring deposits and well scales and their main components, [B] elements concentrated in minerals and amorphous substrates, [C] enhanced concentrations of elements in silica sinter and occurrences in subsurface altered rock and [D] materials adhering on fresh ash fragments from the 1995-1996 Ruapehu eruption.

In summary, the chemical compositions of melt inclusions, rock, mineral precipitates and volcanic ash leachates in the TVZ show that hydrothermal and magmatic-hydrothermal fluids have the propensity to contain enhanced concentrations of a wide number of critical elements including Te, Zn, Ga, As, Ge, Ag, Y, Sr, U, Cu, Cd, Co, Cr, Dy, Li, B, Mg, P, Sc, V, Ni, Zr, Nb, Mo, Sn, Sb, W, Au, Hg, Tl, Pb, Bi and Nd although not all, as yet, have been analyzed or detected in the fluids (Figs. 7A and B).

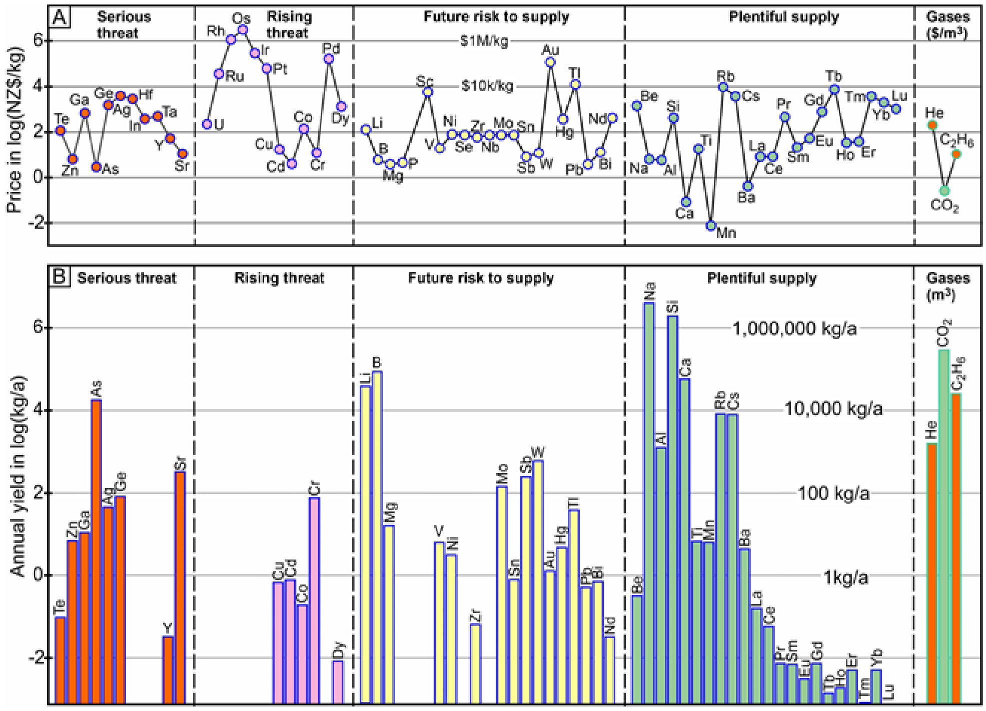

Figure 7: [A] International market prices of elements in log(NZ$/kg) and [B] estimated annual yield of elements, in log(kg), from fluids of a typical TVZ geothermal system.

3.2 Fluid discharges

As much as possible, the yield of elements from a typical TVZ hydrothermal discharge is calculated from downhole samples (Ritchie, 1973; Goguel, 1988; Simmons et al, 2016). In the absence of downhole measurements for rare earth elements (Wood, 2003) it is assumed that surface discharge and downhole concentrations are the same. Calculation of the annual mass of various elements produced by a typical geothermal system in the TVZ assumes a median flowrate of 3 x 10^6 m^3/a and a gas:aqueous fluid ratio of 3:7. Market prices of critical elements and selected non-critical elements are shown in Fig. 7A and the annual mass (kg) produced in a typical TVZ geothermal system shown in Fig. 7B.

The highest yield of elements from aqueous fluids of a typical TVZ geothermal system, at >100kg/a include from lowest to highest: Mo, Sb, Sr, W, Al, Cs, Rb, As, Li, Ca, B, Si and Na. There are also three sets of elements that warrant further study: (1) Au, Ga, Tl, Ag and Ge, despite low yields at only ~1-75 kg/a, because of high market prices, (2) Rb and Cs because of high yield from geothermal fluids and high market prices and thus TVZ hydrothermal fluids can be an alternative source for Rb and Cs in the future and (3) Si because silica precipitates act as a sponge for a number of elements as discussed in Section 3.1.3. Amongst gases of economic interest in the TVZ are CO_2 mainly for food processing, C_2H_6 and He; although the abundance of the last two are higher in hydrocarbon-bearing sedimentary systems such as in Taranaki, Northland and the South Island.

4. SUMMARY AND CONCLUSIONS

Without considering costs of extraction from fluids and mineral substrates, production and research, cut-off concentrations for mining elements, and current technological capabilities to extract elements from aqueous solutions or silica precipitates, the monetary value of elements in a typical TVZ fluid discharge is shown in Fig. 8, based on Figs. 7A and B. The estimated value of Mo, As, Ag and CO_2 in fluids from one TVZ system is $10k-100k/a per element; 100k-1M/a for Au, C_2H_6, He, Ge, Tl and B and >1M/a for Li, Na, Cs, Rb and Si. One producing TVZ geothermal system contains ~NZ$850M/a worth of elements or ~NZ$19.5B/a for 23 active hydrothermal systems.

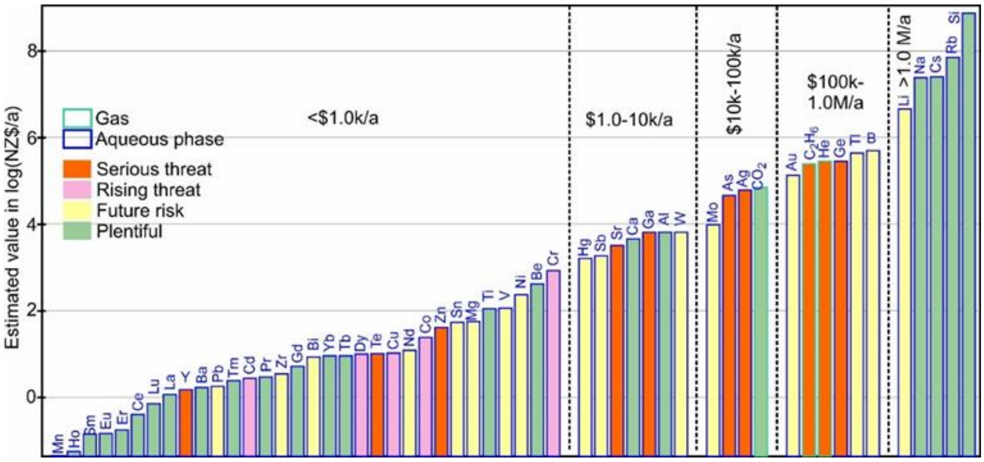

Figure 8: Estimated annual worth of elements in a TVZ geothermal system.

However, as attested by studies of metal and non-metal deposition in geothermal installations, volcanic crater lake deposits and ore mineral deposits, specific conditions are required to induce precipitation or fluid-extraction of specific elements including, among others, changes in fluid flow rates, redox conditions, temperature and pressure, phase separation and fluid mixing. Thus, despite the presence of a wide range of critical elements in the TVZ fluids, only a few can be economically and technologically extracted at present.

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