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Review

Critical Element Concentrations in High Enthalpy Geothermal Fluids in New Zealand

Lucjan Sajkowski [1,*], Rose Turnbull [2] and Karyne Rogers [3]

1 GNS Science, Wairakei Research Centre, Taupo 3384, New Zealand
2 GNS Science, Dunedin Research Centre, Dunedin 9016, New Zealand
3 GNS Science, National Isotope Centre, Gracefield 5010, New Zealand
* Correspondence: l.sajkowski@gns.cri.nz

Abstract: This review compiles publicly available datasets describing the chemical composition of geothermal fluids from eight wells in the Taupo Volcanic Zone (TVZ) and Ngāwhā, New Zealand. Our review allows previously reported geothermal reservoir water compositions at various locations around the TVZ (and Ngāwhā) to be assessed and compared for the first time. The combined data present a new perspective on potential critical elements of geothermal resources and will be a valuable tool for future research projects and investment opportunities. Composition data were used to estimate the annual flux of different elements in New Zealand geothermal systems. Several elements found in New Zealand geothermal fluids are currently considered 'critical' for the transition to a carbon-neutral economy and are present in economically extractable quantities. We estimate that each year, approximately 1100 tons of lithium pass as heat exchange fluids through Wairakei geothermal power station. An overview of the critical elemental capture and extractive potential from New Zealand's geothermal fields is provided.

Keywords: critical elements; geothermal reservoir; geothermal fluid; Taupo Volcanic Zone; extraction; green energy future

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1. Introduction

Building a low-carbon energy ecosystem for Aotearoa, New Zealand, will require access to new resources of specific elements and materials. Elements that play an important role in low-carbon future technologies—many of which are classified as 'critical elements'—are unevenly distributed around the world [1]. Often, 'critical element' supply chains (both for mining and processing) are dominated by a few players that are granted a "near-monopoly" in a small number of countries. While global efforts to secure supply chains of critical elements have focused on traditional mineral ore bodies and material recycling, critical elements are known to occur in geothermal fluids in economically extractable quantities [2–8]. Geothermal fluids used to generate electricity represent a particularly interesting opportunity for critical element extraction, thanks to the existing substantial infrastructure. Although the process of economic recovery of aqueous critical elements presents technical challenges [3,9], it is certainly worth exploring, especially considering the potential added value to producing geothermal power stations [10]. The aim of this review is to extract and compile data from almost 60 years of studies of New Zealand geothermal fluids. This paper offers a comprehensive insight into the composition of New Zealand geothermal fluids and provides potential quantitative extractable estimates of critical element resources. Although some of the geochemical data are dated or were sampled and analyzed using different techniques, they still offer first-order guidance on potential elemental abundances and subsequent extraction opportunities. This is the first study to compile geothermal fluid compositions for such a wide range of elements—previous reviews of geothermal well compositions have focused on the elements of highest abundance and also addressed the most commonly analyzed elements (i.e., Na, K, Ca, Cl, B, SiO_2, Li, Rb, Cs, Mg, Au, Ag, and Cu [8].

1.1. Critical Elements

Critical elements are defined as those that are crucial to society for economic growth and/or national security but which are vulnerable to supply disruption (Figure 1) [11]. They are usually in high demand and have no practical substitutes. As such, the elements deemed 'critical' change through time due to social, technical, and political changes [12]. Presently, most of the elements classified as 'critical' are essential components for clean energy (i.e., solar, wind) and clean technology (i.e., electric vehicles, home battery devices) sectors and are therefore crucial in enabling the move to a global low-carbon economy. There are currently 50 elements and minerals listed as critical in the United States of America (USA) [13]. These are: aluminum, antimony, arsenic, barite, beryllium, bismuth, cerium, caesium, chromium, cobalt, dysprosium, erbium, europium, fluorspar, gadolinium, gallium, germanium, graphite, hafnium, holmium, indium, iridium, lanthanum, lithium, lutetium, magnesium, manganese, neodymium, nickel, niobium, palladium, platinum, praseodymium, rhodium, rubidium, ruthenium, samarium, scandium, tantalum, tellurium, terbium, thulium, tin, titanium, tungsten, vanadium, ytterbium, yttrium, zinc, and zirconium.

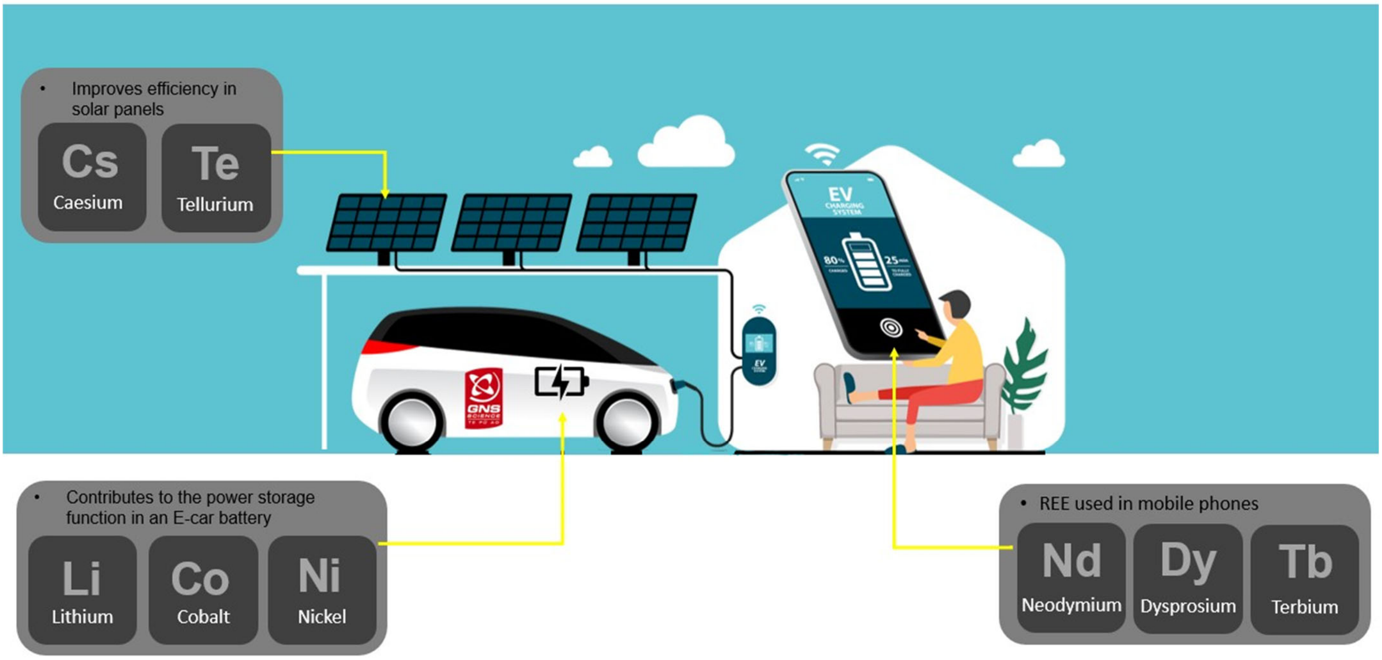

Figure 1. Examples of the use of some critical elements in green technology (electric car batteries, solar panels) and high-tech electronics (i.e., smartphone batteries, magnets, and screens). The examples above include numerous other critical elements not shown that are essential to their various technologies (e.g., electric vehicles).

In comparison, the European Union defined its own list of critical materials (elemental groups and minerals) [14,15], including many of the elements listed as 'critical' by the US Geological Survey (USGS), but also including bauxite, borate, coking coal, natural rubber, phosphate rock, phosphorus, silicon metal, and strontium.

New Zealand does not currently have a list of elements considered 'critical' for societal, economic, and/or national security reasons. However, the necessity for the development of such a list has been recognized as a part of a plan to secure affordable resources to meet New Zealand's future mineral and energy needs. As part of the Ministry of

Business, Innovation and Employment's (MBIE) 2019–2029 Resource Strategy for New Zealand, a list of critical minerals specific to New Zealand is in development [16].

1.2. Extraction of Critical Elements from Geothermal Fluids

Growing demand for carbon-neutral renewable energy is generating an incentive to grow geothermal developments worldwide. New Zealand is no different, and geothermally generated electricity accounts for c. 20% of New Zealand's total electricity supply, with new field developments still ongoing. In addition to generating electricity, geothermal fluid can also be used as a direct source of heat energy in industrial, commercial, and residential sectors. In Iceland, geothermal heating utilizing geothermal fluids piped into buildings has provided heating and hot water for >90% of all of Iceland's buildings for more than 20 years [17]. In New Zealand, geothermal heat is used to dry timber, manufacture milk powder, and heat glasshouses for horticultural purposes.

Well-managed geothermal resources are a source of clean, reliable, and sustainable energy. Once geothermal fluid has been extracted from a production well and has been used to generate electricity or supply heat, the energy-depleted fluid is reinjected back into the reservoir through reinjection wells some distance from the production well. The reinjected fluid flows through the fractured reservoir network (i.e., permeable zones in the rock), extracting more thermal energy from the rocks and mixing with the reservoir fluid as it flows back towards the production well [18–22].

In recent years, research has begun to examine the potential for the commercial extraction of various elements from geothermal fluids (Figure 2), (i.e., [3,4,6,23,24]. This new and emerging industry has the potential to develop into a significant multi-million-dollar industry both in New Zealand and internationally. However, multidisciplinary collaborative research is necessary to assist in removing implementation barriers [25]. Despite promising fluid compositions and the substantial volume of geothermal fluid production at numerous geothermal fields in the Taupo Volcanic Zone (TVZ), the additional opportunity for critical element extraction at a commercial scale in New Zealand is yet to be realized for minerals other than silica.

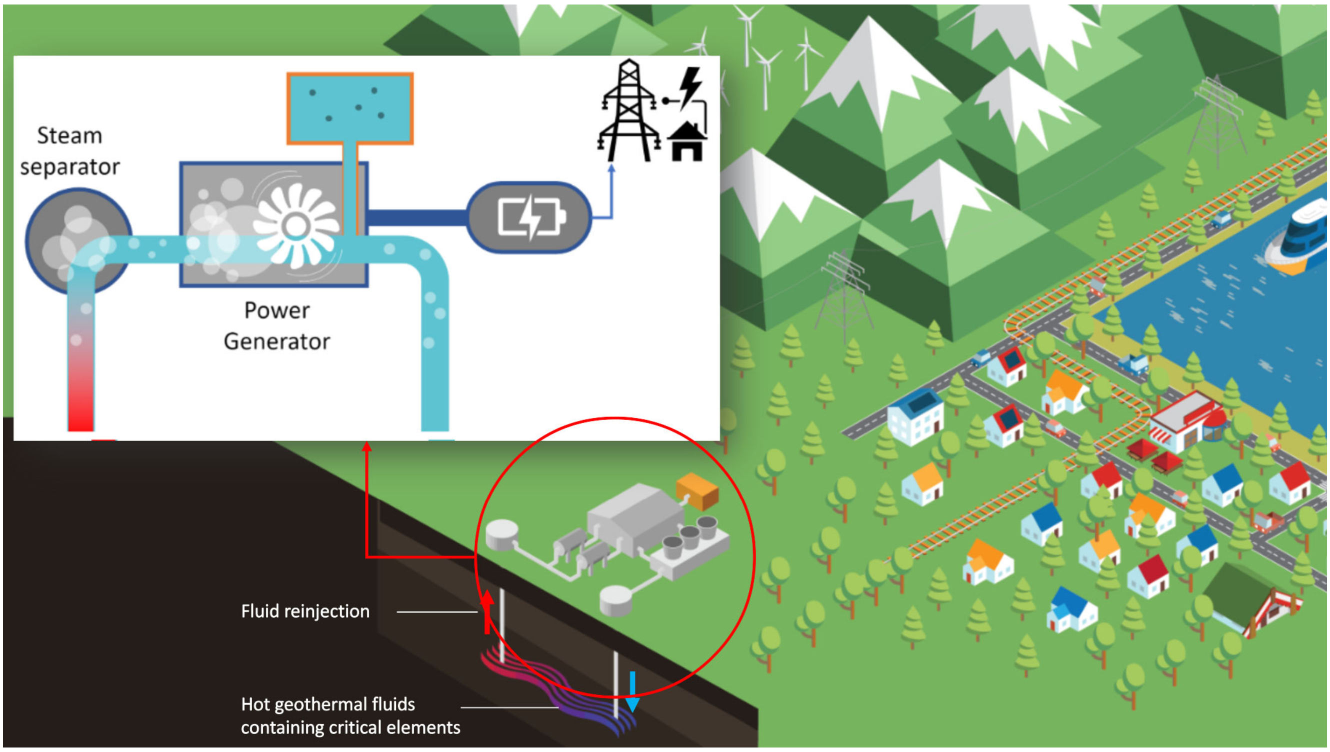

Figure 2. Cartoon highlighting the co-existence of geothermal energy production and critical element extraction from geothermal fluids (i.e., lithium).

1.3. Recovery of Elements from Geothermal Fluids

The concept of multi-element extraction from geothermal fluid is not new. In the 1960s, extraction of lithium, sodium, and potassium from the Wairakei geothermal field was considered [26]. In the early 1980s, a pilot plant at Wairakei was set up to separate solids (e.g., calcium silicate) from geothermal fluid [10]. Subsequently, over the years, many researchers and engineers have revisited the opportunity for mineral extraction from geothermal fluids [3,5,6,8,9,25,27–31].

Today a sustainable silica extraction plant is in operation at the Ohaaki geothermal power station in New Zealand, with a lithium extraction plant in the pilot stages of operation. In the USA, at Salton Sea, California, three companies are developing chemical processes to extract lithium in economic quantities from geothermal fluids [32]. Similarly, other countries, including the United Kingdom (UK) and Italy, are exploring opportunities to extract elements from geothermal fluids [33–35], and in Germany, the first example of battery-grade lithium has already been produced from geothermal fluids [36].

2. New Zealand High-Temperature Geothermal Systems

Historical well water compositions from eight currently operated, high-temperature geothermal fields, Ohaaki, Kawerau, Mokai, Ngatamariki, Ngāwhā, Rotokawa, Tauhara, and Wairakei (Figure 3, with Ngāwhā field in the insert), are compiled. New Zealand's high-temperature geothermal systems are restricted to the TVZ except for Ngāwhā, which is located in Northland (Figure 3). The TVZ is an active continental volcanic arc/back-arc basin, resulting from subduction of the Pacific Plate beneath the Australian Plate along New Zealand's North Island [37]. It is a region of active extension and crustal thinning, with high-heat flow and productive rhyolitic volcanism [38,39]. The TVZ extends from Ruapehu in the south to Whakaari/White Island in the northeast and is flanked and underlain by basement metasedimentary rocks (greywacke and argillite) of the Mesozoic Torlesse and Waipapa composite terranes [38,40]. The northern and southern ends of the TVZ are dominated by volcanics of andesitic composition, while the central segment is dominated by rhyolitic compositions [41,42]. Most of the high-temperature geothermal systems are located within rocks of rhyolitic composition, though lithologies are variable (i.e., rhyolitic ignimbrites and lavas interbedded with lacustrine and fluvial sediments [39].

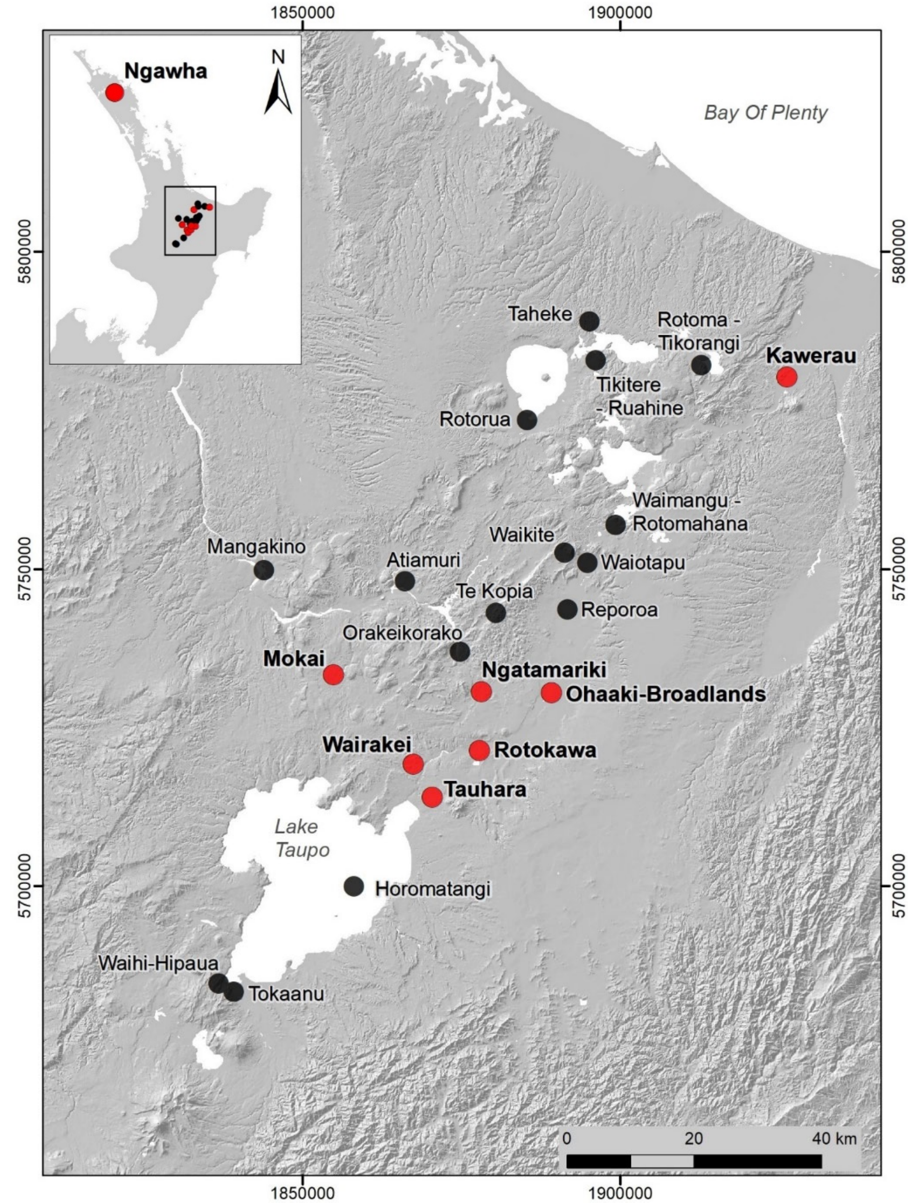

Figure 3. Location of New Zealand geothermal areas; Ngāwhā in northern New Zealand and the TVZ, as discussed in this report. Fields with fluid compositional data listed in Table 1 are indicated by a red circle and listed in bold.

The Ngāwhā geothermal system occurs in the north of the North Island and is hosted within Permian-Triassic basement metasedimentary rocks of the Waipapa Composite Terrane [43]. Quaternary felsic volcanism is proposed as the heat source for the Ngāwhā geothermal system [39].

More than twenty defined geothermal fields have been identified within the TVZ (Figure 3), seven of which are in current use to generate electricity and have geothermal fluid temperatures exceeding 230 °C (Table 1).

Table 1. Maximum reported temperature of geothermal reservoir fluids for geothermal fields considered in this review.

	Wairakei–Tauhara	Kawerau	Rotokawa	Ngatamariki	Ohaaki–Broadlands	Mokai	Ngāwhā
Max Temperature	280 °C [44]	310 °C [45]	337 °C [46]	>280 °C [47]	307 °C [48]	>300 °C [44]	230 °C [49]

Composition of New Zealand Geothermal Fluids

The composition of New Zealand's deep geothermal fluids (i.e., high-temperature fluid, which is enriched in chemical components) is reduced, near-neutral pH chloride waters predominantly of meteoric origin with occasional evidence of limited magmatic fluid components [50–52]. Geothermal fluid composition is influenced by temperature, pressure, host rock, and mixing between various fluid types [19]. Therefore, the fluid composition of each geothermal field has its own unique chemical signature. The major solutes include Na, Si, K, Al, Fe, Mg, and Al (i.e., rock-forming elements) and magmatic volatiles such as Cl, CO_2, and H_2S. Fluid interaction with surrounding rocks results in leaching of other elements such as Cs, Rb, or rare earth elements (REE) [8,53]. It is important to note that even if the concentrations of elements in geothermal fluids are quite low (i.e., at ppm to ppb levels), their potential economic value may still be substantial, especially in the context of the large volumes of fluids that are circulated each year through geothermal power stations.

Table 2 shows a compilation of published and unpublished data from the selected New Zealand geothermal fields, showing the elemental concentration (ppm = mg L^{-1}, ppb = μg L^{-1}) of geothermal fluids measured at each site. The data presented in this review were collected and analyzed between 1967 and 2016 by multiple authors (for references, see Appendix A). The data extracted from these reports vary in their analytical techniques and sampling approach, as some samples were collected from different depths and others from separated fluids. Special caution has to be taken for Nd, Sm, Gd, and Er values as these authors reported that some of them were present as contamination in sampling containers [2,8,9,47,53–67]. Furthermore, the compiled elemental data may not directly reflect the stable element fluxes for each geothermal system (i.e., element concentrations may vary with time, especially with continued extraction of fluids for geothermal power generation, which may deplete the overall potential critical element resource). Therefore, while the compiled results are indicative only, they constitute a good starting point for understanding and comparing critical element geochemistry of fluids from some New Zealand geothermal fields and provide a foundation for future research.

Table 2. Elemental content or range of various geothermal fluids from nine different geothermal fields in New Zealand. For detailed references, see Appendix A.

Element	Wairakei	Kawerau	Rotokawa	Ngatamariki	Ohaaki–Broadlands	Mokai	Ngāwhā
Aluminium ppm	1.5	0.02–1.1	0.2–1.8	n.d.	0.3–0.5	0.5	0.3
Antimony	19–182	480–540	1.3–230	13–27	360–384	15–1242	125–1070
Arsenic	2941–3700	3120–4900	1180–1400	94–470	1540–3090	3227–3850	770
Barium ppm	<	<–0.3	<–0.7	n.d.	<–0.1	<	0.8
Bismuth	n.d.	n.d.	n.d.	n.d.	0.3	n.d.	n.d.
Boron ppm	21–37	57–78	14.6–30	23	38–60	20.5–40	1063
Bromine ppm	5.9–10.6	3.2–4.5	1.15	0.8–1.4	5.9	4.3–8.0	5
Cadmium	<–0.55	0.7–1	<–13.3	0.15–0.37	0.02–14.4	<7	<–0.19
Caesium ppm	1.3	0.6	1.6	1.7	1	6.1	0.8
Calcium ppm	18	0.5–1	0.5	3.5	0.3–5.7	5.7–8.9	5.5
Cerium	1.1–41.5	0.3–1.6	1.5–3.4	n.d.	0.4–400	0.7–3.5	6.2–15.7
Chlorine ppm	1991	1028	1099	1441	1172	3540	1465
Chromium	0.3–24	120–520	0.3–41	40–73	40	0.3–107	2.5–19
Cobalt	<–12.6	<	<–12.5	n.d.	<–8.0	<	29.6–30.6

Copper	<0.2–2400	490–2520	<0.1–19,800	2587–3298	600	0.2–4000	750–4700
Dysprosium	0.2–5.2	<–0.2	0.2–0.4	n.d.	<–32.4	<–0.5	1.2–4.9
Erbium	<–11.4	<–0.1	0.2–0.3	n.d.	<–12.8	<–0.4	<–2.1
Europium	0.1–7.2	<–0.1	0.2–0.3	n.d.	<–11	<–0.3	2.8–5.9
Gadolinium	<–24.8	0.1–0.2	0.2–0.4	n.d.	<–47	<–0.6	<–6.6
Gallium	0.2	n.d.	5.6	n.d.	0.6	n.d.	n.d.
Germanium	3–87	n.d.	n.d.	n.d.	3–4	n.d.	n.d.
Gold	<–0.26	0.03–2.2	<–37	< 0.1–1.2	<–1.5	<–1.0	<–1.03
Holmium	0.7–3.9	<–0.1	0.1	n.d.	<–5.4	<–0.1	0.2–0.9
Iodine ppm	0.11–0.19	0.2–0.35	0.05–0.7	0.35–0.54	0.3	0.81–0.25	0.7–0.8
Iron ppm	0.012–0.8	<–0.1	<–0.06	<–0.1	0.25	0.05–1.6	0.1
Lanthanum	0.3–18.6	0.2–0.9	0.9–1.8	n.d.	0.2–239	0.4–1.6	3.2–8.1
Lead	4.5–26	27–41	536–808	7.4–13.2	1.3–21	0.3–211	<–13
Lithium ppm	12.7	6.3	7.9	9.1	11.8	29	12.3
Lutetium	<–1.2	<	<	n.d.	<–1.5	<–0.1	0.1–0.2
Magnesium ppm	0.01	0.01	0.01	0.06	0.01	0.03	0.2–0.3
Manganese	0.7–87	260–780	105–215	238–275	0.009–0.32	50–186	0.02–200
Mercury	<–2.82	44–78	<–5.18	0.73–3.40	12.82	<–1.11	<–39.8
Molybdenum	6.7–102	6–12.5	14–16	9.8–10.4	12	25–30	0.8–8.5
Neodymium	<–22	<	1.1–5.2	n.d.	<–228	<–1.9	<–13.3
Nickel	1–520	68–277	0.5–433	0.5–1.4	0.1–0.2	2.9–2480	0.7–255
Phosphorus ppm	0.1	0.1	<	n.d.	0.1–0.2	0.1	0.4
Potassium ppm	180	119	96–110	183	98	487	72–83
Praseodymium	0.1–4.7	<–0.3	0.2–0.4	n.d.	<–58	<–0.4	0.7–2.4
Rubidium ppm	2.2	0.7	2.1	1.6	1.5	4.9	0.3
Samarium	<–4.0	0.1–0.3	0.3–1.0	n.d.	<–48	0.2–0.8	<–4.1
Selenium	<	18–26	12–19	0.8–2.0	<	n.d.	17.3
Silicon (as SiO2) ppm	618	954	1163	935	829	1070	461
Silver ppb	<0.1–14.1	1.4–33.6	1110–2400	8–22	2.7–8	248–310	0.1–19.1
Sodium ppm	1090–1217	789	633	892	919	1783	1043
Strontium ppm	0.1	0.1	0.2	n.d.	0.3	0.1	1.2
Tellurium	<–4.5	2–3.9	<–2940	3.4–4	1.3	0.2–94	<–0.66
Terbium	<–3.8	<	<–0.1	n.d.	<–6.4	<–0.1	0.2–0.9
Thallium	2.5–10.6	3.0–7.5	0.9–4.1	0.4–1.3	4.1–10	9.7–15	0.4–4.7
Thulium	<–0.9	<	<	n.d.	<–1.7	<–0.1	0.1–0.3
Tin	<–10.1	18–31	<–2.9	2.6–2.8	0.5–11.1	<–3.2	<–1.9
Titanium	<	<	<	n.d.	<	<	<
Tungsten	37–220	46–110	40–190	34–40	30–480	15–190	80–150
Uranium	0.1–1.0	<–0.1	0.2–0.4	n.d.	0.1–6.2	0.2–0.3	0.9–6.7

Vanadium	<–1.2	<–14	2–7.8	<	<–8.3	<–4.4	<
Ytterbium	0.1–3.9	<–0.2	0.2–0.3	n.d.	<–10.1	0.2–0.7	0.4–1.9
Yttrium	1.0–18.9	0.3–1.3	1.8–3.6	n.d.	0.2–160	0.8–2.1	14–34
Zinc	<–243	730–880	100–880	1772–2295	1–440	<–500	6–146
Zirconium	<	<	<–193	n.d.	<	<	<

At the time of writing this report, to our knowledge, no data were available for: Be, Hf, In, Ir, Nb, Os, Pd, Pt, Re, Rh, Ru, Sc, S, and Ta. <–# below detection limit (to see detection limits refer to Appendix A). n.d.—no data were found. Only a small amount of data was available for Tauhara, hence not listed. Data reported in ppb = ug L^{-1} otherwise marked as 'element ^{ppm}' ppm = mg L^{-1}.

It is important to note that different elements behave differently within geothermal fluids. Some of the elements can be transported as very soluble species (e.g., B, Cl, K, Na), while others are mostly deposited in the fracture systems and alteration zones beneath the surface (e.g., Fe, Mn). Some elements travel to the surface of geothermal systems and are deposited as precipitates around natural features (i.e., hot springs, geysers, mud pools). Note that precipitation occurs because of changing conditions of the transported fluid from depth to the surface (change in temperature, pressure, pH, Eh). These precipitates can contain a range of elements, such as Au and Ag precipitates or Ga-rich muds, found around natural features of the Rotokawa geothermal system [2] or Au deposits at Waiotapu [57].

When geothermal fluid travels through the pipeline infrastructure of a geothermal power station, it undergoes physical (temperature, pressure) and chemical changes (due to CO_2 or H_2S degassing, acid-dosing, or use of anti-scalants). These changes increase the mobility of some elements or deposition of others. Elements can be deposited as silica scales, metal sulfides, metal oxides, or alloys (e.g., Au or electrum). These deposits have been reported at wellheads, separators, heat exchangers, two-phase pipelines, and/or reinjection pumps in several geothermal systems [68]. In fact, the major solid by-product in geothermal power generation is silica scale and compounds from pipeline corrosion.

3. Critical Element Abundance in New Zealand's Geothermal Fluids

The concentration of minor and trace elements in New Zealand's geothermal fluids ranges from <1 ppt (ng L^{-1}) up to several ppm, depending on the element. Figure 4 plots the highest published concentrations for each of the measured elements in New Zealand's geothermal fluids (Wairakei, Kawarau, Rotokawa, Mokai, Ohaaki–Broadlands, Ngāwhā, Ngatamariki, and Tauhara) ordered by atomic number (see Table 2 for the range in concentrations and references therein). The data for most of the trace elements should be considered only as qualitative, and some concentrations are close to detection limits (see Table 2).

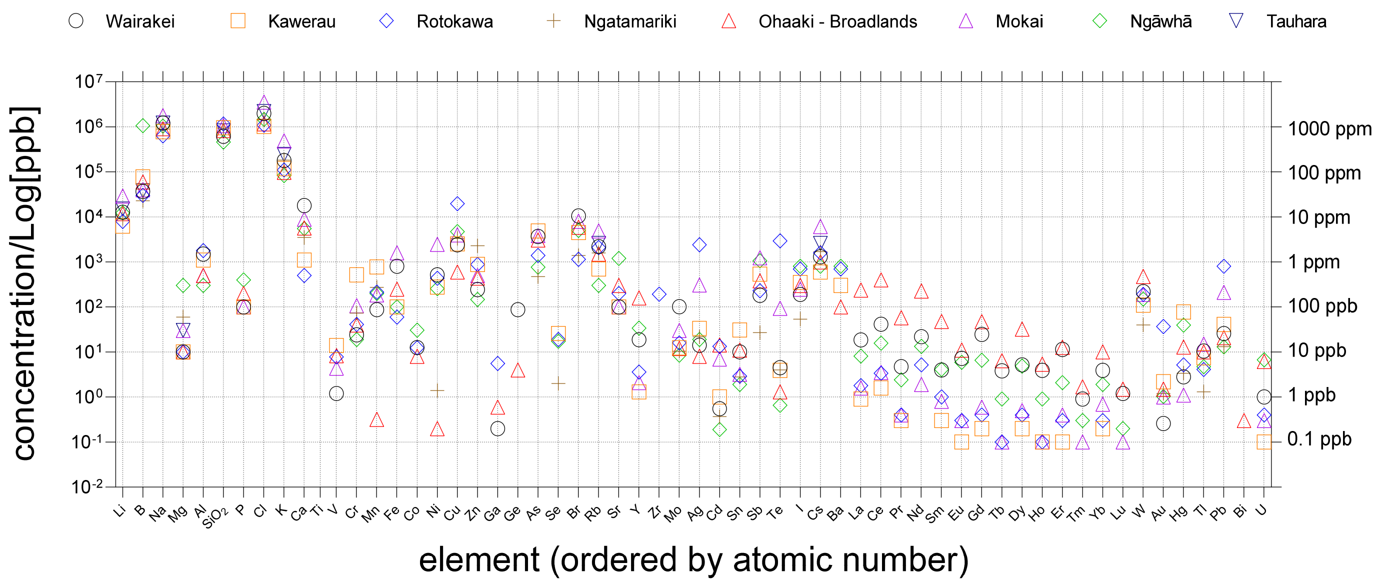

Figure 4. Comparison of elemental concentration in New Zealand's geothermal fluids (logarithmic scale). Values shown represent the highest measured concentrations of elements reported by different authors (see references in Appendix A) and are ranked by atomic mass.

Zirconium and titanium concentrations are below detection limits (with the exception of Rotokawa field). Ba and Bi have been recorded at low concentrations, in the range of <0.01 to 0.1 ppb. Concentrations of Ga, Ho, Lu, Pr, Sm, Tb, Tm, U, V, and Yb are in the range of <0.1 to 10 ppb, and Cd, Ce, Co, Dy, Er, Eu, Gd, Ge, Au, La, Mo, Hg, Se, Tl, Sn, and Y between <0.1 ppb and 100 ppb. Sb, As, Ce, Cr, Cu, I, Fe, Mg, Pb, Mn, Nd, Ni, P, Ag, Sr, Te, W and Zn concentrations show a wide range of <1 ppb to several ppm, most likely associated with the sampling location and sampling technique. Elements Br, Cs, Ca, Li, and Rb are typically present at >1 ppm levels. Note that downhole samples collected at depth show significantly higher concentrations of some elements, including Ag, Cu, Pb, Cd, Zn, and Ni, when compared to samples collected at the wellhead. This reflects the loss of some trace elements from fluid while flowing upwards, towards the wellbore.

Other major elements are present at high ppm concentrations (Cl, Na, Si, B, and K), with the exception of Ngāwhā where B is the third most abundant dissolved constituent. High B concentration is sourced from the argillite/greywacke basement rock or volcanic source associated with the heat source [69].

Alkali metals Li, Na, K, Rb, and Cs are abundant in New Zealand's geothermal fluids compared to other elements. TVZ southern geothermal fields, Mokai, Wairakei and Tauhara, are shown to be relatively enriched in these elements in comparison to the eastern geothermal fields at Kawerau, Ohaaki, and Rotokawa. Whereas the alkaline-earth major metals Ca and Mg and trace metals Ba and Sr are at low ppm levels in all fields, with the exception of Ca in Wairakei and Mokai.

The transition metals and metalloids are particularly unevenly distributed. Specifically, the Ohaaki field stands out with low Mn, Ni, Ga, Ge, and Te concentrations and elevated REE and W. Rotokawa's geothermal fluid is relatively enriched in Mn, Ni, Ga, Te, Ag, and Au but depleted in REE. The differences are related to available transporting complexes, reservoir rocks, temperatures, and most likely amount of magmatic fluid input. More details on these distinctions can be found in [53,70].

Theoretical Quantities of Critical Elements in Geothermal Fluids

Despite the low relative concentrations of many critical elements within New Zealand geothermal fluids, it is worth considering their quantities in the context of the significant volumes of fluids that pass through geothermal power stations annually. The consented annual take for different geothermal fields and the estimated annual element flux are presented in Table 3. Element flux has been calculated for several species and is given based on the highest recorded concentration multiplied by the consented fluid taken for the specific producing geothermal field.

Table 3. Consented annual take (t/yr) for producing geothermal fields in New Zealand and annual flux in tons for selected elements.

Filed	Consented Annual Take (t/yr)	Cl	Na	SiO_2	K	Li	B	Cs	Rb	Nd	Eu	Tb	Dy	Yb	W
Wairakei	89,425,000	178,045	108,830	55,265	16,097	1136	3309	116	197	1.97	0.64	0.34	0.47	0.35	19.7
Kawerau	58,283,200	59,915	45,985	55,602	6936	367	4546	35	41	0.00	0.01	0.00	0.01	0.01	6.4
Rotokawa	23,907,500	26,274	15,133	27,804	2630	189	717	38	50	0.12	0.01	0.00	0.01	0.01	4.5
Ngatamariki	21,900,000	20,761	19,535	13,447	4008	199	197	37	n.d	0.00	0.00	0.00	0.00	0.00	0.9
Ohaaki–Broad-lands	14,600,000	17,111	13,417	12,103	1431	172	876	15	22	3.33	0.16	0.09	0.47	0.00	7.0
Mokai	14,600,000	51,684	26,032	15,622	7110	423	584	89	72	0.03	0.00	0.00	0.01	0.15	2.8
Ngāwhā	9,125,000	13,368	9517	4207	757	112	9700	7	3	0.12	0.05	0.01	0.04	0.01	1.4
Tauhara	77,745,000 *	169,951	94,538	62,896	18,970	1174	2954	202	202	n.d.	n.d.	n.d.	n.d.	0.02	n.d.

* Tauhara has been consented for 213,000 t/d, including Tauhara II; however, this consent is not expected to be exercised for several years; n.d.—no data.

The calculated mass flux indicates both the fluid mass flow and concentration. For example, the greatest SiO_2 annual flux has been calculated for the Kawerau geothermal field, despite that field not having the highest contested take. Similarly, at Ngāwhā, boron concentration is so high that annual boron discharge is 9700 t/yr, more than double the next highest discharge from Kawerau.

On the other hand, the Wairakei and Tauhara geothermal fields, with the highest consented fluid mass discharge, have by far the highest total mass of Cl, Na, K, Li, Cs, and Rb flux in comparison to other geothermal fields. Growing demand for lithium has accelerated the exploration of new Li resources, with around 98 million tonnes being available worldwide and 130,000 tonnes being mined in 2022 alone [1]. Therefore, New Zealand's annual Li mass flux has the potential to constitute about 3% of the current annual world supply. Flux values are particularly interesting for rubidium and cesium, as less than 200,000 tons (each) of these elements were thought to be available in Australia, Canada, China, and Namibia [71]. This suggests that up to 0.29% and 0.27% of the world's Rb and Cs resources, respectively, could be supplied by environmentally friendly extraction from New Zealand geothermal fluids. While currently these resources may be sub-economic, extraction techniques already exist [72], and the growing demand for these elements can and should accelerate this resource utilization. Moreover, it has been reported that demand for Rb is limited by scarce supply, hence, new resources could lead to expanded commercial applications [73].

Table 3 reveals a notable difference in the potential REE (Nd, Eu, Tb, Dy, and Yb) annual mass discharged for the Wairakei and Ohaaki–Broadlands geothermal fields, as they discharge the greatest amounts of these critical elements. For context, annual production of Nd reported in 2017 was 7300 tons and 400 tons of Eu [3]. Therefore, if the reported REE concentrations are correct, the Wairakei and Ohaaki-Broadlands geothermal fields possess an enormous potential to become a relevant REE supply. Finally, global tungsten production volume for 2021 was 79,000 tonnes [74]. Therefore, the potential annual produced mass from New Zealand geothermal fields equates to around 0.05% of the annual global production. The full table of calculated annual mass flux of all reported elements is available in Appendix B.

4. Concluding Remarks

This review briefly summarizes and consolidates published historical data on critical element concentrations in New Zealand geothermal fluids. The data confirm that most elements currently classified as ‘critical’ are present in measurable quantities. The total flux of various species, in tonnes per year, has been calculated using the geothermal fluid taken for each individual geothermal field. The elemental flux calculations constitute one of the first attempts to quantify the potential extractable critical element resources within New Zealand geothermal fluids.

Our data compilation and analysis highlight significant elemental flux in New Zealand geothermal systems and signals that these elements are not evenly distributed across fields. The highest concentrations and fluxes of Ag, Au, and Te were recorded from the Rotokawa and Mokai fields, while the highest REE concentrations are present in fluids from the Wairakei and Ohaaki-Broadland fields.

Extraction of critical elements from geothermal fluids presents many benefits, in particular, the opportunity to extract these elements in an environmentally benign and sustainable way. Combined element extraction and power generation can also offset the extraction costs. Even if current economic constraints hinder the viability of critical element extraction, this may rapidly change with growing demand for more desirable elements and ongoing research and development in element extraction techniques globally.

Nevertheless, it is important to note that the geothermal well concentrations presented here represent a historical snapshot of the potential for a geothermal system to host critical element resources. Regretfully, this data compilation (and associated knowledge) is mostly outdated, as many of the wells were analyzed more than 20 years ago when laboratory techniques were limited (as modern instruments now have much lower detection limits). To more accurately assess the economic commercialization of a critical element extraction industry from geothermal fluids in New Zealand, more research, including standardized sampling and analysis of fluids from all of New Zealand’s producing high-temperature geothermal fields, is required. New testing will provide more precise elemental flux rates and will enable better correlations between critical element concentrations and the various characteristics of each geothermal system to be made (i.e., influence of reservoir host-rock lithology and other factors on controlling the potentially critical element endowment of geothermal fluids).

Once new data verifying critical element concentrations for each geothermal system have been obtained, further work could include the development or adoption of specific element extraction techniques, studies to assess the life cycle of critical elements in geothermal reservoirs and, therefore, their long-term viability, and finally, an economic assessment for a geothermal critical element extractive industry in Aotearoa-New Zealand.

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Appendix A

Table A1. New Zealand's Geothermal Fluid Composition References List.

Element	Symbol	Source	Element	Symbol	Source
Aluminium	Al	[9,65]	Mercury	Hg	[2,53,54,64]
Antimony	Sb	[53–55,64]	Molybdenum	Mo	[53,62]
Arsenic	As	[53–55,64]	Neodymium	Nd	[65]
Barium	Ba	[65]	Nickel	Ni	[53,56,66]
Bismuth	Bi	[56]	Phosphorus	P	[65]
Boron	B	[8,64,75]	Potassium	K	[53]
Bromine	Br	[53]	Praseodymium	Pr	[65]
Cadmium	Cd	[53,65,66]	Rubidium	Rb	[8,75]
Caesium	Cs	[8,75]	Samarium	Sm	[65]
Calcium	Ca	[9,47]	Selenium	Se	[53]
Cerium	Ce	[65]	Silicon	Si	[8]
Chlorine	Cl	[8]	Silver	Ag	[2,8,53,54,76]
Chromium	Cr	[53]	Sodium	Na	[8]
Cobalt	Co	[65]	Strontium	Sr	[59,65]
Copper	Cu	[2,8,53,55,66,76]	Tellurium	Te	[53]
Dysprosium	Dy	[65]	Terbium	Tb	[65]
Erbium	Er	[65]	Thallium	Tl	[53,55,56,64]
Europium	Eu	[65]	Thulium	Tm	[65]
Gadolinium	Gd	[65]	Tin	Sn	[53,56]
Gallium	Ga	[59,61]	Titanium	Ti	[65]
Germanium	Ge	[56,59,62]	Tungsten	W	[53,56]
Gold	Au	[8,53,54]	Uranium	U	[65]
Holmium	Ho	[65]	Vanadium	V	[31,65,66]
Iodine	I	[53,66]	Ytterbium	Yb	[65]
Iron	Fe	[9,63]	Yttrium	Y	[65]
Lanthanum	La	[65]	Zinc	Zn	[53,62,66,77]
Lead	Pb	[66,77]	Zirconium	Zr	[65]
Lithium	Li	[8,75]			
Lutetium	Lu	[65]			
Magnesium	Mg	[8,65,75]			
Manganese	Mn	[53,63,66]			

Appendix B

Table A2. Annual Flux in Tons per Year for Elements Reported in Table 2. Only Maximum Values Have Been Caculated. n.d.—no data.

	Wairakei	Kawerau	Rotokawa	Ngatamariki	Ohaaki–Broadlands	Mokai	Tauhara	Ngāwhā
Aluminium	134.138	64.112	43.034	591.300	7.300	7.300	n.d.	2.738
Antimony	16.275	31.473	5.499	10.293	5.606	18.133	n.d.	9.764
Arsenic	331	286	33	3	45	56	n.d.	7
Barium	0.001	17.485	16.735	0.000	1.460	0.146	n.d.	7.300
Bismuth	0.000	n.d.	0.000	0.504	0.004	n.d.	n.d.	n.d.
Boron	3309	4546	717	197	876	584	2954	9700
Bromine	948	262	27	31	86	117	n.d.	46
Cadmium	0.049	0.058	0.318	0.037	0.210	0.102	n.d.	0.002
Caesium	116.253	34.970	38.252	37.230	14.600	89.060	202.137	7.300
Calcium	1609.650	58.283	11.954	81.030	83.220	129.940	n.d.	50.188
Cerium	3.711	0.093	0.081	1.599	5.840	0.051	n.d.	0.143
Chlorine	178,045	59,915	26,274	20,761	17,111	51,684	169,951	13,368
Chromium	2.146	30.307	0.980	1.533	0.584	1.562	n.d.	0.173
Cobalt	1.127	n.d.	0.299	72.226	0.117	0.000	n.d.	0.279
Copper	214.620	146.874	473.369	0.000	8.760	58.400	n.d.	42.888
Dysprosium	0.465	0.012	0.010	0.000	0.473	0.007	n.d.	0.045
Erbium	1.019	0.006	0.007	0.000	0.187	0.006	n.d.	0.019
Europium	0.644	0.006	0.007	0.000	0.161	0.004	n.d.	0.054
Gadolinium	2.218	0.012	0.010	0.000	0.686	0.009	n.d.	0.060
Gallium	0.018	n.d.	0.134	0.000	0.009	n.d.	n.d.	n.d.
Germanium	7.780	n.d.	0.000	0.026	0.058	n.d.	n.d.	n.d.
Gold	0.023	0.128	0.885	0.000	0.022	0.015	n.d.	0.009
Holmium	0.349	0.006	0.002	0.000	0.079	0.001	n.d.	0.008
Iodine	16.991	20.399	16.735	1182.600	4.380	3.650	n.d.	7.300
Iron	71.540	5.828	1.434	2.190	3.650	23.360	n.d.	0.913
Lanthanum	1.663	0.052	0.043	0.000	3.489	0.023	n.d.	0.074
Lead	2.325	2.390	19.317	0.289	0.307	3.081	n.d.	0.119
Lithium	1136	367	189	199	172	423	1174	112
Lutetium	0.107	n.d.	n.d.	0.000	0.022	0.001	n.d.	0.002
Magnesium	0.894	0.583	0.239	1.314	0.146	0.438	2.332	2.738
Manganese	7.780	45.461	5.140	6.023	0.005	2.716	n.d.	1.825
Mercury	0.252	4.546	0.124	0.074	0.187	0.016	n.d.	0.363
Molybdenum	9.121	0.729	0.383	0.228	0.175	0.438	n.d.	0.078
Neodymium	1.967	n.d.	0.124	0.000	3.329	0.028	n.d.	0.121
Nickel	46.501	16.144	10.352	0.031	0.003	36.208	n.d.	2.327
Phosphorus	8.943	5.828	n.d.	0.000	2.920	1.460	n.d.	3.650
Potassium	16,097	6936	2630	4008	1431	7110	18,970	757
Praseodymium	0.420	0.017	0.010	0.000	0.847	0.006	n.d.	0.022
Rubidium	196.735	40.798	50.206	0.000	21.900	71.540	202.137	2.738
Samarium	0.358	0.017	0.024	0.000	0.701	0.012	n.d.	0.037
Selenium	0.000	1.515	0.454	0.044	0.000	n.d.	n.d.	0.158
Silicon (as SiO_2)	55,265	55,602	27,804	13,447	12,103	15,622	62,896	4207
Silver	1.261	1.958	57.378	0.482	0.117	4.526	n.d.	0.174
Sodium	108,830	45,985	15,133	19,535	13,417	26,032	94,538	9517
Strontium	8.943	5.828	4.782	0.000	4.380	1.460	n.d.	10.950
Tellurium	0.402	0.227	70.288	0.088	0.019	1.372	n.d.	0.006

Terbium	0.340	n.d.	0.002	0.000	0.093	0.001	n.d.	0.008
Thallium	0.948	0.437	0.098	0.028	0.146	0.219	n.d.	0.043
Thulium	0.080	n.d.	0.000	0.000	0.025	0.001	n.d.	0.003
Tin	0.903	1.807	0.069	0.061	0.162	0.047	n.d.	0.017
Titanium	n.d.	n.d.	0.000	0.000	0.000	n.d.	n.d.	0.000
Tungsten	19.674	6.411	4.542	0.876	7.008	2.774	n.d.	1.369
Uranium	0.089	0.006	0.010	0.000	0.091	0.004	n.d.	0.061
Vanadium	0.107	0.816	0.186	0.219	0.121	0.064	n.d.	0.000
Ytterbium	0.349	0.012	0.007	0.000	0.147	0.010	n.d.	0.017
Yttrium	1.690	0.076	0.086	0.000	2.336	0.031	n.d.	0.310
Zinc	21.730	51.289	21.039	50.261	6.424	7.300	n.d.	1.332
Zirconium	0.000	n.d.	4.614	0.000	0.000	0.000	n.d.	0.000

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