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Geothermal waters from the Taupo Volcanic Zone, New Zealand: Li, B and Sr isotopes characterization

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Abstract

In this study, we report chemical and isotope data for 23 geothermal water samples collected in New Zealand within the Taupo Volcanic Zone (TVZ). We analyzed major and trace elements including Li, B and Sr and their isotopic compositions ($\delta^7\text{Li}$, $\delta^{11}\text{B}$, $^{87}\text{Sr}/^{86}\text{Sr}$) in high temperature geothermal waters collected from deep boreholes in different geothermal fields (Ohaaki, Wairakei, Mokai, Kawerau and Rotokawa geothermal systems). Lithium concentrations are high (from 4.5 to 19.9 mg/L) and lithium isotopic compositions ($\delta^7\text{Li}$) are very homogeneous, being comprised between -0.5 and +1.4‰. In particular, it is noteworthy that, except the samples from the Kawerau geothermal field having slightly higher $\delta^7\text{Li}$ values (+1.4‰), the other geothermal waters have a very constant $\delta^7\text{Li}$ signature around a mean value of 0‰ \pm 0.6 (2 σ , n=21). Boron concentrations are also high and relatively homogeneous for the geothermal samples, falling between 17.5 and 82.1 mg/L. Boron isotopic compositions ($\delta^{11}\text{B}$) are all negative, and display a range between -6.7 and -1.9‰. These B isotope compositions are in agreement with those of the Ngawha geothermal field in New Zealand. Li and B isotope signatures are in a good agreement with a fluid signature mainly derived from water/rock interactions involving magmatic rocks with no evidence of seawater input. On the other hand, strontium concentrations are lower and more heterogeneous and fall between 2 and 165 $\mu\text{g/L}$. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.70549 to 0.70961. These Sr isotope compositions overlap those of the Rotorua geothermal field in New Zealand, also confirming that some geothermal waters (with more radiogenic strontium) have interacted with bedrocks from the metasedimentary basement. Each of these isotope systems on their own reveals important information about particular aspects of either water source or water/rock interaction processes, but, considered together, provide a more integrated understanding of the geothermal systems from the TVZ in New Zealand.

Keywords: Geothermal waters, New Zealand, Lithium isotopes, Boron isotopes, Strontium isotopes

5 102 words (without references and captions)

1. INTRODUCTION

In the present work, we report chemical and isotope data for 23 geothermal water samples from the Taupo Volcanic Zone (TVZ) in New Zealand. Chemical and isotope data were analyzed for these deep geothermal waters in order to provide further constraints on the characterization of the associated deep geothermal reservoirs. The present study aims therefore to characterize the fluids from the geothermal systems for the TVZ and, more specifically, to constrain the nature and origin of these fluids: two essential parameters for the characterization of a geothermal resource.

Major and trace elements are first investigated in order to determine the chemical signature of the TVZ geothermal samples. A multi-isotopic approach is then used to provide additional information for the characterization of these waters. Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) are investigated in order to better constrain the signature of the reservoir the waters come from, given that Sr isotopes are a good tracer of water origin for groundwaters and geothermal waters (Négrel et al. 1997, Négrel 1999, Millot et al. 2007). In addition, we also determined Li and B isotopic compositions of the TVZ geothermal waters with the objective of evaluating the utility of these isotopic tools to constrain the water/rocks interactions. Indeed, the isotopic composition of boron ($\delta^{11}\text{B}$) is determined in an attempt to elucidate the source and process controlling B in geothermal waters (Aggarwal et al. 2003), and the use of Li isotopic systematics ($\delta^7\text{Li}$) is also explored, following recent papers indicating that Li isotopes seem to be an effective tracer of water/rock interactions in geothermal waters (Millot et al. 2007, Millot and Négrel 2007, Millot et al. 2010a).

One of the objectives of the present study is also to compare the different information that can be obtained using a multi-isotopic approach for the characterization of geothermal waters, more precisely, how the combination of these isotopic tracers could help in deciphering the water-rock interaction processes. However, it is important to keep in mind that each isotopic system can only provide information concerning the chemical behavior of the element, but considered together, this multi-isotope approach can provide a more integrated understanding of the TVZ geothermal system in New Zealand.

2. THE TAUPO VOLCANIC ZONE

Geothermal systems occur in many parts of New Zealand. The conventional geothermal resources of New Zealand are currently utilized to depths between 1 and 3 km, and temperatures up to 330°C. High temperature geothermal fields ($T > 250^\circ\text{C}$) are principally located in the TVZ (Figure 1), with another high temperature field at Ngawha in Northland. Moderate to low and very low temperature systems ($T < 250^\circ\text{C}$) are more widely scattered.

75 Some are associated with areas of young volcanism: in Northland, Hauraki Plains, and the
76 coastal Bay of Plenty. Many hot springs, particularly in the South Island, are associated with
77 faults and tectonic features. The TVZ is 20-80 km wide and extends from Mt Ruapehu in the
78 south to the Okataina Volcanic Center in the north and continues 200 km offshore. The zone
79 is flanked by thick aprons of welded pyroclastic flows that form shallow dipping plateaus.
80 Situated in the middle of the North Island of New Zealand, the TVZ is an area of both
81 volcanic and geothermal activity. Rhyolitic volcanic activity in the area is thought to have
82 commenced 1.6 Ma ago. The enhanced activity in the region is a result of an actively
83 extending back-arc rift, due to the subduction of the Pacific plate beneath the North Island of
84 New Zealand. This area is characterized by an extremely high heat flow. The average heat
85 flux from the central zone of the TVZ, which contains most of the geothermal fields, is about
86 700 mW/m² (Bibby et al. 1995).

87 Within the TVZ, the different geothermal fields are distributed in two bands approximately 20
88 km apart. It was estimated by Bibby et al (1995), that 75% of the heat flow occurs in the
89 eastern band and 25% in the west. Samples were collected from five geothermal fields within
90 the TVZ: Kawerau, Rotokawa and Ohaaki from the eastern side, and Mokai and Wairakei
91 from the western side (Figure 1).

92 Temperatures of over 300°C are found within the fluids of the geothermal systems within the
93 TVZ, generally within the eastern fields e.g. Kawerau (315°C) and Rotokawa (330°C)
94 (Kissling and Weir 2005). Maximum temperatures at Wairakei reach 265°C (Kissling and
95 Weir 2005), with Mokai (326°C).

96 Giggenbach (1995) used the variations of H₂O, CO₂ and Cl in discharges from six
97 geothermal systems within the TVZ to identify the existence of two distinct types of deep
98 water supply. Falling along the eastern side of the TVZ: Kawerau, Ohaaki and Rotokawa
99 display higher gas contents than the fields on the western side, including Mokai and Wairakei
100 (illustrated by CO₂/Cl ratios above 3.9 ±1.5 vs. 0.14 ±0.1). According to Giggenbach (1995),
101 the higher ratios were described as being of andesitic rock origin, with the lower ratios
102 originating from rhyolitic material. The excess of volatiles present in fluid discharges from
103 geothermal and volcanic systems along convergent plate boundaries are likely to be derived
104 preferentially from the marine sedimentary fraction of subducted material (Giggenbach
105 1995).

106 The Mokai geothermal system lies 25 km northwest of Lake Taupo, and is thought to be 10
107 km², based on resistivity measurements (Kissling and Weir 2005).

108 The Rotokawa geothermal system lies 10 km northeast of Lake Taupo and has an area of 25
109 km², based on resistivity measurements (Hunt and Bowyer 2007, Heise et al. 2008). A mix of
110 Paleozoic and Mesozoic greywackes form the basement of the system, with a mix of

111 ignimbrites and rhyolite lavas forming overlying layers, which are in turn covered by
112 Holocene tuff (Krupp et al.1986, Wilson et al. 2007).

113 Hydrothermally altered greywacke sandstones dominate the basements at both the Kawerau
114 and Ohaaki geothermal fields, however characterization by Wood et al. (2001) has shown
115 that, despite similar lithologies, there are very different petrological characteristics between
116 the two. As a result, the Ohaaki greywackes are analogous, for their bulk compositions, to
117 granite, and the Kawerau greywackes to quartz diorite. The basement at Ohaaki also differs
118 from those of the other fields due to the occurrence of (approx. 3%) argillite in fine partings
119 (Wood et al. 2001).

120 In Table 1, the geothermal samples are listed with their origin (geothermal system), the
121 borehole depth (m) and deep temperature (°C) estimated by chemical geothermometry.

122

123

3. ANALYTICAL METHODS

124

3.1. Major and trace elements

125

126
127 The samples were collected, after filtration and acidification on site, by MRP and Contact
128 Energy, from the production pipeline using a fluid sampling separator. These geothermal
129 sites are managed by Contact Energy Limited, the Tuaropaki Power Company, the
130 Rotokawa Joint Venture and Mighty River Power Limited. All chemical analyses were
131 performed in the BRGM laboratories using standard water analysis techniques such as Ion
132 Chromatography (Cl), Inductively Coupled Plasma-Atomic Emission Spectroscopy (Li, B and
133 Sr), Inductively Coupled Plasma-Mass Spectrometry (Ca and Mg), and Flame Emission
134 Spectrometry (Na, K, Ca and SiO₂). Major species and trace elements were determined on
135 conditioned samples, i.e., after filtration at 0.2 µm for the major anions, and after filtration at
136 0.2 µm and acidification with Suprapur HNO₃ acid (down to pH = 2) for the major cations and
137 trace elements.

138 Accuracy and precision for major and trace elements was verified by repeated
139 measurements of standard materials during the course of this study: namely Ion96-3 and
140 LGC6020 for cations and anions and pure Li, B and Sr standard solutions (Merck). The
141 accuracy of the major and trace element data is approx. ± 10%.

142

3.2. Lithium isotopes

143

144
145 Lithium isotopic compositions were measured using a Neptune Multi Collector ICP-MS
146 (Thermo Fischer Scientific). ⁷Li/⁶Li ratios were normalized to the L-SVEC standard solution
147 (NIST SRM 8545, Flesch et al. 1973) following the standard-sample bracketing method (see

148 Millot et al. 2004 for more details). The analytical protocol involves the acquisition of 15 ratios
149 with 16 s integration time per ratio, and yields in-run precision better than 0.2‰ ($2\sigma_m$). Blank
150 values are low, (i.e. 0.2%), and 5 minutes wash time is enough to reach a stable background
151 value.

152 The samples were prepared beforehand with chemical separation/purification by ion
153 chromatography in order to produce a pure mono-elemental solution. Chemical separation of
154 Li from the matrix was achieved before the mass analysis using a cationic resin (a single
155 column filled with 3 mL of BioRad AG® 50W-X12 resin, 200-400 mesh) and HCl acid media
156 (0.2N) for 30 ng of Li. Blanks for the total chemical extraction were less than 30 pg of Li,
157 which is negligible, since it represents a 10^{-3} blank/sample ratio.

158 Successful quantitative measurement of Li isotopic compositions requires 100% Li recovery.
159 The column was, therefore, frequently calibrated and repeated analysis of the L-SVEC
160 standard processed through columns shows 100% Li recovery and no induced isotope
161 fractionation due to the purification process.

162 The accuracy and reproducibility of the entire method (purification procedure + mass
163 analysis) were tested by repeated measurement of a seawater sample (IRMM BCR-403)
164 after separation of Li from the matrix, for which we obtained a mean value of $\delta^7\text{Li} = +30.9\text{‰} \pm$
165 0.3 (2σ , $n=7$) over the analysis period. This mean value is in good agreement with our long-
166 term measurement ($\delta^7\text{Li} = +31.0\text{‰} \pm 0.5$, 2σ , $n=30$, Millot et al. 2004) and with other values
167 reported in the literature (see, for example, Millot et al. 2004 for a compilation with $\delta^7\text{Li}$ values
168 for seawater ranging from +28.9 to 33.9‰). Consequently, based on long-term
169 measurements of a seawater standard, we estimate the external reproducibility of our
170 method to be around $\pm 0.5\text{‰}$ (2σ).

171

172 **3.3. Boron isotopes**

173

174 Boron isotopic compositions were determined on a Finnigan MAT 261 solid source mass
175 spectrometer in a dynamic mode. B isotope compositions were determined on conditioned
176 samples (after filtration at 0.2 μm). For these samples, water volumes corresponding to a
177 mass of 4 μg of B was processed using a two-step chemical purification through Amberlite
178 IRA-743 selective resin. The boron aliquot sample (2 μg) was then loaded onto a Ta single
179 filament with graphite, mannitol and Cs, and the B isotopes were determined by measuring
180 the Cs_2BO_2^+ ion. The total boron blank is less than 10 ng. The values are given using the δ -
181 notation (expressed in ‰) relative to the NBS951 boric acid standard. The $^{11}\text{B}/^{10}\text{B}$ of replicate
182 analyses of the NBS951 boric acid standard after oxygen correction was 4.05122 ± 0.00122

183 (2σ , $n=27$) during this period. The reproducibility of the $\delta^{11}\text{B}$ determination is $\pm 0.3\text{‰}$ (2σ) and
184 the internal uncertainty is better than 0.3‰ ($2\sigma_m$).

185 The accuracy and reproducibility of the whole procedure were verified by the repeated
186 measurements of the IAEA-B1 seawater standard (Gonfiantini et al. 2003) for which the
187 mean $\delta^{11}\text{B}$ value obtained is $+39.22\text{‰} \pm 0.32$ (2σ , $n=33$), in agreement with the accepted
188 value for seawater ($\delta^{11}\text{B} = +39.5\text{‰}$, see data compilation reported by Aggarwal et al. 2004).

189

190 **3.4. Strontium isotopes**

191

192 Chemical purification of Sr ($\sim 3 \mu\text{g}$) was performed using an ion-exchange column (Sr-Spec)
193 before mass analysis according to a method adapted from Pin and Bassin (1992), with total
194 blank $< 1 \text{ ng}$ for the entire chemical procedure. After chemical separation, around 150 ng of
195 Sr was loaded onto a tungsten filament with tantalum activator and analysed with a Finnigan
196 MAT 262 multi-collector mass spectrometer. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to an
197 $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194. An average internal precision of $\pm 10^{-5}$ ($2\sigma_m$) was obtained and the
198 reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements was tested by repeated analyses of the
199 NBS987 standard, for which we obtained a mean value of 0.710243 ± 0.000010 (2σ , $n=9$)
200 during the period of analysis.

201

202 **3.5. Chemical geothermometry**

203

204 The concentrations of most dissolved elements in geothermal waters depend on the
205 groundwater temperature and the weathered mineralogical assemblage (White 1965, Ellis
206 1970, Truesdell 1976, Arnórsson et al. 1983, Fouillac 1983). Since concentrations can be
207 controlled by temperature-dependent reactions, they could theoretically be used as
208 geothermometers to estimate the deep temperature of the water. In the present study, deep
209 temperature estimates were calculated based on SiO_2 concentrations following silica
210 geothermometer based on quartz, chalcedony, α or β cristobalite and amorphous silica
211 solubility (Fournier and Rowe 1966, Helgeson et al. 1978, Arnórsson et al. 1983). These
212 temperature estimates agree well with downhole measurements and with previous data
213 reported in the literature (Hedenquist 1990, Christenson et al. 2002).

214

215

4. RESULTS AND COMMENTS

216

217 **4.1. Major and trace elements**

218

219 Geothermal waters are commonly characterized by examining the behavior of the major
220 elements (Table 1). In this context, Figure 2 illustrates the relationship between Cl,
221 considered as a conservative element, and Na, which is largely controlled by water/rock
222 interactions. Whereas Cl concentrations range between 666 and 2834 mg/L, Na
223 concentrations range between 388 and 1477 mg/L. From a general point of view, we observe
224 a good relationship between Na and Cl (Figure 2), indicating that the geothermal waters
225 display a large range of salinity, with Na and Cl concentrations increasing from Rotokawa,
226 Kawerau, Ohaaki, and Wairakei up to the samples from Mokai.

227 Other major elements range from 72 to 338 mg/L for K, from 0.005 to 0.028 mg/L for Mg, and
228 from 0.1 to 27.7 mg/L for Ca. Anions concentrations range between 2.6 and 74.8 mg/L for
229 SO₄ and between 1.1 and 5.9 mg/L for Br. Silica concentrations are high, ranging from 384 to
230 1169 mg/L.

231 Concerning trace elements, and those of interest for the present work: Li concentrations are
232 high, ranging from 4.5 to 19.9 mg/L. B concentrations are also high, ranging between 17.5
233 and 82.1mg/L (BR49, Ohaaki). If we exclude the sample with the highest concentration, B
234 contents are homogeneous, falling between 17.5 and 42.3 mg/L. Finally, Sr concentrations
235 are clearly lower, ranging from 0.002 to 0.165 mg/L. The lithium, boron and strontium
236 concentrations are in agreement with the data reported in the literature for worldwide
237 geothermal waters (Mossadik 1997, Williams et al. 2001, Aggarwal et al. 2003, Millot et al.
238 2007, Millot and Négrel 2007, Millot et al. 2009, Millot et al. 2010a).

239 Because Na is mainly controlled by water/rock interactions, it is interesting to also investigate
240 the relationships between Na and Li, B and Sr (Figure 3). Firstly, it can be observed (Figure
241 3a), that all the geothermal waters define a general positive relationship between Na and Li,
242 which suggests that, like Na, Li is mainly controlled by water/rock interactions. Secondly and
243 by contrast, when B concentrations are plotted against Na (Figure 3b), different trends
244 emerge. Indeed, we can observe different positive correlations between B and Na, meaning
245 that B is also controlled by water/rock interactions, but there is not a single general trend at
246 the scale of the whole TVZ as observed for Li. From that graph (Figure 3b) geothermal
247 samples can be divided into different groups of samples: thus, the geothermal waters from
248 Kawerau and Rotokawa seem to define a single trend, those from Ohaaki are different, and
249 finally, those from Mokai and Wairakei seem to also plot on a single trend. These trends
250 correlate with the spatial distribution of geothermal fields within the TVZ. The geothermal
251 systems from Mokai and Wairakei are located in the western side of the TVZ, and those from
252 Kawerau, Rotokawa and Ohaaki are located in the eastern side of the TVZ. Finally, when Sr
253 concentrations are plotted as a function of Na (Figure 3c), it seems that there is no global link
254 between these two elements, except that the geothermal waters from Kawerau and
255 Rotokawa show a positive relationship.

256 Additional information can also be obtained when the concentrations of trace elements are
257 plotted as a function of the deep temperature of the water calculated by chemical
258 geothermometry (Figure 4). Both Li and B concentrations appear to be relatively constant
259 and independent of the temperature of the fluid. On the other hand, Sr concentrations appear
260 to be anti-correlated with the temperature of the fluid (Figure 4b). Such a feature strongly
261 suggests that dilution is occurring in the system by mixing of shallower and colder waters.
262 However, it is also likely that the lower Sr contents can also be controlled by calcite
263 precipitation. Finally, in Figure 4d, SiO₂ concentrations and deep temperature show a strong
264 correlation ($R^2 = 0.84$) but this is an induced correlation, due to the fact that, deep
265 temperature estimates were calculated based on SiO₂ concentrations following silica
266 geothermometers.

267

268 **4.2. Li-B-Sr isotopes**

269

270 Li isotopes are reported in Table 1 and lithium isotopic compositions ($\delta^7\text{Li}$, ‰) are very
271 homogeneous. For all the samples, the range of variation for $\delta^7\text{Li}$ values is small (1.9‰ in
272 total) ranging between -0.52 and +1.42‰, respectively, for sample BR9 (Ohaaki) and KA37
273 (Kawerau). Omitting the two samples from Kawerau, which have slightly higher $\delta^7\text{Li}$ values
274 (+1.42 and +1.38‰), the other geothermal waters have a very constant $\delta^7\text{Li}$ signature around
275 a mean value of 0‰ \pm 0.6 (2 σ , n=21). This small range of variation (\pm 0.6‰) is almost the
276 same as our external reproducibility of our method for Li isotopes analysis (\pm 0.5‰, 2 σ ,
277 section 3.2.). This result means that lithium has either the same origin in these fluids and/or
278 the process(es) that control Li isotope fractionation is (are) the same for all the geothermal
279 water samples under consideration. Compared to scarce literature data for geothermal
280 waters (Millot and Négre 2007, Millot et al. 2007, 2009, 2010), geothermal waters from the
281 TVZ display low $\delta^7\text{Li}$ values.

282 B isotopes are also reported in Table 1. The range of $\delta^{11}\text{B}$ values is of 4.8‰ in total, from -
283 6.70‰ (RK14, Rotokawa) to -1.92‰ (WK235, Wairakei). A plot of B isotopes ($\delta^{11}\text{B}$, ‰) as a
284 function of B concentrations (Figure 5b) shows that, with the exception of sample BR49
285 (Ohaaki) having the highest B concentrations, there is no large variation of both B isotopes
286 and concentrations. However, Rotokawa and Ohaaki geothermal waters have the lowest $\delta^{11}\text{B}$
287 values, and, by contrast, geothermal waters from Wairakei, Mokai and Kawerau have the
288 highest $\delta^{11}\text{B}$ values. Geothermal samples from this study can be compared with literature
289 data from the Ngawha geothermal field (Aggarwal et al. 2003) for B isotopes. The Ngawha
290 geothermal field is the only high temperature geothermal field in New Zealand that is located
291 outside the TVZ. It is located on the central axis of the Northland peninsula in a Quaternary–

292 Holocene basaltic field (Kaikohe volcanic field). Measurements of water samples from the
293 Ngawha geothermal system fall within a limited range of $\delta^{11}\text{B}$ values between -3.9 and -
294 3.1‰, overlapping the TVZ data.

295 Sr isotopes are also reported in Table 1. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.70549 (WK245,
296 Wairakei) to 0.70961 (BR49, Ohaaki). Sr isotopes are plotted as a function of Sr
297 concentrations in Figure 5c and show no general trend or any relationship with the spatial
298 distribution of the samples (eastern vs. western location). However, it is noteworthy that
299 geothermal waters from the Wairakei field display the most constant $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, between
300 0.70549 and 0.70574. Sr isotope data reported here are in agreement with those of Graham
301 (1992) for the Rotorua geothermal waters (0.70514-0.70791) and for the Ohaaki geothermal
302 field site (0.70746, Grimes et al. 2000) also located in New Zealand.

303

304

5. DISCUSSION

305

306 Collectively, the lithium, boron and strontium isotopes can be used to identify the different
307 sources contributing to the Li-B-Sr isotopic signature and to determine the main processes
308 controlling these elements and their isotopes in the geothermal waters of the TVZ.

309 First, Sr isotopes are investigated in the present work in order to better define the signature
310 of the reservoir the geothermal waters came from, given that Sr isotopes are a good tracer of
311 water origin for groundwaters and geothermal waters (Goldstein and Jacobsen 1987, Négrel
312 et al. 1997, Négrel 1999, Négrel et al. 2000). Second, lithium and boron isotopic
313 compositions ($\delta^7\text{Li}$ and $\delta^{11}\text{B}$) are also considered in order to provide further constraints on the
314 origin of Li and B in these geothermal waters.

315 As already mentioned, Sr isotopes display a large range in the geothermal waters of the TVZ
316 (from 0.70549 to 0.70961). In addition, we also observed in the previous section that if
317 dilution processes happen in the system (by shallow, colder waters), it could probably explain
318 the distribution of Sr concentrations. On the other hand, the higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in
319 geothermal waters are close to the value of modern seawater ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70917$, Dia et al.
320 1992). Collectively, these observations could reflect dilution of geothermal waters by
321 seawater (cold and shallow water input with high Sr isotopic ratio). A seawater mixing
322 calculation is displayed in Figure 6, in which $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are plotted vs. Cl/Sr ratios. The
323 geothermal end member is chosen to be sample RK5 (Rotokawa), which has both the lowest
324 $^{87}\text{Sr}/^{86}\text{Sr}$ and the highest Cl/Sr ratios, and is, thus, representative of geothermal waters being
325 least affected by potential seawater contribution. No significant contribution of seawater for
326 strontium is observed in the geothermal systems of the TVZ, it means that Sr and its isotopes
327 are mainly controlled by the signature of the bedrocks themselves.

328 As already mentioned in section 2., the TVZ is an area of rhyolitic volcanic activity and
329 hydrothermal altered sediments (greywackes) form the basement of the system. On the left
330 side of Figure 6, we show the ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the bedrocks of the system:
331 volcanic country rocks (rhyolite, ignimbrite and breccia, 0.7049-0.7057) reported by Graham
332 (1992), basalts for the TVZ (0.7026-0.7052, Gamble et al. 1993) and metasedimentary
333 basement rocks that have $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.705 for greywackes up to 0.725 for
334 argillites (Graham 1992). Therefore it is likely that the most radiogenic Sr isotope ratios are
335 the result of a significant contribution of waters having interacted with bedrocks having more
336 radiogenic strontium like metasedimentary basement rocks.

337 Finally, when $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the TVZ fluids are compared to literature data for other
338 geothermal fluids (Figure 7a), the geothermal waters from the TVZ are similar to those of
339 Graham (1992) for the Rotorua geothermal waters in New Zealand (0.70514-0.70791), but
340 are significantly different from those of Iceland, which have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging between
341 0.7032 and 0.7042 (Millot et al. 2009). However, all of the geothermal waters display a
342 similar range for Cl/Sr ratios, except for those of the Rotokawa geothermal field, which have
343 higher Cl/Sr ratios. It is very likely that the significant difference in the Sr isotopes signature
344 between the geothermal systems from New Zealand and those from Iceland is related to the
345 signature of the volcanic basement rocks. New Zealand volcanic activity commenced 1.6 Ma
346 ago, allowing in-growth of radiogenic Sr from Rb, whereas the geothermal systems in Iceland
347 are located in the central volcanic area, which is only < 0.8 Ma old.

348 Boron isotopes ($\delta^{11}\text{B}$) range from -6.70‰ to -1.92‰ in the geothermal waters from the TVZ,
349 these values are in a good agreement with a volcanic origin of the waters ($< 0\text{‰}$: Barth 1993,
350 2000). In addition, according to Aggarwal et al. (2003) for the Ngawha geothermal field, the
351 relatively low $\delta^{11}\text{B}$ values for the fluids implies no significant marine input into the geothermal
352 reservoir and this is also in accord with other geochemical data, e.g. average Cl/B = 53
353 compared to seawater Cl/B = 4839. In Figure 7b, it is important to note that the worldwide
354 geothermal waters have a $\delta^{11}\text{B}$ signature almost entirely comprised between -10 and 0‰ ,
355 with the exception of the samples from Reykjanes and Svartsengi geothermal fields in
356 Iceland, for which the contribution of seawater is significant (Millot et al. 2009). And, like the
357 Na concentration (Figure 3), the Cl/B is also variable according to the location of the
358 geothermal field.

359 Lithium isotopic compositions ($\delta^7\text{Li}$, ‰) are very homogeneous for the geothermal waters of
360 the TVZ. In Figure 7c, we can compare Li isotope data for TVZ geothermal waters with
361 geothermal waters from Iceland (Millot et al. 2009) and with geothermal systems from the
362 Guadeloupe and Martinique islands (volcanic islands belonging to the Lesser Antilles arc,
363 French West Indies, Millot et al. 2010a). The geothermal waters from the TVZ are distinct

364 from those of other geothermal systems. Indeed, the geothermal waters from the TVZ display
365 the lowest $\delta^7\text{Li}$ yet reported for geothermal waters, but they also have the lowest Cl/Li ratios.
366 In addition, whereas the geothermal fields from Iceland and French West Indies can have a
367 significant contribution of Li from seawater (Millot et al. 2009, 2010b), it is obvious that
368 seawater has no influence on the composition of the geothermal waters from New-Zealand.
369 Several studies of Li-isotope behaviour in near-surface environments have shown that $\delta^7\text{Li}$
370 values do not directly reflect the signature of the bedrock, but instead are controlled by
371 fractionation during water/rock interactions during the formation of secondary minerals of
372 alteration (Huh et al. 1998, 2001, 2004, Pistiner and Henderson 2003, Rudnick et al. 2004,
373 Kısakürek et al. 2004, 2005, Pogge von Strandmann et al. 2006, Vigier et al. 2009, Teng et
374 al. 2010, Lemarchand et al. 2010, Millot et al. 2010b). And it has been suggested that
375 the $\delta^7\text{Li}$ signature in the liquid might be controlled by the preferential retention of light lithium
376 isotope (^6Li) into secondary mineral phases during the weathering processes. It has also
377 been shown that the fractionation of lithium isotopes during water/rock interactions also
378 depends on temperature because different secondary minerals might control the uptake or
379 release of lithium in secondary minerals depending on the temperature of interaction and the
380 associated dissolution/precipitation reaction (Chan and Edmond 1988, Chan et al. 1992;
381 1993; 1994; Chan et al. 2002). All geothermal fluids from the TVZ show homogeneous and
382 low $\delta^7\text{Li}$ values, indicating that temperature is probably not the main factor in controlling the
383 Li isotopic composition of the geothermal fluids. Rather, it is more likely that the consistent
384 low $\delta^7\text{Li}$ values in these geothermal fluids could reflect Li leaching from the same source
385 rock. When plotted on isotope vs. isotope diagrams (Figure 8), the following conclusions can
386 be reached: i) Li isotope signatures are very homogeneous and do not allow the
387 discrimination of any geothermal field, suggesting that the fluids are well-mixed for Li and
388 that it is the process of water/rock interaction at high temperature that is the main factor that
389 determine both Li and its isotopes distribution in geothermal waters of the TVZ; ii) B isotopes
390 are less homogeneous, and some differences could exist between the geothermal fields;
391 although B and its isotopes are also mainly controlled by water/rock interaction processes,
392 there is a small difference for $\delta^{11}\text{B}$ values between geothermal waters from Rotokawa and
393 Ohaaki on the one hand and those from Mokai, Wairakei and Kawerau on the other hand; iii)
394 the Sr isotopes signatures vary widely and confirm distinction between waters from different
395 locations. From a general point of view, the geographical distribution of the samples within
396 the TVZ (eastern vs. western location) shows that it could affect B and Sr but not Li isotopes,
397 meaning that it is likely that the fluids are well-mixed for Li and less for B and Sr. In addition,
398 for Sr isotopes, the isotopic signal also depends on the type of basement rocks.
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6. CONCLUSIONS

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The main conclusions of the Li-B-Sr isotopes characterization of the geothermal waters from the Taupo Volcanic Zone are:

- Lithium concentrations are high (ranging from 4.5 to 19.9 mg/L) and lithium isotopic compositions ($\delta^7\text{Li}$) are homogeneous ranging between -0.5 and +1.4‰. Li isotope tracing shows that the input of seawater is negligible in these geothermal waters and that Li and its isotopes are mainly controlled by equilibrium exchange with magmatic rocks at high temperature.
- Boron concentrations are also high (17.5 and 82.1 mg/L) and relatively homogeneous and boron isotopic compositions ($\delta^{11}\text{B}$) are all negative, ranging from -6.7 to -1.9‰. This B isotope signature is in a good agreement with a fluid signature derived mainly from water/rock interactions involving magmatic rocks and no seawater input.
- Strontium concentrations (0.02 to 0.165 mg/L) are lower and more heterogeneous while $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range between 0.70549 and 0.70961. These Sr isotope compositions are similar to those of local magmatic bedrocks and the highest Sr isotope ratios are the result of a significant contribution of waters having interacted with bedrocks having more radiogenic strontium like, metasedimentary basement rocks.

Each of these isotope systems on their own reveals important information about particular aspects of either water source or water/rock interaction processes, but, considered together, provide a more integrated understanding of the geothermal systems from the TVZ in New Zealand. However, the combination of Li, B and Sr isotopic systems highlights the complexity of the study of these geothermal waters, and the use of only one isotopic tool could lead to an incomplete characterization of the geothermal waters.

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427

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608

609 **Table caption**

610

611 **Table 1**

612

613 Sample list including geothermal site, sample i.d., latitude and longitude coordinates, depth
614 of borehole (m), deep temperature estimates given by geothermometry (°C) and date of
615 sampling. Major and trace elements concentrations (mg/L) in the geothermal water samples
616 are also reported in this table and Li, B and Sr isotopic compositions. d.l. is the detection limit
617 (5 µg/L for Mg). Individual errors ($2\sigma_m$) are also reported for isotopic data.

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619

620 **Figure captions**

621

622 **Figure 1**

623 Geothermal samples location. These geothermal waters were sampled by Contact Energy
624 Limited for Ohaaki and Wairakei geothermal systems and by Mighty River Power Limited
625 (MRP) for Mokai, Kawerau and Rotokawa geothermal systems respectively.

626

627 **Figure 2**

628 Cl concentrations (mg/L) plotted as a function of Na concentrations (mg/L).

629

630 **Figure 3**

631 Li, B and Sr concentrations (mg/L) plotted as a function of Na concentrations (mg/L). The
632 dashed lines represent the 2σ uncertainty on the linear correlations.

633

634 **Figure 4**

635 Li, Sr, B and SiO₂ concentrations (mg/L) plotted as a function of the deep temperature (°C)
636 estimated by geothermometry. Correlations have been added as well as a 2σ interval of
637 confidence.

638

639 **Figure 5**

640 a: Li isotopes plotted as a function of Li concentrations (mg/L). The errors bars correspond to
641 the external reproducibility of our method for Li isotopes analysis $\pm 0.5\text{‰}$, 2σ .

642 b : B isotopes plotted as a function of B concentrations (mg/L). The errors bars correspond to
643 the external reproducibility of our method for B isotopes analysis $\pm 0.3\text{‰}$, 2σ .

644 c : Sr isotopes plotted as a function of Sr concentrations (mg/L). The errors bars are included
645 within the sample symbol and correspond to the external reproducibility of our method for Sr
646 isotopes analysis ± 0.000020 , 2σ .

647

648 **Figure 6**

649 Sr isotopes plotted as a function of Cl/Sr massic ratio. Fields for volcanic country rocks, TVZ
650 basalts and metasedimentary basement rocks have also been added, see text for comments.

651

652 **Figure 7**

653 a : Sr isotopes plotted as a function of Cl/Sr massic ratio. Comparison with geothermal
654 waters from Rotorua geothermal system (Graham 1992) and geothermal systems from
655 Iceland (Millot et al. 2009).

656 b : B isotopes plotted as a function of Cl/B massic ratio. Comparison with geothermal waters
657 from Ngawha geothermal system (Graham 1992), Yellowstone (Palmer and Sturchio 1990)
658 and geothermal systems from Iceland (Millot et al. 2009).

659 c : Li isotopes plotted as a function of Cl/Li massic ratio. Comparison with geothermal waters
660 from Iceland (Millot et al. 2009) and from the Antilles (French West Indies, Millot et al.
661 2010a).

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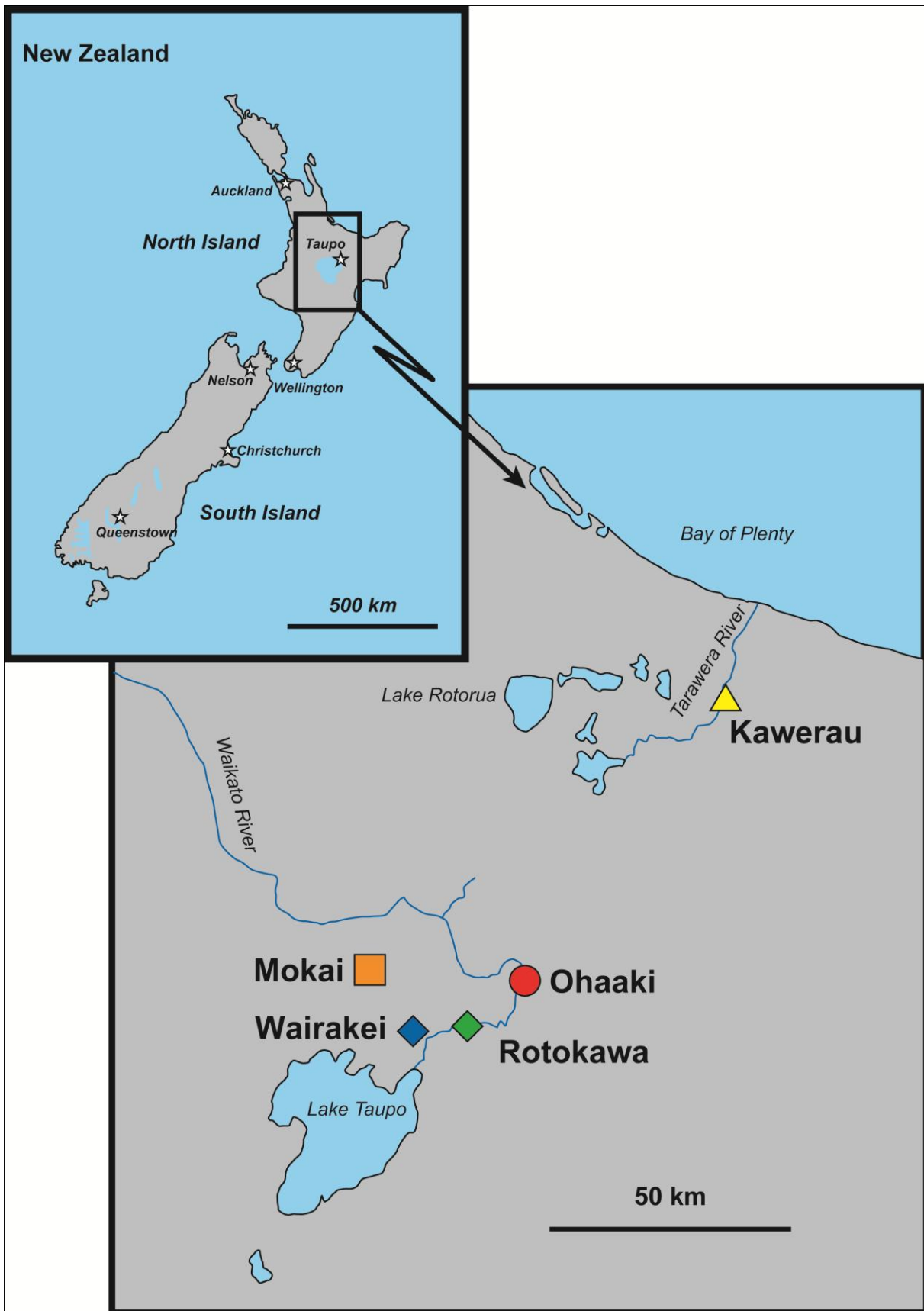
663 **Figure 8**

664 Multi-isotopic (Li-B-Sr) characterization of geothermal waters from the Taupo Volcanic Zone.

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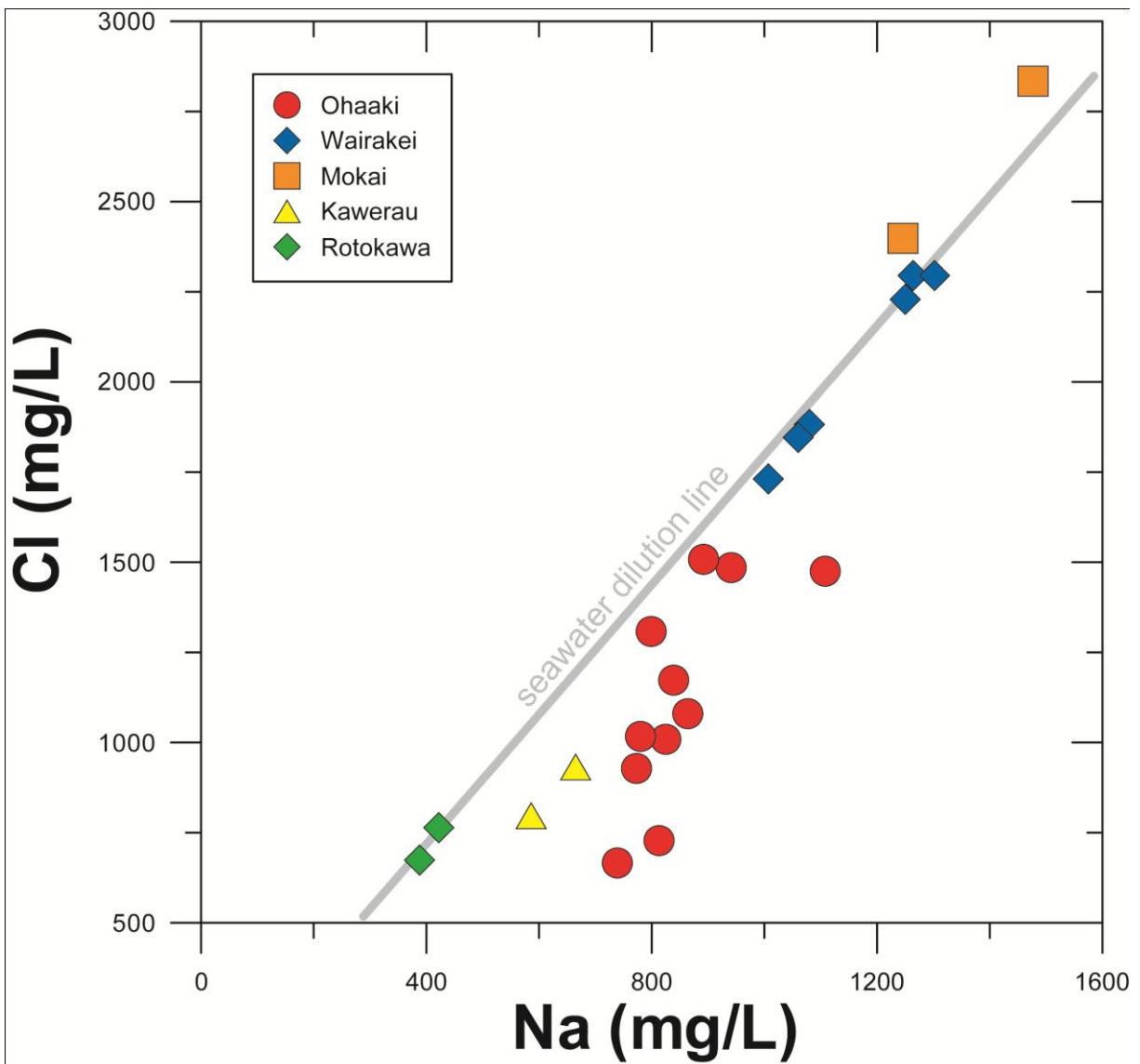
667 Figure 1



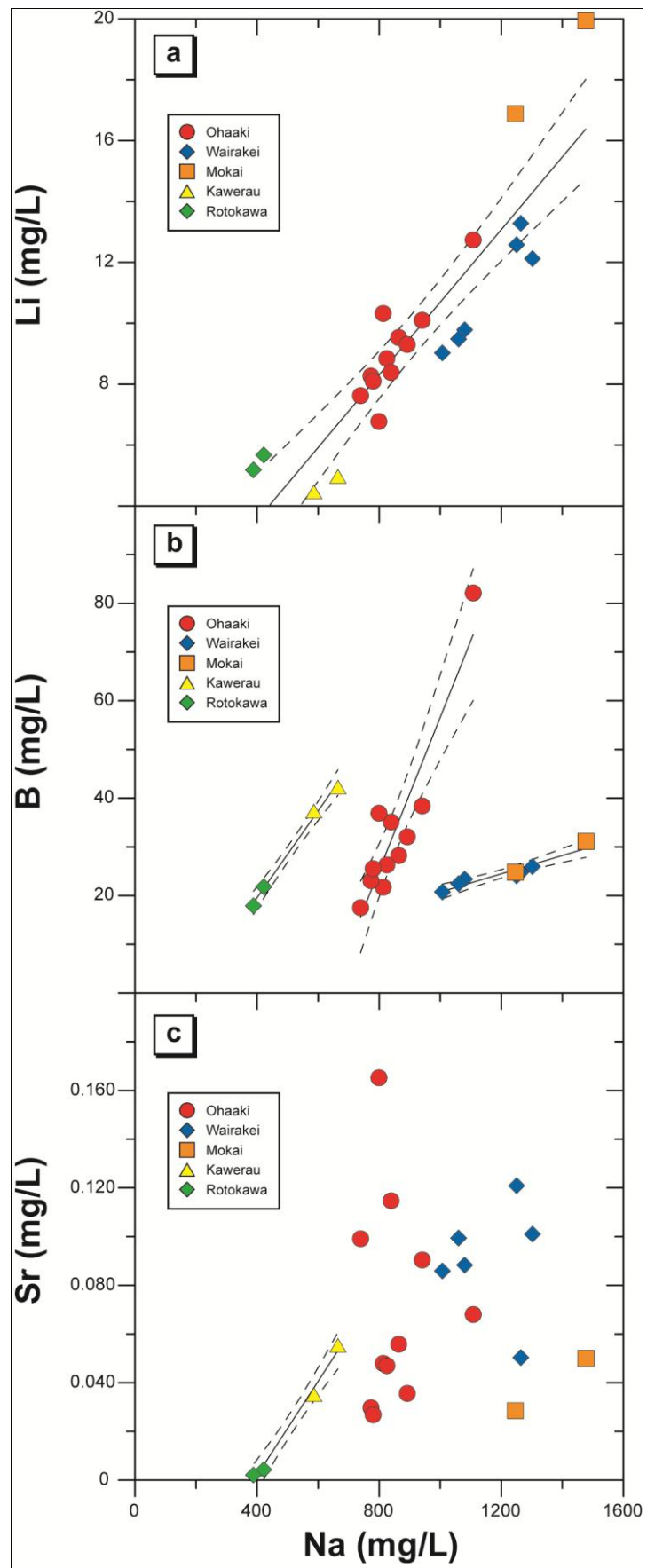
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670 Figure 2



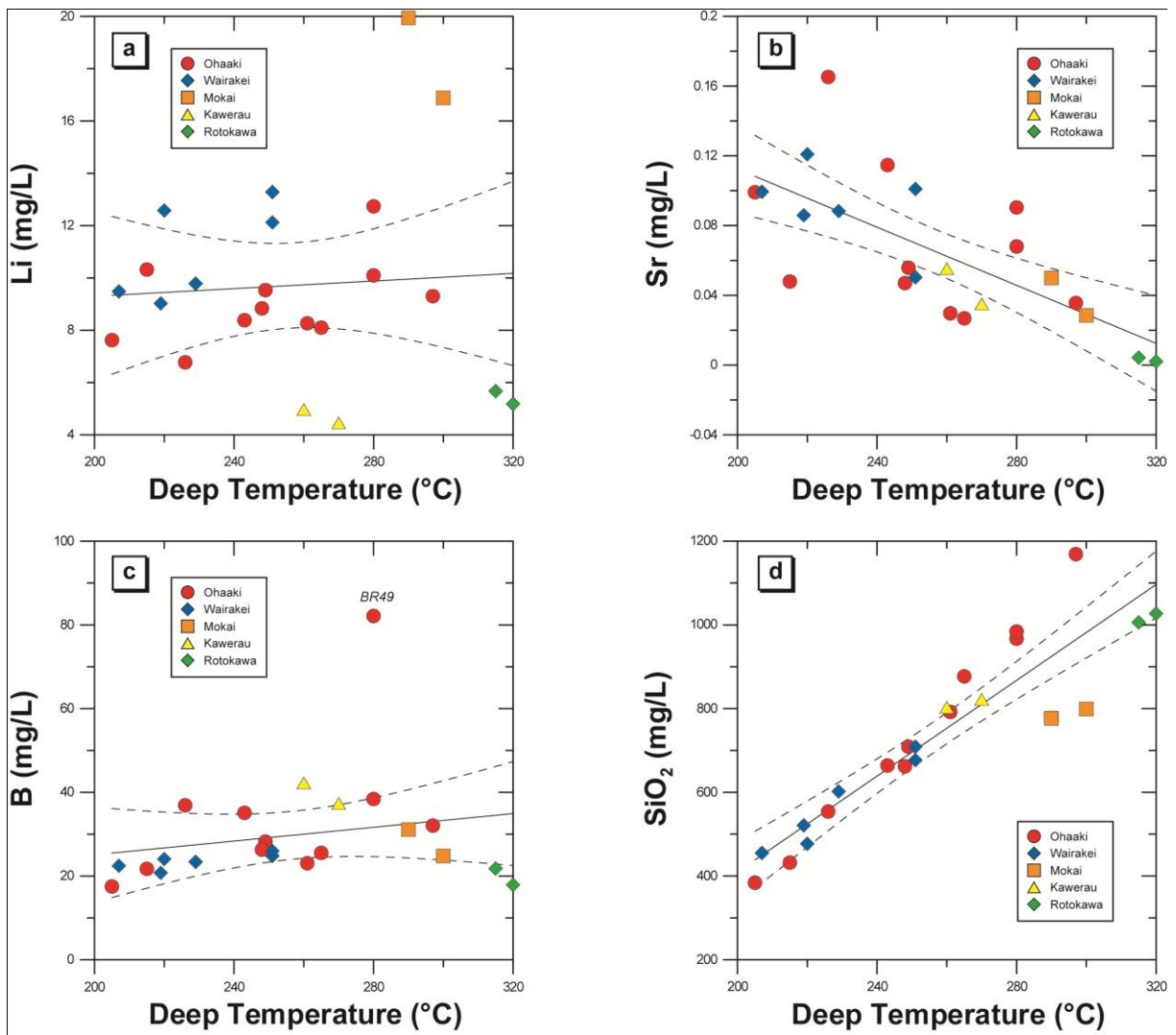
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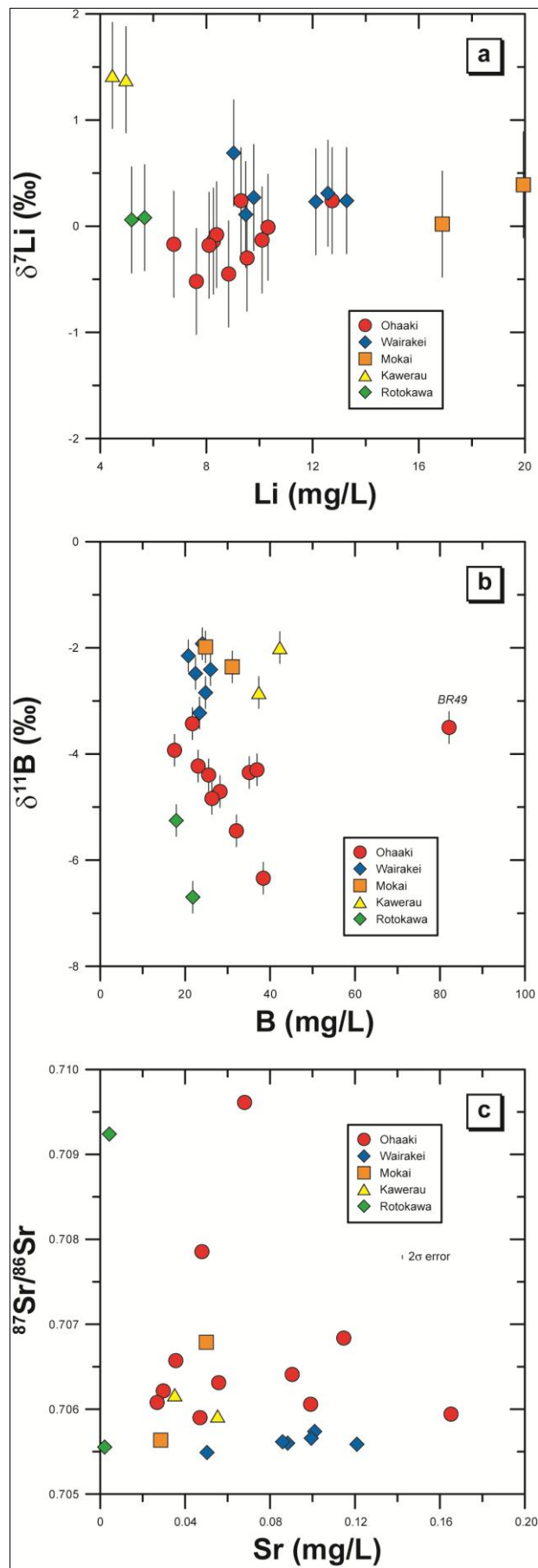
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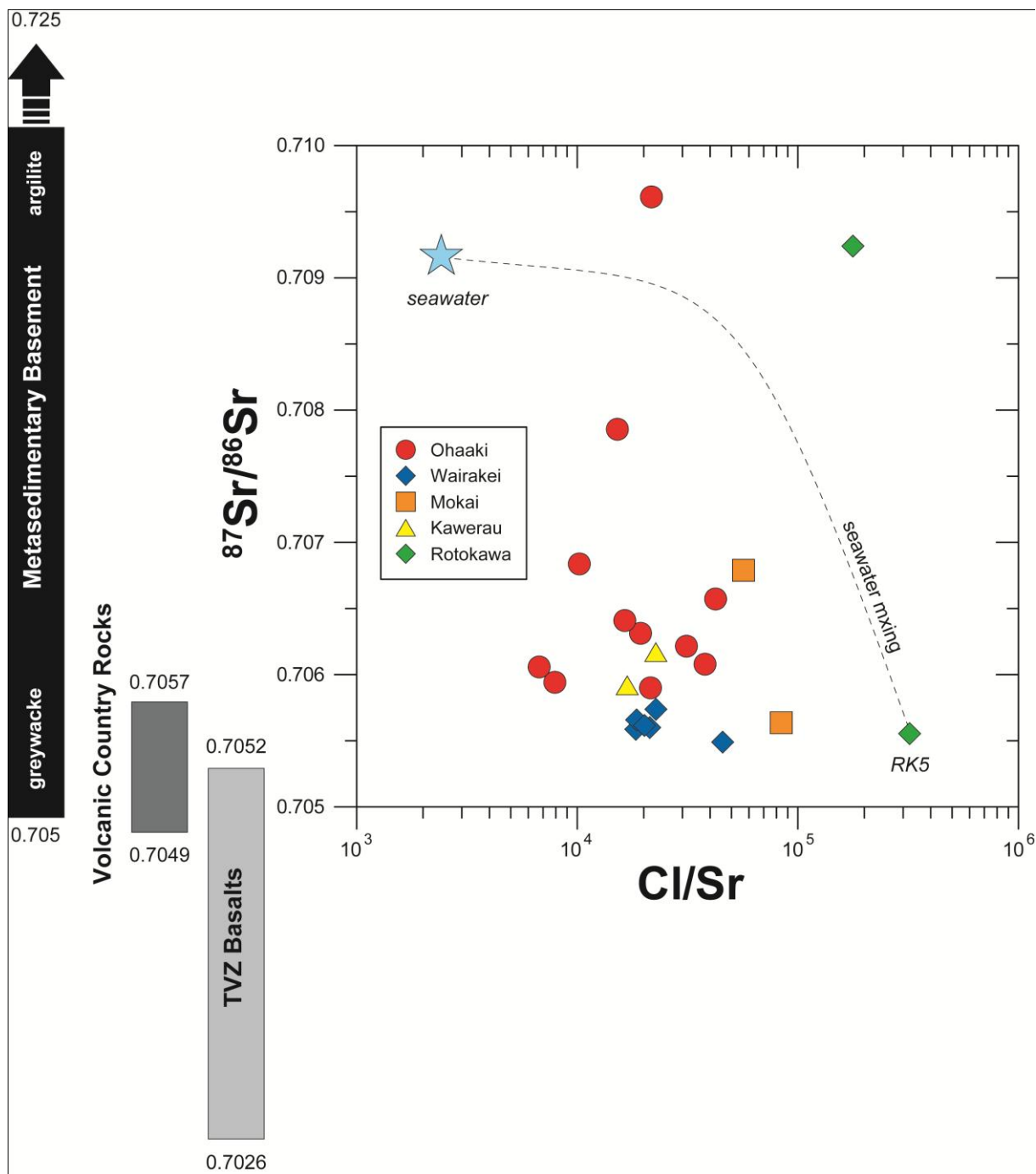
688 Figure 4



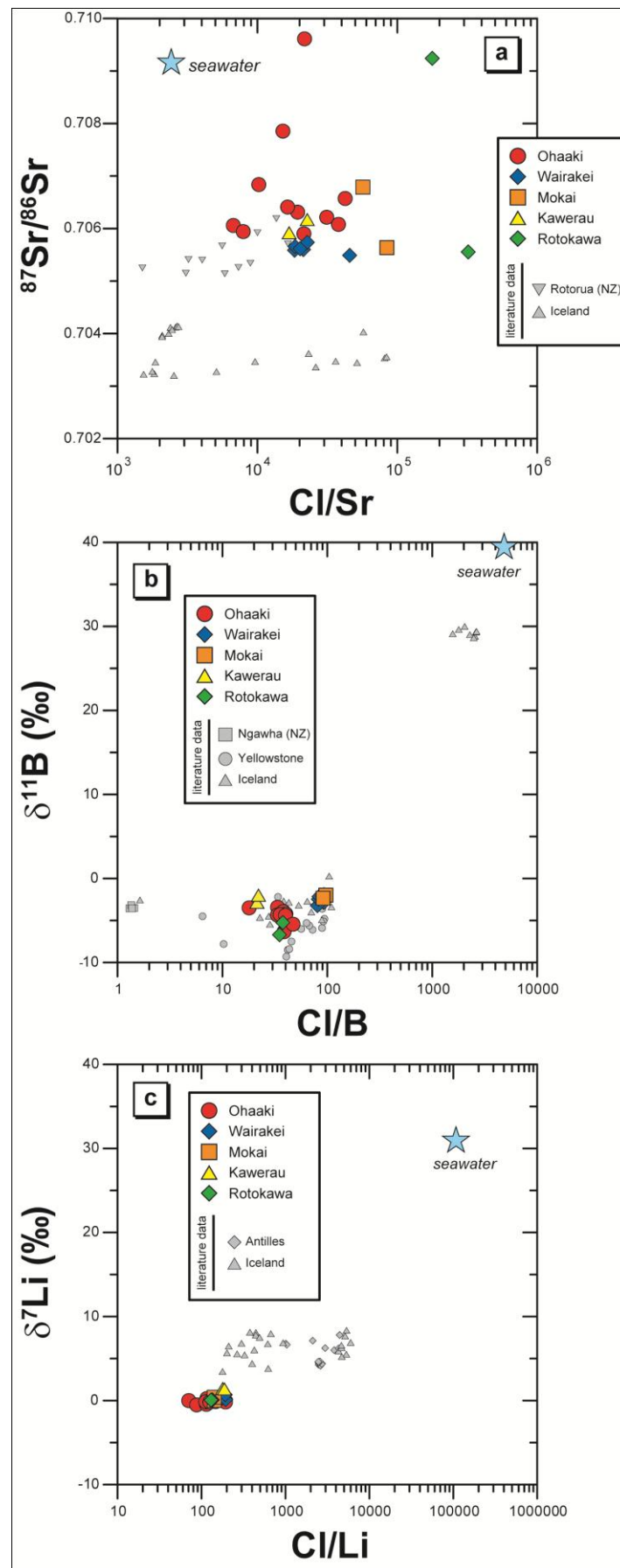
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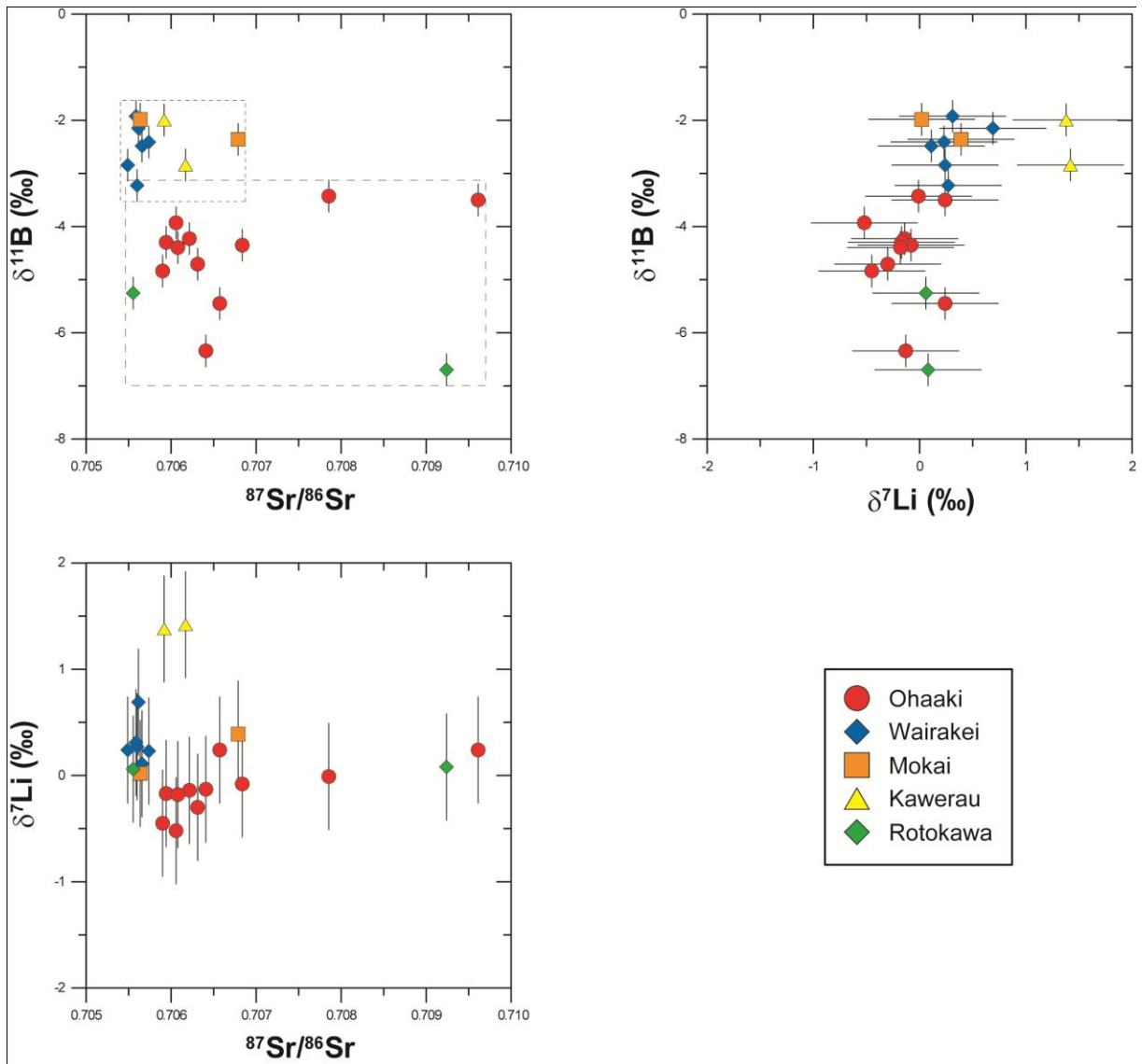
706 Figure 6



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718 Figure 8



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| Geothermal system | | Well ID | Coordinates | | borehole depth | deep temperature | DATE | Na | K | Mg | Ca | Cl | SO ₄ | Br | SiO ₂ | Li | B | Sr | δ ⁷ Li | 2σ _m | δ ¹¹ B | 2σ _m | ⁸⁷ Sr/ ⁸⁶ Sr | 2σ _m |
|-------------------|-------|-------------|--------------|-----------|----------------|------------------|------|-------|--------|--------|------|------|-----------------|------|------------------|-------|-------|-------|-------------------|-----------------|-------------------|-----------------|------------------------------------|-----------------|
| | | | latitude | longitude | m | °C | mg/L | mg/L | μg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L | μg/L | ‰ | ‰ | ‰ | ‰ | | |
| Ohaaki | BR25 | S 38°31'58" | E 176°18'43" | 680 | 215 | 07/10/2004 | 813 | 94 | < d.l. | 0.106 | 728 | 19 | 2 | 432 | 10.32 | 21.71 | 47.9 | -0.01 | 0.12 | -3.43 | 0.09 | 0.707855 | 0.000006 | |
| Ohaaki | BR49 | S 38°32'16" | E 176°18'37" | 1270 | 280 | 04/10/2005 | 1108 | 206.5 | 8.4 | 2.143 | 1475 | 4 | 3.7 | 967 | 12.74 | 82.13 | 68 | 0.24 | 0.16 | -3.50 | 0.08 | 0.709612 | 0.000006 | |
| Ohaaki | BR9 | S 38°31'11" | E 176°18'24" | 1000 | 205 | 03/04/2006 | 739 | 72.2 | 8.3 | 1.647 | 666 | 74.8 | 1.9 | 384 | 7.62 | 17.50 | 99.1 | -0.52 | 0.14 | -3.93 | 0.06 | 0.706058 | 0.000009 | |
| Ohaaki | BR22 | S 38°31'10" | E 176°18'34" | 670 | 249 | 03/04/2006 | 864 | 137.4 | 5.3 | 1.758 | 1080 | 58.8 | 3.1 | 709 | 9.53 | 28.22 | 55.8 | -0.30 | 0.24 | -4.71 | 0.07 | 0.706312 | 0.000007 | |
| Ohaaki | BR20 | S 38°31'18" | E 176°18'36" | 1000 | 248 | 23/04/2007 | 825 | 110.2 | 15.4 | 1.859 | 1009 | 60.5 | 3 | 662 | 8.84 | 26.31 | 47 | -0.45 | 0.22 | -4.84 | 0.08 | 0.705900 | 0.000007 | |
| Ohaaki | BR54 | S 38°31'06" | E 176°18'35" | 1430 | 261 | 01/05/2007 | 773 | 121.4 | < d.l. | 1.624 | 928 | 43.5 | 2.7 | 792 | 8.27 | 23.06 | 29.7 | -0.14 | 0.20 | -4.23 | 0.11 | 0.706215 | 0.000007 | |
| Ohaaki | BR44 | S 38°31'53" | E 176°19'06" | 760 | 243 | 28/08/2007 | 839 | 102.2 | 5.1 | 2.146 | 1173 | 12.4 | 3.2 | 664 | 8.38 | 35.10 | 114.7 | -0.08 | 0.18 | -4.35 | 0.09 | 0.706837 | 0.000007 | |
| Ohaaki | BR14 | S 38°37'06" | E 176°19'19" | 590 | 226 | 31/08/2007 | 799 | 81.1 | 25.4 | 12.625 | 1308 | 3.9 | 3.7 | 554 | 6.77 | 36.91 | 165.2 | -0.17 | 0.24 | -4.30 | 0.07 | 0.705942 | 0.000007 | |
| Ohaaki | BR48 | S 38°31'06" | E 176°17'53" | 1360 | 265 | 28/09/2007 | 780 | 136.1 | < d.l. | 1.872 | 1017 | 41.3 | 2.8 | 877 | 8.10 | 25.53 | 26.8 | -0.18 | 0.12 | -4.39 | 0.07 | 0.706079 | 0.000007 | |
| Ohaaki | BR60 | S 38°31'10" | E 176°17'54" | 1800 | 280 | 23/07/2008 | 941 | 199.2 | 8.9 | 2.686 | 1485 | 10.2 | 4.4 | 984 | 10.10 | 38.40 | 90.4 | -0.13 | 0.10 | -6.34 | 0.07 | 0.706409 | 0.000008 | |
| Ohaaki | BR66 | S 38°31'01" | E 176°18'17" | 1880 | 297 | 03/09/2008 | 892 | 220.5 | 27.9 | 3.003 | 1508 | 9.5 | 4.3 | 1169 | 9.30 | 32.06 | 35.6 | 0.24 | 0.26 | -5.45 | 0.08 | 0.706572 | 0.000006 | |
| Wairakei | WK245 | S 38°37'04" | E 176°02'59" | 800 | 251 | 07/09/2008 | 1264 | 217.4 | < d.l. | 10.923 | 2295 | 34.1 | 5.4 | 709 | 13.28 | 24.81 | 50.3 | 0.24 | 0.14 | -2.84 | 0.09 | 0.705490 | 0.000009 | |
| Wairakei | WK70 | S 38°37'22" | E 176°04'22" | 600 | 229 | 08/10/2008 | 1080 | 146.1 | 8.6 | 20.434 | 1882 | 35 | 4.5 | 602 | 9.78 | 23.39 | 88.3 | 0.27 | 0.30 | -3.23 | 0.08 | 0.705600 | 0.000008 | |
| Wairakei | WK247 | S 38°36'55" | E 176°03'20" | 2300 | 251 | 05/03/2007 | 1302 | 213.2 | 7.5 | 27.667 | 2295 | 34 | 5.8 | 677 | 12.12 | 25.97 | 101 | 0.23 | 0.12 | -2.41 | 0.09 | 0.705738 | 0.000007 | |
| Wairakei | WK235 | S 38°36'53" | E 176°03'23" | 700 | 220 | 04/03/2008 | 1250 | 175.6 | 9.2 | 20.911 | 2229 | 33.7 | 5.6 | 477 | 12.58 | 24.06 | 120.9 | 0.31 | 0.18 | -1.92 | 0.09 | 0.705587 | 0.000008 | |
| Wairakei | WK28 | S 38°37'32" | E 176°04'09" | 600 | 207 | 14/04/2008 | 1060 | 139.3 | 16.7 | 21.261 | 1846 | 44.4 | 4.6 | 455 | 9.48 | 22.44 | 99.4 | 0.11 | 0.18 | -2.48 | 0.12 | 0.705658 | 0.000008 | |
| Wairakei | WK24 | S 38°37'21" | E 176°04'18" | 600 | 219 | 30/07/2008 | 1007 | 128.2 | 7.2 | 20.247 | 1731 | 34.9 | 4.3 | 521 | 9.03 | 20.75 | 85.9 | 0.69 | 0.18 | -2.15 | 0.08 | 0.705616 | 0.000007 | |
| Mokai | MK3 | S 38°31'34" | E 175°56'23" | 1679 | 300 | 24/02/2009 | 1246 | 288.6 | 14.6 | 7.965 | 2398 | 11.7 | 5.6 | 799 | 16.88 | 24.79 | 28.5 | 0.02 | 0.16 | -1.98 | 0.09 | 0.705636 | 0.000006 | |
| Mokai | MK7 | S 38°31'36" | E 175°55'34" | 2252 | 290 | 25/02/2009 | 1477 | 338.2 | 27.2 | 12.086 | 2834 | 6.6 | 5.9 | 777 | 19.94 | 31.10 | 50 | 0.39 | 0.16 | -2.36 | 0.09 | 0.706789 | 0.000007 | |
| Kawerau | KA37 | S 38°03'52" | E 176°43'34" | 1306 | 270 | 29/01/2009 | 586 | 92.9 | < d.l. | 1.891 | 797 | 26.4 | 2 | 822 | 4.46 | 37.34 | 35.1 | 1.42 | 0.18 | -2.84 | 0.06 | 0.706170 | 0.000009 | |
| Kawerau | KA19 | S 38°03'32" | E 176°43'07" | 1108 | 260 | 28/01/2009 | 665 | 99.4 | 6.9 | 2.468 | 932 | 14.6 | 2 | 803 | 4.97 | 42.28 | 55.3 | 1.38 | 0.16 | -1.99 | 0.06 | 0.705919 | 0.000007 | |
| Rotokawa | RK14 | S 38°36'33" | E 176°11'25" | 2500 | 315 | 08/04/2009 | 422 | 126.7 | < d.l. | 1.632 | 764 | 2.6 | 1.3 | 1006 | 5.67 | 21.80 | 4.3 | 0.08 | 0.16 | -6.70 | 0.06 | 0.709240 | 0.000007 | |
| Rotokawa | RK5 | S 38°36'31" | E 176°11'40" | 2783 | 320 | 07/04/2009 | 388 | 112.1 | < d.l. | 1.232 | 674 | 3.9 | 1.1 | 1027 | 5.18 | 17.90 | 2.1 | 0.06 | 0.20 | -5.25 | 0.07 | 0.705554 | 0.000007 | |