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Possible Mineral-Water Interactions Delimiting Li Geothermometry in Geothermal Systems

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ABSTRACT

In the Taupo Volcanic Zone (TVZ) hydrothermal systems, smectite, chlorite, quartz, albite, illite and Ca-aluminosilicates contain measurable concentrations of Li (3.6 to 210 mg/kg) whilst Li in hydrothermal calcite is below detection limits. The affinity for Li by hydrothermal minerals in the TVZ, from highest to lowest is: smectite > quartz > chlorite > illite ~ albite ~ Ca-aluminosilicates >> calcite where calcite is a Li-rejecting mineral as opposed to the other Li-receptor minerals. The presence of both Li-rejecting and Li-acceptor minerals regulate the Mg/Li and Na/Li ratios of hydrothermal aqueous fluids. In addition, the temperature-dependent transitions from smectite to illite, chlorite to illite, opal CT to quartz and the increase in Mg in Mg-Fe chlorites affect the concentration and mobilization of Li indicating that these mineral transformations can also control the Mg/Li or Na/Li ratios in aqueous fluids. Without modifications, the Mg-Li geothermometer cannot be used in the TVZ but may be applicable to systems where the main alteration process at <200°C ± 20°C involves the transition of smectite to illitic clays and transformation of chlorite to illite, with limited quartz deposition. Several different alteration processes have opposing effects on the Na/Li ratios of aqueous fluids in the Taupo Volcanic Zone including: dissolution of glass and plagioclase to form phyllosilicates and albite (<Na/Li); albitization, silicification, chloritization and intense argillization (>Na/Li); deposition of calcite (<Na/Li). All these alteration assemblages can be affected by variations in the gas contents and fluid pH, permeability and hydrological processes which can vary from hydrothermal systems to system. Because Li is a trace element in minerals, it is sensitive to slight variations in conditions and may be one of the reasons why the Li geothermometers appear to be site-specific. Both geothermometers cannot be ascribed to a simple interchange between Li and Mg or Na in minerals. The trend of decreasing Mg/Li or Na/Li ratios with temperature exhibited by the Mg-Li and Na-Li geothermometers can be replicated by counterbalancing deposition of chlorite + quartz (for Mg-Li) or albite + quartz (for Na-Li) with deposition of the Li-rejecting calcite and/or illite (which accommodates less Li than chlorite, quartz or albite).

1. INTRODUCTION

The most robust and reliable geothermometers for aqueous fluids (e.g., Fournier, 1981; Giggenbach, 1988; Arnorsson et al, 1983) used in assessing active hydrothermal systems are derived from thermodynamically-based mineral solubilities (SiO_2) and ion-exchange between feldspars (Na-K geothermometry) or phyllosilicates and feldspars (K-Mg geothermometry), albeit each with its own limitations (e.g., Arnorsson, 1985; Kharaka and Hanor, 2003). In contrast, empirical and semi-empirical geothermometers such as the Na-K-Ca (Fournier and Truesdell (1973), Mg-corrected Na-K-Ca (Fournier and Potter, 1979); Na-Li and Mg-Li (e.g., Fouillac and Michard, 1981), calibrated from field measurements, are not always reliable in predicting subsurface temperatures and appear to be site-specific.

Field observations (e.g., Fouillac and Michard, 1981) and experimental studies (Ellis and Mahon, 1964 and 1967) have clearly shown an increase in Li concentrations as temperatures rise in hydrothermal and sedimentary formation aqueous fluids. However, unlike the SiO_2 and alkali-cation geothermometers, which can be correlated with chemical equilibrium of widespread and relatively abundant specific minerals, authigenic neoformed Li-rich minerals are rarely reported in hydrothermal and sedimentary environments. So far, the only Li-rich minerals reported in active hydrothermal systems are lepidolite in Yellowstone forming at 130-140°C (Bargar et al, 1973) and elbaite, a Li-rich tourmaline, depositing at >300°C in magmatic-hydrothermal systems in the Philippines (Reyes et al, 2003). Because these Li-rich minerals are rare in hydrothermal systems, both will have limited impact on Li water-rock equilibria.

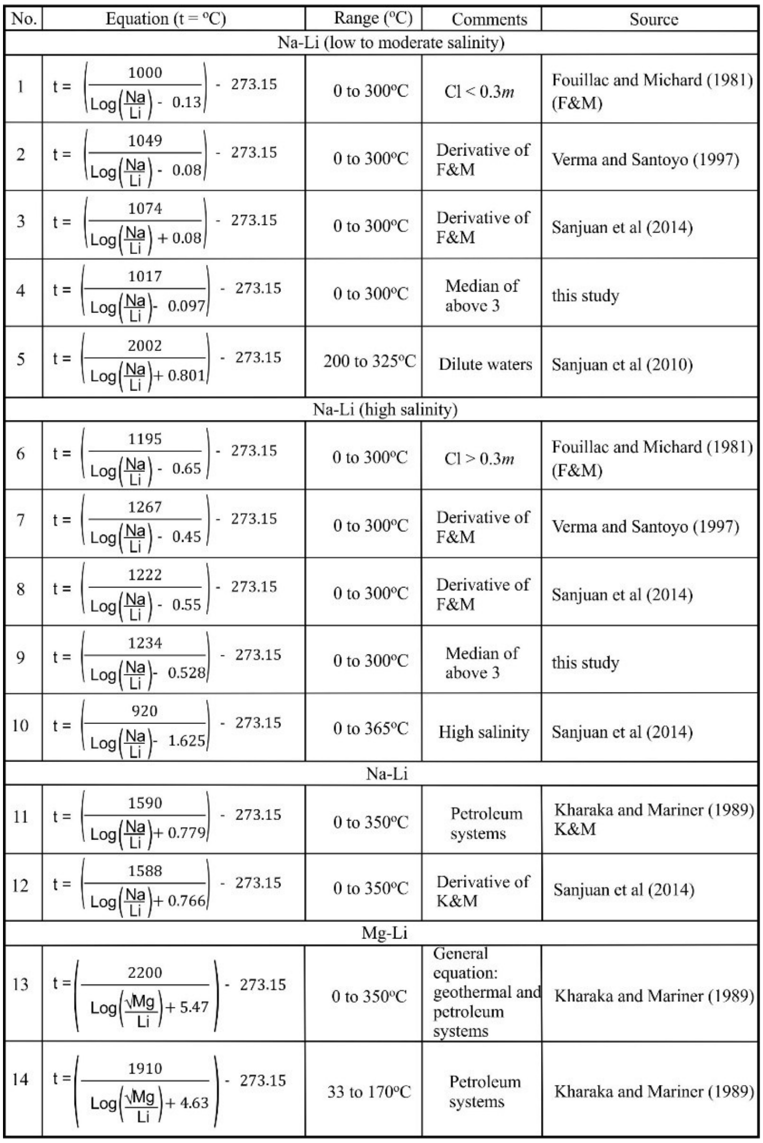
Lithium, unlike Na, K and Mg occur as a trace element in most rocks. To explain any chemical equilibria that may govern Li redistribution between rock and aqueous fluids Fouillac and Michard (1981) invoked the model of a “soluble” Li that is not sequestered in any neoformed mineral except in smectites (Ellis and Mahon, 1967). However later studies, prompted by more sensitive analytical equipment and techniques, showed that apart from being incorporated in smectites (e.g., Seyfried et al, 1984), low concentrations of Li can also occur in hydrothermal minerals such as zeolites, celadonite, quartz and chlorite (Goguel, 1983; Sturchio et al, 1986).

The objective of this paper is to evaluate the redistribution of Li between aqueous fluids and various protoliths and minerals in the high-temperature hydrothermal systems in the Taupo Volcanic Zone (TVZ) that may cause the tendency for Li geothermometers to be site specific.

To understand the main rock sources and pathways of Li in high temperature hydrothermal systems of the TVZ, representative samples of protoliths (rhyolite, andesite, basalt and greywacke) on the surface and hydrothermally altered rhyolite, andesite and greywacke cores and cutiings from deep geothermal wells were collected. All samples were analyzed in detail under a petrographic microscope and major oxides in selected minerals determined using an electron microprobe. Lithium concentrations in powdered rock and individual minerals in polished thin sections were analyzed with a proton beam at GNS-Science, utilizing Nuclear Reaction Analysis (Trompetter et al, 1999). The limit of detection for Li in these experiments is 3.6 mg/kg (Reyes and Trompetter, 2012).

2. LITHIUM GEOTHERMOMETERS

Of the five Na-Li geothermometers and the five derivatives from the original equations (Table 1), the most widely used for geothermal and petroleum systems is based on Fouillac and Michard (1981) for low-moderate (Cl<0.3m) and high Cl (Cl>0.3m). These were derived from a wide range of high- and low-temperature geothermal systems in volcanic and sedimentary environments and sedimentary formation waters. Extreme outliers in Icelandic geothermal systems were deemed by Fouillac and Michard (1981) to be due to interaction with basalt. Two Na-Li geothermometers, showing again a dichotomy between dilute and high-Cl aqueous fluids, were devised specifically for geothermal systems in basaltic rift-type systems (Sanjuan et al, 2010 and 2014). These were successfully used in subaerial systems such as Iceland and Djibouti and subsea systems in the Mid-Atlantic Ridge and East Pacific Rise. Unlike the previous geothermometers, the Na-Li geothermometer of Kharaka and Mariner (1989) is based on formation waters in petroleum systems and hence not suitable for geothermal systems (Kharaka and Hanor, 2003). The general equation for the Mg-Li geothermometer (equation 13 in Table 1) was derived from both geothermal and formation aqueous fluids in contrast to the more restricted Mg-Li geothermometer for petroleum systems (Kharaka and Mariner, 1989).



No.	Equation (t = °C)	Range (°C)	Comments	Source
Na-Li (low to moderate salinity)				
1	$t = \left(\frac{1000}{\text{Log}\left(\frac{Na}{Li}\right) - 0.13}\right) - 273.15$	0 to 300°C	Cl < 0.3*m*	Fouillac and Michard (1981) (F&M)
2	$t = \left(\frac{1049}{\text{Log}\left(\frac{Na}{Li}\right) - 0.08}\right) - 273.15$	0 to 300°C	Derivative of F&M	Verma and Santoyo (1997)
3	$t = \left(\frac{1074}{\text{Log}\left(\frac{Na}{Li}\right) + 0.08}\right) - 273.15$	0 to 300°C	Derivative of F&M	Sanjuan et al (2014)
4	$t = \left(\frac{1017}{\text{Log}\left(\frac{Na}{Li}\right) - 0.097}\right) - 273.15$	0 to 300°C	Median of above 3	this study
5	$t = \left(\frac{2002}{\text{Log}\left(\frac{Na}{Li}\right) + 0.801}\right) - 273.15$	200 to 325°C	Dilute waters	Sanjuan et al (2010)
Na-Li (high salinity)				
6	$t = \left(\frac{1195}{\text{Log}\left(\frac{Na}{Li}\right) - 0.65}\right) - 273.15$	0 to 300°C	Cl > 0.3*m*	Fouillac and Michard (1981) (F&M)
7	$t = \left(\frac{1267}{\text{Log}\left(\frac{Na}{Li}\right) - 0.45}\right) - 273.15$	0 to 300°C	Derivative of F&M	Verma and Santoyo (1997)
8	$t = \left(\frac{1222}{\text{Log}\left(\frac{Na}{Li}\right) - 0.55}\right) - 273.15$	0 to 300°C	Derivative of F&M	Sanjuan et al (2014)
9	$t = \left(\frac{1234}{\text{Log}\left(\frac{Na}{Li}\right) - 0.528}\right) - 273.15$	0 to 300°C	Median of above 3	this study
10	$t = \left(\frac{920}{\text{Log}\left(\frac{Na}{Li}\right) - 1.625}\right) - 273.15$	0 to 365°C	High salinity	Sanjuan et al (2014)
Na-Li				
11	$t = \left(\frac{1590}{\text{Log}\left(\frac{Na}{Li}\right) + 0.779}\right) - 273.15$	0 to 350°C	Petroleum systems	Kharaka and Mariner (1989) K&M
12	$t = \left(\frac{1588}{\text{Log}\left(\frac{Na}{Li}\right) + 0.766}\right) - 273.15$	0 to 350°C	Derivative of K&M	Sanjuan et al (2014)
Mg-Li				
13	$t = \left(\frac{2200}{\text{Log}\left(\frac{\sqrt{Mg}}{Li}\right) + 5.47}\right) - 273.15$	0 to 350°C	General equation: geothermal and petroleum systems	Kharaka and Mariner (1989)
14	$t = \left(\frac{1910}{\text{Log}\left(\frac{\sqrt{Mg}}{Li}\right) + 4.63}\right) - 273.15$	33 to 170°C	Petroleum systems	Kharaka and Mariner (1989)

Table 1: List of Na-Li and Mg-Li geothermometers with solutes expressed in mg/kg. Versions using molal concentrations are converted to mg/kg.

The various Na-Li geothermometers and experimental results (Ellis and Mahon, 1964 and 1967) are compared in a Na-Li-K ternary diagram (Figure 1). In general, based on experimental results (Ellis and Mahon, 1964 and 1967), dilute aqueous fluids show increasing Li concentrations with respect to the volcanic and greywacke protoliths as water-rock interaction time and temperatures increase (arrow in Figure 1). In both low-moderate and high Cl aqueous fluids, Li increases with temperature as Na decreases. At a given temperature, Li concentrations relative to Na are higher in low-moderate Cl compared to high-Cl aqueous fluids suggesting that high fluid salinities, or more specifically higher Na fluids, cause a greater retention of Li in the rock either by retarding dissolution of Li-bearing minerals, enhancing deposition of Li-accepting minerals or delaying deposition of secondary Na aluminosilicates such as albite. Most of the high temperature neutral pH spring and well discharges in the Taupo Volcanic Zone hydrothermal systems, with Cl concentrations of 0.001 to 0.091m, plot at 100°-350°C between the Kharaka and Mariner (1989) and Fouillac and Michard (1981) curves for Cl<0.3m with the majority occurring at 220°-350°C. The one neutral pH fluid from Raoul Island, a volcano (Giggenbach, 1995), that plots on the high Cl curve of Sanjuan et al (2014) is likely affected by seawater (Christenson et al, 2007). Other neutral pH outliers often have high HCO_3/Cl ratios at >0.2 to 11.4. Acidic volcanic and geothermal aqueous fluids are widely scattered showing that mere rock dissolution has little correlation with Na-Li geothermometry (Figure 1).

The regression line x in Figure 1, fitting most of the Taupo Volcanic Zone data, shows a very narrow range of Na/Li ratios at >200°C ± 20°C. The change from a higher slope from 20°-200°C to a shallower slope at >200°C ± 20°C may indicate a change in the type and abundance of minerals that accept or reject Li in their crystal lattices.

A comparison of measured stable maximum well temperatures and temperatures calculated from the Na-K, Na-Li (Cl<0.3m) and Mg-Li geothermometers is shown in Figure 2. As indicated by previous workers (e.g., Giggenbach, 1995) the Na-K geothermometer is the most reliable with 78% of the data falling within ±25°C of measured temperatures. Only 50% of the Na-Li temperatures by Fouillac and Michard (1981) correlate with measured temperatures in contrast to about 45% using the Verma and Santoya (1997) and Sanjuan et al (2014) geothermometers and 54% when equation 4 (Table 1) is used. Mg-Li temperatures show little correlation with measured well temperatures. The Na-Li geothermometer of Fouillac and Michard (1981) overestimates subsurface temperatures by as much as 120°C and underestimates by as much as 45°C compared to the Mg-Li geothermometer which overestimates by 165°C and underestimates by 95°C. Although the Na-Li and Mg-Li geothermometers have been successfully used to evaluate temperatures in several geothermal and petroleum systems in other parts of the world (e.g., Fouillac and Michard, 1981; Land and Macpherson, 1992; Sanjuan et al 2014 and 2016), there are geothermal systems, other than the TVZ, where these geothermometers have also proven less plausible than the Na-K geothermometer (e.g., Grimaud et al, 1985; Verma et al, 2008) or the Na-K-Ca geothermometer (Davisson et al, 1994). The Mg-Li geothermometer was configured using aqueous fluids in sedimentary basins (Kharaka and Mariner, 1989) and may account for its failure in the TVZ where volcanic rocks are the major source of water-rock interaction. On the other hand, the Na-Li geothermometer by Fouillac and Michard (1981) has a 50% success in predicting reservoir temperatures in the TVZ.

Lithium isotopes in aqueous fluids of various TVZ geothermal systems have similar values with a median of 0‰ ± 0.6 indicative of high temperature water-rock interaction with volcanic rocks with no evidence for seawater contribution (Millot et al, 2012). Giggenbach (1995) also surmised a similar source for aqueous fluid solutes such as Li and Cs except for specifying andesite as a source rock in the east and rhyolite-basalt in the west of the TVZ. If Li contents in aqueous fluids of the TVZ is modulated by water-rock interaction rather than the introduction of extraneous fluids, then what are the compositions of the source rocks and their corresponding altered rock? What processes during hydrothermal alteration affect Li redistribution between aqueous fluids and rock?

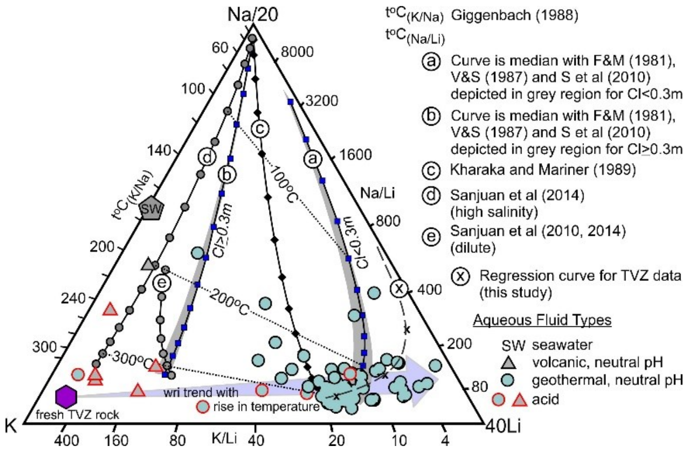


Figure 1: Relative Na, Li and K concentrations of neutral pH and acidic geothermal and volcanic aqueous fluids in the Taupo Volcanic Zone superimposed on the various Na/Li geothermometric curves a, b, c, d and e with Na/K temperatures shown on the left side. Lithium concentrations in aqueous fluids increase as temperatures rise regardless of the original lithology (light violet arrow) based on water-rock interaction (wri) experiments of Ellis and Mahon (1964 and 1967).

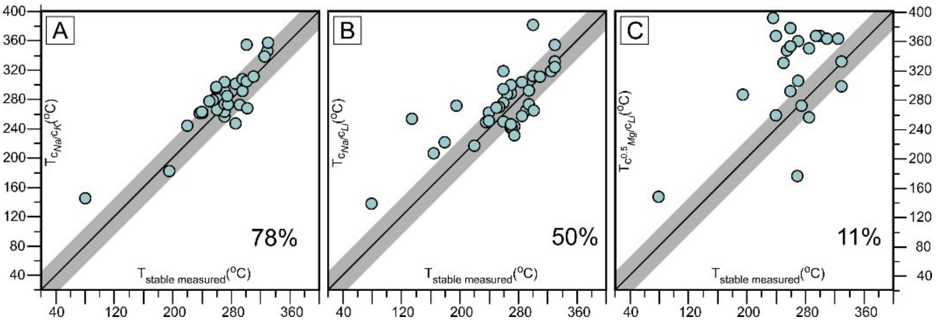


Figure 2: Stable measured well temperatures of geothermal wells in the Taupo Volcanic Zone vs the [A] Na-K (Giggenbach, 1988), [B] Na-Li for dilute aqueous fluids (equation 1 in Table 1, Fouillac and Michard, 1981) and [C] Mg-Li (equation 13 in Table 1; Kharaka and Mariner, 1989) geothermometers. Grey region is ±25°C.

3. LITHIUM CONCENTRATIONS IN ROCKS

Lithium is a trace element in most rocks. Of the fresh volcanic rocks (Table 2A) in the TVZ (Ewart and Taylor, 1968; Goguel, 1983; Reyes and Trompetter, 2012; this study), rhyolite has the highest Li content with a median of 38 mg/kg (range: 9-100 mg/kg) and basalt the lowest (median: 10 mg/kg, range: 7-22 mg/kg). Andesite is midway between the two volcanic rocks with a median of 19 mg/kg (range: 4-41 mg/kg). The general increase in Li with SiO_2 concentrations in volcanic rocks follows a similar trend worldwide (e.g., Ryan and Langmuir, 1987). The median of six surface greywacke samples is 35 mg/kg (range: 20-56 mg/kg).

The median Li concentrations of hydrothermally altered rhyolite are 1.2x higher, at 45 mg/kg (Table 2B), and altered andesite 1.3x higher, at 24 mg/kg Li than their respective unaltered counterparts. Median Li concentrations between hydrothermally altered greywacke from well cores/cuttings and protoliths are similar at 36 mg/kg. Results from Goguel (1983) also showed a 1.5x increase in Li concentrations in altered rhyolite and 3x in altered andesite relative to their protoliths. The general increase in Li concentrations from protolith to hydrothermally altered volcanic rock suggests deposition of mineral receptors that scavenge Li from hydrothermal aqueous fluids and/or preferential retention of Li in the rock. Although these bulk results appear to be in conflict with the experimental results of Ellis and Mahon (1964 and 1967) and field studies by, e.g., Fouillac and Michard (1981) detailed study of mineral distribution and Li-receptor minerals indicate more complex redistribution patterns.

The distribution and abundance of primary and secondary mineral in hydrothermally altered rhyolite, andesite and greywacke and Li concentrations are shown in Figure 3 and compared with alteration rank, related to temperature-dependent assemblages, and alteration intensity defined by the percentage of alteration to primary volcanic components. The general correspondence of alteration rank in volcanic rocks with stable measured well temperatures indicate that hydrothermal alteration is recent, an assumption used in the absence of fluid inclusion measurements. In this paper volcanic rocks with >45% primary minerals with or without glassy matrix still extant has low alteration intensity and those with <45% high intensity. Because of the similarity in detrital and hydrothermal mineral assemblages in greywacke, alteration rank is difficult to assess and thus measured well temperatures are used in the evaluation. The mineralogy and temperature range of the seven alteration ranks in Figure 3 are defined as follows (Reyes and Trompetter, 2012; Reyes, in prep.): (1) smectite $\pm$ kaolinite $\pm$ opal CT/opal A (<120°C), (2) chlorite + smectite + illite-smectite (120°-180°C), (3) chlorite + quartz + illite-smectite (180°-220°C), (4) illite + chlorite + quartz (220°-240°C), (5) illite + chlorite + quartz + incipient to fine-grained epidote (epidote is $\leq$5% of rock) $\pm$ adularia (240°-270°C), (6) illite + chlorite + quartz + adularia + epidote (epidote is 5-15% of the rock; 270°-320°C) and (7) illite + chlorite + quartz + well-crystalline replacement and vein epidote (epidote >15% of rock) $\pm$ actinolite/tremolite $\pm$ biotite $\pm$ magnetite (>320°C). All predicted temperatures are $\pm$20°C.

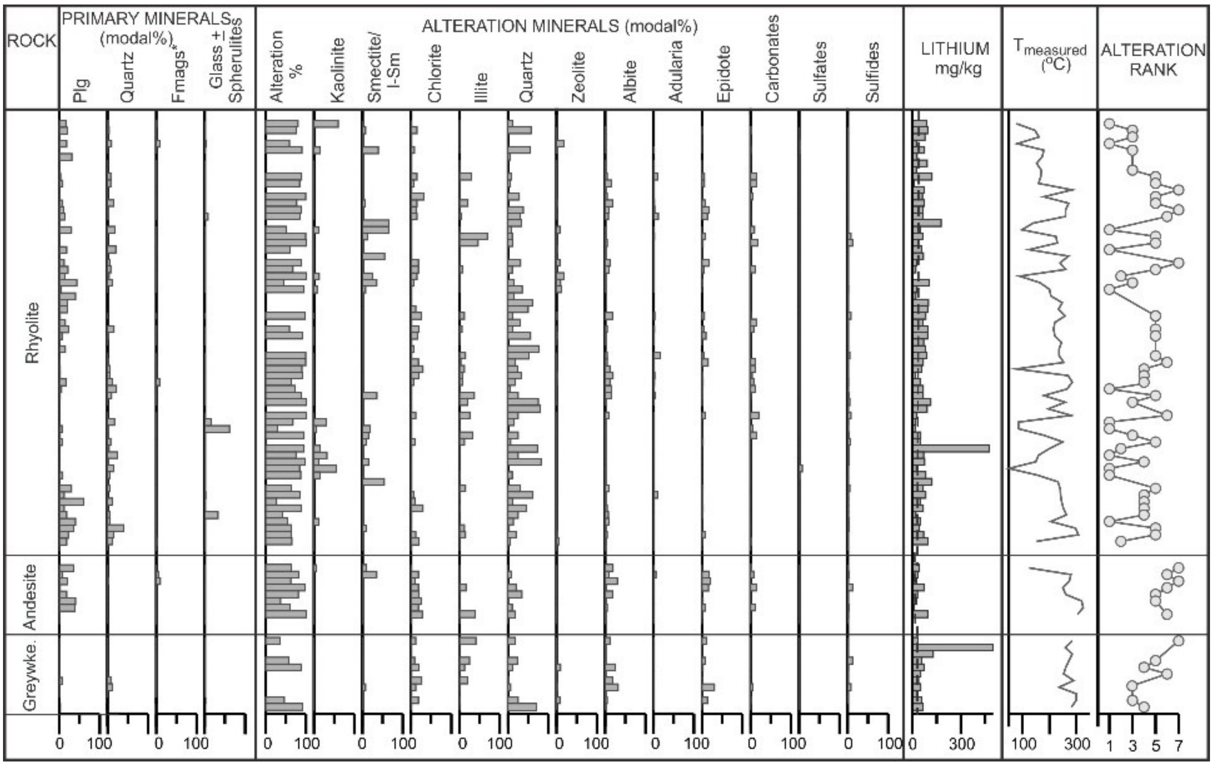


Figure 3: Variations in modal % of primary and hydrothermal minerals in altered rocks of the TVZ and corresponding Li concentrations, measured stable well temperatures and alteration rank. Broken vertical lines are median Li concentrations for the respective protoliths. Alteration ranks based on mineral assemblages (see Reyes and Trompetter, 2012) are: (1) <120°C, (2) 120-180°C, (3) 180-220°C, (4) 220-240°C, (5) 240-270°C, (6) 270-320°C and (7) >320°C.

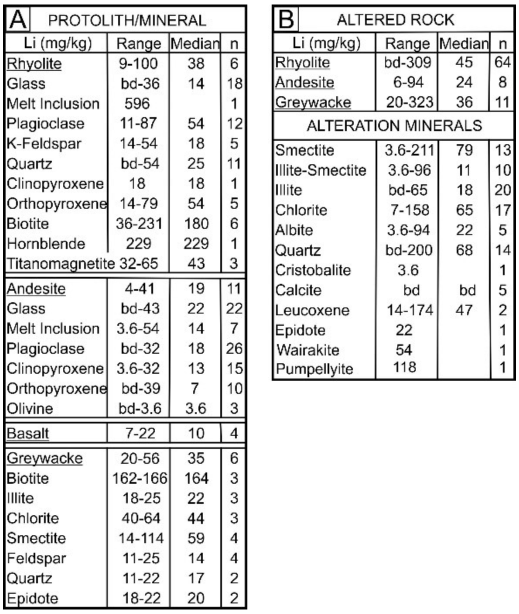
Thus, detailed petrological studies (Figure 3) generally show that Li decreases in the altered rock by 15% to 70% relative to the protolith in hydrothermally altered andesite and rhyolite with <45% alteration minerals and mineral assemblages indicative of temperatures <200° $\pm$ 20°C. Where alteration minerals comprise >55% of the rock and alteration assemblages indicate deposition temperatures of >200° $\pm$ 20°C, Li concentrations in altered rock increase, on average, by 120% regardless of whether the altered rock is andesite, rhyolite or greywacke. Thus, more Li is preferentially partitioned into the aqueous fluids at lower temperatures and lower alteration intensity. The highest gains in Li in the rock occur where secondary quartz or chlorite + quartz comprise >25% by volume of the rock. Apart from quartz, calc-silicate deposition also increases relative Li contents of hydrothermally altered greywacke.

4. LITHIUM IN MINERALS

4.1 Protolithic and Hydrothermal Mineral Li contents

Median Li concentrations in rhyolitic primary components vary from 43 mg/kg in titanomagnetite to 180 mg/kg in biotite with as high as 229 mg/kg in hornblende. Median Li contents in corresponding andesite minerals are lower than for rhyolite. Andesitic plagioclase has a median Li concentration of 18 mg/kg in contrast to 54 mg/kg in rhyolite; 13 mg/kg for andesitic clinopyroxene and 18 mg/kg for its rhyolitic counterpart; 7 mg/kg for andesitic orthopyroxene and 54 mg/kg for rhyolitic orthopyroxene. Lithium in rhyolite is preferentially partitioned into the minerals hence all rhyolitic minerals have higher Li concentrations than the rhyolitic glassy mesostasis (median: 14 Li mg/kg) in contrast to andesite where the glassy matrix is more enriched, at 22 mg/kg Li, relative to its minerals (Table 2A). Hence Li is more incompatible in andesite than rhyolite. Median Li contents in detrital minerals in surface greywacke range from 14 to 164 mg/kg. The phyllosilicates have the highest median Li concentrations varying from 22 mg/kg in illite, 44 mg/kg in chlorite, 59 mg/kg in smectite and 164 mg/kg in biotite.

The highest Li concentrations in hydrothermal minerals (Table 2B) occur in smectite (up to 210 mg/kg), quartz (up to 200 mg/kg), pumpellyite (118 mg/kg), chlorite (up to 158 mg/kg) and leucoxene (174 mg/kg), a Si- and Ti-rich amorphous material replacing Ti-magnetite. Lithium concentrations are as high as 96 mg/kg in interlayered illite-smectite decreasing to 65 mg/kg in illite. Albite concentrations are as high 94 mg/kg, higher than wairakite (54 mg/kg) and epidote (22 mg/kg). However, Li contents in calcite are below experimental detection limits suggesting that Li does not easily substitute for Ca^{+2} in hydrothermal carbonates although very low concentrations in sedimentary calcite are often reported (e.g., Fuger et al, 2019). Hydrothermal chlorite, smectite and illite have higher Li concentrations than detrital phases. Similarly, hydrothermal quartz is more enriched in Li than magmatic and detrital counterparts (Table 2B).



A PROTOLITH/MINERAL			
Li (mg/kg)	Range	Median	n
Rhyolite	9-100	38	6
Glass	bd-36	14	18
Melt Inclusion	596		1
Plagioclase	11-87	54	12
K-Feldspar	14-54	18	5
Quartz	bd-54	25	11
Clinopyroxene	18	18	1
Orthopyroxene	14-79	54	5
Biotite	36-231	180	6
Hornblende	229	229	1
Titanomagnetite	32-65	43	3
Andesite	4-41	19	11
Glass	bd-43	22	22
Melt Inclusion	3.6-54	14	7
Plagioclase	bd-32	18	26
Clinopyroxene	3.6-32	13	15
Orthopyroxene	bd-39	7	10
Olivine	bd-3.6	3.6	3
Basalt	7-22	10	4
Greywacke	20-56	35	6
Biotite	162-166	164	3
Illite	18-25	22	3
Chlorite	40-64	44	3
Smectite	14-114	59	4
Feldspar	11-25	14	4
Quartz	11-22	17	2
Epidote	18-22	20	2

B ALTERED ROCK			
Li (mg/kg)	Range	Median	n
Rhyolite	bd-309	45	64
Andesite	6-94	24	8
Greywacke	20-323	36	11
ALTERATION MINERALS			
Smectite	3.6-211	79	13
Illite-Smectite	3.6-96	11	10
Illite	bd-65	18	20
Chlorite	7-158	65	17
Albite	3.6-94	22	5
Quartz	bd-200	68	14
Cristobalite	3.6		1
Calcite	bd	bd	5
Leucoxene	14-174	47	2
Epidote	22		1
Wairakite	54		1
Pumpellyite	118		1

Table 2: Range and median concentrations of Li (mg/kg) in [A] surface samples of fresh volcanic rocks, glass and primary minerals, and in greywacke and detrital minerals; [B] hydrothermally altered rhyolite, andesite and greywacke and hydrothermal minerals (Reyes and Trompetter, 2012; this study).

In summary, Mg-rich hydrothermal aluminosilicates such as chlorite, smectite and pumpellyite generally have higher Li concentrations than hydrothermal albite, K-bearing phases such as illite and interlayered illite-smectite, and Ca-bearing aluminosilicates. Li commonly substitutes for Mg in a range of minerals from low-temperature smectites (Seyfried et al, 1984) to metamorphic and magmatic phases (Penniston-Dorland et al, 2017) because of their similarity in atomic radii despite the difference in charges (Kharaka and Mariner, 1989). The lower Li concentrations of hydrothermal K-, Ca- and Na-aluminosilicates relative to Mg-rich minerals may in part be due to the large difference between the Li atomic radius and that of K^+, Na and Ca^{+2} (Cambridge Structural Database).

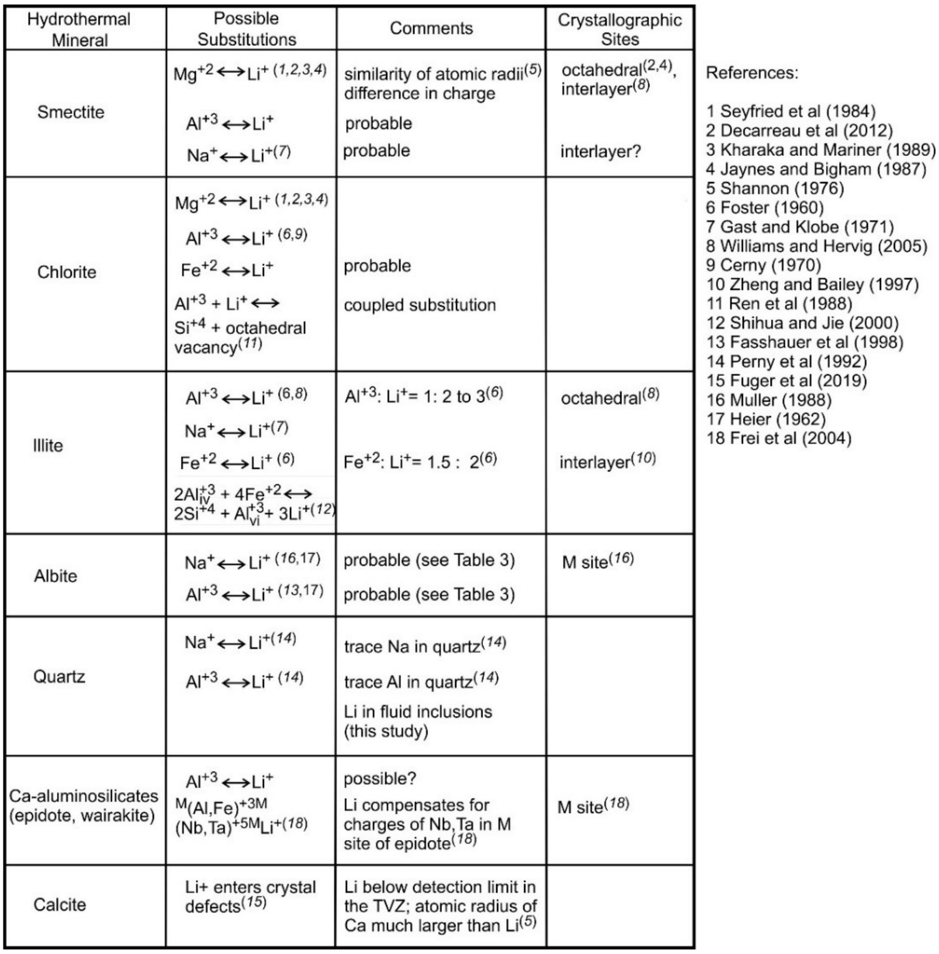
4.2 Hydrothermal Mineral Compositions and Possible Li Substitutions

Major oxides in illite, smectite, chlorite and albite were analysed to determine any correlation with Li concentrations (Table 3). Measured well temperatures at the sample depths are about 250°C. There is a strong negative correlation of Li with Na_2O in all four minerals and with Al_2O_3 in albite. In illite, a K-rich mineral, a minor component such as Fe^{2+} contents, not K^+, decrease as Li increases. Negative correlation of Li with CaO and K_2O occurs mainly in smectite where Li, Ca^+, and K^+ may interact within the interlayer sites (Brindley, 1980). Variations in oxides with Li concentrations in the minerals may not necessarily be caused by substitution with Li per se but a concatenation of elemental shuffling within the various crystal sites, e.g., to balance charges within the phyllosilicate layers as Li enters crystal sites (Table 4).

Mineral	Source	Depth (m)	SiO_2	Al_2O_3	FeO (t)	MgO	CaO	Na_2O	K_2O	Li
			%							mg/kg
Illite	Well KA-26, Kawerau	396	42.89	30.41	1.79	1.29	0.26	0.25	7.91	8
Illite	Well KA-26, Kawerau	396	47.44	34.15	1.73	1.44	0.34	0.18	9.28	28
Smectite	Well WK-19, Wairakei	1100	34.65	21.79	9.83	4.08	0.80	0.12	4.20	39
Smectite	Well WK-19, Wairakei	1100	31.96	22.60	17.83	6.27	0.42	bd	3.12	72
Chlorite	Well WK-19, Wairakei	1100	21.84	17.51	27.65	9.68	0.54	bd	0.09	20
Chlorite	Well WK-19, Wairakei	1100	28.53	17.63	20.00	6.93	0.41	2.03	0.22	36
Chlorite	Well WK-19, Wairakei	1100	25.47	18.72	28.95	11.2	0.15	0.16	0.11	61
Chlorite	Well WK-19, Wairakei	1100	22.81	17.77	28.39	9.96	0.21	0.1	0.07	77
Albite	Well WK-19, Wairakei	1100	66.13	21.42	bd	0.05	1.34	10.59	bd	22
Albite	Well WK-19, Wairakei	1100	66.19	19.59	0.36	0.11	1.68	10.08	0.12	94

Table 3: Partial electron microprobe analysis of major oxides (%) and proton probe measurement of Li (mg/kg) in selected hydrothermal minerals (this study).

As shown in Table 4, Li occupies sites in the octahedral and interlayers of phyllosilicates where it can substitute for Mg, Al and Na in smectite, with the addition of Fe in chlorite. Coupled substitutions for chlorite have been reported (Ren et al, 1988) where Li and Al partly substitute for Si and occupy a vacancy in the octahedral site. In the case of illite, Shihua and Jie (2000) proposed a coupled substitution of Al + Fe with Si + Al + Li. A few studies demonstrate the capacity for Li to substitute for Na or Al in feldspars in metamorphic rocks (Heier, 1962) and for Na during ion exchange experiments, albeit sluggish (Muller, 1988). Although Li has been reported in epidote (Frei et al, 2004) and wairakite (Goguel, 1983, this study) little is known regarding its accommodation in the crystals. It is possible that, similar to occurrences in albite and the phyllosilicates, Li can substitute for Al in these aluminosilicates. Frei et al (2004) suggested that Li may enter the M site of epidote to compensate for charge imbalances caused by the insertion of HFS (High Field Strength) elements such as pentavalent Nb and Ta.



Hydrothermal Mineral	Possible Substitutions	Comments	Crystallographic Sites
Smectite	$Mg^{+2} \leftrightarrow Li^{+}$ (1,2,3,4) $Al^{+3} \leftrightarrow Li^{+}$ $Na^{+} \leftrightarrow Li^{+}$(7)	similarity of atomic radii(5) difference in charge probable probable	octahedral(2,4), interlayer(8) interlayer?
Chlorite	$Mg^{+2} \leftrightarrow Li^{+}$ (1,2,3,4) $Al^{+3} \leftrightarrow Li^{+}$ (6,9) $Fe^{+2} \leftrightarrow Li^{+}$ $Al^{+3} + Li^{+} \leftrightarrow Si^{+4}$ + octahedral vacancy(11)	probable coupled substitution	
Illite	$Al^{+3} \leftrightarrow Li^{+}$ (6,8) $Na^{+} \leftrightarrow Li^{+}$(7) $Fe^{+2} \leftrightarrow Li^{+}$ (6) $2Al_{iv}^{+3} + 4Fe^{+2} \leftrightarrow 2Si^{+4} + Al_{vi}^{+3} + 3Li^{+}$(12)	Al^{+3}: Li^{+}= 1: 2 to 3(6) Fe^{+2}: Li^{+}= 1.5 : 2(6)	octahedral(8) interlayer(10)
Albite	$Na^{+} \leftrightarrow Li^{+}$ (16,17) $Al^{+3} \leftrightarrow Li^{+}$ (13,17)	probable (see Table 3) probable (see Table 3)	M site(16)
Quartz	$Na^{+} \leftrightarrow Li^{+}$(14) $Al^{+3} \leftrightarrow Li^{+}$ (14)	trace Na in quartz(14) trace Al in quartz(14) Li in fluid inclusions (this study)	
Ca-aluminosilicates (epidote, wairakite)	$Al^{+3} \leftrightarrow Li^{+}$ $^{M}(Al,Fe)^{+3M}(Nb,Ta)^{+5M}Li^{+}$(18)	possible? Li compensates for charges of Nb,Ta in M site of epidote(18)	M site(18)
Calcite	Li+ enters crystal defects(15)	Li below detection limit in the TVZ; atomic radius of Ca much larger than Li(5)	

References:

1 Seyfried et al (1984)
2 Decarreau et al (2012)
3 Kharaka and Mariner (1989)
4 Jaynes and Bigham (1987)
5 Shannon (1976)
6 Foster (1960)
7 Gast and Klobe (1971)
8 Williams and Hervig (2005)
9 Cerny (1970)
10 Zheng and Bailey (1997)
11 Ren et al (1988)
12 Shihua and Jie (2000)
13 Fasshauer et al (1998)
14 Perny et al (1992)
15 Fuger et al (2019)
16 Muller (1988)
17 Heier (1962)
18 Frei et al (2004)

Table 4: How Li can be accommodated in the main hydrothermal minerals in the TVZ.

Because of its cramped structure, quartz has limited tolerance for impurities that include Al, H, Li, Na, Fe, K and Ti. These impurities are preferentially introduced along growth zones and maintain electrical neutrality in the crystal (Heaney, 1994, Perny et al, 1992), with Li preferentially substituting for Na and Al (Perny et al, 1992). Quartz can accommodate as much as 15000 mg/kg Al (Heaney, 1994). During our measurements Li counts were higher where the proton beam impinged against fluid inclusions. Although fluid inclusions visible under a petrographic microscope were avoided it is still possible that some of the high Li values for quartz may be affected by optically undetectable fluid inclusions. Similar to quartz, impurities such as Na and Li are accommodated in crystal defects along growth zones of calcite (Fuger et al, 2019). However, unlike quartz, Li contents of calcite in the TVZ hydrothermal systems are below detection limits of the experimental set-up.

5. DISCUSSION

5.1 Factors Affecting Lithium Mobility during Hydrothermal Alteration

5.1.1 Mineralogy of Protoliths

Higher Li concentrations do not necessarily equate to higher production of Li from a volcanic rock. In experiments done by Ellis and Mahon (1964 and 1967), the higher Li concentration extracted from andesite compared to rhyolite, based on this present study, can be attributed to Li being preferentially held in the andesitic glassy matrix as opposed to minerals in rhyolite. Glass is more susceptible to hydrothermal alteration, especially at the initial stages of hydrothermal alteration. Thus, the more incompatible Li is in a volcanic rock, the higher the extractability during hydrothermal fluid influx. The same experiments by Ellis and Mahon (1964 and 1967) showed that low concentrations of Li were extracted by aqueous fluids from greywacke. This can be attributed to the similarity in the detrital minerals in the rock with subsequent hydrothermal phases including smectite, illite, chlorite, feldspars, quartz and epidote, where Li is largely reshuffled during recrystallization of the same minerals rather than undergoing the sequential dissolution to deposition of neoformed mineral process in volcanic rocks. Thus, the propensity for rocks to release Li into aqueous fluids from highest to lowest is: andesite to rhyolite to greywacke.

5.1.2 Alteration Products of Protolithic Minerals

The predilection of Li to be scavenged by aqueous fluids or incorporated into Li-receptor minerals are evaluated for rhyolite and greywacke. An increase in Li concentrations relative to the initial rock component indicates preferential incorporation of the trace element into the hydrothermal mineral, and a relative decrease implies preferential partitioning into aqueous fluids.

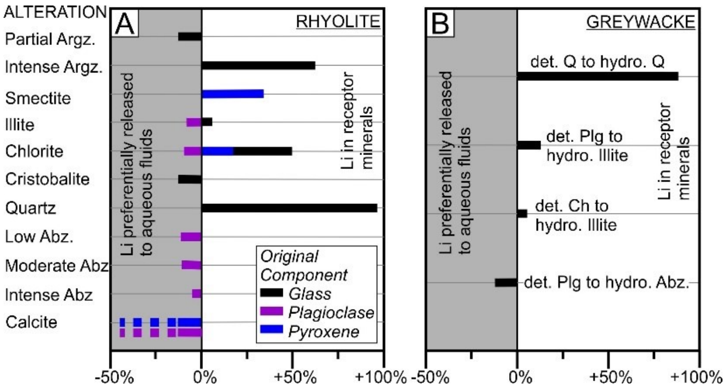


Figure 4: Redistribution of Li between alteration and aqueous fluids during hydrothermal alteration of [A] the glassy mesostasis, primary plagioclase and pyroxene phenocrysts in rhyolite and [B] recrystallization of detrital minerals (det.) in greywacke to hydrothermal (hydro.) phases. % refer to change in Li contents from the original material set at 0%. Abz: albitization, Argz: argillization, Ch: chlorite, Plg: plagioclase, Q: quartz

During the hydrothermal alteration of rhyolite (Figure 4A), Li is preferentially incorporated by illite or chlorite when replacing the glassy mesostasis but is mobilized to the aqueous solutions when replacing plagioclase. This difference may be due to the chemical compositions of the protolithic minerals. Deposition of chlorite and illite would only require a reshuffling of chemical components already present in the glass. In contrast, the replacement of plagioclase by illite or chlorite is preceded by dissolution of plagioclase, releasing Li to the aqueous solutions, followed by deposition of illite and chlorite which then incorporate whatever Li is readily available in the immediate environment of deposition.

Hydrothermal alteration of rhyolitic plagioclase tends to release Li into aqueous fluids but at varying proportions, with deposition of calcite causing the highest relative Li-enrichment in the aqueous fluids, followed by low intensity of albitization, moderate albitization, chlorite, illite and intense albitization. Lithium has the least affinity for calcite with illite and chlorite less so, hence the preferential partitioning into the liquid at various degrees. Although initial albitization of plagioclase preferentially releases Li from the mineral, the affinity of Li for albite increases as albitization of plagioclase intensifies, supporting measurements (Table 3) that Li may substitute for Na (e.g., Gast and Klobe).

In greywacke, albitization of detrital plagioclase preferentially releases Li into the aqueous solutions (Figure 4B), similar to rhyolitic plagioclase. However, the recrystallization of quartz and illite from their clastic progenitors or illite replacement of plagioclase tends to bind Li into the corresponding hydrothermal minerals.

In summary, the fluid mobility of Li is dependent on the compositions of the compositions of the protolithic phase and its alteration product and the intensity of alteration. Quartz is a consistent scavenger for Li unlike chlorite, smectite and illite. In contrast to quartz, calcite consistently shows limited, if any, affinity for Li.

5.1.3 Fluid Throughput and Permeability

The redistribution of Li between rock and water, using a Rayleigh distillation model equation from Bebout et al (1993), was calculated (Reyes and Trompetter, 2012) using rhyolite, andesite and greywacke data from Ellis and Mahon (1964 and 1967), assuming a closed system. The weight fraction of aqueous fluids to rock, from 0 to 1, is used as a proxy for permeability or porosity. Calculations show that Li concentrations in andesite, rhyolite and greywacke increase as the water fraction increases suggesting that high water throughput or high permeability/porosity enhances deposition of Li-receptor minerals such as chlorite and quartz.

5.1.4 Temperature

Some of the most common and abundant alteration minerals in the TVZ are smectite, quartz, chlorite, and illite, replacing primary rock components or occurring in veins and vugs. Illite is initially deposited in active hydrothermal systems at 220° ± 20°C , quartz at 180° ± 20°C and chlorite at 120° ± 20°C (e.g., Browne, 1978; Reyes, 2000). On average, smectite persists only up to 150 ± 20°C at moderate to high permeability. Albitization of plagioclase is widespread but not abundant and occurs throughout the temperature range although deposition of albite in vugs in the TVZ occurs at about 180°C± 20°C (Browne, 1978; Reyes, 2000).

The measured Li contents in chlorite, quartz, illite and albite in the TVZ (Figure 5) are extrapolated to 350°C and are only indicative trends, until more measurements are available. Data points are based on measurements where stable well temperatures (±5°C) are at 120°C, 180°C, 250°C and/or 280°C.

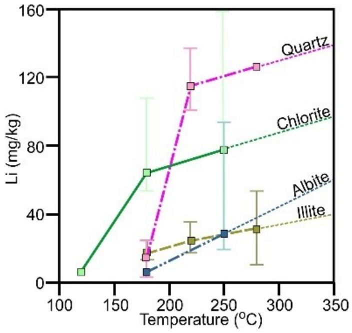


Figure 5: General changes in Li concentrations of hydrothermal quartz, chlorite, albite and illite as stable measured well temperatures rise. Bars indicate range for an average of measurements.

Li-receptivity of chlorite, quartz, illite and albite (albitized plagioclase) increase as temperatures rise, with quartz incorporating more Li into its structure than any of the other three minerals at any temperature. A similar trend was observed in quartz data by Goguel (1983). However, it is likely that the presence of fluid inclusions also contributes to quartz Li concentrations, although microscopically visible fluid inclusions were avoided during our measurements. Illite shows the least change in Li-receptivity with temperature and this is probably because Li preferentially substitutes for trace elements in illite such as Na and Fe (Table 3) rather than the major cation K^+. The general increase in Li concentrations in chlorite and albite is related to the amount of Mg or Na, respectively, available for Li substitution. Based on this premise, then the trends observed for these minerals (Figure 5) are supported by studies showing that Mg in Mg-Fe chlorites increase with temperature (Caritat et al, 1993) and albitization increases as temperatures rise (Perez et al, 2005). From measurements in this study and because of their prevalence and abundance, chlorite and quartz are the likely main Li-receptors in hydrothermal aqueous solutions in the TVZ at a given temperature, with albite and illite less effective Li scavengers.

The shift from cristobalite (opal CT) to quartz replacing the glassy mesostasis (Figure 4) changes Li from being fluid-mobile at <120°C, the temperature at which cristobalite is stable in hydrothermal systems (Section 3), to rock bound at ≥180°C when quartz starts to precipitate. Lithium concentrations decrease notably from smectite to interlayered illite-smectite or illite which are deposited at <150°C, 150°C to 180°C and >220°C, respectively, in active hydrothermal systems (Browne, 1978).

In summary, based on Table 2, and Figures 3, 4 and 5, the efficiency of hydrothermal minerals to incorporate Li into their crystal lattices, from most to least efficient, are: smectite > quartz > chlorite > illite ~ albite ~ Ca-aluminosilicates >> calcite.

5.2 Mineral controls on the Mg-Li and Na-Li geothermometers

There is little correlation between well discharge enthalpies (and corresponding temperatures), with the Kharaka and Mariner (1989) Mg-Li geothermometer temperature curve. But the plot of well discharges show three trends that may be explained by mineralogical transformations that affect relative Mg and Li concentrations in aqueous fluids (Figure 6A). The transformation of smectite or Mg-Fe chlorite to interlayered illite-smectite (a in Figure 6A) at <200°C and chlorite to illite (b in Figure 6A) at >200°C, preferentially liberates Li from minerals, decreasing Mg/Li ratios in the aqueous fluids, as temperatures rise. As smectite is transformed to K-bearing phases such as interlayered illite-smectite at higher temperatures, Li loses its niche in the octahedral or interlayer sites, and preferentially stays in solution. In hydrothermal systems, much more so than in sedimentary basins, quartz is pervasive and abundant at >200°C ± 20°C, especially in permeable zones, and competes with chlorite scavenging Li. As temperatures increase and more quartz and chlorite are deposited, more Li is incorporated into the minerals resulting to an increase in Mg/Li ratios in the aqueous fluids (c in Figure 5) but with the increase in Mg/Li counterbalanced by calcite, which rejects Li (d in Figure 6A)

The Kharaka and Mariner (1989) temperature curve is generally offset to higher Mg/Li ratios than discharge well compositions implying that corrections applicable to the TVZ and its specific hydrothermal mineral assemblages is possible. But at present, the lack of consistency of the Mg-Li geothermometer with stable measured temperatures and other geothermometers suggest that the Kharaka and Mariner Mg-Li geothermometer is probably most suitable for hydrothermal systems where the main alteration process involves the alteration of smectite and chlorite to illitic clays, with limited quartz deposition. In the TVZ these processes occur at a maximum temperature of about 220°C, just when illite is being deposited, preferably in low permeability zones.

Well discharge Na/Li ratios cluster close to and along the Na-Li temperature curve of Fouillac and Michard (1981) for low to moderate Cl aqueous fluids at >220°C within a range of about ± 60°C (Figure 6B), in contrast to the widely spread distribution of Mg/Li ratios along the Mg-Li temperature curve (Figure 6A). Because the glassy mesostasis and plagioclase, which are Na-rich phases in the protoliths, are abundant and widespread then the dissolution of the protolithic phases contributes to regulating the Na/Li ratios in the TVZ hydrothermal aqueous fluids, as much as the deposition of albite, especially at the initial stages of alteration or in low-permeability zones.

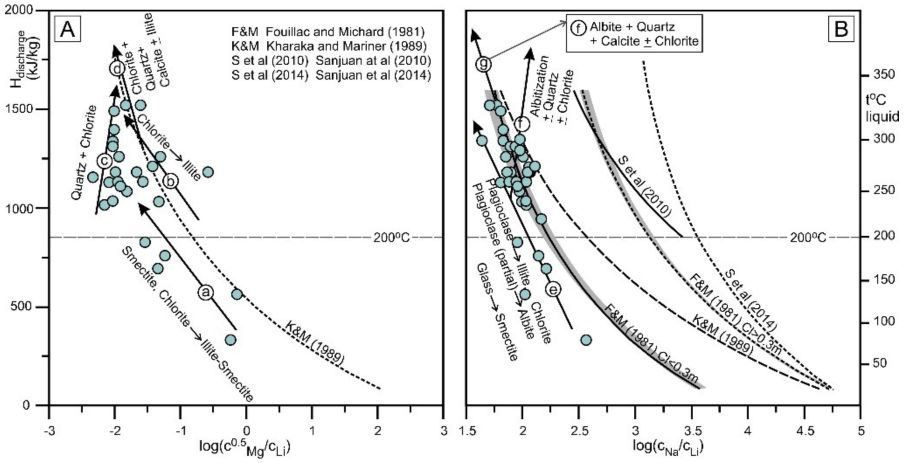


Figure 6: Probable hydrothermal mineral alteration associated with changes in the [A] $\log(c^{0.5}_{Mg}/c_{Li})$ and [B] $\log(c_{Na}/c_{Li})$ with enthalpy (kJ/kg) or temperature of aqueous fluids discharging from geothermal wells in the Taupo Volcanic Zone. Arrows point towards decreasing Mg/Li or Na/Li ratios and higher temperatures.

At the initial stages of hydrothermal alteration, the Na/Li ratio of aqueous fluids decreases when Li is released from the glassy mesostasis as it is partially altered to smectite at <150°C and from plagioclase as it is partly dissolved and then recrystallized to chlorite at >120°C and illite at >220°C (Figure 4A; e in Figure 6B). However, as argillization intensifies and smectite abundance increases, more Li would be incorporated into the smectite crystal lattice resulting to an increase in the Na/Li ratio of the aqueous fluids. Similarly, the Na/Li ratio of aqueous fluids decreases with partial albitization of plagioclase but the intensification of albitization results to the preferential sequestration of Li from the aqueous fluid (Figure 4B) resulting to higher aqueous fluid Na/Li ratios.

The intensification of albitization per se, with or without chlorite and quartz deposition, as temperatures rise would increase the Na/Li ratios (f in Figure 6B) of the aqueous fluids. However, deposition of calcite, a common hydrothermal mineral in the TVZ which hardly accepts Li in its lattice, would offset the effects of Li sequestration by quartz, chlorite and albite (g in Figure 6B) resulting to a decrease in aqueous fluid Na/Li ratios as temperatures increase, similar to the trend shown by the well discharges and the Na-Li temperature curve.

The changes in the Na/Li ratio of aqueous fluids with temperature is a product of a wide number of alteration processes involving dissolution of major aluminosilicate protolithic phases containing Na and Li, followed by deposition of secondary minerals that either incorporate or reject Li in their structures including not only albite but also quartz, chlorite and calcite. The effects of alteration are further modified by alteration intensity and the composition of the original phase being replaced. Although more Li apparently substitutes for Na as albitization intensifies and as the temperature of albitization increases (Figure 5) it is not possible to solely attribute the Na-Li geothermometer to albitization but must include the effects of Li-rejectors such as calcite and Li-acceptors such as quartz, chlorite, illite and Ca-aluminosilicates.

6. CONCLUSIONS

The redistribution of Li between rock and aqueous fluids in a high-temperature geothermal systems in the TVZ, pervaded by silica-saturated neutral pH aqueous fluids, is dependent on the chemical and mineralogical compositions of the protolithic minerals, the stage of alteration (initial dissolution of rock accompanied by low degree of alteration, to pervasive mineral transformations, to recrystallization of hydrothermal minerals), and the composition and abundance of hydrothermal mineral assemblages which are, in part, dependent on temperature and permeability.

In hydrothermal systems, smectite, chlorite, quartz, albite and illite, are some of the most abundant and pervasive alteration minerals containing measurable concentrations of Li (3.6 to 210 mg/kg) and are thus candidates for regulating the Mg/Li and Na/Li ratios of hydrothermal aqueous fluids. The temperature-dependent transitions from smectite to illite, chlorite to illite, opal CT to quartz and the increase in Mg in Mg-Fe chlorites affect the concentration and mobilization of Li indicating that these mineral transformations can control the Mg/Li or Na/Li ratios. However, Li is a trace element and at present its distribution in Li-acceptor minerals is not well known. Although Figure 5 shows that Li concentrations in Li-acceptor minerals increase with temperature, the plot is based on too few samples with several points exhibiting large ranges. Lithium also appears to be an opportunistic cation, preferentially substituting for the most compatible cations in a mineral assemblage within its vicinity. The presence of major Li-receptor minerals, such as smectite, chlorite and quartz, minor Li-receptors such as albite and illite, and the main Li-rejecting mineral calcite regulate the fluid mobility of Li in a hydrothermal system.

At present the Mg/Li geothermometer of Kharaka and Mariner (1989) cannot be used in the TVZ but may be applicable to low-permeability systems where the main alteration process involves the transition of smectite to illitic clays and transformation of chlorite to illite, with limited quartz deposition where temperatures are <200ºC ± 20ºC. However, the TVZ well discharges exhibit a defined offset at >220ºC from the Mg-Li temperature curve indicating that corrections to the published equation of Kharaka and Mariner (1989) can be applied to suit TVZ conditions.

Temperatures derived from the Na-Li geothermometer is consistent with stable measured temperatures (+25ºC) for 50% of the TVZ well discharge samples in this study. Unlike Mg/Li, the Na/Li ratio in aqueous fluids is affected by alteration intensity, composition of protolithic rock phases (glass, plagioclase), the abundance and prevalence of Li-acceptor minerals (smectite, chlorite, quartz, illite, albite) and the counteracting effect of the Li-rejecting mineral calcite. Substitution of Li for Na in albite results to a trend that contrasts with the Na-Li temperature curve of Fouillac and Michard (1981) and well discharges. But the presence of calcite (which mostly rejects Li) and illite (which has less affinity for Li than quartz or chlorite) with albite can result to decreasing Na/Li ratios with increasing temperature. However, albite maybe widespread in the TVZ but are not as abundant as smectite, chlorite, quartz and calcite. Hence the Li concentration in the aqueous fluids is probably regulated by several different alteration processes that have opposing effects on the Na/Li ratios of the aqueous fluids including: dissolution of glass and plagioclase to form phyllosilicates and albite (<Na/Li); albitization, silicification, chloritization and intense argillization (>Na/Li); deposition of calcite and/or illitization (<Na/Li). All these alteration assemblages can be affected by variations in the gas contents and fluid pH, permeability and hydrological processes which can vary from hydrothermal systems to system. Because Li is a trace element in minerals, it is sensitive to slight variations in system conditions and may be one of the reasons why the Mg-Li and Na-Li geothermometers appear to be site-specific.

Essentially, the Mg-Li and Na-Li geothermometers break down upon deposition of abundant quartz but are most useful in hydrothermal systems with low permeability where clays and phyllosilicates prevail and the sequestration of Li by Li-acceptor minerals such as smectite, chlorite, quartz and albite is counterbalanced by deposition of abundant calcite and/or illite.

REFERENCES

Arnorsson, S.: The Use of Mixing Models and Chemical Geothermometers for Estimating Underground Temperatures in Geothermal Systems, *Journal of Volcanology and Geothermal Research,* **23**, (1985), 299-335.

Arnorsson, S., Gunnlaugsson, E. and Svavarsson, H.: The Chemistry of Geothermal Waters in Iceland. II. Mineral Equilibria and Independent Variables Controlling Water Compositions, *Geochimica et Cosmochimica Acta*, **47**, (1983), 547-566.

Bargar, K.E., Beeson, M.H., Fournier, R.O., and Muffler, L.J.P.: Present-day Deposition of Lepidolite from Thermal Waters in Yellowstone National Park, *American Mineralogist*, **58**, (1973), 901-904.

Bebout, G.E., Ryan, J.G., and Leeman, W.P.:B-Be Systematics in Subduction-Related Metamorphic Rocks: Characterization of the Subducted Component, *Geochimica et Cosmochimica Acta*, **51**, (1993), 2227-2237.

Brindley, G.W.: Order-disorder in Clay Mineral Structures, In: Brindley, G.W., Brown, G. (Eds.), Crystal structures of Clay Minerals and their X-ray identification. Mineralogical Society Monograph 5, London, (1980), 125-196.

Browne, P.R.L.: Hydrothermal Alteration in Active Geothermal Fields, *Annual Review Earth and Planetary Sciences*, **6**, (1978), 229-250.

De Caritat, P., Hutcheon, I., and Walshe, J.L.: Chlorite Geothermometry: A Review, *Clays and Clay Minerals*, **41**, (1993), 219-319.

Cerny, P.: Compositional Variations in Cookeite, *The Canadian Mineralogist*, **10(4)**, (1970), 636-647.

Christenson, B.W., Werner, C., Reyes, A.G., Sherburn, S., Scott, B.J., Miller, C.A., Rosenberg, M.D., Hurst, A.W., and Britten, K.: Hazards from Hydrothermally Sealed Volcanic Conduits, *Eos,* **88(5)**, (2007), 53-55.

Davisson, M.L., Presser, T.S., and Criss, R.E.: Geochemistry of Tectonically Expelled Fluids from the Northern Coast ranges, Rumsey Hill, California, USA, *Geochimica et Cosmochimica Acta*, **58**, (1994), 1687-1699.

Decarreau, A., Vigier, N., Palkova, H., Petit, S., Viellard, P, and Fontaine, C.: Partitioning of Lithium between Smectite and Solution: An Experimental Approach, *Geochimica et Cosmochimica Acta*, **85**, (2012), 314-325.

Ellis, A.J., and Mahon, W.A.J.: Natural Hydrothermal Systems and Experimental Hot Water/Rock Interactions, *Geochimica et Cosmochimica Acta*, **28**, (1964), 1323-1357.

Ellis, A.J., and Mahon, W.A.J.: Natural Hydrothermal Systems and Experimental Hot Water/Rock Interactions (Part II), *Geochimica et Cosmochimica Acta*, **31**, (1967), 519-538.

Ewart, A., Taylor, S.R., and Capp, A.C.: Trace and Minor Element Geochemistry of the Rhyolitic Volcanic Rocks, Central North Island, New Zealand, *Contributions to Mineralogy and Petrology*, **18**, (1968), 76-104.

Fasshauer, D.W., Chatterjee, N.D. and Cemic, L.: A Thermodynamic Analysis of the System $LiAlSiO_4$-$NaAlSiO_4$-Al_2O_3-SiO_2-H_2O based on New Heat Capacity, Thermal Expansion, and Compressibility Data for Selected Phases, *Contributions to Mineralogy and Petrology*, **133**, (1998), 186-98.

Foster, M.D.: Interpretation of the Composition of Lithium Micas, *Professional Paper U.S. Geological Survey*, **354-E**, (1960), 115-147.

Fouillac, C., and Michard, G.: Sodium/Lithium Ratio in Water Applied to Geothermometry of Geothermal Reservoirs, *Geothermics*, **10**, (1981), 55-70.

Fournier, R.O.: Application of water geochemistry to Geothermal Exploration and Reservoir Engineering, In: Rybach, L. and Muffler, L.J.P (Eds.), Geothermal Systems: Principles and Case Histories, Wiley, New York, 109-143.

Fournier, R.O., and Potter R.W.: Magnesium Correction to the Na–K–Ca Chemical Geothermometer, *Geochimica Cosmochimica Acta*, **43**, (1979), 1543–1550.

Fournier, R.O., and Truesdell, A.H.: An Empirical Na-K-Ca Chemical Geothermometer for Natural Waters, *Geochimica Cosmochimica Acta*, **37**, (1973), 1255-1275.

Frei, D., Liebscher, A., Franz, G. and Dulski, P.: Trace Element Geochemistry of Epidote Minerals, *Reviews in Mineralogy and Geochemistry*, **56**, (2004), 553-605.

Fuger, A., Konrad, F., Leis, A., Dietzel, M., and Mavromatis, V.: Effect of growth rate and pH on Lithium Incorporation in Calcite, *Geochimica Cosmochimica Acta*, **248**, (2019), 14-24.

Gast, R.G., and Klobe, W.D.: Sodium-Lithium Exchange Equilibria on Vermiculite at 25^{o}C and 50^{o}C, *Clays and Clay Minerals*, **17**, (1971), 311-319.

Giggenbach, W.F.: Geothermal Solute Equilibria. Derivation of Na-K-Mg-Ca Geoindicators, *Geochimica et Cosmochimica Acta,* **52**, (1988), 2749-2765.

Giggenbach, W.F.: Variations in the Chemical and Isotopic Composition of Fluids Discharged over the Taupo Volcanic Zone, *Journal of Volcanology and Geothermal Research,* **68**, (1995), 89-116.

Goguel, R.: The Rare Alkalis in Hydrothermal Alteration at Wairakei and Broadlands, Geothermal Fields, N.Z., *Geochimica et Cosmochimica Acta,* **47**, (1983), 429-437.

Grimaud, D., Huang, S., Michard, G., and Zhang, K.: Chemical Study of Geothermal Waters of Central Tibet (China), *Geothermics*, **14**, (1985), 35-48.

Heaney, P.J.: Structure and Chemistry of the Low-Pressure Silica Polymorphs, In: Heaney, P.J., Prewitt, C.T. and Gibbs, G.V. (Eds), Silica Physical Behavior, Geochemistry and Material Applications, *Reviews in Mineralogy*, **29**, Mineralogical Society of America, (1994), 1-40.

Heier, K.S.: Trace Elements in Feldspars, a Review, *Norsk Geolisk Tidsskrift*, **42**, (1962), 415-455.

Jaynes, W.F. and Bigham, J.M.: Charge Reduction, Octahedral Charge, and Lithium Retention in Heated, Li-Saturated Smectites, *Clays and Clay Minerals*, **35**, (1987), 440-448.

Kharaka, Y.K., and Hanor, J.S.: Deep Fluids in the Continents: I. Sedimentary Basins, In: Turekian, K.K., and Holland, H.D. (Eds): *Treatise on Geochemistry*, (2003), Elsevier Sciences, 499-540.

Kharaka, Y.K., and Mariner, R.H.: Chemical Geothermometers and Their Application to Formation Waters from Sedimentary Basins, In: Naeser, N.D., and McCulloh, T.H. (Eds.): *Thermal History of Sedimentary Basins*, (1989), Springer -Verlag, New York, 99-117.

Land, L.S., and Macpherson, G.L.: Geothermometry from Brine Analyses: Lessons from the Gulf Coast, U.S.A., *Applied Geochemistry*, **7**, (1992), 333-340.

Millot, R., Guerrot, C., Innocent, C., Negrel, Ph., and Sanjuan, B.: Chemical Multi-Isotopic (Li-B-Sr-U-H-O) and Thermal Characterization of Triassic Formation Waters from the Paris basin, *Chemical Geology*, **283**, (2011), 226-241.

Muller, G.: Preparation of Hydrogen and Lithium Feldspars by Ion Exchange, *Nature*, **332**, (1988), 435-436.

Penniston-Dorland, S., Liu, X-M., and Rudnick, R.L.: Lithium Isotope Geochemistry, *Reviews in Mineralogy and Geochemistry*, **82**, (2017), 165-217.

Perez, R.J., and Boles, J.R.: An Empirically Derived Kinetic Model for Albitization of Detrital Plagioclase, *American Journal of Science*, **305**, (2005), 312-343.

Perny, B., Eberhardt, P., Ramseyer, K, Mullis, J. and Pankrath, R.: Microdistribution of Al, Li and Na in α Quartz: Possible Causes and Correlation with Short-Lived Cathodoluminescence, *American Mineralogist*, **77**, (1992), 534-544.

Ren, S., Eggleton, R.A., and Walshe, J.: The Formation of Hydrothermal Cookeeite in the Breccia Pipes of the Ardlethan Tin Field, New South Wales, Australia, *Canadian Mineralogist*, **26**, (1988), 407-412.

Reyes, A.G.: Petrology and Mineral Alteration in Hydrothermal Systems: From Diagenesis to Volcanic Catastrophes, *United Nations University, Iceland,* (2000), 77 p.

Reyes, A.G., and Trompetter, W.J.: Hydrothermal Water-Rock-Interaction and the Redistribution of Li, B and Cl in the Taupo Volcanic Zone, New Zealand, *Chemical Geology*, **314-317**, (2012), 96-112.

Reyes, A.G., Grapes, R., and Clemente, V.C.: Fluid-Rock Interaction at the Magmatic-Hydrothermal Interface of the Mount Cagua Geothermal System, Philippines, In: Simmons, S.F., and Graham, I.J.: Volcanic, Geothermal, and Ore-Forming Fluids : Rulers and Witnesses of Processes within the Earth, *Special Publication Society of Economic Geologists*, **10**, (2003), 197-222.

Ryan J.G., and Langmuir C.H.: The systematics of Lithium Abundances in Young Volcanic Rocks, *Geochimica et Cosmochimica Acta* **51**, (1987), 1727-1741.

Sanjuan, B., Millot, R., Asmundsen, R., Brach, M., and Giroud, N.: Use of Two New Na/Li Geothermometric Relationships for Geothermal Fluids in Volcanic Environments, *Chemical Geology*, **389**, (2014), 60-81.

Sanjuan, B., Millot, R., Brach, M., Asmundsen, R., and Giroud, N.: Use of a New Sodium/Lithium (Na/Li) Geothermometric Relationship for High-Temperature Dilute Geothermal Fluids from Iceland, Enhancement of Steam Phase Relative

Permeability Due to Phase Transformation Effects in Porous Media, *Proceedings*, World Geothermal Congress, Bali, Indonesia (2010),

Seyfried Jr, W.E., Janecky, D.R. and Mottl, M.J.: Alteration of the Oceanic Crust: Implications for Geochemical Cycles of Lithium and Boron, *Geochimica et Cosmochimica Acta,* **48**, (1984), 557-569.

Shannon, R.D.: Revised Effective Ionic Radii and Systematic Studies of Interactive Distances in Halides and Chalcogenides, *Acta Crystallographica*, **A32**, (1976), 751-766.

Shihua S., and Jie, Y.: Actual Fe-Li Mica Series as a Series with $\square_{VI}$ Constant but not Al_{IV} or Al_{VI}, *Mineralogical Magazine*, **64**, (2000), 755-775.

Sturchio, N.C., Muehlenbachs, K., and Seitz, M.G.: Element Redistribution during Hydrothermal Alteration of Rhyolite in an Active Geothermal System: Yellowstone Drill Cores Y-7 and Y-8, *Geochimica et Cosmochimica Acta,* **50**, (1984), 1619-1631.

Trompetter, W.J., Reyes, A.G., Vickridge, I.C., Markwitz, A.: Lithium and Boron Distributions in Geological Samples, *Nuclear Instruments and Methods in Physics Research B*, **158**, (1999), 568-574.

Verma, S.P., and Santoyo, E.: New Improved Equations for Na/K, Na/Li and SiO_2 Geothermometers by Outlier Detection and Rejection, *Journal of Volcanology and Geothermal Research*, **79**, (1997), 9-23.

Verma, S.P., Pandarinath, K., and Santoyo, E.: SolGeo: A New Computer Program for Solute Geothermometers and its Application to Mexican Geothermal Fields, *Geothermics*, **37**, (2008), 597-621.

Williams, L.B., and Hervig, R.L.: Lithium and Boron Isotopes in Illite-Smectite: The Importance of Crystal Size, *Geochimica et Cosmochimica Acta,* **69**, (2005), 5705-5716.

Zheng, H., and Bailey, S.W.: Refinement of the Cookeite “r” Structure, *American Mineralogist*, **82**, (1997), 1007-1013.