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Use of Heavy Metals and Trace Elements in Groundwater as a Tool for Mineral Exploration: A Case Study from Udawalawe, Sri Lanka

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Abstract: The geochemistry of regional groundwater has been utilized worldwide to discover subsurface mineral deposits, though it has not yet been practiced in Sri Lanka. The present study focuses on utilizing geochemistry of groundwater in the Udawalawe area of south-central Sri Lanka where two serpentinite bodies exist within the high-grade crystalline basement. This area is in the proximity of the litho-tectonic boundary between two metamorphic complexes. Thus, the scope of the study is to uncover geological and geochemical anomalies of potential mineralization. Mode of occurrences and petrography of exposed serpentinite bodies and physico-chemical properties of groundwater were investigated to establish a relationship between regional groundwater geochemistry and geological anomalies. The pH and electrical conductivity of groundwater were measured in-situ and concentrations of Al, Ba, Be, Cs, Cu, Fe, Li, Mn, Pb, Rb, Sr and Zn were analysed using atomic absorption and emission spectroscopy. The present study reveals that concentrations of these elements are significantly higher close to serpentinite bodies with Cu and Zn having the highest concentrations. Elevated concentrations of Al, Ba, Be, Fe, Li, Pb, Rb and Sr were also noted. Relatively higher concentrations of Be, Cu, Li, Mn, Pb, Rb and Zn in groundwater in the area between the two exposed serpentinite bodies indicate the possible occurrence of a subsurface mineral deposit in the area. These results indicate the importance and feasibility of the application of regional groundwater geochemistry as a tool for uncovering subsurface mineral deposits. Detailed observations of groundwater flow patterns, facies changes, and associated element mobility could effectively help in accurate demarcation of the lateral extents of mineral deposits.

Key words: Mineral exploration, groundwater geochemistry, heavy metals, trace elements, serpentinite.

Introduction

Groundwater that is in contact with bedrock for a prolonged period is enriched with many ions including trace elements and heavy metals due to the water-rock interaction (Nordstrom et al., 1989; Saxena and Ahmed, 2001; de Caritat et al., 2005; Dehnavi et al., 2011). Though their behaviour in groundwater is not yet fully understood, the non-conservative characteristics of trace elements have drawn the attention of many researchers (Banks et al., 1999; Janssen and Verweij, 2003; Johannesson et al., 2005). Trace elements, heavy metals and rare earth elements (REE) present in groundwater are used to study the water-rock interaction and in regional geochemical and geological mapping (Banks et al., 1999; de Caritat et al., 2005). Their behaviour and distribution in groundwater is useful in aquifer demarcation, distinguishing the origin of water

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and groundwater flow path tracing (Ronnback et al., 2003; Tweed et al., 2006; Féraud et al., 2009; Biddau et al., 2009). Further, heavy metals, trace elements and REEs are indicators of the geologic signature of aquifers (Reimann and Birke 2010; Pelpitiya et al., 2012).

Geophysical methods coupled with remote sensing are widely used tools for mineral exploration. However, a significant uncertainty is associated with geophysical means of mineral deposits, which are intermingled with the country rock. Costly infrastructure as well as the requirement of expert knowledge are negative characteristics of these methods (Lowrie 2007). However, metallic elements and trace elements in groundwater are possible indicators, which can be used to identify subsurface mineral deposits at a lower cost and with less expertise than whole rock geochemical analysis (Banks et al., 1999; Caron et al., 2008; Navarro et al., 2011). Therefore, the use of trace elements of regional groundwater as a tool for mineral exploration has increasingly become the alternative method (Banks et al., 1999; Johannesson et al., 2005; Tweed et al., 2006; Caron et al., 2008; Navarro et al., 2011). Another advantage of this method is that it has the potential of assessing mineral occurrences in a short time frame.

Though groundwater geochemistry has not been used as a tool for mineral exploration in Sri Lanka, it is already globally accepted and practiced elsewhere such as Oslo, Central Mexico and Dandenong Ranges – Australia (Banks et al., 1999; Johannesson et al., 2005; Tweed et al., 2005; Caron et al., 2008; Navarro et al., 2011). Therefore, the present study focuses on exploring the feasibility of such studies in Sri Lanka. The Udawalawe region in Sri Lanka was selected, since the area is known for occurrences of serpentinite exposures (Dissanayake, 1982; Tennakone et al., 2009). Greenish coloured serpentinite consists of fibrous and platy serpentine found at Udawalawe. Tremolite, diopside, enstatite and quartz are the common minerals found (Dissanayake and Riel, 1978). Higher content of hypersthene (> 46.0%), olivine (>4.5%) and magnetite (>3.0%) occupy the mineral content (Dissanayake, 1982). Mafic, siliceous and calcic dykes are present in some exposures. Al, Mn, Pb and Zn are the most abundant elements in Udawalawe serpentinite (Dissanayake, 1982).

This mineral occurrence has the same features of serpentinites found worldwide (Hewawasam et al., 2014). Heavy metals and trace elements such as Al, Ba, Be, Cs, Cu, Fe, Li, Mn, Pb, Rb, Sr and Zn were selected for analysis because elements such as Ba, Cs, Pb, Rb and Sr are abundant in the upper crust (Taylor and McLennan, 1985; Mclennan, 2001; Willbold and Stracke, 2006). Ba, Pb, Rb and Sr are also abundant in tectonic settings such as plate margins and the study area is located closer to such a tectonic setting (Munasinghe and Dissanayake, 1979; Bhatia and Crook, 1986). Serpentinite rocks consist of the aforementioned elements. Furthermore, Li, Rb and Sr among the selected elements are highly mobile, thus they could easily be detected in the groundwater (Taylor and McLennan, 1985; Rudnick and Gao, 2003). The present study suggests a cost-worthy geochemical technique for mineral exploration. Therefore, this research aims to utilize heavy metals and trace elements in regional groundwater in fractured crystalline aquifers as a tool for locating unexposed mineral deposits and for identifying geological anomalies.

Study Area

Physiography and Geology

Udawalawe serpentinite bodies are exposed at the surface at Ginigalpelessa (GGP) and Indikolapelessa (IKP), two regions that are about 4 km apart (Figure 1). Only species of trees that are tolerant of the unusual soil chemistry are present (Rajakaruna and Bruce, 2002). On the contrary, the rest of the study area has usual vegetation patterns including the area between two outcrops. The area is a flat terrain with rolling topography to the south. Weathered serpentinite bodies and lateritic fragments cover most of the surface of the area. The serpentinite rocks have been derived from igneous process, while the hosts are high grade metamorphic rocks of the Highland Complex (Dissanayake and Riel, 1978; Dissanayake, 1982; Cooray, 1984). Outcrops of deposits are ultramafic hyperbyssal rocks mainly composed of olivine, pyroxene, magnetite and chromite (Dissanayake and Riel, 1978; Dissanayake, 1982). Cobalt and manganese are rich in the lateritic overburden, while nickel and lead are high in the parent rocks (Dissanayake, 1982). The Ginigalpelessa exposure extends approximately 4 km^2 and is intermingled with charnockitic gneiss on the north and hornblende biotite gneiss on the south. Indikolapelessa exposures are associated with hornblende biotite gneiss and biotite hornblende gneiss. Other rock types found in the study area include granitic gneiss, charnockitic gneiss and marble. Both deposits are located in the immediate proximity of the lithotectonic boundary between Highland and Vijayan Complexes (Kroner et al., 1991; Cooray, 1994). Many mineral deposits, geologic anomalies and thermal

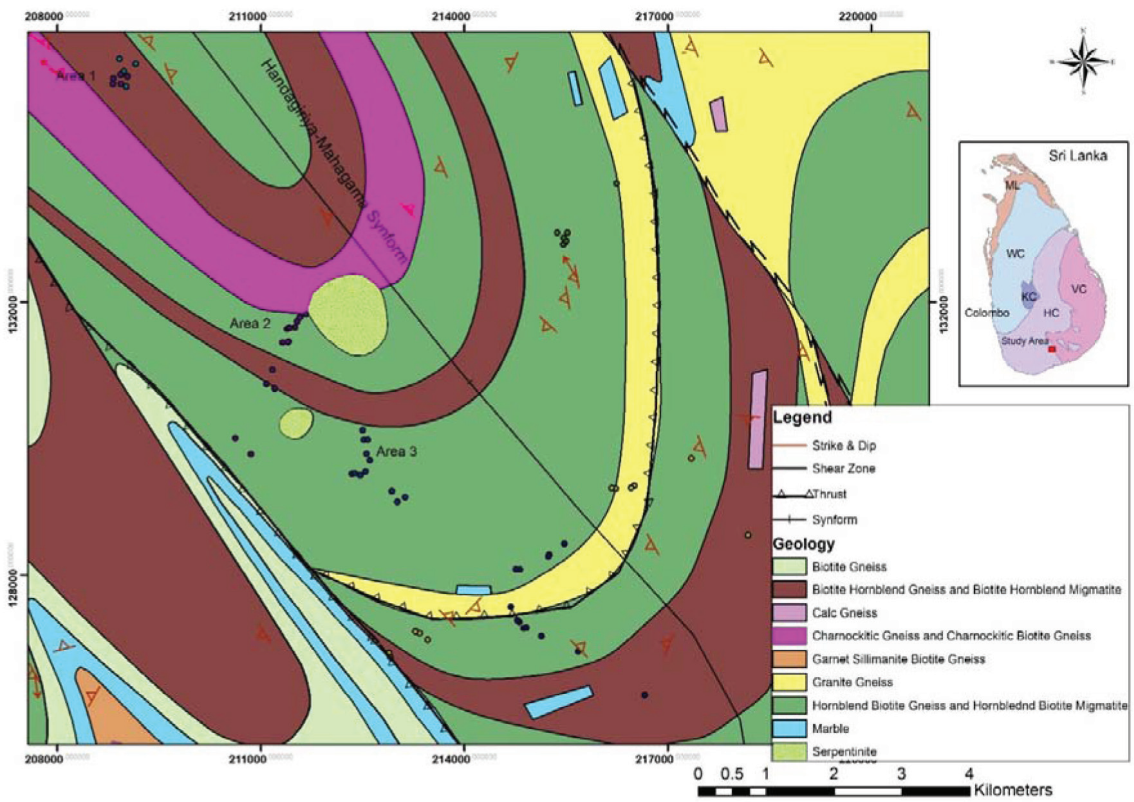

Figure 1: Inset of simplified geological map of Sri Lanka (after Cooray, 1994), showing location of the investigated area and geological map of the area with sample locations (WC: Wanni Complex; KC: Kadugannawa Complex; HC: Highland Complex; VC: Vijayan Complex).

springs are found along the boundary (Munasinghe and Dissanayake, 1979; Cooray and Berger, 1980; Munasinghe and Dissanayake, 1980; Cooray, 1984; Dissanayake and Jayasena, 1988). Structurally, these bodies lie on the Handagiriya-Mahagama synform, which is plunging NW-SE direction. The synform is bounded by two shear zones which are trending in same direction east and west.

Geochemistry and Hydrogeology

Groundwater in Sri Lanka is divided into four types based on its geochemistry (Dissanayake and Weerasooriya, 1986). Those are calcium, magnesium, sodium/potassium and non-dominant cations types which are associated with non-dominant anions, chloride, sulphate, and bicarbonate anion types (Dissanayake and Weerasooriya, 1986). The groundwater in the study area is of the Ca and Mg type with chloride as the anion (Dissanayake and Weerasooriya, 1986). The total hardness of groundwater in dug wells and tube wells varies across a wide range (7 to 3579 mgL^{-1} as $CaCO_3$) with an average of 395 mgL^{-1} during the wet season and 40–90 mgL^{-1} during the dry season (Hiscock, 2005). This variation can be attributed to dilution due to recharge from irrigation canals (Hiscock, 2005; Prado et al., 2010).

A narrow alluvial aquifer is present in the western margin of the area along the Walawe River. The rest of the area can be considered to be shallow regolith aquifers in fractured hard rocks (Panabokke and Perera, 2005; Villholth and Rajasooriyar, 2009). Thus, oxic groundwater condition prevails (Panabokke and Perera, 2005; Jayawardana et al., 2010). The major surface water sources of the area are lakes which are interconnected by irrigation canals. Fractured crystalline aquifers host regional and intermediate groundwater regimes (Panabokke and Perera, 2005; Villholth and Rajasooriyar, 2009). While the main recharge source is rainfall, fractures that run from the highlands also recharge these aquifers (Dissanayake and Weerasooriya, 1986; Hiscock, 2005; Prado et al., 2010). On an average, the groundwater level is approximately 25 feet below the ground surface during the dry season. However, the canals and lakes also recharge the groundwater creating a complex hydrogeological setting (Prado et al., 2010). Shallow groundwater levels have been observed in the northwest corner of the area (Prado et al., 2010). Based on the flow data and geologic setting, the flow direction of groundwater can be deduced as being in a north-east direction (Prado et al., 2010).

Material and Methods

Petrographical, mineralogical and hydrogeological data from previous works were gathered (Dissanayake, 1982; Prado et al., 2010). Tube wells and dug wells were selected for sampling as their depth can reach intermediate or regional groundwater regimes (Figure 1). Water was extracted by manual pumping and samples were collected in PETF bottles with two replicates. All samples were immediately acidified following collection. The pH and electrical conductivity of water were measured in situ with a Thermo® Orion 3 Star pH/EC meter. Al, Ba, Be, Cs, Cu, Fe, Li, Mn, Pb, Rb, Sr and Zn were analysed via atomic absorption and emission spectroscopy (Varian SpectrAA 240 and GTA 120). In order to minimize instrument error, the replicates for each sample were analysed. The average values of these measurements were calculated for each sample. The addition of 1 mL of 1M KCl solution was required to enhance the atomization of Al, Ba and Sr. The instrument was calibrated with authenticated standards (Fluka™ 1000 ppm). Analyses with AAS followed APHA Standard Methods (APHA, 2005). Elements in canonical ratios such as Ba/Rb, Sr/Rb and Sr/Ba were analysed to facilitate better interpretation (Taylor and McLennan, 1985; Bhatia and Crook, 1986; Rollings, 1993; Ranasinghe et al., 2005).

Principal component analyses (PCA) were performed to establish any interrelationship among concentrations of elements found in the groundwater. PCA can be used for compressing higher dimensional data sets to lower dimensional ones for data analysis, visualization, feature extraction, or data compression (Lukibisi and Lanyasunya, 2010). It is applied in assessing multi-element geochemical data of various types, because it reveals the correlation structure of the elements, governed by the rock-water interaction (Bhatia and Crook, 1986; Deverel and Millard, 1988; Chandrajith et al., 2001; Thamó-Bozsó and Kovács, 2007; Jayawardana et al., 2012). Minitab 14 (Minitab Inc.) software was utilized for the analysis. Pearson data correlation was calculated in order to generate the correlation matrix. Non-correlated element data were removed from the correlation matrix. Three component PC analysis was performed in order to keep the eigenvalue below 1. PC 1 was considered for the analysis since it represented 42% of the total population.

Results and Discussion

The pH of the groundwater is within the range of 6.5 to 8.2 with the average of 7.4. The electrical conductivity of the groundwater varies from 187.5 μScm^{-1} to 728.0 μScm^{-1} with the average of 532.9 μScm^{-1}. Data analysis revealed that elements such as Al, Be, Fe, Mn, Pb, Rb and Sr are in higher concentrations at some localities. Further, three regions of anomalies were identified: 2 km north east of the GGP deposit (*area 1*), in the immediate vicinity of GGP and IKP deposits (*area 2*) and 1 km south of GGP (*area 3*) (Figure 1). The electrical conductivity of groundwater in these three areas varies between 500 μScm^{-1} and 550 μScm^{-1}. Concentration range, mean and standard deviation of water samples at each anomaly are shown in Table 1. Though 67 wells were sampled, only about 30 wells represent all three areas. Geochemical analysis of the same serpentinite indicates that except for Be and Li, other elements are also present in elevated concentrations (Dissanayake, 1982).

Previous studies have not paid attention to analysing Be and Li in serpentinite rock, soil or groundwater (Dissanayake, 1982; Tennakone et al., 2009). However, the results clearly showed that except for Be, the elemental concentrations in groundwater of *Area 2* are at elevated levels. Some of them exceed the SLS 843:2003 and CODEX drinking water quality standards. It is an indication of good hydraulic connectivity between the deposit and surroundings of *Area 2*. Maximum Be concentration is highest in *Area 1*. That is four fold higher concentrations than that of *Area 2*. This implies that there may be a different source of Be in *Area 2*. Maximum Ba concentrations are similar in areas 1 and 2, but were less than that of *Area 3*. Comparatively, except for Ba, other elemental concentrations in groundwater were lower in *Area 3*. Even though *Area 3* is closer to the deposit, groundwater geochemistry shows that it is influenced less by the intrusive rocks probably due to the groundwater flow direction. Thus, the higher Ba concentration may be due to the weathering of an individual mineral occurrence. Therefore, this data set itself could be utilized to predict geologic anomalies.

PCA and Inter-Element Correlation

Three-component PCA was selected as they explain more than 80% of variation in the data. Factor 1 of PCA of *Area 2* shows a clear correlation among Al, Ba, Be,

Table 1: Summary of elemental concentration (ppm) in groundwater at areas 1, 2 and 3 (*n* is number of samples)

	Area 1 (n = 10)				*Area 2 (n = 9)*				*Area 3 (n = 9)*			
	Min	*Max*	*Mean*	*Std. Dev.*	*Min*	*Max*	*Mean*	*Std. Dev.*	*Min*	*Max*	*Mean*	*Std. Dev.*
Fe	0.000	0.149	0.042	0.048	0.037	0.647	0.196	0.194	0.027	0.139	0.050	0.033
Cu	0.016	0.020	0.018	0.001	0.027	0.115	0.045	0.026	0.028	0.031	0.029	0.001
Zn	0.004	0.097	0.025	0.030	0.004	0.281	0.052	0.083	0.003	0.013	0.006	0.003
Li	0.020	0.030	0.026	0.003	0.041	0.054	0.046	0.005	0.044	0.055	0.047	0.003
Mn	0.000	0.170	0.038	0.052	0.010	0.404	0.073	0.118	0.010	0.103	0.027	0.029
Be	0.393	1.210	0.662	0.249	0.152	0.340	0.216	0.068	0.225	0.359	0.295	0.041
Pb	0.00	0.05	0.00	0.01	0.13	0.24	0.16	0.04	0.12	0.37	0.18	0.07
Al	3.91	5.90	5.10	0.64	4.82	8.18	6.23	1.14	3.94	6.94	5.46	0.88
Rb	0.05	0.08	0.07	0.01	0.16	0.17	0.16	0.00	0.16	0.16	0.16	0.00
Sr	0.087	0.324	0.148	0.068	0.200	0.632	0.338	0.124	0.167	0.566	0.320	0.121
Ba	0.0051	0.0082	0.0065	0.0009	0.0073	0.0085	0.0081	0.0004	0.0081	0.0094	0.0086	0.0005

Li, Mn and Rb and a negative correlation with Cu, Fe, Pb, Sr and Zn (Figure 2). Thus, it can be assumed that some of lithophile elements including Ba, Rb, Al, Li, Be and Mn are leaching from the serpentinite bodies (Horstman, 1957; Marschall et al., 2007; Vils et al., 2011). Negatively correlated ferromagnesian (Fe and Mg) and chalcophile (Cu, Pb and Zn) elements may be mainly due to the weathering of the bed rocks such as hornblende biotite gneiss and hornblende biotite migmatitic gneiss (Figure 1).

Zn, Cu and Pb are negatively loaded in three factors. These chalcophiles have similar geochemical behaviour in groundwater. Fe shows different loading at each factor. Factors 2 and 3 for Ba, Be, Li and Mn are comparatively low thus, factor 1 is sufficient to describe the geochemical behaviour of those elements. Al shows different loading at factors 1 and 2, which may be due to its lower mobility in the environment (Taylor and McLennan, 1985; Roser, 2000; Rudnick and Gao, 2003). The factor 3 lower value for Rb is negligible. However, different loading at factors 1 and 2 may be due to its high mobility. Geochemical behaviour of Sr in groundwater can also be explained similar to that of Rb, because it has high mobility (Taylor and McLennan, 1985; Rollings, 1993; Rudnick and Gao, 2003).

On the contrary, PC1 for areas 1 and 3 are different from each other and from *Area 2* (Figure 2). It implies that the areas 1 and 3 may have little or no influence by the serpentinite rocks or there may be geological anomalies. In *Area 1*, ferromagnesian and chalcophile elements are not correlated well with each other. It may be due to the low solubility and low residence time of Fe (Taylor and McLennan, 1985; Roser, 2000; Rudnick and Gao, 2003). Further, Sr shows a negative correlation with most elements. It may be due to the fact that Sr is highly soluble and has a high residence time in water (Taylor and McLennan, 1985; Rudnick and Gao, 2003). Apatite, carbonate minerals, sphalerite and garnet in the bed rock are most likely the dominant mineral hosts for those elements (Jayawardana et al., 2012).

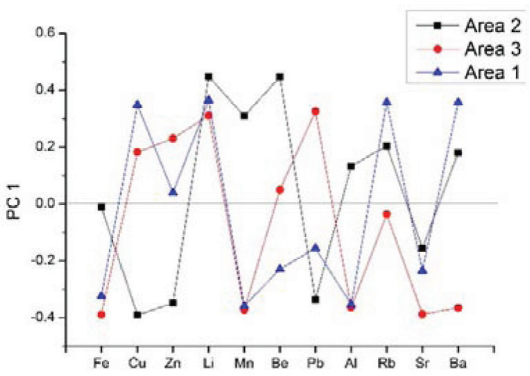

Figure 2: PC1 of ***Area 1, 2 and 3*****.**

For both areas 1 and 3, Li is positively loading with Cu and Zn. Weathering of chalcophile elements and Na or K replaced by Li in feldspars or biotites may be giving rise to this trend (Pelig-Ba, 1998). Since lithium is highly mobile, it may escape to the groundwater through weathering of feldspars and biotites (Pelig-Ba, 1998; Yoon, 2010; Figueroa et al., 2012). The areas 1 and 3 are underlain by biotite hornblende gneiss and hornblende biotite gneiss, respectively (Figure 1). Therefore, biotite rich rocks may also be a source for them. Mn and Al exhibit a negative relationship with each other at both sites. However, being a transition element, a comparison between these two elements are not possible (Rollings, 1993). Al in water may be due to leaching from clay minerals. Be and Pb are negatively correlated with each other in *Area 1* and vice versa in *Area 3*. Being associated with REE, Be and Pb are less mobile (Taylor and McLennan, 1985; Borovec, 1993; Rudnick and Gao, 2003). Thus, they may show similar correlations. Be is found in muscovite and plagioclase in granites. Thus, Be is enriched in most pegmatites (Navratil et al., 2002; Armiento et al., 2012). Beryl or chrysoberyl, which are found in pegmatites, may also be probable sources for Be. Further, positive correlation of Be and Li in samples from *Area 3* indicate that they may have been derived from pegmatites (Pelig-Ba, 1998). Lithophiles, including Ba and Rb, are positively correlated in *Area 1* and vice versa in *Area 3*. They might have been originated from different sources. However, it is noteworthy that both areas 2 and 3 are underlain by the same rock types, hornblende biotite gneiss and hornblende biotite migmatite. Therefore, detailed geological mapping is necessary to identify the particular sources for *Area 3*.

Elemental Ratio Correlation

The Pearson product-moment coefficient of correlation can be utilized to establish further correlation between element ratios (Rollings, 1993). P values indicate that Sr:Rb and Sr:Ba element pairs have higher correlations in all three areas. It is over 0.43, 0.96 and 0.73 in areas 1, 2 and 3, respectively. In areas 2 and 3 those element pair ratios show stronger linear relationships than in *Area 1* (Figures 3 and 4). The strong linear relationship between elemental pairs may be due to the higher saturation of Sr, Rb and Ba in groundwater in *Area 2*. It implies that this particular area is directly connected with serpentinite bodies. In addition to that, Ba:Rb element pairs show a linear relationship with elemental ratio in *Area* 2. However, it is not the same relationship as Sr:Rb and Sr:Ba. The high concentration of Sr may be the dominant factor in these correlations. Concentrations of these three elements are relatively higher in *Area* 3 than in *Area 1*. Therefore, there is a better correlation of element pair ratios in *Area 3* (Figures 5, 6 and 7). Elemental ratios show that Sr concentration may be the decisive factor of controlling the Sr:Rb:Ba correlations. Furthermore, these correlations are useful in distinguishing groundwater geochemistry in areas 1 and 3. Therefore, it could be that those two areas may be underlain by some geologic anomalies. The linear behaviour of the above element pair ratios indicates possible gem deposits (Ranasinghe et al., 2005).

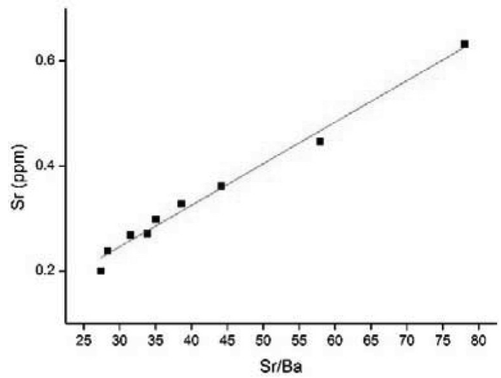

Figure 3: Canonical ratio of Sr:Ba at *Area* 2.

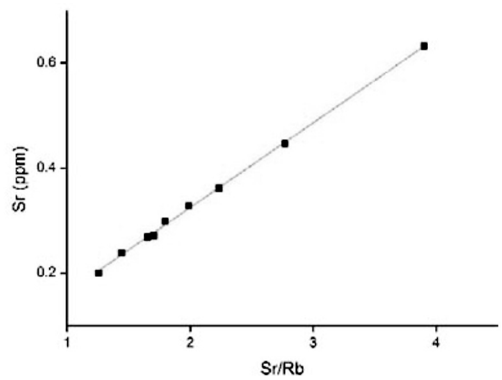

Figure 4: Canonical ratio of Sr/Rb at *Area* 2.

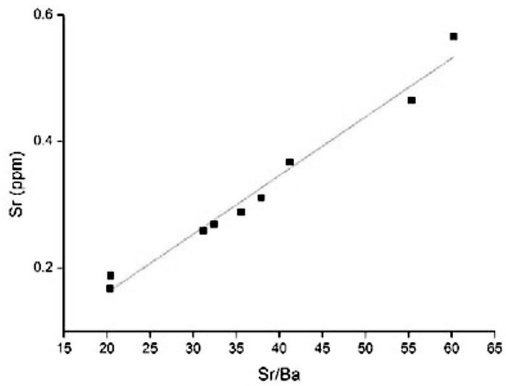

Figure 5: Canonical ratio of Sr:Ba at *Area* 3.

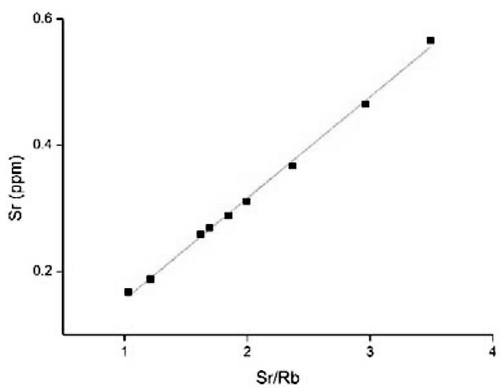

Figure 6: Canonical ratio of Sr:Rb at *Area* 3.

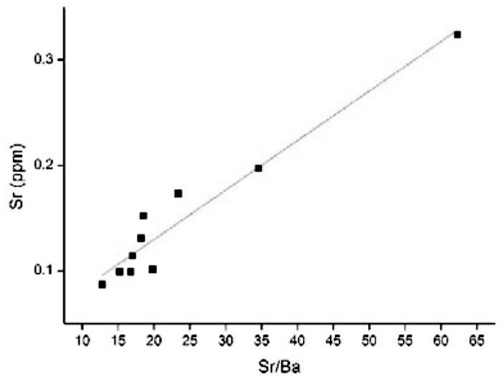

Figure 7: Canonical ratio of Sr:Ba at *Area* 1.

Conclusions

Principal component analysis indicates that the elements in the groundwater in *Area 2* may have been leached from the serpentinite rocks. However, the sources for such anomalies in areas 1 and 3 are not clear. Since there is no hydrogeologic connection between these areas, the groundwater geochemistry in each area represents the in-situ geologic conditions. The higher correlations of canonical ratios in *Area 2* could be a result of higher elemental migration from serpentinite rocks whereas the higher correlation of canonical ratios in *Area 3* indicates the possibility of gem deposits. The results of the study emphasise the fact that heavy metals and trace elements in the groundwater can be used effectively as a tool for locating unearthed mineral deposits or geologic anomalies.

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