Article

Using rare earth elements (REE) to study the origin of ore-fluids associated with granite intrusions

Xue-Ming Yang

Manitoba Geological Survey, 360-1395 Ellice Avenue, Winnipeg, MB R3G 3P2, Canada; eric.yang@gov.mb.ca

Received: May 2, 2019; Accepted: date; Published: date

Abstract: A practical method is presented to estimate rare earth elements (REE) concentrations in magmatic vapour phase (MVP) in equilibrium with water-saturated granitic melts based on empirical fluid-melt partition coefficients of REE (k_P^{REE}). The values of k_P^{REE} can be calculated from a set of new polynomial equations linking to the chlorine molality (m_{Cl}^v) of the MVP associated with granitic melts, which are established via a statistical analysis on the existing experimental dataset. These equations may be applied to the entire pressure range (0.1 to 10.0 kb) within the continental crust, suggesting that light REEs behave differently in magmatic fluids, i.e. either being fluid compatible with higher m_{Cl}^v or fluid incompatible with lower m_{Cl}^v values. In contrast, heavy REEs are exclusively fluid incompatible and partition favourably into granitic melts. Consequently, magmatic fluids tend to be rich in LREE relative to HREE, leading to REE fractionation during the evolution of magmatic hydrothermal systems. Maximum k_P^{REE} value for each element is predicted and presented in a REE distribution diagram constrained by the threshold of m_{Cl}^v. REE contents of the granitic melt is approximated by whole-rock analysis, so that REE concentrations in the associated MVP would be estimated from the value of k_P^{REE} given chemical equilibrium retains. Two examples are provided respectively, to show the use of this method as a REE tracer to fingerprint the source of ore-fluids responsible for the Lake George intrusion-related Au-Sb deposit in New Brunswick (Canada), and for the Bakircay Cu-Au (-Mo) porphyry systems in northern Turkey.

Keywords: REE distribution pattern; REE fluid-melt partition coefficient; granite; intrusion-related gold system; porphyry copper (gold) system

1. Introduction

Using rare earth elements (REE) to study the origin of ore-fluids associated with granite (*sensu lato*) intrusions has been made possible and attractive, thanks to the progress in a number of high P-T experiments on REE partitioning between magmatic vapour phases and granitic melts [1-3]. This technique has been proved reliable and cost-effective in probing the sources of ore-fluids associated with granite intrusions [4-5].

Experimental studies indicate that REE fluid-melt partition coefficient k_P^{REE} (see Table 1 for the explanations of symbols) is dominantly dependent upon fluid composition (i.e. chlorine molality m_{Cl}^v), and is also controlled to some extent by melt composition (e.g., ASI) and pressure (1.25 to 10.0 kb), but is not notably affected by temperature (750 to 950 °C) [3]. In a strongly peraluminous (ASI >1.1) granitic melt system associated with a fluid phase with a large range of m_{Cl}^v from 0.1 to 6.0 *M*, the values of k_P^{La} range from ca. 0.035 to 0.150. In contrast, in a moderately peraluminous (ASI = 1.0 to 1.1) to metaluminous (ASI <1.0) melt system associated with fluid phase with the same m_{Cl}^v range, k_P^{La} values range from ca. 0.005 to 1.5 [2-3]. These experimental observations suggest that k_P^{La} values could be estimated over a range of X-P conditions.

It is well-known that granitic melts could lose a magmatic vapour phase (MVP; Table 1), shown as trapped fluid inclusions in primary quartz phenocrysts [6-9] to surrounding country rocks during cooling, resulting in hydrothermal alteration and sometimes mineralization (e.g., porphyry Cu-Au (Mo), intrusion-related Au). As much as 5 wt% water containing various metals and/or ligands may

Table 1. Symbols used in this paper.

Symbol	Explanation
ASI	Aluminum saturation index that is expressed as molar ratio of Al/(Ca+Na+K) of granitic melts (or granites)
C_{Cl}^{m}	Chlorine content (wt.%) of granitic melt
C_{REE}^{m}	REE concentration of granitic melt, e.g., C_{La}^{m} stands for La content (ppm) in the melt
C_{REE}^{v}	REE concentration of magmatic fluid (or magmatic vapour phase; see below MVP)
k_P^{Cl}	Chlorine partition coefficient between magmatic fluid and granitic melt, that is defined by the ratio of m_{Cl}^{v}/m_{Cl}^{m}
k_P^{REE}	REE partition coefficient between magmatic fluid and granite melt; for example, k_P^{La} denotes La partition coefficient defined by C_{La}^{v}/C_{La}^{m} ratio, and so on
m_{Cl}^{m}	Chlorine molality of granitic melt
m_{Cl}^{v}	Chlorine molality of magmatic fluid (i.e. aqueous vapour phase)
MVP	Magmatic vapour (or volatile fluid) phase

be lost to the surroundings upon cooling of granite magmas during their ascent and emplacement [10]. This may be concentrated to form an ore deposit if the geological settings are favourable. The composition of MVP (or magmatic fluids) can be modelled by studying ore-forming elements (e.g., Cu, Mo) partitioning between the MVP and granitic melts through high PT experimental and empirical investigations [11-13]. Therefore, it is possible to determine what roles are played by the magmatic fluids associated with granitic magmas in mineralization by comparing the geochemical data (e.g., REE) of ore deposits and associated alteration with the composition of simulated magmatic fluids based on the fluid-granitic melt partitioning data.

This paper presents the procedures of how to calculate REE concentrations of MVP based on a set of new polynomial equations that can be used for estimation of REE fluid-granitic melt partition coefficients over a wide range of P-T-X conditions. This technique is then used for tracking the sources of ore-fluids responsible for the formation of two typical mineral deposits; 1) the Lake George intrusion-related Sb-Au-W-Mo deposit (New Brunswick, Canada) characterized by low to medium salinity ore-fluids; and 2) the Bakircay Cu-Au (-Mo) porphyry system in northern Turkey, that may have been formed by ore-fluids with medium to high salinities.

2. Methodology

An element partition coefficient between MVP and granitic melt is defined by the ratio of its concentration in the MVP to that in the melt [1, 14; Table 1]. For instance, the REE partition coefficient k_P^{REE} between MVP and silicate melt can be expressed as the ratio of C_{REE}^{v}/C_{REE}^{m}; similarly, chlorine partition coefficient k_P^{Cl} is defined as the ratio of m_{Cl}^{v}/m_{Cl}^{m} (Table 1). The partition coefficient is dimensionless, and is controlled by various variables, such as pressure, temperature, and composition of magmatic-hydrothermal systems [1-3, 5, 10-16]. It is also noted that the value of k_P^{Eu} could be effected by oxygen fugacity (fO_2) of the system in question, because Eu has two valences (i.e. Eu^{3+}, Eu^{2+}) that depend upon fO_2 [1, 3].

Estimates of REE concentration of magmatic fluid are made based on empirical values of k_P^{REE} obtained by the new equations presented in this study (see below); using the REE data of fresh bulk-rock samples to approximate that of the granitic melt in equilibrium with the magmatic fluid, and altered rock, which resulted from the interaction or reaction of the fresh rock with the magmatic fluid. Thus, the signature of magmatic fluids may be recognized to some extent by following the method presented in this study.

2.1. Relationship of REE fluid-granitic melt partition coefficient k_P^{REE} to chlorine molality m_{Cl}^v

How to calculate REE partition coefficients k_P^{REE} between magmatic aqueous fluid and granite melt was presented by [5] according to the experimental results [1-2]. It could be described by a linear function of cubic power of m_{Cl}^v, but the Eu fluid-granitic melt partition coefficient k_P^{Eu} is related to the fifth power of m_{Cl}^v when the aqueous fluids have relatively low values of m_{Cl}^v. This confirms the experimental observations by [1-2]. The mathematic relationships of k_P^{REE} to the low range of m_{Cl}^v of aqueous fluids were provided on the basis of a least square regression analysis of the experimental dataset. However, such a linear relationship cannot extend to higher values of m_{Cl}^v (e.g., >3.5 *M*), which was also noticed by [3]. Therefore, it is necessary to re-assess the existing experimental data presented in [1-3]. Here, these datasets (Supplementary Table 1) are plotted on Figure 1, using La to represent LREE and Yb to represent HREE (note: the other REEs are not shown). To best fit the dataset, a set of new polynomial equations linking k_P^{REE} with m_{Cl}^v can be obtained for each of REE as shown in Table 2, although more experimental data are required to fill the data gap. Remarkably, these equations display relatively higher correlation coefficients (R^2 ranging from 0.943 to 0.969; see Table 2) when compared with those (R^2 ranging 0.90 to 0.95) presented by [5]. Based on the equations presented in Table 2 respectively for La and Yb, k_P^{La} can be readily calculated, for example, for the magmatic fluid with m_{Cl}^v value of 1.0 *M*, to be 0.054; and k_P^{Yb} to be 0.024.

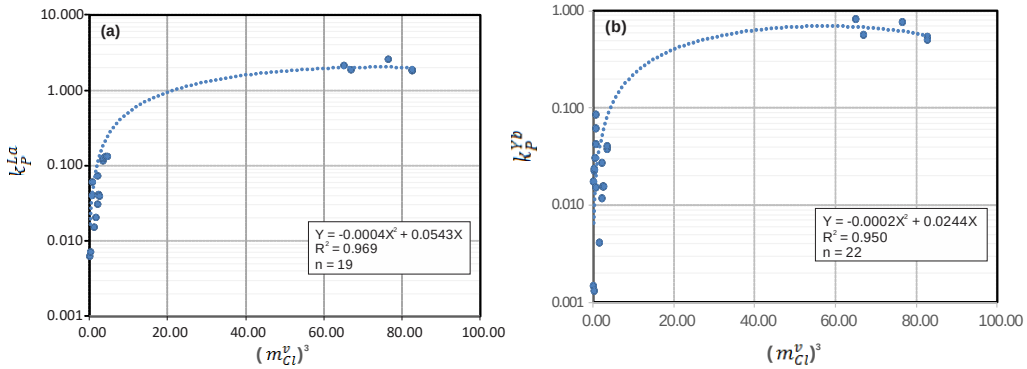

Figure 1. Plot of REE fluid-granitic melt partition coefficient k_P^{REE} versus chlorine molality m_{Cl}^v of magmatic vapour (fluid) phase: (a) k_P^{La} versus $(m_{Cl}^v)^3$, and (b) k_P^{Yb} versus $(m_{Cl}^v)^3$. Data used for this plot from [1-3] (Supplementary Table 1). In each of the equation, Y denotes k_P^{REE}; x represents $(m_{Cl}^v)^3$, except for Eu where *e* is $(m_{Cl}^v)^5$ (Table 2); R is correlation coefficient; and n is the number of experimental dataset. It is worth noting that the uncertainties of such estimation for k_P^{REE} using the equations listed in Table 2 are not well constrained, although they must have been within the errors of the original dataset [1-3], i.e. ±0.025 for LREE, and ±0.030 for HREE.

The REE fluid-granitic melt partition coefficients k_P^{REE} data used for the statistical analysis of this study (Supplementary Table 1) were acquired under the experimental conditions of 4.0 kb, 800°C and quartz-fayalite-magnetite buffer by [1], at 2.0 kb and 800°C by [2], and experiments at 0.2 to 10 kb and 750 to 950°C by [3]. Numerical analysis of these dataset strongly suggest that k_P^{REE} is dominantly controlled by chlorine molality m_{Cl}^v of the fluids in equilibrium with the granitic melts, consistent with the observations by [1-3]. The experiment work indicates that k_P^{REE} values are not influenced by temperature, although the pressure effect appears to be notable (i.e. the values of k_P^{REE} for trivalent REEs would increase with decreasing pressure). Interestingly, Borchert et al. (2010) [3] have pointed out that the pressure (ranging from 2.0 to 9.0 kb) effect on k_P^{La} values is not discernible for peraluminous granitic melts, although such an effect is slightly manifest for metaluminous melts. For instance, the value of k_P^{La} increases from 0.03 at 3.0 kb to 0.12 at 7.0 kb when a fluid with m_{Cl}^v of 6.0 *M* associated with a metaluminous granitic melt [3]. Obviously, more high P-T experiments are required to cover a range of pressures at least from lower to upper continental crust. Furthermore, it has been well constrained that k_P^{Cl} is only pressure dependent [10]. Consequently, the value of m_{Cl}^v

Table 2. Relationship of REE fluid-granite melt partition coefficients (k_P^{REE}) to chlorine molality (m_{Cl}^v) of magmatic fluids [note: x denotes $(m_{Cl}^v)^3$ in the equations except for Eu in which instead of x, a different variable e is used that equals to $(m_{Cl}^v)^5$].

REE	Equation for estimating k_P^{REE}	Correlation coefficient (R^2)	Number of the experimental data used for polynomial analysis (n)
La	$k_p^{La} = -0.0004x^2 + 0.0543x$	0.969	19
Ce	$k_p^{Ce} = -0.0005x^2 + 0.0649x$	0.964	20
Nd	$k_p^{Nd} = -0.0004x^2 + 0.0588x$	0.958	13
Sm	$k_p^{Sm} = -0.0004x^2 + 0.0519x$	0.950	13
Eu	$k_p^{Eu} = -0.0000007e^2 + 0.0017e$	0.956	20
Gd	$k_p^{Gd} = -0.0003x^2 + 0.0419x$	0.943	22
Tb	$k_p^{Tb} = -0.0003x^2 + 0.0413x$	0.956	13
Ho	$k_p^{Ho} = -0.0003x^2 + 0.0338x$	0.965	11
Yb	$k_p^{Yb} = -0.0002x^2 + 0.0244x$	0.950	22
Lu	$k_p^{Lu} = -0.0002x^2 + 0.0207x$	0.962	13

in magmatic fluids is only related to pressure (Table 1), which is the main controlling factor on values of k_P^{REE} (Table 2). Therefore, these equations (Table 2) may be used to calculate k_P^{REE} values for a wide range of pressure (0.1 to 10.0 kb) within the continental crust, and to estimate REE concentrations of magmatic fluids, although the limitation of such a practical simulation should be kept in mind.

A virtual examination of Figure 1 suggests that the value of k_P^{REE} would approach its maximum with increasing $(m_{Cl}^v)^3$ to a certain value, or a threshold. When $(m_{Cl}^v)^3$ is much smaller than this threshold, k_P^{REE} is in linear relationship to the variable as described by [1-2, 5]. As long as m_{Cl}^v of a magmatic fluid reaches the threshold, the value of k_P^{REE} would reach the maximum and then appear to remain constant regardless how much the concentration of chlorine in the fluid is increased. This conclusion is also achieved by a numerical analysis (i.e. differentiation) of the equations listed in Table 2. This practise is able to predict the $(m_{Cl}^v)^3$ threshold and maximum k_P^{REE} value for each individual element (Table 3). Obviously, the implication of such thresholds and (or) parameters needs further discussed, and tested by more experimental work because the existing dataset used in this paper (Supplementary Table 1) are limited. Albeit the data limitation, the functions presented in Table 2 appear to be applicable to covering the entire pressure range within the continental crust (e.g., 0.1 to 10.0 kb) owing to the fact that maximum k_P^{REE} values rely only upon the chlorine molality thresholds $(m_{Cl}^v)^3$ of magmatic fluids (Figure 2; Table 3) regardless pressures of the

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 3 June 2019 doi:10.20944/preprints201906.0020.v1

Peer-reviewed version available at Minerals 2019, 9, 426; doi:10.3390/min9070426

fluid-melt systems in question. Here, it is recommended that the maximum value of k_P^{REE} for each REE be used to simulate REE contents of magmatic fluid once the chlorine molality of the fluid reaches the threshold.

Table 3. Predicted chlorine molality thresholds $(m_{Cl}^v)^3$ of magmatic fluids (note: for Eu, it should be $(m_{Cl}^v)^5$) and maximum values of REE fluid-granite melt partition coefficients of k_P^{REE} from this study.

REE	Threshold $(m_{Cl}^v)^3$ of fluid [except for Eu that is $(m_{Cl}^v)^5$]	m_{Cl}^v of fluid (M)	Maximum value of k_P^{REE}
La	67.88	4.08	1.843
Ce	64.90	4.02	2.106
Nd	73.50	4.19	2.161
Sm	64.88	4.02	1.684
Eu	1214.29	4.14	1.961
Gd	69.83	4.12	1.463
Tb	68.83	4.10	1.421
Ho	56.33	3.83	0.952
Yb	61.00	3.94	0.744
Lu	51.75	3.73	0.536

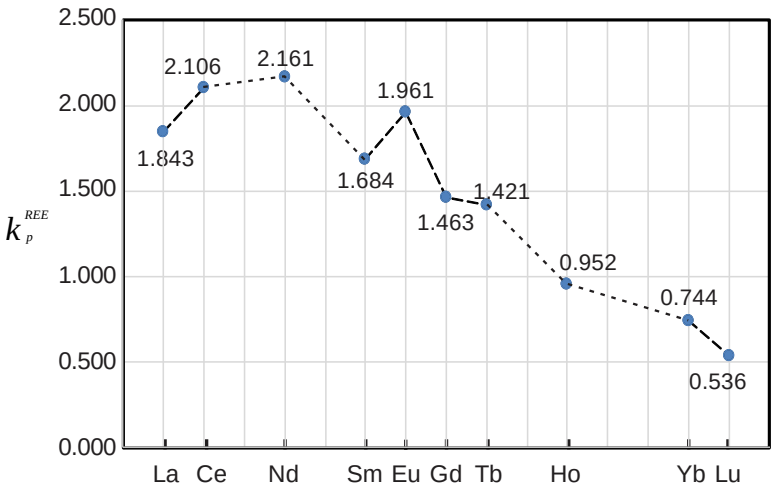

Figure 2. Plot of the predicted maximum values of REE partition coefficients k_P^{REE} between magmatic fluids and granitic melts based on the equations in Table 2. Number marked on the graph is the maximum value of predicted k_P^{REE} for each element, e.g., La equals to 1.843.

Figure 2 indicates that REE partitioning between magmatic fluids and granite melts must have resulted in LREE enrichment relative to HREE in the fluids, consistent with the observations of alteration halos associated with the Cu-Au (-Mo) porphyry systems [4], intrusion-related Au systems [5], and of natural fluid inclusions [6]. Also, it is likely that the fluids with relatively low m_{Cl}^v values would display a negative Eu anomaly as indicated by the relationship of k_P^{REE} to m_{Cl}^v (Table 2), unless their m_{Cl}^v values are close to the threshold that would result in a positive Eu anomaly. However, this effect could be influenced by the value of m_{Cl}^v that is a function of pressure [10; 14-17]. Maximum partition coefficients for other REE (e.g., Pr, Dy, Er, Tm) may be obtained by extrapolation from the data presented in Figure 2. Further stretching on this, nevertheless, is not

encouraged, although such a practice would provide a basis for future experiment work to determine their respective values experimentally.

Furthermore, the equations (Table 2) can also be used for evaluation of REE behaviour in a fluid-granitic melt system. When the value of k_P^{REE} is ≥1.0, REE is fluid compatible and prefers partitioning into the magmatic fluid. Otherwise, REE is granitic melt compatible when k_P^{REE} is <1.0. LREE (e.g., La) would not become fluid compatible until the value of $(m_{Cl}^v)^3$ is higher than 21.97 (i.e. m_{Cl}^v ≥2.80 *M*, which is obtained by solving the equation when k_P^{La} equals to 1.0; see Figures 1a and 3). In other words, La would be fluid incompatible and favours granite melt if the fluid has the m_{Cl}^v value below 2.80 *M*. Therefore, LREE behaves differently in the fluid-granite melt system, depending upon the value of m_{Cl}^v of the magmatic fluid. Interestingly, Eu requires much higher m_{Cl}^v value to become fluid compatible than the other LREE, indicating that it is melt compatible in equilibrium with magmatic fluids with low m_{Cl}^v, and therefore, such fluids commonly have negative Eu anomaly. If magmatic fluids reach thresholds $(m_{Cl}^v)^3$ (Table 3; Figure 2), they would display positive Eu anomaly. HREE (e.g., Yb), however, is typically fluid incompatible and prefers partitioning into granite melt (Figure 1b), and the maximum value of k_P^{Yb} is 0.744 when $(m_{Cl}^v)^3$ is equal to its threshold of 61.00 (or m_{Cl}^v = 3.94 *M*) for the fluids associated with granite melts, leading to REE fractionation that LREE are enriched relatively to HREE during evolution of magmatic hydrothermal systems.

More recently, Song et al. (2016) [18] found that REEs prefer partitioning into carbonate melt with fluid–melt partition coefficients <1.0 at 1–2 kb and 700–800 °C, leading to relative HREE enrichment compared to LREE. Their experimental work suggests that REE fractionation in the fluid-carbonatite melt system distinctly differs from that in the fluid-granite melt system as discussed in this study.

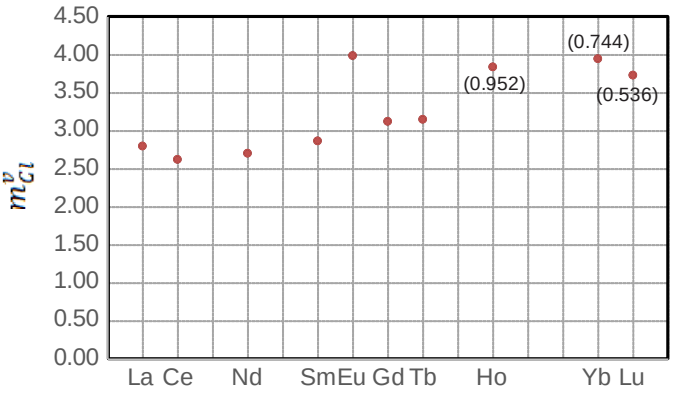

Figure 3. Diagram of m_{Cl}^v values required for k_P^{REE} ≥1.0 so that LREEs become fluid compatible, whereas HREEs are exclusively fluid incompatible and prefer partitioning into granitic melts because their k_P^{REE} are always <1.0 and would reach maximum values (as shown by number; Table 3) when $(m_{Cl}^v)^3$ values achieve their respective threshold.

2.2. Calculation of chlorine molality m_{Cl}^v

As pointed out by [17], it is not easy to obtain chlorine concentration in granite melt. To make it simple, the chlorine molality m_{Cl}^m (unit in *M* or moles/kg) of granitic melt can be calculated by chlorine content of granite as indicated by the equation below.

$$m_{Cl}^m = (C_{Cl}^m \div 35.5) \times [(100 - C_{Cl}^m) \div 1000] \quad (1)$$

where chlorine content C_{Cl}^m in granitic melt is approximated by the analysis of whole-rock sample and its unit is in wt%.

Such an exercise of using eq. 1 to calculate chlorine molality m_{Cl}^v of a granite sample would provide a minimum value of the corresponding granitic melt, because a large amount of chlorine may have been lost from the melt during cooling [10, 16]. This is unavoidable because of high

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 3 June 2019 doi:10.20944/preprints201906.0020.v1

Peer-reviewed version available at Minerals 2019, 9, 426; doi:10.3390/min9070426

chlorine partition coefficient between MVP and granitic melt at magmatic conditions [14-15, 17]. Table 4 shows the results of calculation by using two examples.

Table 4. Calculation of REE concentrations in magmatic fluid.

	Lake Geoge granodiorite [5]		Bakircay granodiorite [4]		
	A	B	D	E	
La (ppm)	30.9	30.9	12.7	12.7	
Ce	51.2	51.2	25.8	25.8	
Nd	13.7	13.7	12.1	12.1	
Sm	4.2	4.2	2.17	2.17	
Eu	1.08	1.08	0.54	0.54	
Gd	4.8	4.8	2.24	2.24	
Tb	0.8	0.8			
Dy			2.25	2.25	
Er			1.16	1.16	
Yb	2.2	2.2	1.1	1.1	
Lu	0.3	0.3			
Cl	1000	15 wt% $NaCl_{eqv.}$ in fluid inclusion [7]	17 wt% $NaCl_{eqv.}$ in primary inclusion	52% $NaCl_{eqv.}$ in fluid inclusion, 18.52 *M* >Threshold	
Calculation of REE fluid-granitic melt partition coefficient					***Equation***
m_{Cl}^{m}	0.028				1
m_{Cl}^{v}	1.23	3.02	3.50	>Threshold	2
k_P^{Cl}	43.5				at 2 kb [10]
k_p^{La}	0.099	1.189	1.593	1.843	from Table 2
k_p^{Ce}	0.118	1.405	1.863	2.106	from Table 2
k_p^{Nd}	0.107	1.313	1.786	2.161	from Table 2
k_p^{Sm}	0.094	1.123	1.490	1.684	from Table 2
k_p^{Eu}	0.005	0.381	0.700	1.961	from Table 2
k_p^{Gd}	0.076	0.924	1.245	1.463	from Table 2
k_p^{Tb}	0.075	0.908	1.219	1.421	from Table 2
k_p^{Ho}	0.061	0.702	0.898	0.952	from Table 2
k_p^{Yb}	0.044	0.519	0.678	0.744	from Table 2
k_p^{Lu}	0.038	0.418	0.520	0.536	from Table 2
Calculation of REE concentrations (ppm) in MVPs					
C_{La}^{v}	3.05	36.74	20.23	23.41	
C_{Ce}^{v}	6.04	71.92	48.08	54.33	
C_{Nd}^{v}	1.47	17.98	21.61	26.15	
C_{Sm}^{v}	0.40	4.72	3.23	3.65	
C_{Eu}^{v}	0.01	0.41	0.38	1.06	
C_{Gd}^{v}	0.39	4.73	1.43	3.28	
C_{Tb}^{v}	0.06	0.73			
C_{Yb}^{v}	0.10	1.14	0.75	2.14	
C_{Lu}^{v}	0.01	0.14			

A more accurate chlorine molality m_{Cl}^{m} of granite melt may be obtained by using the methods proposed by Piccoli et al. [13], but their methods require chemical composition data of apatite, or bulk composition of aplite associated with the main granite intrusion. Here, using the value of m_{Cl}^{m} obtained by eq. 1 and chlorine partition coefficient k_P^{Cl} [10, 14-15] one can readily estimate the value of chlorine molality m_{Cl}^{v} of the aqueous vapour phase in equilibrium with the granite melt at

magmatic P-T conditions. As mentioned above, $k_P^{Cl} = m_{Cl}^v/m_{Cl}^m$, is a function of pressure and independent of temperature within the continental crust [10-11]. Thus, m_{Cl}^v can be obtained from equation 2 below, if m_{Cl}^m is given (column A in Table 4).

$$m_{Cl}^v = k_p^{Cl} \times m_{Cl}^m \quad (2)$$

Chlorine partition coefficients k_P^{Cl} between chloride-bearing fluids and granitic melts were determined experimentally under pressure of 2 to 8 kb and near 700 and 750°C isotherms by Kilinc and Burnham [14], indicating that the k_P^{Cl} values are strongly dependent upon pressure. The values increase from 43.5 at 2 kb to 83.3 at 6 kb, and then decrease sharply to 13.0 at 8 kb. Webster and Holloway (1990) reported a similar result for the pressure range of 2 to 4 kb, although a fluorine-free system has higher k_P^{Cl} values [15]. These experimental data suggest that chlorine prefers to partitioning into aqueous fluids under magmatic conditions. However, experiments also showed that chlorine is compatible to granite melt when it has high fluorine (>7 wt%) and low chlorine (0.12 wt%) contents at 2 kb and 1000°C [15].

Using the salinity data of fluid-inclusions to estimate the chlorine molality m_{Cl}^v is a quick solution regarding the potential problems (e.g., chlorine lost from cooled granitic melts), if the inclusions trapped in minerals are primary magmatic fluids sourced from granite magmas (intrusions). For example, the fluid inclusions trapped in apatite enclosed in a plagioclase crystal from a granodiorite sample collected from the Lake George granodiorite stock represent typical magmatic fluids with medium salinity of 15 wt% $NaCl_{eqv.}$ that is suitable for calculating chlorine molality m_{Cl}^v of the fluids [5, 7] (column B in Table 4). This practice may avoid the complexity of estimating m_{Cl}^m [13, 17] and the use of eq. 2 which relies on the pressure dependant k_P^{Cl} parameter [14, 15-16].

Medium to high salinity fluids (e.g., 17 wt% $NaCl_{eqv.}$, ~3.50 *M* Cl^-; slightly lower salinity than the threshold required for the maximum value of k_P^{Yb}, see Table 3) are commonly associated with porphyry Cu-Au (-Mo) systems [19, 20]. These values may be input into the equations to calculate k_P^{REE} and then to calculate REE concentrations of the magmatic fluids that are presented in column D in Table 4. High salinity fluids responsible for potassic alteration associated with porphyry Cu-Au (-Mo) deposits (52 wt% $NaCl_{eqv.}$, 18.52 *M* Cl^-) [20] have much higher values of m_{Cl}^v than the thresholds (Table 3) required to reach the maximum values of k_P^{REE} for all REE (Table 3; Figure 2). Thus, using the maximum k_P^{REE} values (Table 3) to calculate REE contents in magmatic fluids is reasonable, that is presented in column E also in Table 4.

2.3. Calculation of REE concentration C_{REE}^v in MVP

The REE concentration C_{REE}^v in MVP (magmatic fluids) can be readily calculated in terms of the k_P^{REE} values as described above and bulk-rock (melt) REE content C_{REE}^m. Table 4 shows that, for example, La content (3.05 ppm) in the MVP is computed by multiplying the value of k_P^{REE} (0.099) and La content (30.9 ppm) in the melt that is approxiamted by the analysis of the granite sample (column A in Table 4).

3. Application

Two examples are presented here to show how to calculate REE concentrations in magmatic fluid associated with 1) the Lake George granodiorite stock, which is thought to genetically responsible for the formation of the Sb-Au-W-Mo mineral deposit, New Brunswick (Canada); and 2) the Bakircay Cu-Au (-Mo) porphyry system, Northern Turkey. The Lake George deposit was the largest antimony producer in North America until mid-1990s. It is temporally and spatially associated with the Early Devonian Lake George granodiorite stock [21-27]. The styles of Au mineralization include Au-bearing quartz–carbonate veins, veinlets and stockworks are present within the granodiorite stock, quartz-feldspar dyke, and proximal metamorphic aureole; they are associated with earlier W–Mo mineralization. These characteristics suggest that the Lake George

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 3 June 2019 doi:10.20944/preprints201906.0020.v1

Peer-reviewed version available at Minerals 2019, 9, 426; doi:10.3390/min9070426

granodiorite intrusion and related hydrothermal systems may have ultimately resulted in Au mineralization [21-24, 26], resembling intrusion-related gold systems [7, 27-29].

Table 4 lists the analyses of the Lake George and Bakircay granodiorites, chlorine contents either of bulk analysis or from fluid inclusion salinity data, calculated chlorine molality m_{Cl}^{v}, calculated k_P^{REE} and REE concentrations of magmatic fluids. Other data include the Lake George mineralized quartz-feldspar porphyry [26], Bakircay potassic altered rock [4], and calculated REE contents in magmatic fluids with different m_{Cl}^{v} are tabulated in Supplementary Table 2.

The Lake George granodiorite-normalized REE distribution patterns of magmatic fluids (see Table 4 for the estimated value of C_{REE}^{v} for each element) at chlorine molality m_{Cl}^{v} equals to 1.23 and 3.02 *M*, respectively are plotted in Figure 4a, indicating that REE concentrations in the magmatic fluids are elevated remarkably with increasing the value of m_{Cl}^{v} (Table 4). Also, the REE pattern of the fluid displays a pronounced negative Eu anomaly at m_{Cl}^{v} equal to 1.23 *M*, whereas the Eu anomaly becomes much less pronounced when m_{Cl}^{v} equals to 3.02 *M*. Figure 4b indicates the REE patterns in the calculated magmatic fluid at m_{Cl}^{v} = 3.50 *M* and with thresholds (Table 3), respectively normalized by the Bakircay granodiorite. Although their LREEs are similar, the fluid with the threshold Cl^- molality displays relatively elevated HREE compared to the granodiorite.

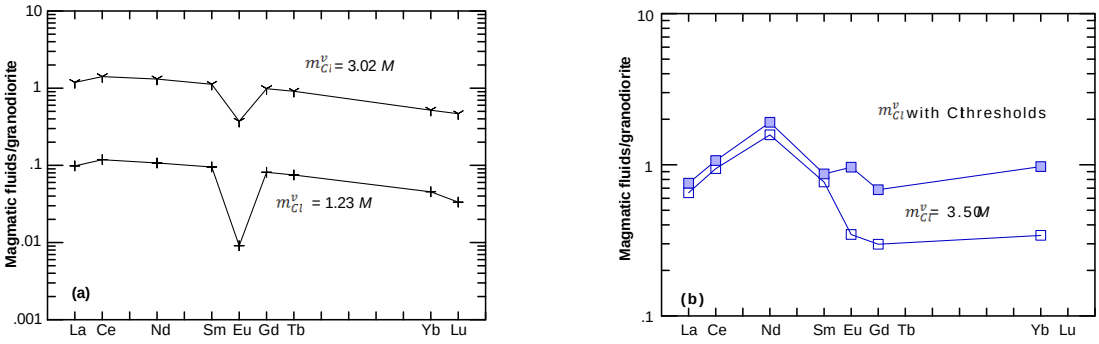

Figure 4. Lake George granodiorite-normalized REE distribution patterns of magmatic fluids with chlorine molality of m_{Cl}^{v} equals respectively to 1.23 to *M* and 3.02 *M* (a), and the Bakircay granodiorite-normalized REE distribution patterns of magmatic fluids with m_{Cl}^{v} values respective of 3.50 *M* and threshold (b). The normalization values in Table 4.

Figure 5a show chondrite-normalized REE patterns for the Lake George granodiorite, mineralized (or altered) quartz-feldspar porphyry and the calculated magmatic fluids, suggesting that these fluids are likely to decouple with the granodiorite although the altered porphyry lacks a Eu anomaly. A higher m_{Cl}^{v} fluid appears to be required to reduce Eu anomaly, which is evident in fluid inclusion studies (i.e. halite-bearing inclusions) [7]. Such fluids with varied m_{Cl}^{v} deriving from progressively cooling magmas would interact the quartz-feldspar porphyry, resulting in reduction to disappearance of Eu anomaly, and in some part (HREE) intersecting with the granodiorite. This process may have produced hydrothermal alteration and simultaneously Au mineralization in the vein stockwork systems [23, 26], consistent with evidence from lithogeochemistry, mineral chemistry, fluid inclusions, and stable isotopes [7, 27-30]. Notably, increasing the values of m_{Cl}^{v} could raise the k_P^{REE} values, thus raises the REE concentration of the ore-fluids, and further reduce its Eu anomaly.

Figure 5b shows the calculated magmatic fluids with m_{Cl}^{v} of 3.50 *M* and with threshold associated with the Bakircay granodiorite melt, and are compared to potassic altered rock that hosts Cu-Mo mineralization [4], indicating that the mineralization is most likely to related to the ore-fluids that have medium to very high salinities. Interaction of such fluids with host rocks would have ultimately resulted in potassic alteration and ore mineral (e.g., chalcopyrite) precipitation. Such magmatic fluids with LREE enriched relatively to HREE, and released from cooling magmas, are consistent with the mass-balance studies by [4] and numerical simulation also based on REE fluid-granitic melt partitioning by [2].

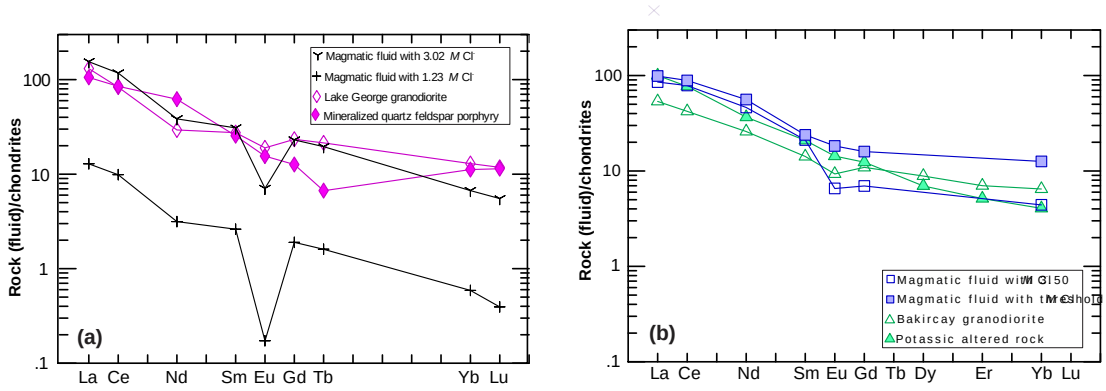

Figure 5. (a) A comparison of chondrite-normalized REE patterns of calculated magmatic fluids, the Lake George granodiorite and mineralized quartz-feldspar porphyry; (b) chondrite-normalized REE patterns of the Bakircay granodiorite, potassic altered rock, and the calculated magmatic fluids. The chondrite normalizing values are from [31].

4. Discussion

The experimental data used for this study has not considered chemical components (e.g., CO_3^{2-}, HS^-) effect on REE partition coefficients k_P^{REE} except for chlorine concentrations of magmatic fluids [1-3], although the recent experiments show that REEs prefer entering carbonate melt [18], that is a different system. Despite the difficulty of determining chlorine molality (m_{Cl}^v) of granite melt [17], this study uses the bulk-rock analysis to estimate the minimum value of m_{Cl}^v in the granitic magma (melt), and also suggests that using salinity data of primary fluid inclusions may be a quick solution to this problem (Table 4).

The method is presented here to estimate rare earth element concentrations in magmatic fluids associated with water-saturated granites (magmas), which are then compared to those in hydrothermal alteration zones related to intrusion-related Au and porphyry Cu-Au (-Mo) deposits, providing clues as to the origin of their ore-fluids and metallogeny. The key is to estimating the empirical values of k_P^{REE} that have been established and can be described by a set of new polynomial equations (Table 2) based on a statistical analysis of the existing experimental dataset (Supplementary Table 1). These equations (Figure 1 and Table 2) suggest that the values of k_P^{REE} would achieve a maximum when the chlorine molality m_{Cl}^v values are equal to the thresholds (Table 3), which provide a theoretical constraint on REE solubility in magmatic fluids containing chloride. When m_{Cl}^v> thresholds, REE chloride complexes (e.g., $LaCl_3$, $EuCl_2^-$, $EuCl_3$, $YbCl_3$) would become unstable at magmatic hydrothermal conditions, and thus some REE minerals (?) may have precipitated. This prediction, however, needs to be tested by experimental work (e.g., using very high salinity solution).

The values of k_P^{REE} in this study are only related to m_{Cl}^v (Table 2) which is linked to k_P^{Cl} that is mainly pressure dependent [14]. Therefore, the equations proposed in this study may be applied to a wide pressure range within the continental crust, given a proper value of k_P^{Cl} at specific pressure [14-16] is used to calculate the value of m_{Cl}^v. As pointed out above, this problem may be readily resolved by using magmatic fluid inclusion data to estimate m_{Cl}^v (Table 4). When the values of m_{Cl}^v reach the thresholds (Table 3), k_P^{REE} would achieve the maximum and therefore must be independent of pressure. Furthermore, LREE and HREE display distinct behaviour in magmatic fluids associated with granitic magmas, leading to their fractionation in the magmatic-hydrothermal systems. The examples given by this study confirm that the calculated magmatic fluids are enriched in LREE relative to HREE (Figure 5), and europium appears to have deviated from the other REEs with either having pronounced negative anomalies (in low to medium m_{Cl}^v fluids) or without notable Eu anomalies (in high m_{Cl}^v fluids). Here, oxygen fugacity is not considered, although it is known that the Lake George granodiorite exhibits characteristics of reduced I-type [27-29] whereas the Bakircay granodiorite is a normal oxidized I-type based on its mineral assemblage [4]. This suggests the behaviour of Eu in the magmatic hydrothermal systems may have been influenced by

redox conditions [1]. The Lake George granodiorite contains primary magmatic pyrrhotite, ilmenite but lacks of magnetite, supporting the conclusion that it is a reduced I-type granite [28-30]. The sulphide would be unstable when interacting with chlorine-bearing magmatic fluids, liberating ore components (e.g., Au, S) and enhancing the ore-fluids [28, 32-35] that may have precipitated ore minerals including Au in a suitable setting, e.g., shear zones, hydrofractures, to form intrusion-related gold mineralization [7, 27-28, 36].

Although intrusion-related Au systems, such as the Lake George Sb-Au-W-Mo mineral deposit, are commonly characterized by low to medium salinity, carbonic, and reduced ore-fluids [7, 35], the presence of high salinity fluids appears required to balance the LREE, Eu anomaly and HREE as observed in the mineralized porphyry [26] and by the modelling presented in this study. Such a high salinity fluid is evident by the occurrence of halite-bearing fluid inclusions [7, 21-22]. On the other hand, porphyry Cu-Au (-Mo) systems are characterized by oxidized, medium to high salinity (or m_{Cl}^{v}) ore-fluids [19-20] associated with the granite intrusions. Such conditions are favourable in promoting Cu enrichment during magmatic-hydrothermal evolution [10-14].

5. Conclusions

LREEs behave differently in magmatic fluids associated with granitic magmas. They are either fluid compatible in higher m_{Cl}^{v} magmatic fluid or granitic melt compatible in low m_{Cl}^{v} magmatic fluid, whereas HREE are exclusively fluid incompatible. Consequently, magmatic fluids tend to be rich in LREE relative to HREE, resulting in REE fractionation during the evolution of magmatic hydrothermal systems.

When the value of $(m_{Cl}^{v})^3$ reaches the threshold, REE fluid-granitic melt partition coefficients k_P^{REE} would achieve their respective maximum value, suggesting that magmatic fluids associated with granitic magmas could not dissolve any more REEs than the predicted maximum concentrations.

Europium behaves differently from the other REEs, requiring much higher m_{Cl}^{v} values to become fluid compatible, and thus the magmatic fluids with low m_{Cl}^{v} would have a negative Eu anomaly.

REE concentrations in magmatic fluids associated with granitic melts (intrusions) may be estimated in terms of the new polynomial equations (Table 2), which are then compared to those of altered and (or) mineralized rocks to study the origin of ore-fluids. This technique is applied to the Lake George Sb-Au-W-Mo mineral deposit, New Brunswick, Canada, and Bakircay Cu-Au (-Mo) porphyry systems in northern Turkey, suggesting that ore-fluids may have been dominated by magmatic fluids, albeit with different chlorine molarities (i.e., the former with low to medium values of m_{Cl}^{v}, and the latter with medium to high values of m_{Cl}^{v}).

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, S1: Supplementary Table 1; S2: Supplementary Table 2.

Funding: This study did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Acknowledgments: Constructive review of an earlier draft of manuscript by Dr. Sean H. McClenaghan is gratefully acknowledged, which greatly improved the manuscript. Discussion with Simon Gagne is appreciated. I thank two anonymous journal reviewers for their constructive comments on the manuscript, which significantly improved the presentation of this study. The Academic Editor of the journal is gratefully acknowledged for handling the manuscript and for encouraging me to resubmit this paper.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Flynn, R.; Burnham, C.W. An experimental determination of rare earth partition coefficients between a chlorite containing vapour phase and silicate melts. *Geochimica et Cosmochica Acta* **1978**, *42*, 685-701.
2. Reed, M.J.; Candela, P.A.; Piccoli, P.M. The distribution of rare earth elements between monzogranitic

melt and the aqueous volatile phase in experimental investigations at 800°C and 200 MPa. *Contributions to Mineralogy and Petrology* **2000**, *140*, 251-262.

3. Borchert, M.; Wilke, M.; Schmidt, C.; Cauzid, J.; Tucoulou, R. Partitioning of Ba, La, Yb and Y between haplogranitic melts and aqueous solutions: An experimental study. *Chemical Geology* **2010**, *276*, 225-240.
4. Taylor, R.P.; Fryer, B.J. Multiple-stage hydrothermal alteration in porphyry copper systems in northern Turkey: The temporal interplay of potassic, propylitic, and phyllic fluids. *Canadian Journal of Earth Sciences* **1980**, *17*, 901-926.
5. Yang, X.M. Calculation of rare earth element patterns in magmatic fluids: Evidence for origin of the Lake George Sb-Au-W-Mo ore deposit, New Brunswick, Canada. *The Open Geology Journal* **2012**, *6*, 19-24.
6. Banks, D.A.; Yardley, B.W.D.; Campbell, A.R.; Jarvis, K.E. REE composition of an aqueous magmatic fluid: A fluid inclusion study from the Capitan Pluton, New Mexico, USA. *Chemical Geology* **1994**, *113*, 259-272.
7. Yang, X.M.; Lentz, D.R.; Chi, G., Kyser, T.K. Fluid-mineral reaction in the Lake George granodiorite, New Brunswick: implications for Au-W-Mo-Sb mineralization. *Canadian Mineralogist* **2004**, *42*, 1443–1464.
8. Harlov, D.E.; Austrheim, H. *Metasomatism and the chemical transformation of rock: Rock-mineral-fluid interaction in terrestrial and extraterrestrial environments*, 1st ed.; Springer-Verlag: Berlin, Germany 2013; pp. 1-16.
9. Mathieu, L.; Racicot, D. Petrogenetic study of the multiphase Chibougamau Pluton: Archaean magmas associated with Cu–Au magmato-hydrothermal systems. *Minerals* **2019**, *9*, 174; doi:10.3390/min9030174
10. Holland, H.D. Granites, solutions, and base metal deposits. *Economic Geology* **1972**, *67*, 281-301.
11. Candela, P.A. Theoretical constraints on the chemistry of the magmatic aqueous phase. In *Ore-bearing granite systems; petrogenesis and mineralizing processes*; Stein, H.J., Hannah, J.L., Eds.; Geological Society of America Special Paper 246, 1990; pp. 11-20.
12. Candela, P.A.; Piccoli, P.M. Magmatic contributions to hydrothermal ore deposits: an algorithm (MVPart) for calculating the composition of the magmatic volatile phase. *Reviews in Economic Geology* **1998**, *10*, 97-108.
13. Piccoli, P.M.; Candela, P.A.; Williams, T.J. Estimation of aqueous HCl and Cl concentrations in felsic systems. *Lithos* **1999**, *46*, 591-604.
14. Kilinc, I.A.; Burnham, C.W. Partitioning of chloride between silicate melt and coexisting aqueous phase from 2 to 8 kilobars. *Economic Geology* **1972**, *67*, 231-235.
15. Webster, J.D.; Holloway, J.R. Partitioning of F and Cl between magmatic hydrothermal fluids and highly evolved granitic magmas. In *Ore-bearing granite systems; petrogenesis and mineralizing processes*; Stein, H.J., Hannah, J.L., Eds.; Geological Society of America Special Paper 246, 1990; pp. 21-34.
16. Webster, J.D.; De Vivo, B. Experimental and modeled solubilities of chlorine in aluminosilicate melts, consequences of magma evolution, and implications for exsolution of hydrous chloride melt at Mt. Somma-Vesuvius. *American Mineralogist* **2002**, *87*, 104-1061.
17. London, D. Estimating abundances of volatile and other mobile components in evolved silicic melts through mineral–melt equilibria. *Journal of Petrology* **1997**, *38*, 1691-1706.
18. Song, W.L.; Xu, C.; Veksler, I.V.; Kynicky, J. Experimental study of REE, Ba, Sr, Mo and W partitioning between carbonatitic melt and aqueous fluid with implications for rare metal mineralization. *Contributions to Mineralogy and Petrology* **2016**, *171*, 1. DOI 10.1007/s00410-015-1217-5
19. Bodnar, R.J. Fluid inclusion evidence for a magmatic source for metals in porphyry copper deposits. Mineralogical Association of Canada **1995**, *Short Course Series 23*, pp. 139–152.
20. Gregory, M.J. A fluid inclusion and stable isotope study of the Pebble porphyry copper-gold-molybdenum deposit, Alaska. *Ore Geology Reviews* **2017**, *80*, 1279–1303.
21. Seal, R.R. II; Clark, A.H.; Morrissy, C.J. Stockwork tungsten (scheelite)-molybdenum mineralization, Lake George, southwestern New Brunswick. *Economic Geology* **1987**, *82*, 1259-1282.
22. Seal, R.R. II; Clark, A.H.; Morrissy, C.J. Lake George, southwestern New Brunswick: a Silurian, multi-stage, polymetallic (Sb-W-Mo-Au-base metal) hydrothermal centre. In *Recent advances in the geology of granite-related mineral deposits*, Taylor, R.P., Strong, D.F., Eds; Canadian Institute of Mining and Metallurgy **1988**, *Special Volume 39*, pp. 252-264.
23. Lentz, D.R.; Thorne, K.G.; Yang, X.M. Preliminary analysis of the controls on the various episodes of gold mineralization at the Lake George antimony deposit, New Brunswick. In *Current Research, New Brunswick Department of Natural Resources and Energy Division 2002, Mineral Resource Report 02-1*, Carroll, B.M.W., Ed.; pp. 55-79.

24. Yang, X.M.; Lentz, D.R.; Chi, G. Petrochemistry of Lake George granodiorite stock and related gold mineralization, York County, New Brunswick. Geological Survey of Canada, *Current Research* **2002**, *2002-D7*, 1-10.
25. McLeod, M.J.; Johnson, S.C.; Krogh, T.E. Archived U-Pb (zircon) dates from southern New Brunswick. *Atlantic Geology* **2003**, *39*, 209–225.
26. Leonard, P.R.R.; Lentz, D.R.; Poujol, M. Petrology, geochemistry, and U-Pb (zircon) age of the quartz-feldspar porphyry dyke at the Lake George antimony mine, New Brunswick: implications for origin, emplacement process, and mineralization. *Atlantic Geology* **2006**, *42*, 13–29.
27. Yang, X.M.; Lentz, D.R. Sulfur isotopic systematics of granitoids from southwestern New Brunswick, Canada: Implications for magmatic-hydrothermal processes, redox conditions, and gold mineralization. *Mineralium Deposita* **2010**, *45*, 795-816.
28. Yang, X.M.; Lentz, D.R.; Sylvester, P.J. Gold contents of sulphide minerals in granitoids from southwestern New Brunswick, Canada. *Mineralium Deposita* **2006**, *41*, 369-386.
29. Yang, X.M.; Lentz, D.R.; Chi, G.; Thorne, K.G. Geochemical characteristics of gold-related granitoids in southwestern New Brunswick, Canada. *Lithos* **2008**, *104*, 355-377.
30. Yang X.M.; Lentz, D.R. Chemical composition of rock-forming minerals in gold-related granitoid intrusions, southwestern New Brunswick, Canada: Implications for crystallization conditions, volatile exsolution and fluorine–chlorine activity. *Contributions to Mineralogy and Petrology* **2005**, *150*, 287-305.
31. Sun, S.-s.; McDonough, W.F. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes; In *Magmatism in the Ocean Basins*, Saunders, A.D., Norry, M.J., Eds.; Geological Society of London 1989, Special Publications 42, pp. 313–345.
32. Keith, J.D.; Whitney, J.A.; Hattori, K.; Ballantyne, G.H.; Christiansen, E.H.; Barr, D.L.; Cannan, T.M.; Hook, C.J. The role of magmatic sulphides and mafic alkaline magmas in the Bingham and Tintic mining districts, Utah. *Journal of Petrology* **1997**, *38*, 1679-1690.
33. Halter, W.E.; Heinrich, C.A.; Pettke, T. Magma evolution and formation of porphyry Cu–Au ore fluids: Evidence from silicate and sulphide melt inclusions. *Mineralium Deposita* **2005**, *39*, 845-863.
34. Stavast, W.J.A.; Keith, J.D.; Christiansen, E.H.; Dorais, M.J.; Tingey, D.; Larocque, A.; Evans, N. The fate of magmatic sulfides during intrusion or eruption, Bingham and Tintic Districts, Utah. *Economic Geology* **2006**, *101*, 329-345.
35. Fan, H.R.; Zhai, M.G.; Xie, Y.H.; Yang, J.H. Ore-forming fluids associated with granite-hosted gold mineralization at the Sanshandao deposit, Jiaodong gold province, China. *Mineralium Deposita* **2003** *38*, 739–750.
36. Yang, X.M. Sulphur solubility in felsic magmas: implications for genesis of intrusion-related gold mineralization. *Geoscience Canada* **2012**, *39*, 17-32.