The Canadian Mineralogist
Vol. 41, pp. 365-382 (2003)

COMPOSITIONAL HETEROGENEITY IN FLUORITE AND THE GENESIS OF FLUORITE DEPOSITS: INSIGHTS FROM LA–ICP–MS ANALYSIS

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Abstract

Fluorite from four fluorite–*REE* mineral deposits has been analyzed by LA–ICP–MS to determine the viability of this method for fluorite and to assess spatial and paragenetic compositional heterogeneity in the fluorite. Two of the deposits studied have an affiliation to an alkaline suite (Gallinas Mountains, New Mexico and Rock Canyon Creek, British Columbia), and two are associated with granites (South Platte, Colorado and St. Lawrence, Newfoundland). We show that LA–ICP–MS is a valid technique for the analysis of fluorite and that the nature of, and controls on, the trace-element content of fluorite are more complex than previously indicated from bulk analyses. Significant, small-scale (less than 2 mm) variation occurs in the trace-element composition of fluorite within individual deposits. Patterns of trace-element enrichment and depletion differ between, but are generally consistent within, individual deposits. Fluorite associated with alkaline magmatism is characterized by a flat to *LREE*-enriched chondrite-normalized *REE* pattern that lacks a negative Eu anomaly and has a positive Y anomaly. Fluorite associated with granitic magmatism is characterized by a flat to *LREE*-depleted chondrite-normalized *REE* pattern that has a negative Eu anomaly and a positive Y anomaly. With the exception of the Eu and Y anomalies, the chondrite-normalized *REE* patterns of the fluorite are similar to those of the associated intrusive rocks. The compositional heterogeneity of fluorite indicates that its use as a guide in classifying mineralization or in mineral exploration should be limited to instances where results of small-scale analyses (LA–ICP–MS) are available.

Keywords: fluorite, LA–ICP–MS, rare-earth elements, hydrothermal fluid, granite, syenite, mineralization.

Sommaire

Nous avons examiné la composition de la fluorite provenant de quatre gisements de fluorite et terres rares par plasma à couplage inductif et spectrométrie de masses avec ablation au laser (LA–ICP–MS) afin d'établir la viabilité de cette approche pour la fluorite et d'en évaluer l'hétérogénéité spatiale et paragénétique. Deux des gisements ont une filiation avec une suite alcaline (Gallinas Mountains, au Nouveau-Mexique, et Rock Canyon Creek, en Colombie-Britannique), et deux sont associés à des granites (South Platte, au Colorado, et St. Lawrence, à Terre-Neuve). Nous démontrons que la technique LA–ICP–MS est propice pour l'analyse de la fluorite, et que la nature des éléments traces présents dans la fluorite, et des contrôles les régissant, sont plus complexes que l'on croyait d'après les résultats sur analyses globales. Des variations importantes des teneurs en éléments traces à courte échelle (moins de 2 mm) sont décelées au sein d'un même gisement. Les tracés d'enrichissement et d'appauvrissement diffèrent d'un gisement à l'autre, mais semblent *grosso modo* conformes au sein d'un seul gisement. La fluorite associée au magmatisme alcalin possède un tracé plat ou enrichi en terres rares légères par rapport aux chondrites; elle est dépourvue d'une anomalie négative en Eu, mais montre une anomalie positive en Y. La fluorite associée au magmatisme granitique possède un tracé plat ou appauvri en terres rares légères, et montre une anomalie négative en Eu et une anomalie positive en Y. A l'exception des anomalies en Eu et Y, les tracés des terres rares normalisés dans la fluorite ressemblent à ceux des roches intrusives associées. A casuse de l'hétérogénéité de la fluorite, son utilisation comme guide d'un certain type de minéralisation en en exploration minérale sera limitée aux cas où il existe des résultats d'une étude des variations à courte échelle, par exemple par LA–ICP–MS.

(Traduit par la Rédaction)

Mots-clés: fluorite, ablation au laser, ICP–MS, terres rares, fluide hydrothermal, granite, syénite, minéralisation.

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INTRODUCTION

The trace-element composition of fluorite from hydrothermal mineral deposits has been used to identify sources of fluid (*e.g.,* magmatic *versus* formation waters), evaluate depositional mechanisms, develop conceptual genetic models, and make inferences about the ore potential of individual deposits and the regions in which they occur (*e.g.,* Möller *et al.* 1976, Richardson & Holland 1979, Eppinger & Closs 1990, Hill *et al.* 2000). Most of these interpretations are based on the bulk composition of fluorite crystals; such crystals commonly show fine-scale color banding (*e.g.,* Strong *et al.* 1984), however, suggesting the possibility that the trace-element distribution varies on a fine scale.

The trace-element composition of minerals, including fluorite, can now be quantitatively determined on small spatial scales (≤10 μm) and to low elemental concentrations (≤μg/g) using laser ablation – inductively coupled plasma – mass spectrometry (LA–ICP–MS) (Jackson *et al.* 1992, Fryer *et al.* 1995). In order to assess the nature and magnitude of fine-scale variations in the trace-element content of fluorite, its composition from four mineral deposits was investigated using LA–ICP–MS analysis: Gallinas Mountains, New Mexico, Rock Canyon Creek, British Columbia, South Platte, Colorado, and St. Lawrence, Newfoundland. These deposits were selected because they represent a spectrum of fluorite-bearing mineral deposits associated with granitic and alkaline magmatism, and all contain multiple generations of fluorite. In this paper, we show that there can be significant variation in the trace-element content of fluorite within deposits at a variety of scales, and that this variation has the potential to provide useful insights into mineralizing processes.

GEOLOGY OF THE MINERAL DEPOSITS SELECTED

Gallinas Mountains, New Mexico

Rare-element mineralization in the Gallinas Mountains district of east-central New Mexico was described by Perhac & Heinrich (1964), Schreiner (1993), and Williams-Jones *et al.* (2000). Fluorite – rare-earth element (*REE*) mineralization is associated with Oligocene felsic intrusive bodies and occurs within breccia pipes and fault-hosted breccias hosted by these intrusive rocks and the country rocks. Fluorite, the predominant mineral in the breccia matrix, occurs with *REE* minerals (mainly bastnäsite), quartz, barite, calcite, pyrite and hematite. In the Pinatosa deposit, a breccia pipe 100 meters wide hosted by quartz syenite, three generations of fluorite (P1, P2 and P3) have been identified (Williams-Jones *et al.* 2000). The earliest, P1, is rimmed and replaced by P2, whereas P3 fluorite replaces and forms the matrix to P1 and P2 fluorite and other minerals. Williams-Jones *et al.* (2000) proposed that the mineralization formed as a result of the progressive mixing of magmatic fluids with formation waters.

Rock Canyon Creek, British Columbia

The Rock Canyon Creek rare-element mineralization in southeastern British Columbia has been described by Pell & Hora (1987), and Samson *et al.* (2000, 2001). Fluorite–*REE* mineralization occurs mainly as an elongate, approximately strata-parallel zone hosted by limestone and dolomite predominantly of Ordovician and Devonian age. Mineralization comprises early, fine-grained, patchy disseminated fluorite and later vein and breccia-matrix fluorite (Samson *et al.* 2001). *REE* minerals (mostly synchysite and parisite) are associated with the early, disseminated fluorite. Barite, quartz, carbonate, pyrochlore and Nb-bearing rutile occur with the fluorite and *REE* minerals (Samson *et al.* 2001). Although a magmatic association has not been documented in the field, the geochemical, mineralogical and isotopic character of the deposit indicates fluid derivation from alkaline magma (Pell & Hora 1987, Samson *et al.* 2001). Precipitation of the disseminated fluorite–*REE* mineralization is considered to have resulted from interaction of F- and *REE*-bearing hydrothermal fluids with carbonate wallrocks (Samson *et al.* 2001). Samples of early purple disseminated fluorite and later yellow and purple, zoned breccia-matrix and vein fluorite were included in this study.

South Platte, Colorado

The South Platte district rare-element mineralization in central Colorado has been described by Simmons & Heinrich (1980), Simmons *et al.* (1987) and Levasseur (1997). The mineralization occurs within concentrically zoned, *REE*–F–Y–Nb–U-enriched granitic pegmatites hosted by the Proterozoic, anorogenic Pikes Peak granitic batholith (Hedge 1970, Simmons & Heinrich 1970, 1980, Simmons *et al.* 1987). Some of the zoned pegmatites contain secondary hydrothermal replacement minerals that include fluorite (Simmons & Heinrich 1970, 1980, Brewster 1986). Six varieties of fluorite have been identified: primary (magmatic) green, and secondary (hydrothermal) purple, colorless, white, brown and gray (Simmons & Heinrich 1980). The deposits occur entirely within, and are genetically linked to, the host granitic batholith. Levasseur (1997) and Levasseur & Samson (1996) interpreted the *REE* in the hydrothermal fluorite to have been leached from the primary green fluorite by magmatic solutions. Samples of green, purple, colorless and white fluorite included in this study were obtained from the White Cloud and Oregon 3 pegmatites.

St. Lawrence, Newfoundland

The St. Lawrence fluorspar deposits in southeastern Newfoundland have been described by Van Alstine (1948), Strong *et al*. (1984) and Collins & Strong (1988). The deposits comprise fluorite veins that mostly occur within the Lower Carboniferous St. Lawrence granitic pluton and related porphyry dikes, but which also extend into the country rocks. The veins are genetically linked to the granitic pluton and formed as open-space fillings in tension fractures caused by cooling of the granite (Van Alstine 1948). Fluorite is the predominant mineral in the veins and has well-developed colored growth-zones (Strong *et al.* 1984). Quartz, calcite, minor chalcopyrite, sphalerite, galena, and rare barite also occur within the veins. Strong *et al.* (1984) and Collins & Strong (1988) presented genetic models in which fluorite deposition occurred as a result of cooling or boiling of fluid, or mixing of formation water with magmatic fluid. Samples of fluorite included in this study were obtained from the Iron Springs, Grebe's Nest and Lawn Barite veins. The Iron Springs vein is located within the St. Lawrence granite, and the Grebe's Nest and Lawn Barite veins are located within a granitic dike and the country rocks to the St. Lawrence granite, respectively (Strong *et al.* 1984, Collins & Strong 1988). A summary of the sample locations and the types of fluorite studied is provided in Table 1.

LA–ICP–MS ANALYSIS

Analysis of fluorite samples from Gallinas Mountains, Rock Canyon Creek, South Platte and the majority of the fluorite samples from St. Lawrence was conducted at the LA–ICP–MS facility in the Great Lakes Institute for Environmental Research at the University of Windsor. Some of the St. Lawrence fluorite samples were analyzed at the LA–ICP–MS facility in the Department of Earth Sciences at Memorial University of Newfoundland. Both facilities are equipped with solid-state, 266 nm Nd-doped yttrium aluminum garnet (Nd–YAG) pulsed lasers. Analyses were performed on doubly-polished wafers bonded to glass slides, and all samples were cleaned prior to analysis by washing with distilled, deionized water and ethanol. Sample ablation was conducted within an argon-filled sampling cell mounted to the stage of a conventional polarizing microscope. The ablated material was transported from the ablation cell to the ICP–MS in argon as the carrier gas. Laser-sampling locations on individual grains of fluorite were selected to minimize the possibility of encountering solid or liquid inclusions. Sampling locations included single spots for samples that exhibited a relatively high degree of visual heterogeneity, such as multiple generations of fluorite (Gallinas Mountains) or growth bands (St. Lawrence, Rock Canyon Creek), and traverses for samples that appeared relatively homogeneous (South Platte and St. Lawrence). Photomicrographs of typical laser-ablation pits and traverses in fluorite from St. Lawrence are provided in Figure 1.

Fluorite analyses conducted at the University of Windsor were performed using a ThermoElemental PlasmaQuad–3 ICP–MS instrument, and those at Memorial University were performed using a Sciex ICP–MS instrument. The fluorite samples were analyzed for most or all of the *REE* as well as several other elements. Calibration of the ICP–MS was accomplished using NIST glass standards 610 and 612. The conversion of the ICP–MS output data (counts/second) to concentration units (μg/g) was accomplished using the LAMTRACE program developed by S.E. Jackson (van

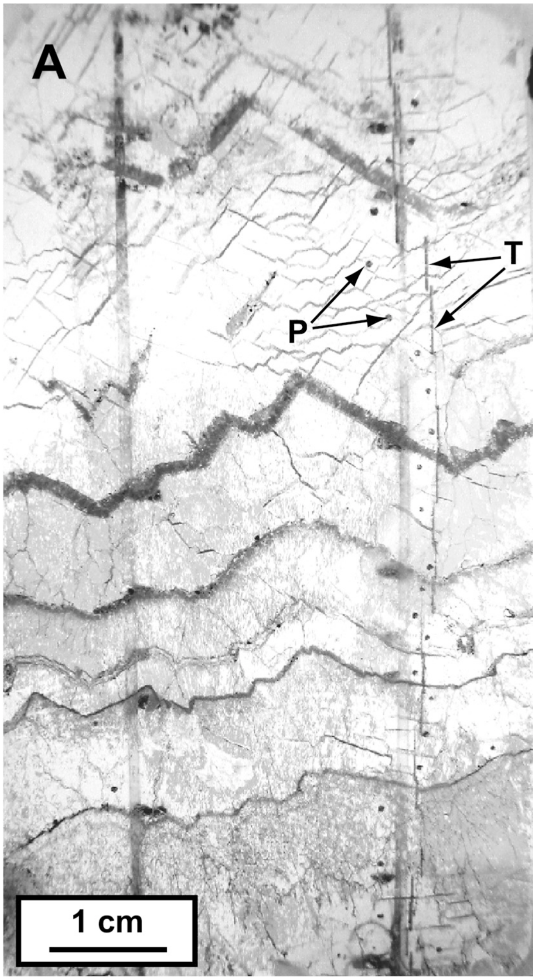

FIG. 1A. Photomicrograph of a thin section of Grebe's Nest vein fluorite from St. Lawrence, Newfoundland showing well-developed parallel growth-bands, laser-ablation pits (P) and traverses (T).

Achterbergh *et al.* 2001). The stoichiometric proportion of Ca in ideal fluorite was used as an internal standard for the calculation of the trace-element abundances. This choice is reasonable, considering that in most cases fluorite comprises over 99% CaF_2 (Deer *et al.* 1992). Elements that readily substitute for Ca (Ce, Sr, and Y) were sought and generally found to occur at total concentrations of less than approximately 0.4 wt.% in our samples. A summary of the equipment specifications and general instrument-operation conditions used during analysis of the fluorite samples is provided in Table 2. An example of time-resolved spectra obtained from green fluorite from South Platte is provided in Figure 2; the plot shows that several elements were detected at significant and relatively uniform count-rates, indicating the presence of these elements within the structure and not as small solid or liquid inclusions within the grains.

ANALYTICAL RESULTS

The results of the LA–ICP–MS analyses are summarized in Tables 3 through 6. Reported in the tables are the types of fluorite analyzed, the average abundance of elements present (reported as μg/g) in concentrations above the detection limits of the analytical method, and the number of analyses performed (*n*). Included in Table 3 is the average composition of the quartz syenite associated with the Gallinas Mountains fluorite–*REE* mineralization, calculated from data presented by Schreiner (1993). Included in Table 5 is the average composition of the Pike's Peak granite associated with the fluorite–*REE* mineralization, calculated from data presented by Smith *et al.* (1999). Included in Table 6 is the average composition of the St. Lawrence granite associated with the fluorite–*REE* mineralization, calculated from previously unpublished data collected by B.J. Fryer.

TABLE 1. THE VARIETIES OF FLUORITE IN THE FOUR DEPOSITS

Deposit	Magmatic fluorite	Hydrothermal fluorite
Alkaline-suite-associated deposits		
Gallinas Mountains	- -	P1 → P2 → P3*
Rock Canyon Creek	- -	Disseminated → Vein and Breccia* Replacement
Granite-associated deposits		
South Platte	Green	Purple and white → Colorless*
St. Lawrence	- -	Grebe's Nest, Iron Springs, Lawn Barite

* Arranged in order of paragenesis.

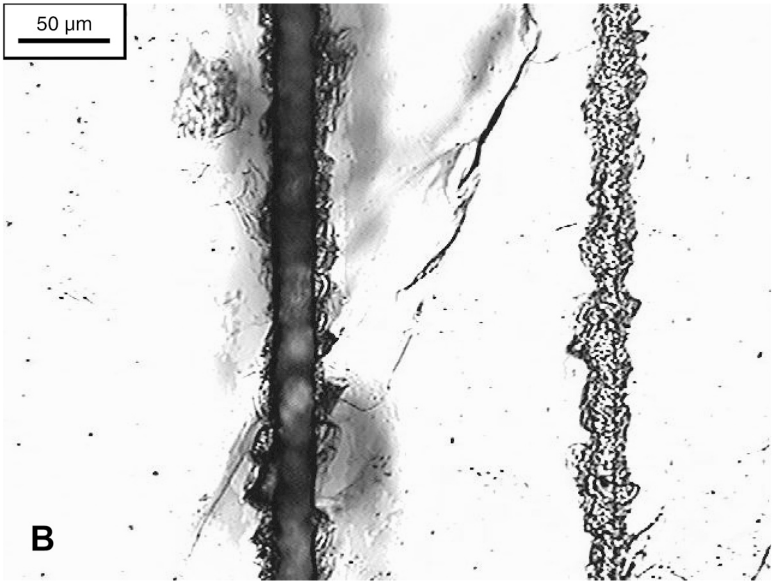

FIG. 1B. Photomicrograph of typical laser traverses in Grebe's Nest vein fluorite. The photomicrograph illustrates how the ablation characteristics of fluorite can be modified by adjusting laser energy. The traverse on the right shows poor ablation-characteristics obtained at low power (5 mJ). The traverse on the left shows good ablation-characteristics obtained at higher power (20 mJ).

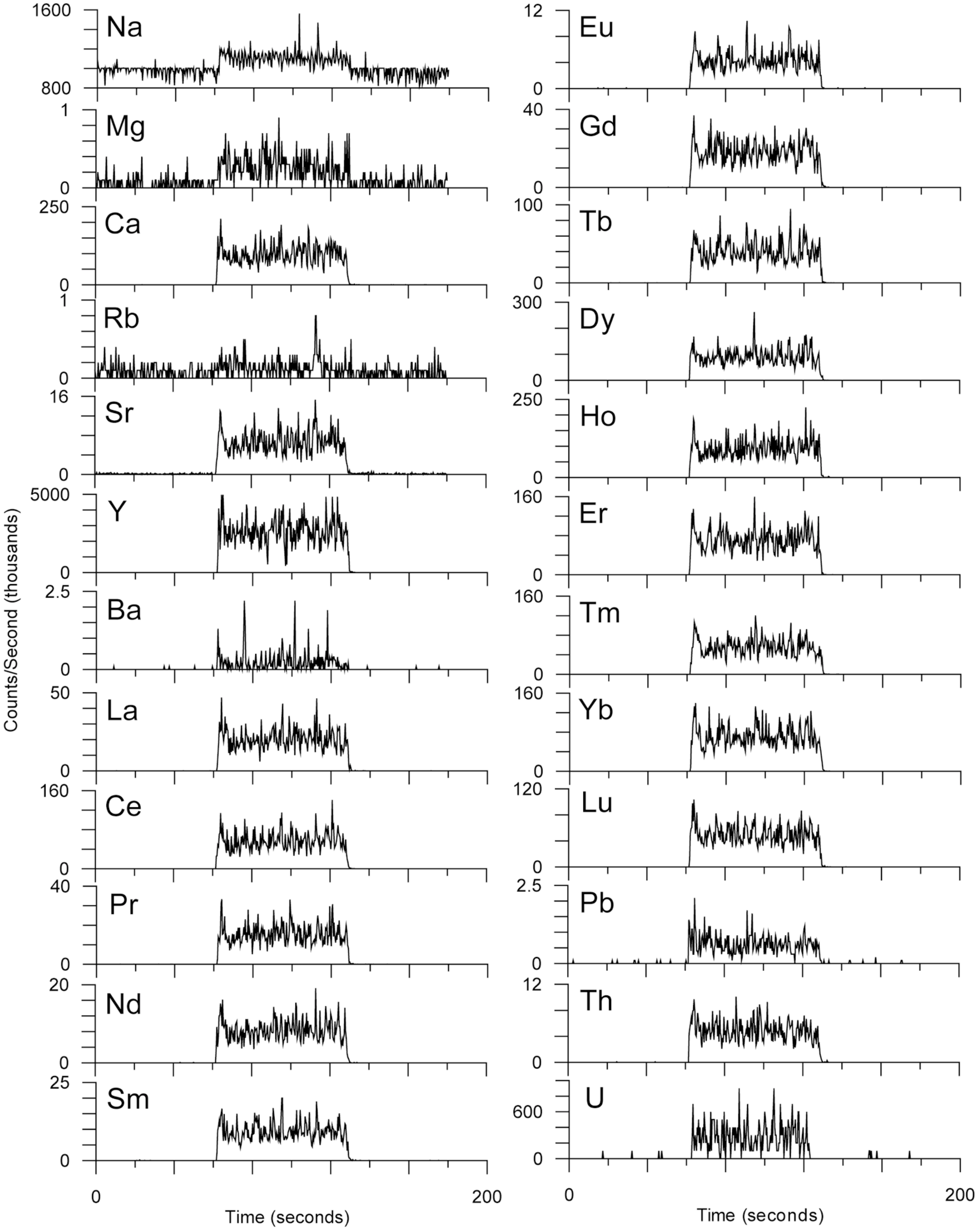

FIG. 2. An example of time-resolved ICP–MS spectra obtained from green fluorite from the South Platte District. In addition to the elements presented in the figure, Si, K, Cu, Zn and Nb were also sought, but were found to be below the lower limit of detection.

SPATIAL AND PARAGENETIC CHANGES IN FLUORITE COMPOSITIONS

Gallinas Mountain

As a result of petrographic analysis of the Gallinas Mountains fluorite–*REE* mineralization, Williams-Jones *et al.* (2000) determined that the sequence of fluorite precipitation was P1, then P2 and, finally, P3. These authors postulated that early in the evolution of the hydrothermal system, the magma that produced the quartz syenite, or a related magma at depth, was the dominant source of fluid. Figure 3A presents the average compositions of P1, P2 and P3 fluorite relative to the average composition of the quartz syenite, based on published data for the syenite from Schreiner (1993). The average compositions of the three generations of fluorite differ from each other and from the quartz syenite. Crystals of P1 fluorite have similar Sr and heavy *REE* (*HREE*), five

TABLE 2. SUMMARY OF INSTRUMENT CONDITIONS

Laser-sampling system		**ICP–MS system**	
Manufacturer	Continuum	Manufacturer	ThermoElemental
Model	Surelite I	Model	PQ3
Wavelength	266 nm	Mode	Peak-jumping
Energy	20 mJ	Dwell time/Isotope	10 ms
Mode	Q-switched	Average sensitivity (solution mode)	200,000,000 counts/s/ppm
Repetition rate	20 Hz		
Pulsewidth	4 to 6 ns	Scan time	150 to 400 ms/scan
Laser-spot diameter	10 to 15 µm		

TABLE 3. SUMMARY OF ANALYTICAL RESULTS ON FLUORITE FROM GALLINAS MOUNTAINS, NEW MEXICO, COMPARED WITH THOSE ON SYENITE

Element	Fluorite P1 $n = 9$	Fluorite P2 $n = 11$	Fluorite P3 $n = 12$	Syenite* $n = 11$
Na µg/g	1380	5270	2740	60700
Mg	10	80	680	500
Si	1070	12220	10200	307500
K	100	170	170	24700
Mn	20	220	1060	0.09
Cu	6.0	6.0	669	9.7
Zn	1.7	4.1	194	29.8
Rb	0.4	0.5	0.7	N.a.
Sr	243	698	2930	194
Y	179	676	2620	58.9
Nb	0.1	1.6	32.2	142
Ba	5.4	1480	10400	1190
La	73	5510	55100	137
Ce	68	4720	45300	214
Pr	5.9	478	4760	< D.L.
Nd	26	1350	13500	58.6
Sm	4.4	140	1070	9.8
Eu	1.2	32.6	264	2.1
Tb	0.8	14.7	95.7	0.7
Dy	4.8	65.8	613	3.0
Ho	1.3	14.1	75.5	1.0
Er	4.2	41.1	209	< D.L.
Tm	0.6	6.3	50.5	< D.L.
Yb	3.4	38	193	5.2
Lu	0.4	4.2	16.4	0.7
Pb	141	605	9110	63.4
Th	0.2	17.2	768	62.3
U	0.3	39.0	344	9.8

< D.L.: concentration below detection limit of the analytical method. N.a.: Sample was not analyzed for this element. * Source: Schreiner (1993).

TABLE 4. SUMMARY OF ANALYTICAL RESULTS ON FLUORITE FROM ROCK CANYON CREEK, BRITISH COLUMBIA

Element	Dissem. fluorite $n = 19$	Vein* fluorite $n = 44$	Element	Dissem. fluorite $n = 19$	Vein* fluorite $n = 44$
Na µg/g	420	390	Nd	3660	83
Mg	4280	680	Sm	117	31.7
Si	1520	1150	Eu	27.5	16.1
K	20	20	Tb	7.8	13.6
Cu	4.6	4.2	Dy	22.5	111
Zn	5.6	11.2	Ho	4.5	23.9
Rb	0.1	0.2	Er	12.5	65.8
Sr	627	648	Tm	2.3	10.4
Y	211	469	Yb	17.0	64.1
Nb	18.1	0.8	Lu	2.4	8.7
Ba	2650	29.4	Pb	6.4	11.8
La	25400	51.7	Th	673	1880
Ce	19200	116	U	0.2	0.7
Pr	1620	17.7			

Dissem.: disseminated. Vein*: vein or breccia.

TABLE 5. SUMMARY OF ANALYTICAL RESULTS ON FLUORITE FROM SOUTH PLATTE, COLORADO, COMPARED WITH THOSE ON GRANITE

Element	Green fluorite $n = 4$	White fluorite $n = 7$	Purple fluorite $n = 6$	Colorless fluorite $n = 9$	Granite* n = 7
Na µg/g	1640	4110	1940	1870	24100
Mg	20	250	220	30	1400
Si	1910	410	890	360	336100
K	10	220	210	20	45900
Cu	0.7	1.8	9.5	1.2	N.a.
Zn	0.3	3.6	2.9	1	90
Rb	0.2	0.6	0.3	0.3	214
Sr	169	45.2	149	208	85.5
Y	8320	2330	993	9770	81.7
Nb	0.1	13.5	10.2	0.1	21.5
Ba	3.9	4.7	4.8	3.2	659.3
La	141	719	104	220	166.5
Ce	232	851	116	370	312.3
Pr	42.9	157	22.5	66	N.a.
Nd	253	499	103	398	133.6
Sm	139	202	42.0	218	23.4
Eu	16.6	5.5	3.9	22.8	1.8
Tb	90.5	32.0	21.7	123	2.6
Dy	693	194	53.8	1010	N.a.
Ho	206	54.9	48.8	247	N.a.
Er	675	203	165	796	N.a.
Tm	97.4	22.2	8.5	144	N.a.
Yb	820	370	208	998	9.0
Lu	114	49.6	28.4	139	1.4
Pb	1.9	11.3	4.2	4.7	N.a.
Th	43.3	258	122	99.1	N.a.
U	0.7	12.8	1.2	0.8	3.3

N.a.: sample was not analyzed for this element. * Source: Smith *et al.* (1999).

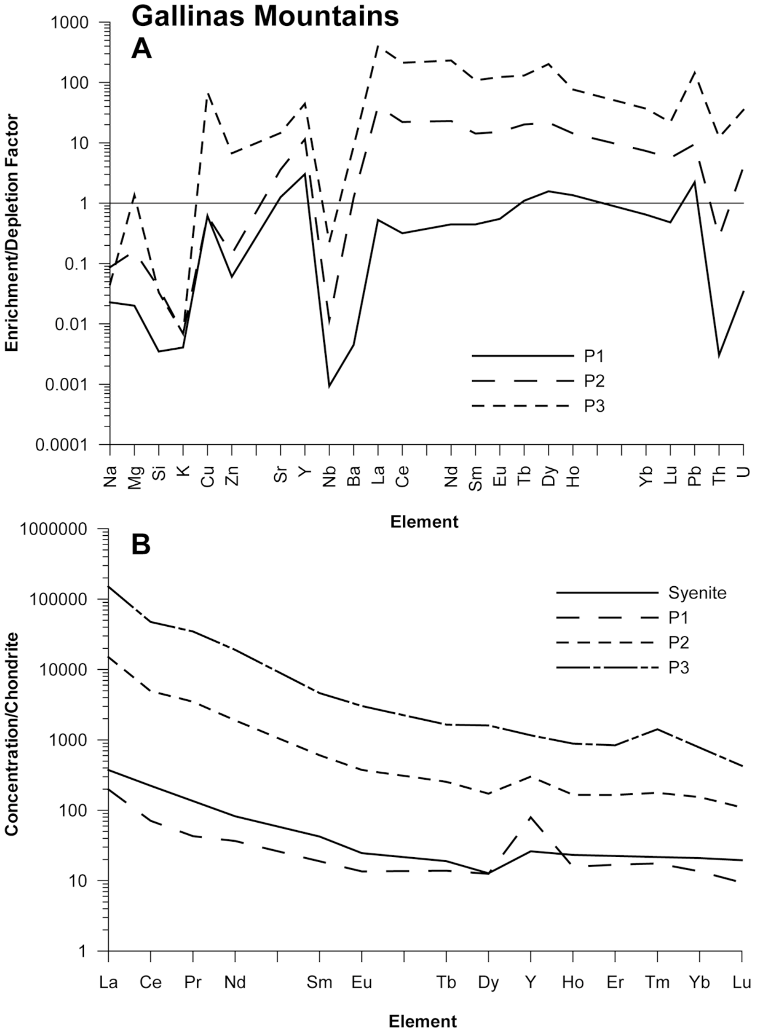

FIG. 3. A. Element enrichment or depletion factors for fluorite P1, P2 and P3 from Gallinas Mountains relative to quartz syenite. These factors are calculated by dividing the average concentration of an element in the fluorite by its average concentration in quartz syenite (Schreiner 1993), and represent the degree of enrichment or depletion of elements in the P1, P2 and P3 fluorite types relative to the quartz syenite. B. Chondrite-normalized *REE* patterns for Gallinas Mountains quartz syenite and fluorite. P1 fluorite has *REE* concentrations and chondrite-normalized *REE* pattern similar to those of the associated syenite. P2 and P3 fluorite have significantly higher *REE* concentrations and are more *LREE*-enriched than P1 fluorite. P1 fluorite has a well-developed, positive Y anomaly, in P2 fluorite, the anomaly is less well-developed, and in P3 fluorite there is no anomaly.

to one thousand times lower Na, Mg, Si, K, Cu, Zn, Nb, Ba, light *REE* (*LREE*), Th and U, and two to three times higher Y and Pb concentrations than the quartz syenite. Crystals of P2 fluorite have five to over one hundred times lower Na, Mg, Si, K, Cu, Zn, Nb and Th and four to forty times higher Sr, Y, *REE*, Pb and U concentrations than the quartz syenite. Crystals of P2 and P3 fluorite have similar or higher concentrations of all of the elements analyzed relative to P1 and P2 fluorite, respectively. Although the relative enrichments and depletions of individual elements vary among the different types of fluorite, the shapes of the enrichment or depletion patterns generally are similar and parallel one another.

The Gallinas Mountains quartz syenite has a relatively flat chondrite-normalized *REE* pattern that is slightly *LREE*-enriched and has a slight, positive Y anomaly (Fig. 3B). Yttrium, which is similar in charge and ionic radius to Ho, has been included between Dy and Ho in the chondrite-normalized *REE* diagrams. P1 fluorite has a similar chondrite-normalized *REE* pattern and *REE* concentrations (particularly the *HREE*) to the quartz syenite, with a distinct, positive Y anomaly. Concentrations of the *REE* in the P1 fluorite and the quartz syenite vary between approximately ten to one hundred times chondrite. The concentrations of all *REE*, but particularly the *LREE*, are higher in P2 fluorite than in P1, and higher still in P3 fluorite. The pronounced positive Y anomaly displayed by P1 fluorite is less pronounced in P2, and absent in P3 fluorite. Concentrations of the *REE* are 10 to 100 times higher in P2 fluorite than in P1 fluorite (approximately 100 to 1,000 times chondrite) and are 10 to 1,000 times higher for P3 fluorite relative to P1 fluorite (approximately 10^2 to 10^5 times chondrite). Unlike the quartz syenite, the chondrite-normalized *REE* patterns for P1, P2 and P3 fluorite all have a slight negative Ce anomaly.

TABLE 6. SUMMARY OF ANALYTICAL RESULTS ON FLUORITE FROM ST. LAWRENCE, NEWFOUNDLAND, COMPARED WITH THOSE ON GRANITE

Element	Grebe's Nest fluorite $n = 48$	Iron Springs fluorite $n = 12$	Lawn Barite fluorite $n = 13$	Granite $n = 2$
Mg µg/g	20	10	N.a.	1030
Si	1000	840	N.a.	361300
Cu	4.6	1030	N.a.	< D.L.
Zn	153	1950	N.a.	29
Rb	0.6	1.7	N.a.	218
Sr	56.1	67.2	184	41.4
Y	2060	3570	1120	68.3
Nb	0.1	0.8	N.a.	55.5
Ba	13.6	6.3	150	40.7
La	21.6	9.7	25.6	45.6
Ce	30.9	15.9	60.9	95.8
Pr	2.7	2.8	9.4	12.0
Nd	44.0	13.2	48.6	45.2
Sm	13.7	7.7	23.0	11.3
Eu	2.0	0.5	3.2	0.2
Tb	1.4	5.0	7.9	1.9
Dy	26.5	36.6	60.0	12.3
Ho	2.0	9.3	12.9	2.6
Er	16.1	24.4	35.8	7.6
Tm	0.6	3.5	4.4	1.2
Yb	11.0	19.1	23.4	7.4
Lu	0.5	2.4	2.2	1.1
Pb	24.0	731	2360	39
Th	0.1	0.1	0.4	19.1
U	0.1	16.6	< D.L.	7

< D.L.: Concentration below detection limit analytical method. N.a.: Sample was not analyzed for this element.

Rock Canyon Creek

In a study of the Rock Canyon Creek fluorite–*REE* mineralization, Samson *et al.* (2001) determined that disseminated fluorite precipitated prior to breccia and vein fluorite. In Figure 4A, we present the average compositions of breccia and vein fluorite relative to disseminated fluorite. The two generations of fluorite have very different average compositions. Relative to disseminated fluorite, breccia and vein fluorite have similar Na, Si, K, Cu, Rb, and Sr, approximately two to seven times higher Zn, Y, *HREE*, Pb, Th, and U, and approximately five to five hundred times lower Mg, Nb, Ba, and *LREE* concentrations.

Disseminated fluorite from Rock Canyon Creek has chondrite-normalized *REE* patterns that are *LREE*-enriched and are approximately ten to one hundred times chondrite (Fig. 4B). The chondrite-normalized *REE* pattern for disseminated fluorite has a slight negative Ce anomaly and positive Y anomaly. Fluorite in the breccia and vein fluorite at Rock Canyon Creek have a flat chondrite-normalized *REE* pattern that is slightly *LREE*-depleted, with a slight negative Y anomaly. Concentrations of the *REE* within breccia and vein fluorite vary between approximately 100 and 300 times chondrite.

South Platte District

In light of petrographic analysis of the South Platte District granitic pegmatites, Levasseur & Samson (1996) and Levasseur (1997) showed that colorless, purple, and white hydrothermal varieties of fluorite replace primary green magmatic fluorite. In Figure 5A, we present the average composition of green, colorless, white and purple fluorite relative to the average composition of the associated Pike's Peak granite, based on published data for the granite taken from Smith *et al.* (1999). Because the fluorite–*REE* mineralization is contained within pegmatites hosted by the granite, the granite is the most likely source of the fluids from which the hydrothermal fluorite precipitated. The average composition of the magmatic and hydrothermal fluorite are significantly different from the host granite, but exhibit similar patterns of enrichment and depletion relative to it. Relative to the average composition of the granite, crystals of primary magmatic and hydrothermal fluorite have similar levels of Sr, La, Ce and U, approximately 10 to 1000 times lower Mg, Si, Zn, Rb, Nb and Ba, and approximately five to 100 times higher Y, Nd, Sm, Eu, Tb, Yb and Lu concentrations. The average composition of the green fluorite is very similar to that of the colorless fluorite, whereas purple and white fluorite display greater compositional variability, compared to green and colorless fluorite.

Relative to magmatic and hydrothermal fluorite, the South Platte District granite has generally lower *REE* abundances and a *LREE*-enriched chondrite-normalized pattern that lacks a negative Ce anomaly, and has negative Eu and Y anomalies (Fig. 5B). Green and colorless generations of fluorite have relatively flat, *HREE*-enriched chondrite-normalized *REE* patterns, with negative Ce and Eu anomalies, a positive Y anomaly, and *REE* concentrations between 500 and 4000 times chondrite. The similarity between the composition of green and colorless fluorite suggests that the colorless fluorite may be altered, relict green fluorite. In general, purple and white generations of hydrothermal fluorite exhibit chondrite-normalized *REE* patterns that are similar to those of green and colorless fluorite, but have *REE* concentrations that are up to 100 times lower, with purple fluorite having the lowest *REE* concentrations (Fig. 5B). White fluorite exhibits a positive Y anomaly, rather than the slight negative Y anomaly exhibited by purple fluorite. With the exception of a few elements (*e.g.*, Y), chondrite-normalized *REE* patterns suggest that replace-

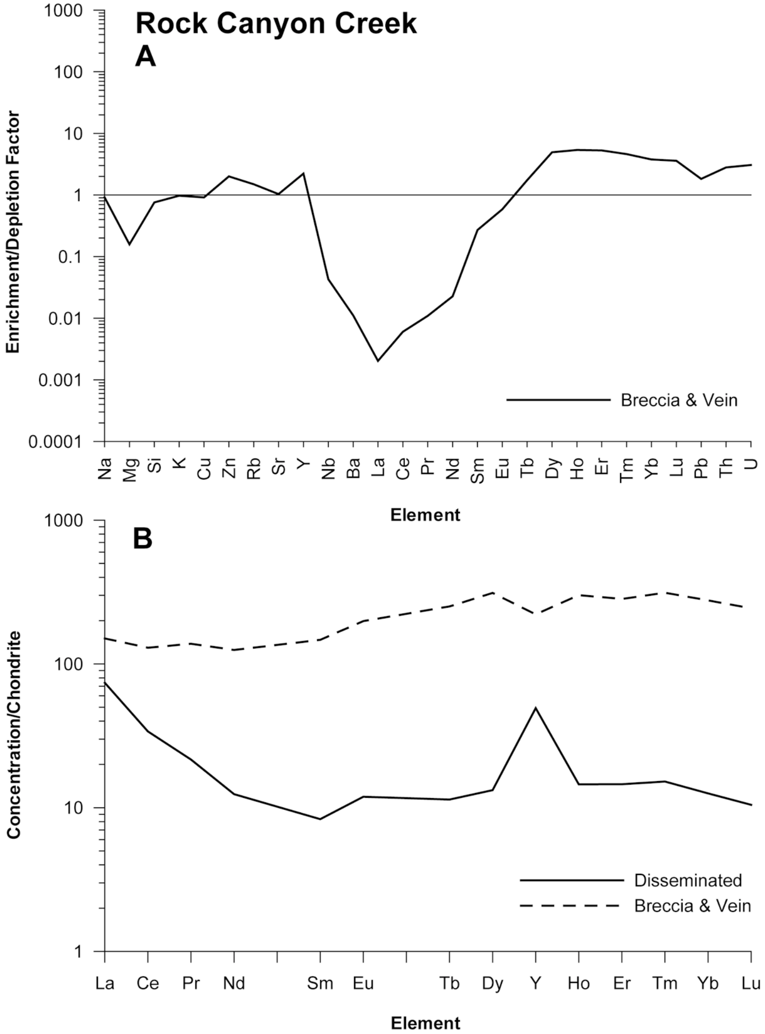

FIG. 4. A. Element enrichment or depletion factors for fluorite in breccias and veins from Rock Canyon Creek relative to disseminated fluorite. These factors are calculated by dividing the average concentration of an element in the breccia and vein fluorite by its average concentration in the disseminated fluorite. B. Chondrite-normalized *REE* patterns for Rock Canyon Creek fluorite. Disseminated fluorite has a slightly *LREE*-enriched pattern with a positive Y anomaly, and breccia and vein fluorite have a flat *REE* pattern with a slight negative Y anomaly.

ment of green fluorite by purple and white fluorite simply resulted in lower concentrations of the *REE* in the replacement fluorite, without significant inter-element fractionation. The similarities in chondrite-normalized *REE* patterns suggest that the composition of the primary fluorite was the predominant control on the compositions of later, hydrothermal fluorite.

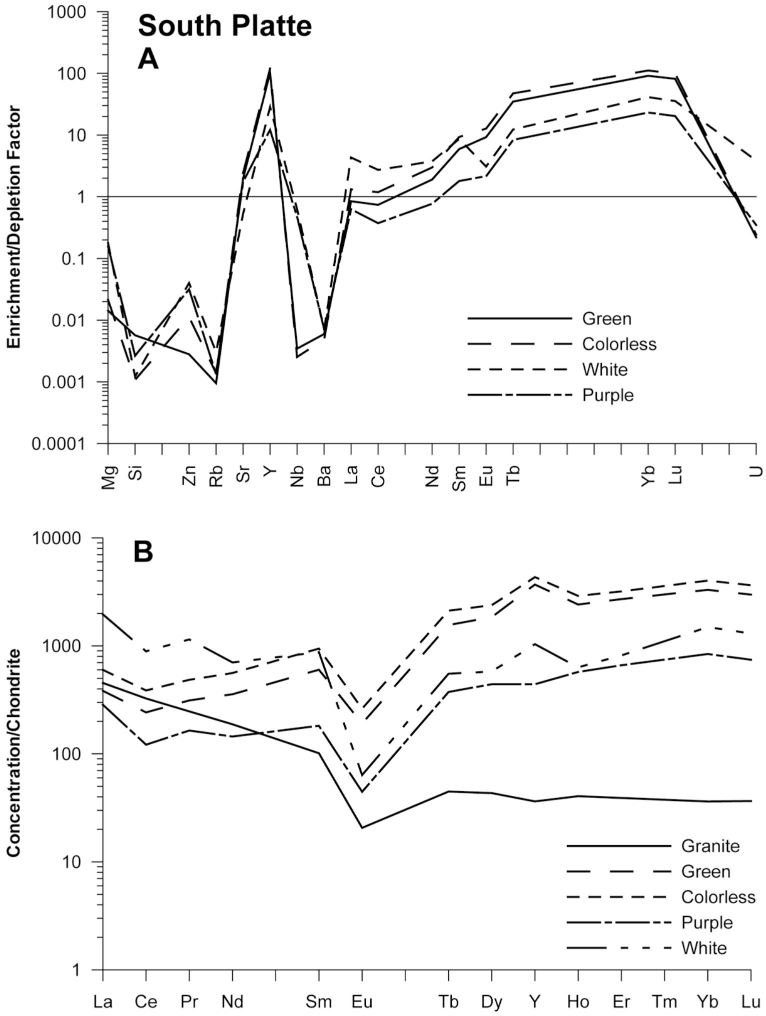

FIG. 5. A. Element enrichment or depletion factors for pegmatite-hosted, magmatic, green and hydrothermal, colorless, purple and white fluorite from the South Platte District relative to the Pikes Peak granite (Smith *et al.* 1999). All types of fluorite show generally similar patterns of elemental enrichment and depletion relative to the associated granite. B. Chondrite-normalized *REE* patterns for fluorite and granite from the South Platte District. The granite has a *LREE*-enriched pattern with a negative Eu anomaly. *REE* patterns and concentrations in colorless, hydrothermal fluorite are identical to those of green, magmatic fluorite. Purple and white hydrothermal fluorite generally have similar *REE* patterns but significantly lower *REE* concentrations than green fluorite. All varieties of fluorite have a negative Eu anomaly. Green and colorless fluorite have a slight negative Y anomaly, whereas purple and white fluorite have a variable, but typically positive Y anomaly.

St. Lawrence

Strong *et al.* (1984) concluded that the St. Lawrence fluorite veins were formed from hydrothermal fluids that were exsolved from the St. Lawrence granite. The veins occur both in the granite (Iron Springs and Grebe's Nest veins) and in the host rocks to the granite (Lawn Barite vein). The occurrence of the fluorite veins within and outside of the granite enables examination of potential large-scale spatial variations in fluorite composition. Figure 6A presents the average composition of fluorite from the Iron Springs, Grebe's Nest and Lawn Barite

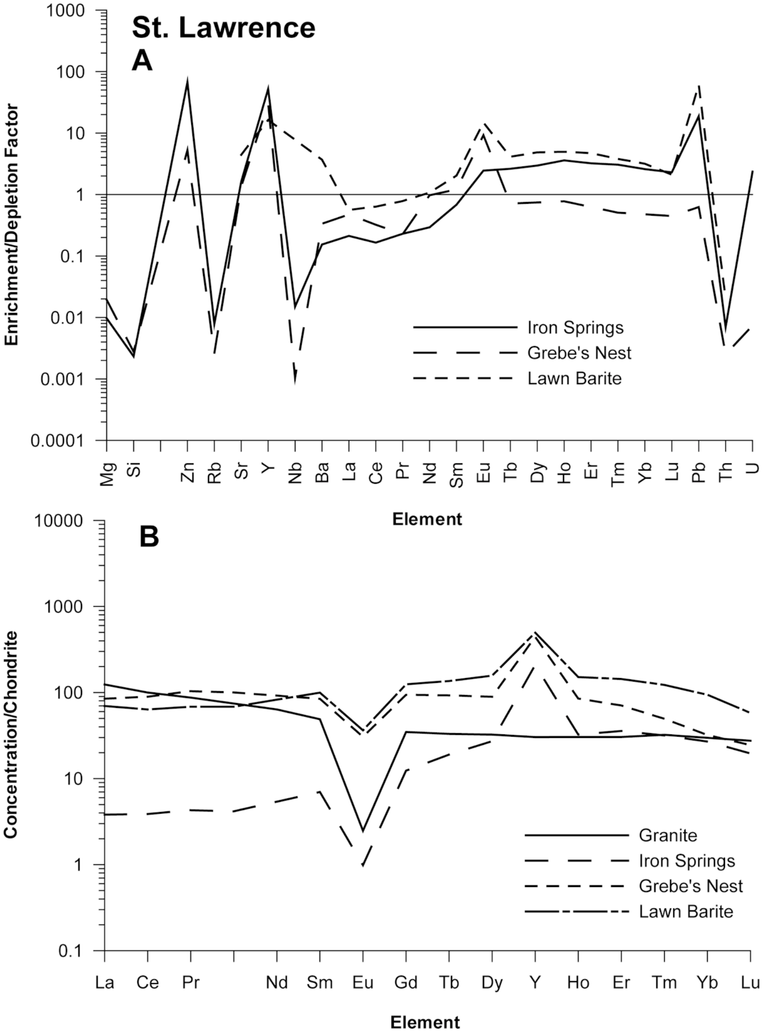

FIG. 6. A. Element enrichment or depletion factors, relative to the St. Lawrence granite, for St. Lawrence Grebe's Nest and Lawn Barite vein fluorite, which occur externally to the granite, and Iron Springs vein fluorite, which is hosted by the granite. All types of fluorite show generally similar patterns of element enrichment and depletion relative to the granite. B. Chondrite-normalized *REE* patterns for St. Lawrence fluorite. Granite-hosted (Iron Springs vein) fluorite has a relatively *LREE*-depleted pattern relative to country-rock-hosted (Grebe's Nest and Lawn Barite veins) fluorite and the granite. The St. Lawrence granite and all varieties of fluorite have a well-developed negative Eu anomaly, and the fluorite has a positive Y anomaly.

veins relative to the average composition of the associated St. Lawrence granite. Relative to the granite, fluorite from those veins generally exhibit similar patterns of elemental enrichment and depletion; crystals of vein fluorite have similar Sr and *REE*, approximately 10 to 1000 times lower Mg, Si, Rb, Nb, Ba and Th, and approximately 10 to 100 times higher Zn, Y, and Eu concentrations. Notable exceptions are Ba, Pb and U. Relative to the granite, Ba is enriched in the Lawn Barite fluorite and depleted in Iron Springs and Grebe's Nest fluorite, Pb is enriched in the Iron Springs and Grebe's Nest fluorite and depleted in Lawn Barite fluorite, and U is enriched in Iron Springs fluorite and depleted in Lawn Barite fluorite. Although the granite has been interpreted to be the source of the hydrothermal fluids and *REE* (Strong *et al.* 1984), veins outside of the granite (*e.g.*, Lawn Barite) have higher average *REE* concentrations than veins within the granite (*e.g.*, Iron Springs). The former are also more *LREE*-enriched than the latter.

In the St. Lawrence granite, *REE* concentrations are between two and one hundred times chondrite, with a chondrite-normalized *REE* pattern that is relatively flat and slightly *LREE*-enriched (Fig. 6B). Fluorite from the Grebe's Nest and Lawn Barite veins has *REE* concentrations between 10 and 1000 times chondrite and relatively flat chondrite-normalized *REE* patterns. Relative to fluorite from the Lawn Barite and Grebe's Nest veins, fluorite from Lawn Barite veins has lower *LREE* concentrations and similar *HREE* concentrations. The chondrite-normalized *REE* patterns for the granite and fluorite all have negative Eu anomalies; only the fluorite has a positive Y anomaly, however.

Fluorite Composition as an Indicator of Geological Affinity

Fluorite from Gallinas Mountains and Rock Canyon Creek, which are associated with alkaline magmatism, are characterized by relatively flat to *LREE*-enriched chondrite-normalized *REE* patterns that lack a Eu anomaly and may or may not show a slight negative Ce anomaly, or slight positive Y anomaly. In the case of Gallinas Mountains, the earliest generation of fluorite (P1) has *REE* abundances and a chondrite-normalized *REE* pattern similar to the associated quartz syenite. In contrast, fluorite from South Platte and St. Lawrence, which are associated with granitic magmatism, are characterized by relatively flat to *HREE*-enriched chondrite-normalized *REE* patterns that have a distinct negative Eu anomaly and a positive Y anomaly. In the case of St. Lawrence, the fluorite has *REE* abundances and chondrite-normalized *REE* patterns that are similar to those of the associated granite, although the granite lacks a positive Y anomaly. At South Platte, the fluorite exhibits *HREE*-enriched chondrite-normalized *REE* patterns that differ markedly from the *LREE*-enriched pattern of the associated granite. Although the absolute concentration of individual elements may vary, the patterns of elemental enrichment and depletion shown by all types of fluorite relative to the associated intrusive rocks are consistent within an individual deposit, regardless of whether the fluorite is primary, *i.e.*, magmatic or secondary and hydrothermal (*e.g.*, South Platte).

Elemental discriminant diagrams have been used in a variety of studies to interpret fluorite compositions, characterize and differentiate fluorite occurrences, and make inferences about the depositional environment and ore potential of individual fluorite deposits and mining districts (*e.g.*, Schneider *et al.* 1975, Möller *et al.* 1976, Eppinger & Closs 1990, Hill *et al.* 2000). Möller *et al.* (1976) used Tb/Ca and Tb/La values to discriminate fluorite occurrences according to their sedimentary, hydrothermal or pegmatitic affinities. Furthermore, they interpreted trends in Tb/Ca and Tb/La as resulting from progressive incorporation of *REE* into fluorite during hydrothermal precipitation, which they refer to as the crystallochemical trend, or from differences in the relative strength of fluorocomplexes, which they refer to as the remobilization trend. Below, we examine the composition of the fluorite analyzed in this study in terms of Tb/Ca and Tb/La values and the fields and trends defined by Möller *et al.* (1976). Use of a constant, stoichiometric abundance of Ca in ideal fluorite (presented as Ca*) as an internal standard for LA–ICP–MS analyses suggests that the use of the Tb/Ca* ratio may be inappropriate. However, varying the Ca* concentration by as much as 10% (±5% from the stoichiometric value), which is unreasonably large considering that the elements that readily substitute for Ca were generally found to occur at total concentrations less than approximately 0.5 wt.% in our samples, shows virtually no effect on the discriminant diagram. Variation in the Ca concentration of fluorite thus is not a relevant variable in discriminating the different occurrences of fluorite discussed here. Plotting Tb *versus* Tb/La would yield comparable results.

Most of the fluorite from Gallinas Mountains plots within the pegmatite field, and each type (P1, P2 and P3) occurs within a relatively well-defined population (Fig. 7A). The change in Tb/Ca* and Tb/La values defined by P1, P2 and P3 fluorite defines a progressive compositional evolution from relatively high Tb/La and low Tb/Ca* (P1 fluorite) to relatively low Tb/La and high Tb/Ca* (P3 fluorite). This evolutionary trend is approximately orthogonal to the crystallochemical trend and is in the opposite direction to the remobilization trend of Möller *et al.* (1976).

Fluorite from Rock Canyon Creek straddles the boundary between the pegmatite and hydrothermal fields (Fig. 7A). Disseminated fluorite plots in a relatively tight cluster, but the vein and breccia fluorite exhibits much greater compositional variation, however, and overlaps the field defined by the paragenetically earlier, disseminated fluorite. Some of the disseminated and vein and breccia fluorite define a compositional trend that parallels the boundary between the pegmatitic and hydrothermal fields and the crystallochemical trend of Möller *et al.* (1976). However, some of the late (vein and breccia) fluorite plots at lower Tb/La and Tb/Ca* values than the early (disseminated) fluorite, suggesting that the composition of some vein and breccia fluorite could be interpreted to define a compositional trend opposite to the crystallochemical trend proposed by Möller *et al.* (1976).

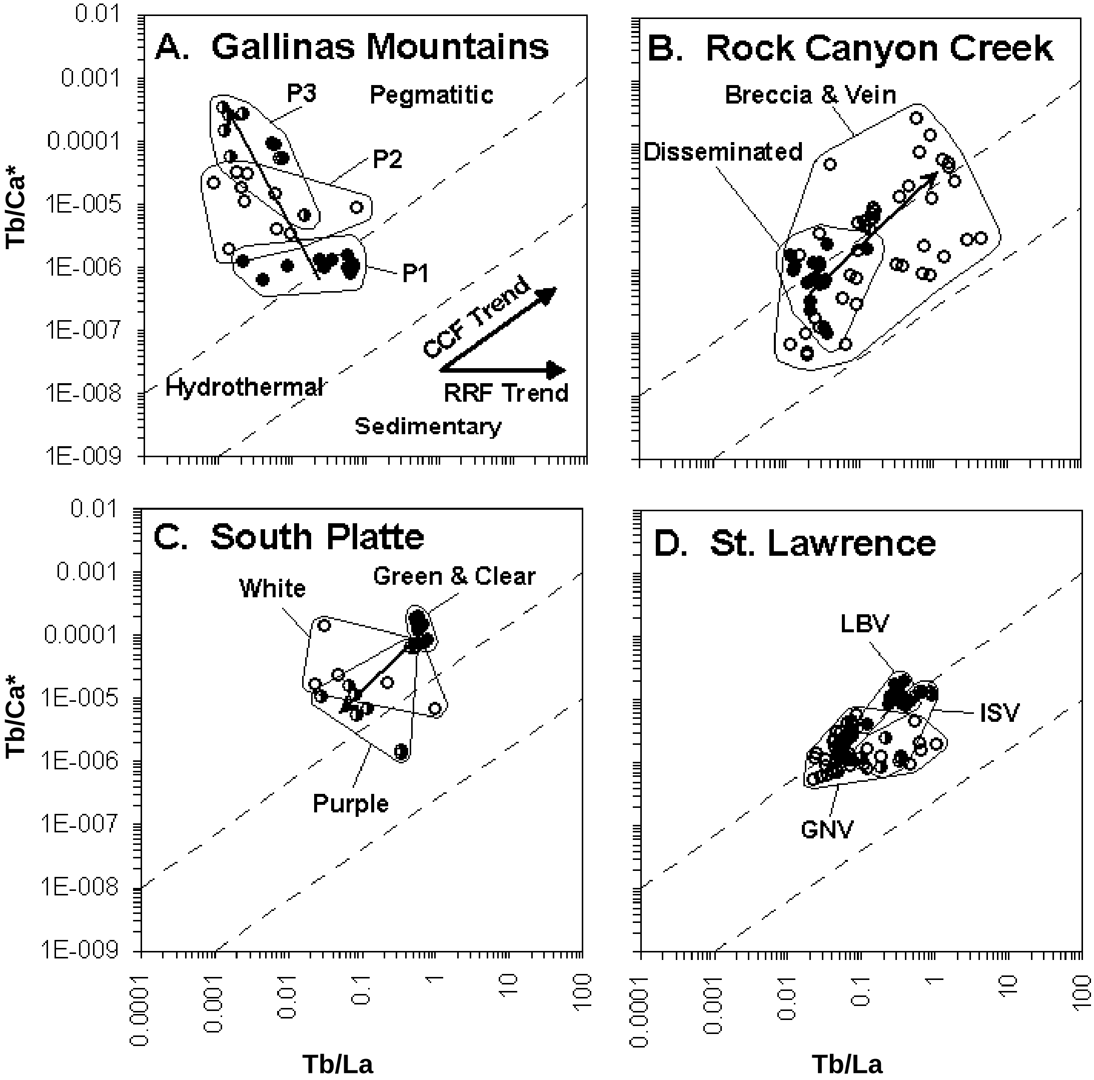

FIG. 7. Log Tb/Ca* and log Tb/La values in Gallinas Mountains (A), Rock Canyon Creek (B), South Platte (C), and St. Lawrence (D) fluorite. Fluorite from Gallinas Mountains and Rock Canyon Creek plot within the hydrothermal and pegmatitic fields of Möller *et al.* (1976). The compositional trends shown by Gallinas Mountains P1 to P2 to P3 and Rock Canyon Creek disseminated and vein and breccia fluorite are indicated by arrows. The compositional trend for Gallinas Mountains fluorite differs from the remobilization (RRF) and crystallochemical (CCF) trends of Möller *et al.* (1976). Fluorite from South Platte and St. Lawrence plot within the hydrothermal and pegmatitic fields of Möller *et al.* (1976). The compositional trend for South Platte green and colorless fluorite to purple and white fluorite is indicated by the arrow. The Iron Springs (ISV), Grebe's Nest (GNV), and Lawn Barite (LBV) veins at St. Lawrence are indicated by the circled fields. The compositional trend for South Platte fluorite also differs from the remobilization (RRF) and crystallochemical (CCF) trends of Möller *et al.* (1976).

The South Platte fluorite plots primarily within the pegmatite field, which is consistent with its occurrence within granite-hosted pegmatites (Fig. 7B). Purple and white fluorite, which replace the green fluorite, have lower Tb/Ca* and Tb/La values than green and colorless fluorite. The compositional range of magmatic and hydrothermal fluorite defines a trend similar in slope, but opposite in direction, to the crystallochemical trend of Möller *et al.* (1976).

Fluorite from the Grebe's Nest and Lawn Barite veins at St. Lawrence plots in a relatively tight cluster within the pegmatite field, whereas fluorite from the Iron Springs vein plots in the hydrothermal field (Fig. 7B). The array of data for fluorite from the Iron Springs vein crudely parallels the crystallochemical trend. In contrast, most of the fluorite from the Grebe's Nest and Lawn Barite veins plot in relatively tight clusters, and systematic trends in composition are not apparent.

Samples of green magmatic and colorless hydrothermal fluorite from South Platte plot entirely within the pegmatite field, as defined by Möller *et al.* (1976). The majority of South Platte purple and white, approximately half of Rock Canyon Creek, and all of Gallinas Mountains P2 and P3 hydrothermal fluorite plot within the pegmatitic field, rather than the hydrothermal field. At St. Lawrence, the granite-hosted Iron Springs vein fluorite plots within the hydrothermal field rather than the pegmatitic field. Therefore, Tb/Ca* and Tb/La values are not a reliable indicator of the geological affinity of hydrothermal fluorite.

The trends in Tb/Ca* and Tb/La values obtained in this study are more complex than can be explained by the crystallochemical and remobilization trends proposed by Möller *et al.* (1976). Trends in the composition of fluorite are opposite to (*e.g.*, South Platte) or inconsistent with (*e.g.*, Gallinas Mountains and St. Lawrence) the remobilization or crystallochemical trends. The controls on trends defined by Tb/Ca* and Tb/La values remain poorly understood.

FLUORITE COMPOSITION AS AN INDICATOR OF SOURCE OF THE HYDROTHERMAL FLUID

Both magmatic and formation waters have been identified from, or proposed to have been involved in, *REE*-bearing hydrothermal systems (*e.g.,* Strong *et al.* 1984, Norman *et al.* 1985, Banks *et al.* 1994, Salvi & Williams-Jones 1992, Palmer & Williams-Jones 1996, Williams-Jones *et al.* 2000, Samson *et al.* 2000). If the composition of fluorite within these deposits is unique to a particular type of ore-forming system (*e.g.*, granitic *versus* alkaline), then compositional data on fluorite from deposits of known affinity could potentially be used to make inferences about the genesis of *REE*-bearing deposits where the source of the hydrothermal fluid is poorly constrained. In the case of South Platte, Gallinas Mountains and St. Lawrence, the composition of green, P1 and Iron Springs vein fluorite, respectively, is considered most likely to represent crystallization from a magma or fluids of predominantly magmatic derivation on the basis of geological, textural and paragenetic relationships and the fluid-inclusion and isotopic data presented by Simmons & Heinrich (1970, 1980), Strong *et al.* (1984), Collins & Strong (1988), Levasseur (1997) and Williams-Jones *et al.* (2000). Such fluorite is characterized by relatively flat chondrite-normalized *REE* patterns that vary from slightly *LREE*-depleted (South Platte green fluorite and St. Lawrence Iron Springs vein fluorite) to slightly *LREE*-enriched, with a weakly to well-developed negative Eu anomaly, and a weakly to well-developed positive Y anomaly. Of these samples of "magmatic" fluorite, those associated with granitic magmatism are characterized by flat to *LREE*-depleted chondrite-normalized *REE* patterns that generally have distinct negative Eu and positive Y anomalies. The chondrite-normalized *REE* patterns of the associated granitic rocks have a distinct negative Eu anomaly but differ from the associated fluorite in being *LREE*-enriched and lacking a positive Y anomaly. The samples of "magmatic" fluorite closely associated with alkaline magmatism (Gallinas Mountains) are characterized by *LREE*-enriched chondrite-normalized *REE* patterns that lack a negative Eu anomaly and have a slight positive Y anomaly. The chondrite-normalized *REE* patterns of the associated alkaline rocks are very similar to the associated fluorite.

For the hydrothermal fluorite in general, distinct compositional differences exist between early- and late-formed fluorite. For example, early, P1 fluorite from Gallinas Mountains has relatively flat chondrite-normalized *REE* patterns with a well-developed positive Y anomaly, and late, P3 fluorite has *LREE*-enriched chondrite-normalized *REE* patterns without a positive Y anomaly. In contrast, the opposite evolutionary trend is observed between early, disseminated and late, breccia and vein fluorite at Rock Canyon Creek. The cause of the differences in the compositional trends of the fluorite is not known, and more comprehensive and systematic analyses of fluorite are required. In addition, other factors need to be evaluated for the deposits in question, including the effect of element partitioning into coprecipitated phases, information on melt/fluid partitioning (*e.g.*, *REE*), aqueous complexation at high temperatures, and fluid composition (*e.g.*, microthermometric and LA–ICP–MS analysis of fluid inclusions).

FLUORITE COMPOSITION AS AN INDICATOR OF EVOLUTION OF THE HYDROTHERMAL FLUID

Multiple generations of fluorite occur in the Gallinas Mountains, Rock Canyon Creek, South Platte, and St. Lawrence deposits (Simmons & Heinrich 1980, Strong *et al.* 1984, Williams-Jones *et al.* 2000, Samson *et al.* 2001). The composition of fluorite within these deposits varies with paragenetic position (Gallinas Mountains, Rock Canyon Creek, and South Platte) or with spatial distribution (St. Lawrence). Also, significant compositional variation occurs within optically homogeneous fluorite. Compared to magmatic fluorite, post-magmatic, hydrothermal fluorite within the South Platte pegmatites is generally characterized by higher concentrations of Mg, K, Cu, Zn, Pb, Th and U, and similar or lower concentrations of Si, Rb, Y, and Ba (Table 5). The variation in Na, Sr, Nb, *REE*, Th, U concentrations is less systematic, and chondrite-normalized *REE* patterns are similar between primary magmatic and hydrothermal, replacement fluorite. It is likely that in some systems, the coprecipitation of *REE*-rich minerals will locally affect fluid composition, and therefore the composition of coprecipitated fluorite (*cf.* Hill *et al.* 2000). In the South Platte District pegmatites, *REE*-bearing minerals (*e.g.*, bastnäsite and synchysite) were interpreted to be coprecipitated with the hydrothermal fluorite (Simmons & Heinrich 1970, 1980). However, fluorite compositions indicate that *REE* fractionation was minimal during replacement of the magmatic fluorite, suggesting that coprecipitation of *REE* minerals did not play a major role in changing the composition of the hydrothermal fluids. Furthermore, as noted above, the evolution in composition from early- to late-formed fluorite is opposite to the crystallochemical trend of Möller *et al.* (1976).

Evolutionary trends in fluorite composition within the South Platte District pegmatites (decreasing Sr, Ba, Y and *REE*) are opposite to trends observed in the Gallinas Mountains, Rock Canyon Creek and St. Lawrence fluorite (increasing Sr, Ba, Y and *REE*), where formation waters (*e.g.*, Strong *et al.* 1984, Williams-Jones *et al.* 2000) or wallrock interaction (*e.g.*, Samson *et al.* 2001) have been interpreted to play a significant role in the formation of the deposits. In addition to elemental enrichment, the compositional evolution of Gallinas Mountains, Rock Canyon Creek and St. Lawrence fluorite is accompanied by significant fractionation of the *REE* (see below). These different trends suggest that the compositional evolution of the South Platte fluorite occurred within a relatively closed system and resulted from factors other than changes in the composition of the hydrothermal fluid (*e.g.*, a reduction in temperature). The compositional variations observed in fluorite at South Platte supports the model proposed by Levasseur (1997) and Levasseur & Samson (1996), in which the composition of late-stage fluorite was controlled by the primary fluorite and not by introduction of fluids derived externally to the granite (*i.e.*, formation waters).

The difference in composition between early- and late-formed hydrothermal fluorite at Gallinas Mountains is generally characterized by higher concentrations of all elements except Cu and Zn for P2 relative to P1 fluorite, and Na, Si and K for P3 relative to P2 fluorite. The *LREE* show particularly significant enrichment from P1 to P2 to P3. Similar enrichment trends, representing spatial variations, occur within the St. Lawrence fluorite veins and are characterized by relatively higher concentrations of most elements within veins hosted by the country rocks (Grebe's Nest and Lawn Barite veins) compared with veins hosted by the St. Lawrence granite (Iron Springs vein) (Table 6). Notable exceptions are Cu, Zn, and Y, which occur in higher concentrations in the Iron Springs vein fluorite. Early, hydrothermal fluorite from Gallinas Mountains (P1) coprecipitated with *REE* minerals (particularly bastnäsite) or replaced bastnäsite (P2 and P3) (Williams-Jones *et al.* 2000). Coprecipitation of *REE* minerals with P1 fluorite could have sequestered the *LREE* preferentially, resulting in relatively low concentrations of the *REE* in the coprecipitated fluorite. Subsequent replacement of the early *REE* minerals likely influenced the composition of P2 and P3 fluorite. In contrast, fluorite is the only mineral within the St. Lawrence fluorite veins that contains significant concentrations of *REE*. Therefore, coprecipitation or replacement of other *REE* minerals cannot have caused the *REE* compositional trends observed within the St. Lawrence veins, and other factors must be considered.

The difference in composition between early- to late-formed hydrothermal fluorite at Rock Canyon Creek is characterized by higher concentrations of Zn, Y, *HREE*, Pb, Th and U, and lower concentrations of Mg, Nb, Ba and *LREE* (Table 4). With respect to the *LREE*, the trend in compositional evolution of fluorite at Rock Canyon Creek is opposite to that observed at Gallinas Mountains. The cause of the different compositional trend at Rock Canyon Creek is presently not understood.

The fluorite with the highest concentrations of trace elements in the Gallinas Mountains (P3 fluorite) is interpreted to have formed during collapse of the magmatic hydrothermal fluid system, at which point the influx of formation waters increased (Williams-Jones *et al.* 2000). Similarly, fluorite with the most significant elemental enrichment in the St. Lawrence deposits (Grebe's Nest and Lawn Barite veins) occurs within veins external to the granite, where the potential influence of country rock or formation waters would be expected to be more significant than in veins hosted by the granite (*i.e.*, Iron Springs vein). Strong *et al.* (1984) and Collins & Strong (1988) determined that the mixing of magmatic and formation waters was a significant factor in the formation of the St. Lawrence fluorite veins. Therefore, elemental enrichments in the fluorite from these deposits could potentially result from contributions from earlier-formed minerals (Gallinas Mountains), formation waters (Gallinas Mountains and St. Lawrence), or be the result of physicochemical conditions promoting the concentration of *REE* within fluorite (complexation effects). The latter may reflect changes in fluid composition associated with the introduction of formation waters into the hydrothermal system. Similar, host-rock or fluid-mixing controls on fluorite composition have been suggested for other fluorite deposits (*e.g.*, Hill *et al.* 2000).

Fluorite Composition as a Guide in Exploration

The LA–ICP–MS results presented indicate that the composition of fluorite, even within an individual deposit, can be highly variable. The range in composition observed within a deposit (*e.g.*, Gallinas Mountains) is as great as, or greater than, the compositional variation observed among some of the deposits studied. Presently, it is not known whether or not the compositional ranges and trends observed in fluorite represent those that might occur in fluorite deposits with other geological affinities. Furthermore, numerous compositional trends can occur within an individual deposit *(e.g.*, St. Lawrence), which may or may not be consistent with compositional trends expected from crystallochemical fractionation or aqueous complexation of the *REE* (*cf*. Möller *et al.* 1976). Therefore, the use of fluorite composition as an indicator of the ore potential of a deposit or region should be approached with care. Complementary data (*e.g.,* isotopic or fluid-inclusion data) would improve the validity of the predictions regarding the ore potential of an individual fluorite deposit or geographic region (*e.g.,* Strong *et al.* 1984, Hill *et al.* 2000).

Recommendations for Further Work

The use of fluorite composition to test genetic models for the deposits considered in this paper, and other deposits, will benefit from a better understanding of the variables controlling fluorite formation and composition. To improve our understanding of the evolution of these ore-forming hydrothermal systems, it is necessary that the following be better understood. 1) Mineral parageneses need to be determined, and quantitative analyses of minerals need to be made in order to assess the potential influence that coprecipitation and replacement of minerals other than fluorite have had on the compositional evolution of fluorite within these hydrothermal systems. 2) It is possible that much of the compositional variation exhibited by fluorite could be controlled by only a few intensive variables (*i.e*., temperature). To better understand the potential effect of intensive variables on the composition of fluorite, additional data (*i.e*., microthermometry) on the hydrothermal system responsible for these deposits are required. 3) The composition of the hydrothermal solutions needs to be determined. Combined microthermometric, LA–ICP–MS, and other types of analyses will lead to quantitative determination of the compositions of fluid inclusions within fluorite and other minerals. Determination of the compositions of the host minerals and fluid inclusions will enable calculation of the distribution coefficients between the hydrothermal solution and minerals in order to assess the role that intensive variables play in controlling fluorite composition (*cf*. Banks *et al.* 1994).

Conclusions

Based on the results of this study, we offer the following conclusions:

1) LA–ICP–MS is an effective method for determining elemental concentrations in fluorite. The ability of LA–ICP–MS to sample small volumes with high sensitivity has enabled the identification of compositional heterogeneities and trends in fluorite not previously documented; bulk analysis of fluorite is inadequate to fully characterize the compositional heterogeneity of fluorite.

2) Differences in composition were observed between early- and late-formed fluorite (Gallinas Mountains, Rock Canyon Creek and South Platte) and between fluorite hosted within granite and country rock (St. Lawrence). The composition of hydrothermal fluorite at South Platte was controlled by the primary magmatic fluorite, and replacement occurred within a relatively closed hydrothermal system. Fluorite from Gallinas Mountains, Rock Canyon Creek and St. Lawrence exhibit compositional trends that may be representative of progressive mixing of hydrothermal fluids or interaction of hydrothermal fluid with wall rocks.

3) Fluorite from granite-associated deposits (South Platte and St. Lawrence) is characterized by relatively flat chondrite-normalized *REE* patterns with a well-developed negative Eu anomaly. Fluorite from alkaline-rock-associated deposits (Gallinas Mountains and Rock Canyon Creek) is characterized by relatively flat to strongly *LREE*-enriched chondrite-normalized *REE* patterns that lack a negative Eu anomaly. The chondrite-normalized *REE* patterns of the associated magmatic rocks are similar to the *REE* patterns for the magmatic or earliest-formed hydrothermal fluorite within these deposits.

4) The variability in fluorite composition observed within these deposits indicates that significantly different conclusions could be drawn on the affinity of the fluorite, and possibly the ore potential of the mineral deposit or region, depending on which fluorite crystal, or part thereof, is sampled. Furthermore, distinctive compositional ranges that might be indicative of a particular geological setting, and which could be used as an exploration tool, were not identified. The Tb/Ca and Tb/La values in fluorite do not appear to be reliable indicators of the affinity of fluorite (*e.g.*, hydrothermal fluorite can be classified as pegmatitic). Therefore, care must be exercised when using fluorite compositions to make inferences about ore potential or affinity.

Acknowledgements

The authors thank C.J. Collins for performing the LA–ICP–MS analyses of the Lawn Barite vein fluorite. The reviews provided by Drs. T. Pettke and A.R.

Campbell resulted in significant improvements to this manuscript. Drs. P.J. Sylvester and R F. Martin are thanked for their editorial handling of the manuscript. This study was supported by NSERC grants to I.M.S., B.J.F. and A.E.W.-J. and by a McGill University graduate student fellowship and a Geological Society of America student research grant to J.E.G.

References

Banks, D.A., Yardley, B.W.D., Campbell, A.R. & Jarvis, K.E. (1994): REE composition of an aqueous magmatic fluid; a fluid inclusion study from the Capitan Pluton, New Mexico, U.S.A. *Chem. Geol.* **113**, 259-272.

Brewster, R.H. (1986): *The Distribution and Chemistry of Rare-earth Minerals in the South Platte Pegmatite District, Colorado, and Their Genetic Implications.* M.S. thesis, Univ. of New Orleans, New Orleans, Louisiana.

Collins, C.J. & Strong, D.F. (1988): A fluid inclusion and trace element study of fluorite veins associated with the peralkaline St. Lawrence Granite, Newfoundland. *Can. Inst. Mining Metall., Spec. Vol.* **39**, 291-302.

Deer, W.A., Howie, R.A. & Zussman, J. (1992): *An Introduction to the Rock-Forming Minerals* (second ed.). Longman Group UK Ltd,, London, U.K.

Eppinger, R.G. & Closs, L.G. (1990): Variations of trace elements and rare earth elements in fluorite: a possible tool for exploration. *Econ. Geol.* **85**, 1896-1907.

Fryer, B.J., Jackson, S.E. & Longerich, H.P. (1995): The design, operation and role of the laser-ablation microprobe coupled with an inductively coupled plasma – mass spectrometer (LAM–ICP–MS) in the Earth sciences. *Can. Mineral.* **33**, 303-312.

Hedge, C.E. (1970): Whole rock Rb–Sr age of the Pikes Peak Batholith, Colorado. *U.S. Geol. Surv., Prof. Pap.* **700B**, 86-89.

Hill, G.T., Campbell, A.R. & Kyle, P.R. (2000): Geochemistry of southwestern New Mexico fluorite occurrences: implications for precious metals exploration in fluorite-bearing systems. *J. Geochem. Explor.* **68**, 1-20.

Jackson, S.E., Longerich, H.P., Dunning, G.R. & Fryer, B.J. (1992): The application of laser-ablation microprobe – inductively coupled plasma – mass spectrometry (LAM–ICP–MS) to *in situ* trace-element determinations in minerals. *Can. Mineral.* **30**, 1049-1064.

Levasseur, R. (1997): *Fluid Inclusion Studies of Rare Element Pegmatites, South Platte District, Colorado.* M.Sc. thesis, Univ. of Windsor, Windsor, Ontario.

________ & Samson, I.M. (1996): Fluid inclusion characteristics of REE–Y–Nb pegmatites, South Platte district, Colorado. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **21**, A56.

Möller, P., Parekh, P.P. & Schneider, H.-J. (1976): The application of Tb/Ca–Tb/La abundance ratios to problems of fluorspar genesis. *Mineral. Deposita* **11**, 111-116.

Norman, D.I., Ting, W., Putnam, B.R., III & Smith, R.W. (1985): Mineralization of the Hansonburg Mississippi-Valley-type deposit, New Mexico: insight from composition of gases in fluid inclusions. *Can. Mineral.* **23**, 353-368.

Palmer, D.A.S. & Williams-Jones, A.E. (1996): Genesis of the carbonatite-hosted fluorite deposit at Amba Dongar, India; evidence from fluid inclusions, stable isotopes, and whole rock – mineral geochemistry. *Econ. Geol.* **91**, 934-950.

Pell, J. & Hora, Z.D. (1987): Geology of the Rock Canyon Creek fluorite/rare earth element showing, southern Rocky Mountains. *British Columbia Ministry of Energy, Mines and Petroleum Resources, Geological Fieldwork 1986, Pap.* **1987-1**, 255-261.

Perhac, R.M.& Heinrich, E.W. (1964): Fluorite–bastnaesite deposits of the Gallinas Mountains, New Mexico and bastnaesite paragenesis. *Econ. Geol.* **59**, 226-239.

Richardson, C.K. & Holland, H.D. (1979): The solubility of fluorite in hydrothermal solutions; an experimental study. *Geochim. Cosmochim. Acta* **43**, 1313-1325.

Salvi, S. & Williams-Jones, A.E. (1992): Reduced orthomagmatic C–O–H–N–NaCl fluids in the Strange Lake rare-metal granitic complex, Quebec/Labrador, Canada. *Eur. J. Mineral.* **4**, 1155-1174.

Samson, I.M., Al-Aasm, I.S. & Zhu, L. (2000): Dolomitization and mineralization in the Rock Canyon Creek fluorite–REE deposit, B.C. *GeoCanada 2000* (*Calgary*), *Program Abstr.*

________, Kerr, I.D. & Graf, C. (2001): The Rock Canyon Creek fluorite–REE deposit, British Columbia. *In* Industrial Minerals in Canada. *Can. Inst. Mining Metall., Spec. Vol.* **53**, 1-10.

Schneider, H. J., Möller, P. & Parekh, P.P. (1975): Rare earth elements distribution in fluorites and carbonate sediments of the East-Alpine Mid-Triassic sequences in the Nordliche Kalkalpen. *Mineral. Deposita* **10**, 330-344.

Schreiner, R.A. (1993): Mineral investigation of the rare-earth-element-bearing deposits, Red Cloud mining district, Gallinas Mountains, Lincoln County, New Mexico. *U.S. Bureau of Mines, Open File Rep.* **99-93**.

Simmons, W.B. & Heinrich, E.W. (1970): Rare-earth–fluorine pegmatites of the South Platte district, Jefferson County, Colorado. *Geol. Assoc. Can. – Mineral. Assoc. Can., Abstr. of Papers*, 48-49.

________ & ________ (1980): Rare-earth pegmatites of the South Platte district, Colorado, *Colorado Geol. Surv., Dep. of Natural Resources, Resource Ser.* **11**.

________, Lee, M.T. & Brewster, R.H. (1987): Geochemistry and evolution of the South Platte granite–pegmatite system, Jefferson County, Colorado. *Geochim. Cosmochim. Acta* **51**, 455-471.

Smith, D.R., Noblett, J., Wobus, R.A., Unruh, D., Douglass, J., Beane, R., Davis, C., Goldman, S., Kay, G., Gustavson, B., Saltoun, B. & Stewart, J. (1999): Petrology and geochemistry of late-stage intrusions of the A-type, mid-Proterozoic Pikes Peak batholith (central Colorado, USA): implications for petrogenetic models. *Precambr. Res.* **98**, 271-305.

Strong, D.F., Fryer, B.J. & Kerrich, R. (1984): Genesis of the St. Lawrence fluorspar deposits as indicated by fluid inclusion, rare earth element, and isotopic data. *Econ. Geol.* **79**, 1142-1158.

van Achterbergh, E., Ryan, C.G., Jackson, S.E. & Griffin, W.L. (2001): Data reduction software for LA–ICP–MS. *In* Laser-Ablation-ICPMS in the Earth Sciences. *Mineral. Assoc. Can., Short Course Ser.* **29**, 239-243.

Van Alstine, R.R. (1948): Geology and mineral deposits of the St. Lawrence area, Burin Peninsula, Newfoundland. *Geol. Surv. Newfoundland, Bull.* **23**.

Williams-Jones, A.E., Samson, I.M. & Olivo, G.R. (2000): The genesis of hydrothermal fluorite–REE deposits in the Gallinas Mountains, New Mexico. *Econ. Geol.* **95**, 327-342.

Received March 1, 2002, revised manuscript accepted February 7, 2003.