The Canadian Mineralogist
Vol. 37, pp. 469-488 (1999)

DOCUMENTATION OF VARIABLE TRACE- AND RARE-EARTH-ELEMENT ABUNDANCES IN CARBONATES FROM AURIFEROUS QUARTZ VEINS IN MEGUMA LODE-GOLD DEPOSITS, NOVA SCOTIA

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ABSTRACT

Samples of vein carbonate from 16 Meguma lode-gold deposits in Nova Scotia have been analyzed by solution chemistry (ICP–MS) and laser ablation micro-analysis (LAM ICP–MS) for their trace- and rare-earth-element (*REE*) abundances in order to assess the potential use of such data to decipher the origin of the mineralization. The gold deposits, hosted by metasedimentary rocks of the Meguma Group, are well suited to such a study because carbonate is the second most abundant phase (after quartz) in these mesothermal lode-gold deposits. Trace-element abundances in the carbonates are low for all elements except Sr (100 to 15 000 ppm), which has larger intra- and inter-deposit variation and is zoned within individual grains (LAM analysis). The *REE* data on vein carbonates are variable, both in terms of abundance (*ca.* 5 to 100 times chondrite) and degree of fractionation, with patterns generally flat to slightly fractionated [$(La/Sm)_N$ and $(Gd/Yb)_N$ both generally ≤1–2] and Eu/Eu* of *ca.* 1 to 2; however, excursions to extreme enrichment in either light or heavy *REE* may occur. The fact that the large chemical variations obtained *via* solution chemistry (*i.e.*, bulk separates) are replicated by LAM ICP–MS analysis precludes putative contamination by micro-inclusions as a critical factor controlling the *REE* content of the carbonates. Instead, a crystal-chemical control is suggested. The data are interpreted to reflect modification of a primary *REE* signature inherited from a reservoir by secondary processes operating at the vein scale. These secondary processes may include one or all of the following: (1) precipitation and dissolution of *REE*-bearing phases, including carbonate, (2) development of narrow wallrock-alteration zones marginal to veins, (3) changes in fluid composition [*i.e.*, pH, $f(O_2)$], (4) recharge of the vein fluid, and (5) rate of fluid flow. Given that the carbonate *REE* patterns deviate markedly from the *REE* signature of the host metasedimentary rocks, the data are in permissive agreement with vein fluids originating from a non-Meguma Group reservoir.

Keywords: carbonates, rare-earth elements, strontium, lode-gold deposits, Meguma Group, Nova Scotia.

SOMMAIRE

Nous avons analysé des échantillons de carbonate provenant de veines de quartz associées à une minéralisation aurifère dans le socle de Meguma, en Nouvelle-Écosse, au moyen de la technique ICP–MS sur solution ainsi qu'avec ablation au laser, afin de déterminer leurs teneurs en éléments traces, y compris les terres rares, et d'évaluer l'origine de la minéralisation à la lumière de ces données. Les gisements aurifères, encaissés dans les roches métasédimentaires du Groupe de Meguma, sont très appropriés pour une telle étude. La fraction carbonatée est deuxième en importance (après le quartz) dans les veines minéralisées mésothermales. Les teneurs en éléments traces des échantillons de carbonate sont faibles, sauf dans le cas du strontium (de 100 à 15000 ppm), qui montre aussi une variation plus importante intra- et inter-gisement, et une zonation intracristalline (analyse LAM). D'après les données sur les terres rares, la fraction carbonatée des veines est variable, à la fois en abondance (*ca.* 5 à 100 fois chondritique) et en degré de fractionnement, avec des spectres horizontaux ou légèrement évolués [$(La/Sm)_N$ et $(Gd/Yb)_N$ en général ≤1–2] et un rapport Eu/Eu* d'environ 1 à 2; on peut toutefois trouver des exemples d'enrichissement extrême en terres rares légères ou lourdes. Le fait que la grande variabilité en composition obtenue sur compositions globales mises en solution soit reproduite dans les résultats d'analyses ponctuelles au laser exclut la possibilité qu'une contamination par des micro-inclusions puisse rendre compte des teneurs en terres rares des carbonates. Il semble plutôt qu'une explication fondée sur la cristallochimie s'applique ici. Les données témoigneraient de la modification d'une signature primaire des terres rares indicative des caratéristiques du réservoir-source par des processus secondaires à l'échelle de veines individuelles, agissant seuls ou non, par

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exemple: (1) précipitation et dissolution de minéraux porteurs de terres rares, y inclus les carbonates, (2) développement de liserés d'altération hydrothermale dans l'encaissant le long des parois des veines, (3) changements dans la composition de la phase fluide [*i.e.*, pH, $f(O_2)$], (4) renouvellement de la phase fluide dans une veine, et (5) variabilité du taux d'écoulement de la phase fluide. Les spectres de terres rares de la fraction carbonatée des veines diffèrent largement de ceux des roches métasédimentaires encaissantes, et permettent l'hypothèse d'un réservoir autre que l'encaissant pour expliquer l'origine de la phase fluide et de la minéralisation.

(Traduit par la Rédaction)

Mots-clés: carbonates, terres rares, strontium, gisements aurifères en veines, Groupe de Meguma, Nouvelle-Écosse.

INTRODUCTION

The lode-gold deposits hosted by the Meguma Group, southern Nova Scotia (Malcolm 1929, Kontak *et al.* 1990a) are typical of slate-belt-hosted lode-gold mineralization in similar lithologies of variable age throughout the world (*e.g.*, Goldfarb *et al.* 1986, Steed & Morris 1986, Sandiford & Keays 1986, Paterson 1986, Cox *et al.* 1991). These deposits are considered either syngenetic–exhalative, synmetamorphic, syndeformational and related to post-tectonic granites, or formed from deep metamorphic fluids generated during terrane accretion [reviews in Nesbitt (1993) and Kerrich & Cassidy (1994)]. The geochemical signature of vein-forming fluids can be used to distinguish between the competing genetic models. However, the majority of studies provide isotopic and fluid inclusion data [reviews in Kerrich (1989) and Nesbitt 1993)], whereas comparatively few chemical data (*i.e.*, on trace elements) have been acquired on vein minerals. We are unaware of any previous detailed study on the trace-element geochemistry of carbonates from lode-gold deposits, although others have analyzed scheelite (Anglin *et al.* 1987, Sylvester & Ghaderi 1997) and tourmaline (King *et al.* 1988) from auriferous veins in Archean deposits to characterize source reservoirs.

In the present study, we focus on the trace-element geochemistry of carbonate minerals from auriferous quartz veins of the Meguma Group (Fig. 1) in order to assess chemical variation among various types of veins within and between gold districts. Carbonates were selected for study since they are the most common vein constituent after quartz; furthermore, on the basis of previous work, carbonates are known to sequester variable amounts of trace and rare-earth elements (*REE*), which are useful in assessing the source reservoir of the vein fluids (*e.g.*, Möller *et al.* 1979, 1984, Jébrak *et al.* 1984, Jébrak 1985, Raimbault 1985, Raimbault *et al.* 1993). Because of the potential influence of putative contaminants in such studies, both bulk- and micro-analytical techniques, the latter using laser-ablation inductively coupled plasma – mass spectrometry (ICP–MS); Jackson *et al.* 1992), were used to acquire data. Results of this study indicate that large variations in trace- (Sr) and rare-earth elements characterize the carbonates on both an intra- and inter-deposit scale. In a companion study, Kontak & Kerrich (1997) have reported on the C, O and Sr isotopic signatures of the same suite of carbonates; these results are integrated with the new geochemical data.

REGIONAL GEOLOGICAL SETTING

The Meguma lode-gold deposits of southern Nova Scotia are located in the Meguma Terrane of the Canadian Appalachians (Fig. 1). The deposits are hosted by Lower Paleozoic metaturbiditic sedimentary rocks of the Meguma Group, which is subdivided into a lower sandstone-dominated unit, the Goldenville Formation, and an overlying shale-dominated unit, the Halifax Formation. These rocks are overlain in the northwest and west by several Silurian – Lower Devonian volcanic and sedimentary formations. The stratigraphic sequence was deformed and metamorphosed (greenschist to upper amphibolite facies) during the mid- to late Devonian Acadian Orogeny (Keppie & Dallmeyer 1987, Muecke *et al.* 1988), which records docking of the Meguma Terrane against ancestral North America; the suture zone is represented by an east–west-trending dextral fault system referred to as the Cobequid–Chedabucto Fault System (Fig. 1). The Meguma Group was intruded at *ca.* 370 Ma by voluminous amounts of metaluminous to peraluminous granite (Reynolds *et al.* 1987) and lesser amounts of gabbroic material (Kontak & Reynolds 1994). The presence of granulite-facies xenoliths within 370 Ma shoshonitic lamprophyres along the eastern shore of the Meguma Terrane (*e.g.*, the Tangier dyke; Eberz *et al.* 1991) and high-grade ortho- and paragneiss in the Liscomb Complex (Fig. 1; Clarke *et al.* 1993) are significant in this study in that they provide insight into the units comprising the lower- and middle crust, respectively, within the Meguma Terrane, and accordingly are relevant in terms of assessing source reservoirs.

THE MEGUMA GOLD DEPOSITS AND OCCURRENCE OF CARBONATE MINERALS

Nature of the vein-type gold deposits

The Meguma gold deposits consist of bedding-concordant, discordant and *ac* vein types [see Henderson &

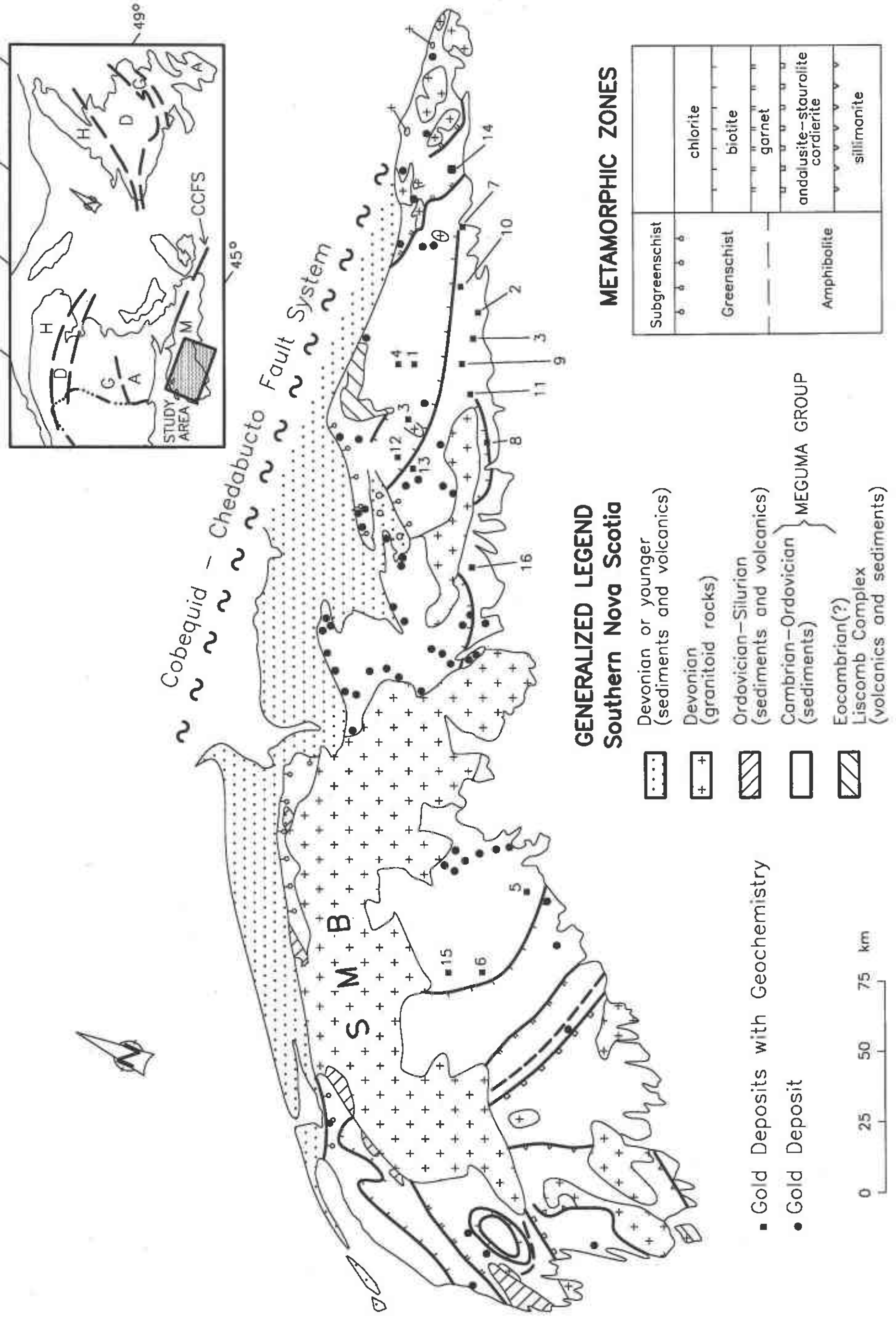

FIG. 1. Geological map of southern Nova Scotia showing the distribution of historical gold deposits within the Meguma Group and location of the deposits studied. Inset map shows the location of the Meguma Terrane (M) in relationship to Nova Scotia and Newfoundland in the northern Appalachians. Other abbreviations are as follows: A Avalon, G Gander, D Dunnage, H Humber terranes; SMB, South Mountain batholith. Deposits indicated by number are as follows: 1) Lochaber, 2) Ecum Secum, 3) Beaver Dam, 4) Fifteen Mile Stream, 5) Leipsigate, 6) Brookfield, 7) Wine Harbour, 8) Tangier, 9) Dufferin, 10) Miller Lake, 11) Sheet Harbour, 12) Caribou, 13) Moose River, 14) Upper Seal Harbour, 15) Molega, 16) Lake Catcha.

Henderson (1986), Mawer (1985) and Horne & Culshaw (1994) for a review of vein nomenclature] that are hosted by metaturbidites of the Goldenville Formation. Where discordant veins dominate, they occupy cross-cutting structural elements such as faults or kink zones (*e.g.*, Caribou deposit; Bell 1948), whereas the more common bedding-concordant veins (Malcolm 1929) are generally found near anticlinal hinge-areas and in the pelitic beds at or near contacts with psammitic beds. It is not unusual for both types of veins to occur within deposit areas and show mutually cross-cutting relationships (Horne & Culshaw 1997). Veins are of variable thickness (1 cm to 1–2 m) and reflect highly variable amounts of strain, such as is typical of mesothermal gold deposits (Hodgson 1989, Cox *et al.* 1991). Vein mineralogy is dominated by quartz, but carbonate and sulfide (arsenopyrite, pyrrhotite, pyrite) phases are consistently present (0.1 to 5 modal %, locally 50–75%); trace amounts of silicates (biotite, muscovite, feldspar, amphibole, garnet, tourmaline), apatite, Bi–Ag tellurides, sulfides (Cu, Pb, Zn) and native gold (fineness >900) also are present (Smith & Kontak 1986, Kontak & Smith 1993). Wallrock alteration marginal to the veins is cryptic to intensely developed, with variable enrichment in quartz, carbonate, sulfides, white mica, biotite and tourmaline. Several of the deposits examined have been dated at *ca.* 370 ± 8 Ma using the $^{40}Ar/^{39}Ar$ technique on hydrothermal vein-bound minerals; these ages are in agreement with field and petrographic relationships that also constrain vein formation to being syn- or post-intrusion of the Late Devonian granites (Kontak *et al.* 1990b, 1993), during a time of late flexural-slip-type folding of the Meguma Group (Horne & Culshaw 1997).

Nature of vein carbonates

Carbonates are present in all vein types and occur as laminae (<1–2 cm) parallel to vein margins, as massive clots within veins, and infilling vugs (10–15 cm across) coexisting with chlorite, sulfides and euhedral quartz (to 10–15 cm), and rarely muscovite and scheelite (Corey 1992, Corey & Mills 1992, Smith & Kontak 1986, Kontak & Smith 1993, this study). Carbonate paragenesis is variable, with the laminated type probably early and the vug-filling carbonate relatively late. In thin section, carbonates are seen as late-stage minerals replacing Ca-rich plagioclase or disseminated in wallrock adjacent to veins. Carbonate grains are mostly cloudy, and white to buff, but additional varieties include shades of pink to red (Tangier), brownish (Brookfield), or transparent crystals (Fifteen Mile Stream, Caribou). There is no systematic relationship between carbonate color and vein type, except that the freshest (*i.e.*, crystal-clear) samples occur in relatively undeformed, paragenetically late veins.

Chemically, the carbonates are calcite, ankerite, dolomite and ferroan dolomite, as discussed in detail by Kontak & Kerrich (1997) and summarized below. Within a single deposit, one type of carbonate dominates, and calcite generally is the most abundant carbonate.

It is emphasized here that this study is broad in scope. Whereas a more detailed examination of carbonates within a deposit may indicate a more complicated paragenesis, our purpose in this work was to examine the regional-scale variations in carbonate geochemistry and processes within the Meguma gold province.

SAMPLE COLLECTION AND ANALYTICAL PROCEDURES

Carbonate-bearing samples were collected during the course of a regional study of these deposits (Smith & Kontak 1986). Where possible, samples were collected from well-characterized localities when exploration development (surface, underground) or outcrop exposure permitted, but in some instances, sampling was restricted to abandoned mines (Sheet Harbour, Molega, West Gore, Lochaber). In general, the number of samples from any one particular deposit reflects accessibility at the time of collection (Beaver Dam, Tangier, Caribou, Fifteen Mile Stream, Moose River). Carbonate samples selected for analysis represent coarse aggregates, in some cases intergrown with chlorite and sulfides. In addition, where sampled, the carbonates dominate the vein assemblage, the only other minerals present being quartz ± chlorite ± sulfides.

Carbonate-rich material was pulverized (–35 to +60 mesh), and high-quality concentrates were hand-picked using a binocular microscope. The separates were then washed in distilled water, dried and crushed to –200 mesh using a mortar and pestle. Powders were analyzed for major cations (Ca, Fe, Mg, Mn, K, Al, Na, Si, P) using wet-chemical methods and atomic absorption spectrophotometry to determine end-member components and to evaluate the importance of impurities (*e.g.*, apatite); where impurities were detected, the concentrates were not used further. In order to verify the type of carbonate, as indicated by the bulk analyses, selected samples were analyzed using a JEOL 733 electron microprobe at Dalhousie University using the following operating conditions: accelerating voltage 15 kV, sample current 10 nA, beam diameter 1–3 μm. The data were reduced to wt.% oxides using a ZAF software package. The same analytical conditions were employed in order to determine the compositions of micro-inclusions within carbonates, after they had been located using back-scattered electron (BSE) imaging. Several samples from each locality also were examined with X-ray diffraction (XRD) to determine the type of carbonate and to obtain semiquantitative compositions (details in Kontak & Kerrich 1997).

Abundances of trace elements, including the rare-earth elements, were determined on carbonate separates using the ICP–MS at Memorial University, Newfoundland, following the procedures outlined in Jenner *et al.* (1990) for solution chemistry. A select few samples ($n = 4$) were chosen for laser-ablation micro-analysis (LAM; Jackson *et al.* 1992), on the basis of the variability of results from solution chemistry, in order to examine in detail the degree of homogeneity within samples and also to assess the potential influence of micro-inclusions on the solution data. Details of the LAM ICP–MS procedures are as outlined in Kontak & Jackson (1995), with the exception that the increased sensitivity of the equipment has reduced the detection limits for the *REE* to below *ca.* 0.5 times chondritic values. Normalizing values used in the chondritic plots are those of Masuda *et al.* (1973).

ANALYTICAL RESULTS

Major-element chemistry and XRD

Results of the chemical analysis of carbonate phases are discussed in detail by Kontak & Kerrich (1997) and summarized below. In general, two types of carbonate can be identified, namely calcite and ferroan dolomite or dolomite; minor magnesian calcite also is present. The maximum amount of Mn recorded in the carbonates was 2.4 wt.% MnO in ferroan dolomite from Caribou; in general, values of <0.8 wt.% MnO are encountered. The scatter in composition of the calcite toward magnesian-rich compositions in some of the samples may in fact reflect intergrowth of trace amounts of dolomite, since the compositions fall on the tie line between end-member calcite and ferroan dolomite. Imaging of some calcite grains in fact supports this suggestion. In the same way, it is possible that some of the variation in the dolomite also reflects trace amounts of calcite intergrown with the dolomite. However, for at least some deposits, this is not the case (*e.g.*, Beaver Dam, Ecum Secum). Whereas some deposits are characterized or dominated by a single carbonate phase on the basis of our sampling (*e.g.*, Beaver Dam, Ecum Secum), in other deposits several discrete carbonate phases may occur (*e.g.*, Tangier, Moose River, Fifteen Mile Stream). In the case of the Tangier deposit, this variation may occur within the same vein and on the scale of a few cm. At the Caribou deposit, dolomite is restricted to bedding-concordant veins, whereas calcite occurs in both bedding-concordant veins and the large discordant stockwork system (see below).

XRD work confirms the presence of the carbonate minerals named and, in addition, indicates that the following carbonate minerals occur where chemical data are not available: (1) dolomite and ankerite at Dufferin, (2) ankerite at Miller Lake, and (3) calcite at Leipsigate and Moosehead. In addition, the much more extensive sampling for XRD work at Beaver Dam indicates that calcite predominates, and that at Tangier, calcite and dolomite are intimately intergrown.

Trace- and rare-earth-element geochemistry of vein carbonate: solution chemistry

Trace-element data, as determined by solution chemistry, have been obtained for 74 carbonate separates from 16 deposits (Table 1, Figs. 2 to 4). [A copy of Table 1 is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.] Levels of trace elements, except for Sr and the *REE*, are systematically low, as is expected for carbonates (Veizer 1983). The relative enrichment in some trace elements (Ba, W, Rb, Pb, Bi; Fig. 2) probably reflects trace amounts of contaminating phases, of which plagioclase, muscovite, scheelite and galena appear to be the most noticeable, albeit still rare in occurrence. The bivariate plot for Ba and Sr (Fig. 2a) indicates that these elements are geochemically decoupled, as also occurs for Sr and W (plot not shown). The data also permit consideration of the role of putative contamination by *REE*-rich phases (*e.g.*, apatite, scheelite, zircon). Examination of the data (Figs. 2c, d, e, f) indicates that such influences are unlikely given simple mass-balance constraints, on the basis of published compositions. This issue is also addressed below utilizing results of the LAM data.

Of all the trace elements, the most enriched is strontium, with values of 50 to *ca.* 15000 ppm (Table 1, Fig. 2). Although some deposits show consistent enrichment in Sr (*e.g.*, Ecum Secum with 4000 to 15000 ppm, av. 9174 ± 4111), there is a considerable range in the data in many suites (*e.g.*, Beaver Dam: 60 to 3990 ppm; Caribou: 112 to 8196 ppm), and yet others where relative depletion occurs (*e.g.*, Tangier av. 194 ± 290). There is no correlation between Sr concentration and either bulk composition of the carbonate or level of other trace elements (*e.g.*, Ba, W, Y, *REE*; Fig. 2).

The *REE* data are summarized for individual deposits in chondrite-normalized plots in Figures 3 and 4. The covariation, or lack thereof, of ΣREE with Zr, W and Sr is examined in Figure 2. The data indicate some variation in terms of ΣREE (< 10 to 322 ppm), Eu/Eu* and degree of fractionation [*i.e.*, $\mathrm{La_N}$, $\mathrm{(La/Sm)_N}$, $\mathrm{(Gd/Yb)_N}$], both on an inter-deposit scale and, where sufficient data exist for individual deposits, also on an intra-deposit scale. For example, more extensive sampling indicates ranges for ΣREE within the Beaver Dam (25 to 215 ppm), Moose River (34 to 322 ppm), Tangier (24 to 136 ppm) and Caribou (31 to 187 ppm) deposits.

In several deposits, only one or two analyses were run. However, at several of these deposits, the absolute abundances and chondrite-normalized patterns are very similar (*e.g.*, Dufferin, Sheet Harbour, Leipsigate, Molega, Brookfield), whereas at others there is a relatively greater variation (*e.g.*, Ecum Secum, Fifteen Mile Stream). There are sufficient analytical data available for the Moose River, Tangier, Caribou and Beaver Dam deposits to examine and identify factors controlling intra- and inter-deposit variability in the *REE* (Fig. 4).

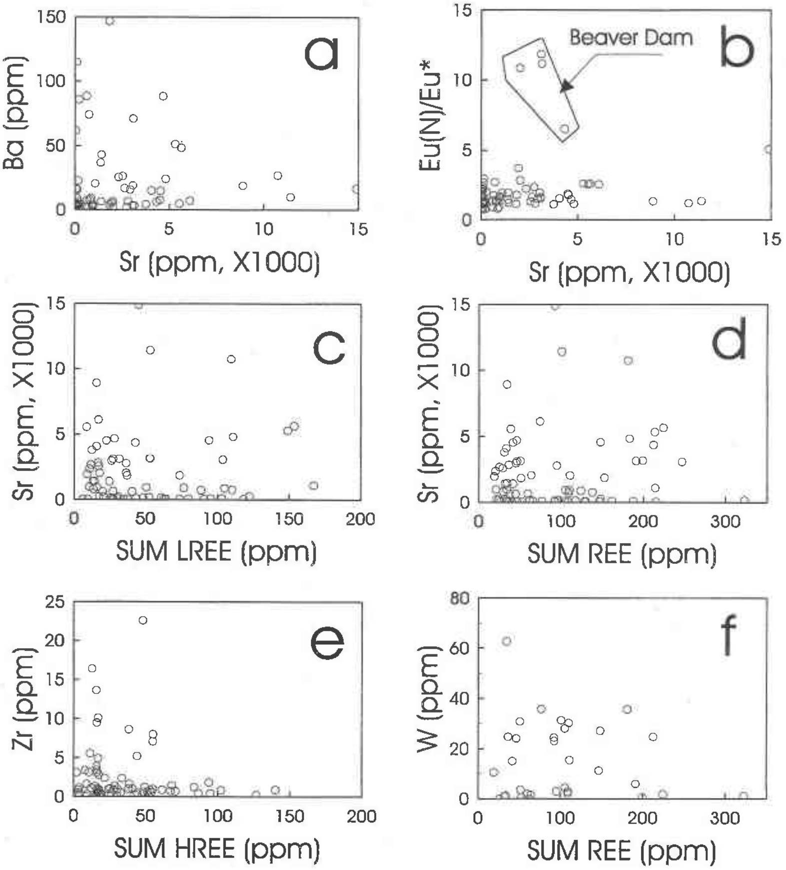

FIG. 2. Selected binary plots of trace-element data for bulk carbonate separates from Meguma gold deposits. The samples with elevated Eu_N/Eu^* values in Figure 2b are for Beaver Dam.

Carbonate samples from *Moose River* display a large overall variation both with respect to ΣREE, degree of fractionation and positive Eu anomaly, such that multiple patterns are present. There is no consistent relationship between the type of carbonate and *REE* content, as patterns for calcite (107, 109) and ferroan dolomite (all remaining samples) overlap. Sample 109 is the most strongly fractionated and is relatively depleted in ΣREE. The profile for sample 109 is, in fact, similar to that observed for samples 131 and 133 at Caribou. There is a general increase in the positive Eu anomaly with increasing ΣREE, especially with samples exhibiting convex profiles.

Carbonate samples from *Tangier* also show large variations of ΣREE, but the profiles are internally more consistent than the samples from Caribou and Moose River, particularly for the light rare-earth elements (*LREE*). There is a well-developed positive Eu anomaly in all samples, and as for Moose River, the highest values are for samples with the greatest enrichment in *REE*. The three samples of calcite (13, 5.3, 90–2) cannot be distinguished from the dolomite samples on the basis of fractionation or abundance of *REE*. Multiple sampling of carbonates from the same hand sample give conflicting results, as carbonates from sample TAN–87–5 (5 and 5.3) have markedly different chondrite-normalized patterns, whereas carbonates from sample TAN–87–3 (3.1, 3.2) are quite similar in their chondrite patterns and ΣREE.

Carbonate samples from *Beaver Dam*, all of which consist of calcite, show a large degree of variation with respect to ΣREE, degree of fractionation and most notably Eu/Eu* values. Different types of veins are represented, but no distinction of their *REE* chemistry is apparent. Samples 100.1, 100A and 100B, which come from the same bedding-concordant vein (*i.e.*, a few m apart), have similar ΣREE and chondritic patterns. The pronounced enrichment of heavy rare-earth elements

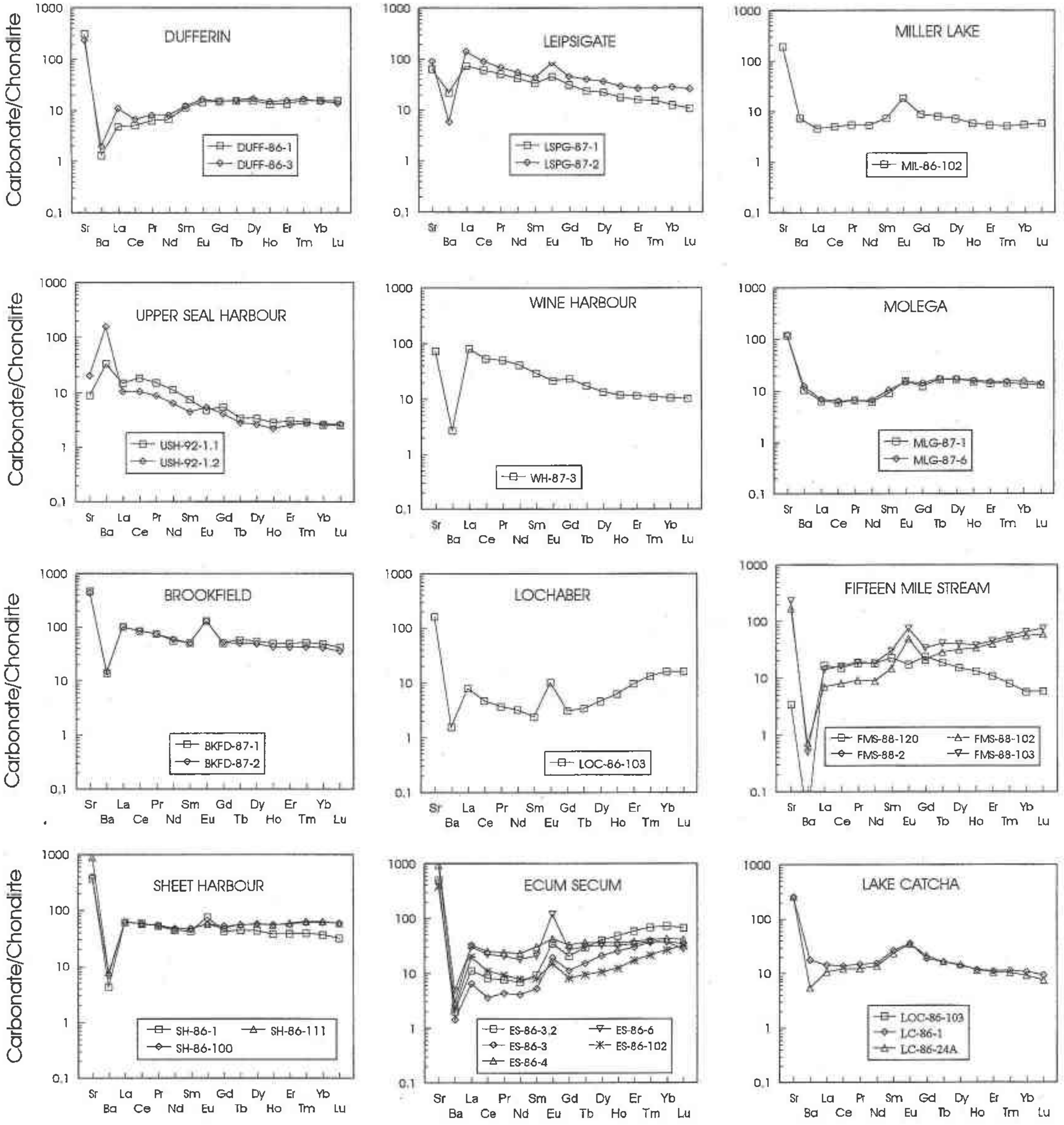

FIG. 3. Extended chondrite-normalized trace- (Sr, Ba) and rare-earth-element plots for carbonate separates from Meguma lode-gold deposits.

(*HREE*) noted for samples 9, 1080 and 161A, which are from discordant veins, cannot be related to micro-inclusions of zircon because these samples have variable Zr contents (23, 112 and < 1 ppm, respectively). These *HREE* patterns are similar to those noted for samples from Tangier (5, 105), Moose River (19.2) and Caribou (48, 134). The positive Eu anomalies in some of the calcite are among the largest observed in the entire dataset for the Meguma gold deposits.

At *Caribou*, the data show an overall variation such that flat, unfractionated (2, 23) to strongly fractionated (133, 131B), concave (48, 134) and convex (101, 88A) patterns are represented. The strongly fractionated patterns are for two of the freshest samples (131B, 133); these carbonates line vugs with coexisting muscovite and chlorite. These two samples also lack a positive Eu anomaly, which is anomalous compared to the rest of the dataset. There is no obvious difference among

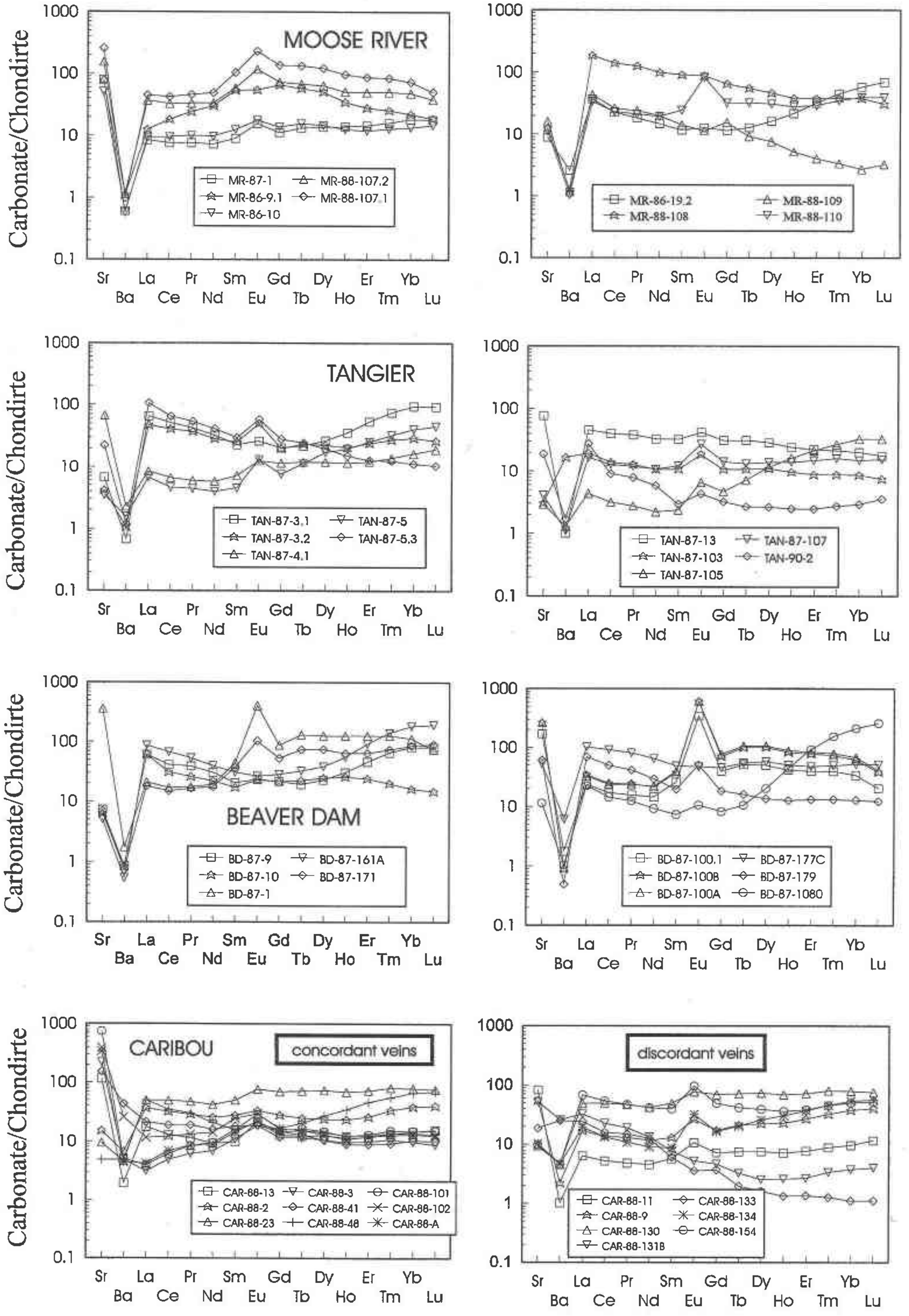

FIG. 4. Extended chondrite-normalized trace- (Sr, Ba) and rare-earth-element plots for carbonate separates from the Moose River, Tangier, Beaver Dam and Caribou lode-gold deposits in the Meguma Group.

samples of bedding-concordant or discordant veins (Fig. 4), or between calcite or ferroan dolomite (*cf.* Jébrak 1985), which incidentally correspond to stockwork and bedding-concordant vein types, respectively. However, for the stockwork or discordant vein samples, there appears to be two trends defined, one of *LREE*-enrichment and strong fractionation (samples 131, 133), and the remainder with a slight concave trend with positive Eu anomalies. Sample 154, from a cross-cutting *ac* vein, has a pattern that is most similar to the second type in the stockwork vein system.

Trace and rare-earth-element geochemistry of vein carbonate: laser-ablation micro-analysis (LAM ICP–MS)

Four carbonate samples, selected on the basis of their variable abundance and fractionation of the *REE* from solution chemistry, were analyzed using LAM ICP–MS to examine in detail the range of trace and *REE* concentrations (Table 2, Fig. 5). With respect to the trace-element data (Sr, Ba, Zr, Y), the following points are noted: (1) Zr is not present above the detection limit of the analysis (*i.e.*, <0.1 ppm); (2) the maximum content of Ba is 16.2 ppm in sample CAR–134, but in the same sample, values range between 0.4 to 16.2 ppm; (3) Y values are highly variable (from 12 to 273 ppm), even within the same sample; (4) the level of Sr ranges from 10 to 5706 ppm, with the greatest variation within a single sample (*i.e.*, 82 to 2040 ppm). The highest Sr contents were found in sample BD–87–100, with all four analyses indicating between 5304 to 5706 ppm. The solution ICP–MS analysis of this sample indicated 3100 ppm, and thus zonation in Sr must exist.

Chondrite-normalized *REE* data obtained by laser ablation (LAM) are compared to the solution-chemistry data for the same four samples in Figure 5. Collectively, the LAM data show a range in both the abundance (*i.e.*, reflect zonation) and fractionation of the *REE*, but most importantly, the LAM data give similar normalized patterns as the solution chemistry. Examination of these patterns indicates the following pertinent information: (1) there is clearly some very dramatic *HREE* enrichment in sample BD–87–161A, and there are variable positive Eu anomalies. Samples with the greatest $\mathrm{Eu}_N/\mathrm{Eu}^*$ values also have the highest Sr and Ba contents and, interestingly, contain Mg (6 and 16 wt. % MgO), whereas the other samples represent end-member calcite; (2) whereas LAM data for sample BD–87–100 average to a value close to that obtained by solution chemistry, the solution-chemistry data for the other carbonate samples are closest to the most enriched LAM result; (3) the variation of the *REE* is generally an order of magnitude more than for either Ba or Sr, a relationship also noted by Kontak & Jackson (1995) for LAM ICP–MS data for hydrothermal calcite associated with Mississippi-Valley-type Zn–Pb mineralization at Gays River, Nova Scotia.

DISCUSSION

Reliability of trace-element analysis of mineral separates

In order to correctly interpret the trace and *REE* data of the carbonates, it is first necessary to ascertain whether or not the solution data approximate the intrinsic composition of the carbonates rather than the influ-

TABLE 2. RESULTS OF LAM–ICP–MS ANALYSES (ppm) OF VEIN CARBONATES, MEGUMA GOLD DEPOSITS, NOVA SCOTIA

Sample	BD-87 161A					BD-87 177C				BD-87 100				CAR-88 134				
Sr	10	24.3	99.1	152.8	69.4	41.8	75.8	34.2	63.6	5460	5329	5706	5304	199.7	112	81.8	1677	2040
Y	15.2	20.5	151.4	221.3	89.5	46.7	78	71.5	26.8	272	187	44.6	125.5	54.2	43	42.7	14.2	11.8
Ba	0.23	0.79	3.1	2.25	0.77	0.73	1.3	1.3	4.6	7.8	7.4	7.6	3.5	16.2	14.5	5.32	0.41	1.9
La	0.71	5.51	10.65	2.35	28.7	18.67	23.25	60.7	13.82	24.79	3.68	1.02	0.65	6.45	9.4	6.9	0.99	1.05
Ce	1.46	10.16	13.92	2.84	60.08	43.99	28.92	141.4	22.52	55.24	5.51	2.75	2.06	9.74	9.05	12.33	2.26	2.13
Pr	0.21	0.93	1.1	0.18	6.72	5.16	4.08	15.94	1.74	7.56	0.57	0.37	1.22	1.09	1.07	1.38	0.35	0.28
Nd	0.78	2.76	3.56	0.47	24.62	18.88	14.9	61.83	5.94	44.61	2.65	2.41	3.26	5.07	4.73	6.03	2.12	1.77
Sm	0.4	0.68	0.58	0.18	6.19	5.77	4.44	13.44	4.64	40.94	2.65	2.15	4.99	1.5	1.61	1.41	1.11	0.92
Eu	0.09	0.39	1.3	0.39	3.17	1.15	2.52	6.83	2.18	101.3	22.36	38.79	29.19	2.68	2.24	1.76	1.16	1.22
Gd	0.29	0.58	1.49	0.76	6.97	4.96	6.57	17.6	2.49	72.25	10.3	5.14	14.25	4.35	3.67	3.46	2.36	1.69
Tb	0.06	0.18	0.59	0.51	1.35	1.07	1.9	3.66	0.75	12.9	3.22	1.29	3.56	1.07	0.87	0.84	0.49	0.36
Dy	0.94	2.27	8.83	14.77	11.35	7.21	12.65	18.14	4.69	74.25	24.83	8.25	23.05	8.71	7.2	6.63	2.76	2.36
Ho	0.52	0.93	4.62	6.73	3.22	1.82	2.84	3.7	1	11.39	5.85	1.59	5.17	2.49	1.85	1.86	0.59	0.48
Er	2.76	4.22	24	35.52	14.7	6.05	6.36	10.18	2.5	30.23	15.83	3.36	10.31	8.25	6.41	5.88	1.5	1.3
Tm	0.79	0.95	5.03	8.43	3.9	1.03	1.19	1.63	0.54	3.72	3.84	0.37	1.49	1.44	1.13	1.02	0.24	0.22
Yb	9.48	12.1	48.99	62.32	42.2	8.83	7.72	12.51	4.27	29.65	24.97	2.56	8.45	12.39	9.96	8.7	1.91	2.1
Lu	1.61	2.23	7.39	9.1	7.22	1.06	0.97	2.04	0.65	1.5	2.31	0.21	0.7	2.07	1.58	1.35	0.32	0.37

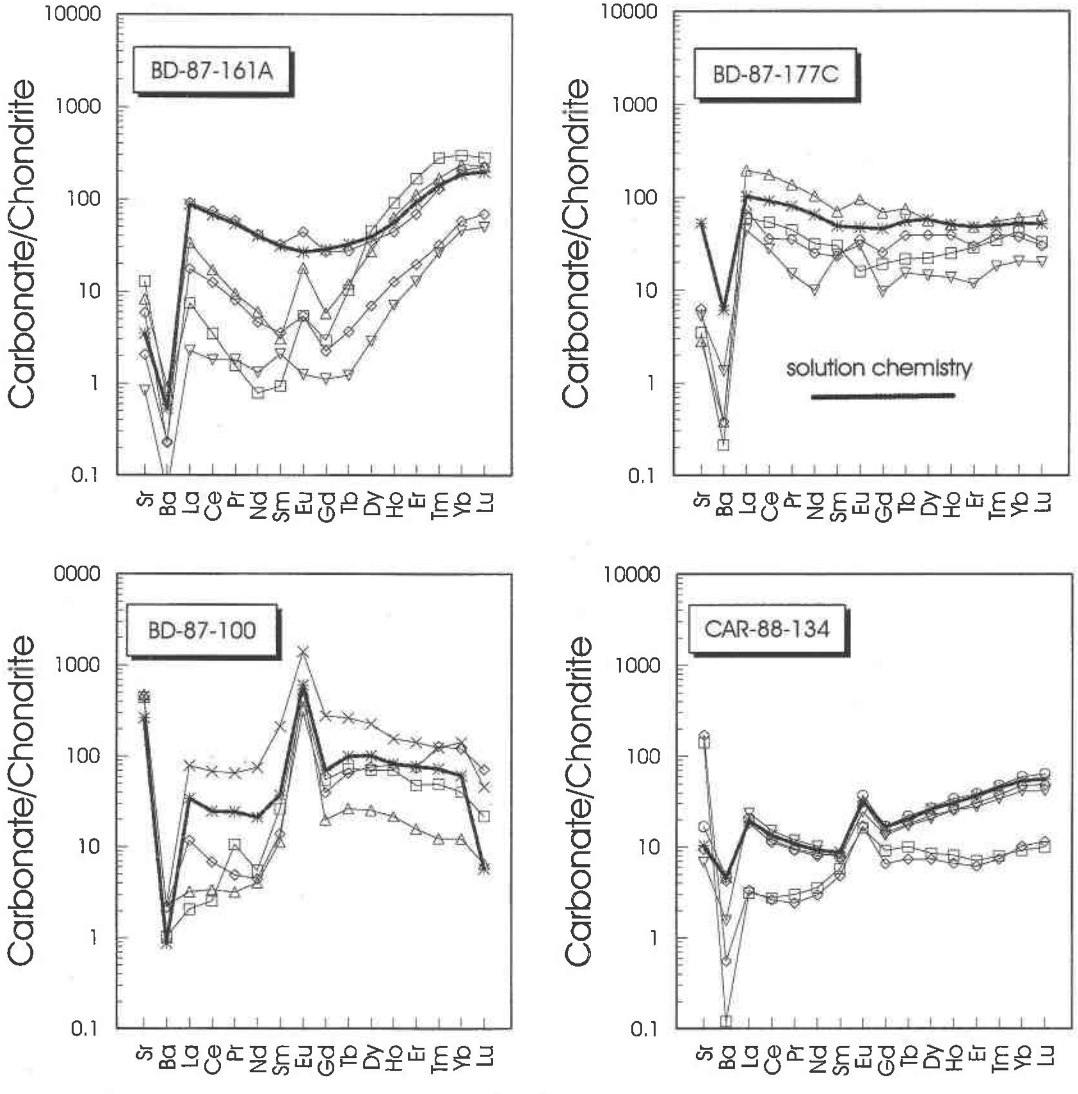

FIG. 5. Extended chondrite-normalized trace- (Sr, Ba) and rare-earth-element plots of LAM ICP–MS data of vein carbonates from Beaver Dam (BD–87–6A, 177C, 100) and Caribou (CAR–88–134) deposits. The solution-chemistry results (solid heavy line) is provided for the bulk separates from the same samples for comparison. Samples from Beaver Dam all consist of calcite except for two datasets in BD–87–161A, which consist of magnesian calcite (6 and 16 wt.% MgO) and are characterized by the steep *HREE* profiles. The sample from Caribou (CAR–88–134) is ferroan dolomite.

ence of micro-inclusions. Although the apparent variability of the *REE* patterns for carbonates within and between deposits shows that putative contamination by micro-inclusions might be responsible, the following points suggest otherwise.

1. Sample preparation was done by dissolving carbonates in dilute HNO_3, which would not readily cause dissolution of such *REE*-rich refractory minerals as zircon, monazite, xenotime, scheelite and apatite.

2. Petrographic examination and imaging analysis of carbonate grain-mounts do indicate the presence of accessory minerals, these being apatite and monazite. However, these phases are rare, and only two grains of monazite were observed out of *ca.* 30 grains examined in detail.

3. Geochemical analysis of wallrocks adjacent to veins (unpubl. data of DJK) does not indicate obvious enrichment of *REE* that might be attributed to element

mobility or growth of accessory minerals, as has been documented, for example, in some massive sulfide deposits, where growth of secondary *REE*-rich phosphates has occurred (Schandl *et al.* 1995, Schandl & Gorton 1991, Gorton & Schandl 1995).

4. Plots in Figure 2 are presented to examine the relationship between possible contamination by micro-inclusions and the *REE* chemistry. There are no obvious patterns present in plots of Zr *versus* $\Sigma HREE$ and Sr *versus* Eu_N/Eu^* that would suggest contamination by micro-inclusions of zircon or scheelite, *even* if they were dissolved during sample preparation (see above). In addition, mass-balance constraints using typical concentrations of *REE* in these minerals (Henderson 1984, Anglin *et al.* 1987, Raimbault *et al.* 1993) also negate the possibility of contamination. The inverse correlation between Ba and Sr precludes plagioclase from contributing to the budget of either of these elements, which is also supported by the negligible contents of Al_2O_3 combined with the known trace-element concentrations in vein plagioclase (Kontak & Smith 1993, and unpubl. data of DJK). As for possible contamination by apatite, the levels of the *REE* in hydrothermal apatite in Meguma veins (Fig. 6) is such that the P_2O_5 contents of the carbonate separates are too low to permit significant contribution to the *REE* budget; data for hydrothermal apatite obtained by others (*e.g.*, Roeder *et al.* 1987, Raimbault *et al.* 1993) reinforce these conclusions. With respect to monazite, it is not possible to quantify its potential influence (*i.e.*, anomalous *LREE* enrichment), although it is known to occur in the vein carbonate in very rare cases. Thus, it is significant to note that where monazite was detected (sample BD–87–177C; LAM ICP–MS results in Fig. 6), there is no indication from the solution chemistry for this same sample (Fig. 4) that monazite is present in sufficient quantities to influence the trace-element results of the carbonate (*i.e.*, no *LREE* enrichment). If contamination by xenotime has influenced the carbonate data, then it is a subtle effect, as samples do not show the marked enrichment in *HREE* expected from this mineral (Fig. 6), except for BD–87–1080 (Fig. 4), and its pattern is not unlike that obtained for the LAM analysis of BD–87–161A (Fig. 5).

5. The general similarity between the chondrite-normalized plots of carbonates from specific deposits suggests that if contamination by micro-inclusions occurred, it would have to be in the same proportions in the different samples. For example, comparison of the Leipsigate and Ecum Secum carbonates indicate *LREE* enrichment in the former *versus HREE* enrichment in the latter for all the samples (Fig. 3). If micro-inclusions are causing the *LREE* and *HREE* enrichments, respectively, then micro-inclusions must be present in the same proportions in all samples.

6. The excellent correlation between solution chemistry and LAM data for four samples with highly variable chondrite-normalized profiles (Fig. 5) indicates that the trace-element data from solution chemistry are not related to contamination by micro-inclusions. On the basis of results for these four samples, we infer that the chondritic profiles in Figures 3 and 4 also indicate a crystal-chemical control for the *REE*.

7. The results of this work are comparable to the large range in the *REE* contents of calcite documented by Kontak & Jackson (1995) on the basis of solution chemistry and subsequently verified with LAM analysis.

From the foregoing discussion, we conclude that whereas some contribution to the trace-element budget may have occurred from micro-inclusions, the extent of such contamination is minor, and it does not account for the highly variable *REE* patterns nor the variable enrichment in Sr. Instead, the variability of some trace elements (Sr, *REE*) is a true reflection of the variable concentration of structurally bound elements, which is a manifestation of the influence of physical and chemical processes.

Nature of the trace and REE variation in the vein carbonates

Trace-element data for carbonates are generally of little use as solute tracers because of their typically low abundances, except for Sr, which often is used as an isotope tracer (*e.g.*, Mueller *et al.* 1991); in this study, the exceptions are Sr and the *REE*. The Sr data indicate that a large range of values can occur within a single deposit (*i.e.*, over two orders of magnitude in concor-

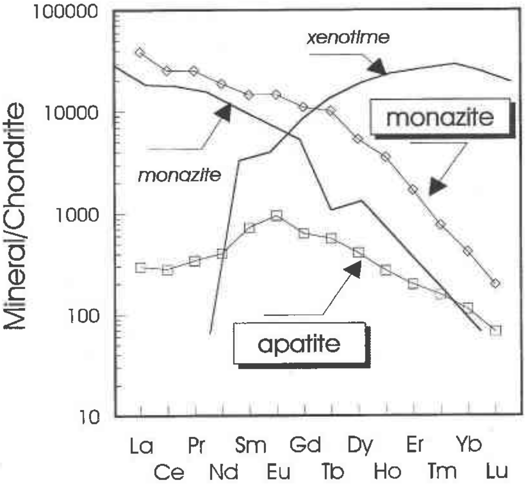

FIG. 6. Chondrite-normalized rare-earth-element plots for accessory mineral phases monazite, apatite and xenotime. The data for the monazite and apatite (labeled) are from gold veins in this study (LAM ICP–MS data), and the reference lines for xenotime and monazite are from Schandl & Gorton (1991).

dant veins at Caribou; Fig. 4) and that there are substantial differences between deposits. This scale of enrichment exceeds that which has been attributed to the influence of precipitation rate or sector zoning (Lorens 1981, Reeder & Grams 1987, Möller *et al.* 1991) and, therefore, some other process or processes may have been involved. In addition, given that the partition coefficient (K_d) of Sr for calcite is *ca.* 0.025, on the basis of both natural sampling (McCaig *et al.* 1995) and laboratory studies (Lorens 1981, Stoessel *et al.* 1987), the fluid must have been relatively enriched in Sr at certain times. Although the nature of this variation along with that of the *REE* is addressed below, we suggest that the broad variation in Sr hints at a possible regional enrichment of Sr, a geochemical feature that has been noted with respect to isotopic and geochemical studies of vein-gold deposits by others (King 1989, King & Kerrich 1989, Mueller *et al.* 1991). Finally, the enrichment of Sr documented in both the solution and LAM ICP–MS data indicates that the carbonate fraction, in addition to apatite (Ayers & Watson 1993), is an important repository of Sr in hydrothermal settings.

In contrast to the other trace elements, the *REE* offer some constraints with regards to the nature and location of source-rock reservoir(s), as well as providing information on *REE*-complexing in the fluid (Wood 1990). The *REE* content of a hydrothermal fluid should reflect the *REE* distribution within the source region where the fluid equilibrated, the *REE*-complexing ligands present in the fluid, and exchange of *REE* with wallrock conduits between the source and the deposit. In addition, the *REE* content of hydrothermal minerals will depend on the distribution coefficients (K_d) for the *REE* between the fluid and host mineral, and the K_d of other minerals precipitating from the same fluid. Although quartz is the most abundant mineral in the Meguma veins, this mineral is deficient in *REE* (*e.g.*, Peucker-Ehrenbrink & Schnier 1992) and thus will not affect the *REE* signature of the carbonates. The possible role of accessory mineral phases is alluded to below. Given the variability of the data, in many ways analogous to data reported for other hydrothermal vein carbonates (Möller *et al.* 1979, 1984, Möller & Morteani 1983, Jébrak 1985), it is difficult to interpret the patterns for the Meguma vein carbonates (Figs. 2, 3, 4) as simply reflecting precipitation in an open system from a chemically uniform fluid. Therefore, before discussing the origin and implications of the patterns, a few points are worth noting.

1. Except for a few samples, negative Ce anomalies are lacking; therefore, a source incorporating abundant oxidized material, such as marine sediments (Henderson 1984), can be eliminated as a reservoir or contaminant.

2. Small to significant positive Eu anomalies characterize almost all the samples, which signifies the following: (1) a suitable source or vein wallrock enriched in Eu, such as would occur if abundant, Eu-rich feldspar were present; and (2) the appropriate temperatures (250°C) and oxidation [$f(O_2)$] conditions prevailed such that Eu^{2+} dominated over Eu^{3+} (Sverjensky 1984, Wood 1990), with subsequent substitution for Ca^{2+} in carbonate. The variation in Eu/Eu* might indicate possible changes in $f(O_2)$, which has been documented in other hydrothermal systems (*e.g.*, Jébrak *et al.* 1984, Raimbault *et al.* 1993). Depletion of Eu in the fluid owing to precipitation of another phase is not considered a viable explanation, given the absence of suitable phases (*e.g.*, feldspar) at most of the deposits.

3. Experimental work has shown that the partitioning of *REE* in carbonates is most strongly affected by the abundance of *REE* in solution (*i.e.*, the ratio *REE*/Ca^{2+}) rather than other factors such as rate of precipitation or [CO_3^{2-}] (Terakado & Masuda 1988, Zhong & Mucci 1995). In addition, Zhong & Mucci (1995) have demonstrated that K_d decreases systematically from $10^{3.6}$ for La to $10^{1.9}$ for Yb, indicating that *LREE* are most strongly partitioned into calcite.

4. Experimental and empirical data indicate that some variability of carbonate *REE* data may be attributable to the complexities of trace-element partitioning, which includes temperature, fluid chemistry, fractionation in the fluid due to mineral precipitation, dissolution of vein minerals and rate of fluid flow through the vein (*e.g.*, Lorens 1981, Möller & Morteani 1983, Möller *et al.* 1991, Ayers & Watson 1993).

5. Because low levels of trace elements, particularly of the *REE*, are transported in solution, the fluid will not take on the trace-element signature of the wallrock unless very high fluid:rock ratios are attained (Michard 1989, Ayers & Watson 1993, Wood & Williams-Jones 1994) or fluid flow occurred over an extended interval of time (*e.g.*, Mungall *et al.* 1987). In addition, a change in the pH of the fluid due to fluid:rock interaction will also influence the *REE* concentrations. For example, an increase in *LREE* of the fluid occurs as pH decreases (Michard 1989, Smedley 1991).

In consideration of the above factors and overall features of the Meguma vein deposits, the chondritic *REE* profiles obtained from solution and LAM analyses are considered to reflect both primary and secondary processes, as summarized in Figure 7.

Primary processes: On the basis of analysis of hydrothermal fluids (Michard & Albarède 1986, Michard *et al.* 1983, Michard 1989) and model calculations (Wood & Williams-Jones 1994), it has been demonstrated that non-magmatic fluids are deficient in terms of *REE* contents. Similar conclusions were reached by Möller *et al.* (1979, 1984) on the basis of natural occurrences of carbonate. Given that the vein-forming fluids responsible for Meguma veins are of metamorphic origin, it would be expected that the fluids would be deficient in the *REE*. Thus, it is interesting to note that the abundances of *REE* in the carbonates from the Meguma veins correspond to those of inferred metamorphic origin by Möller and coworkers and are depleted relative

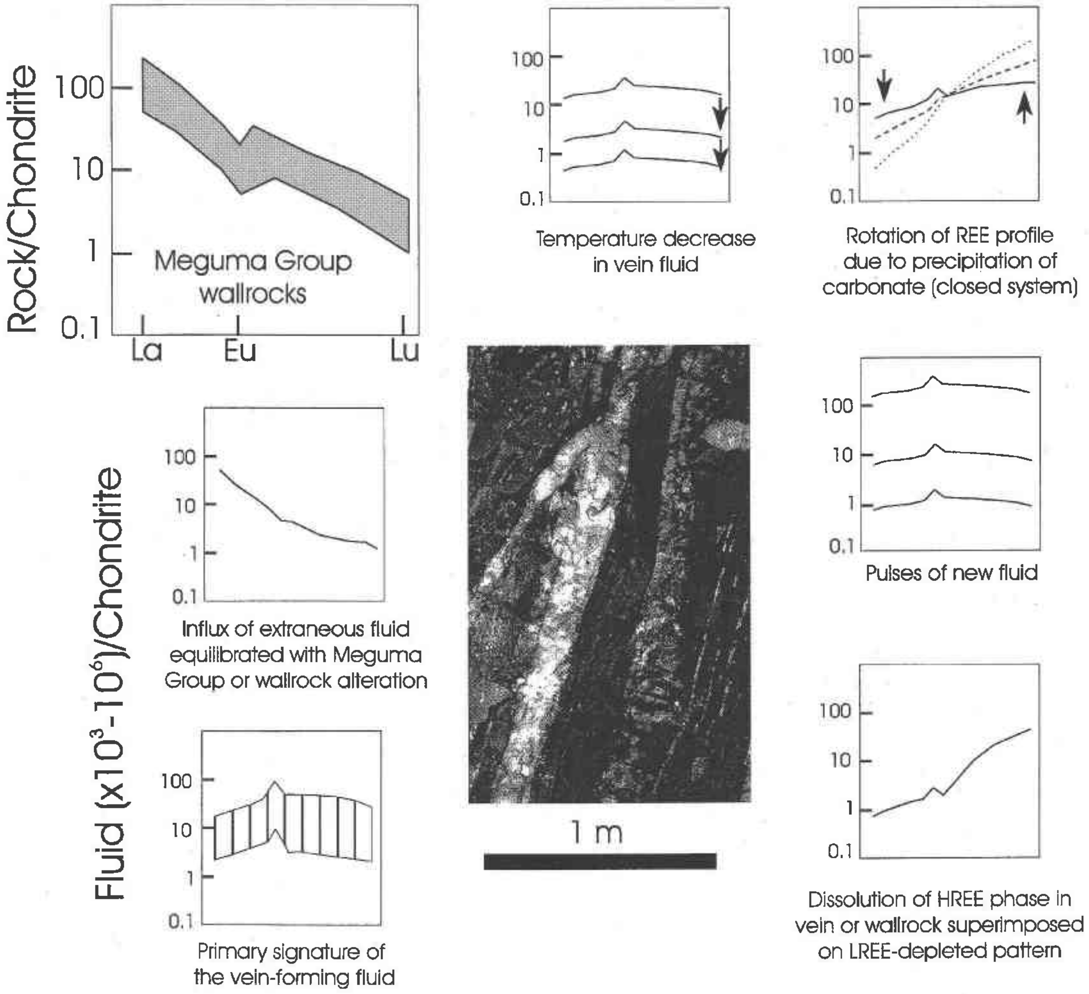

FIG. 7. Schematic diagram summarizing some of the changes in the *REE* signature of the vein fluid that result from physical–chemical changes in the vein–wallrock environment, as discussed in the text. Pattern for the Meguma Group is from Kontak & Smith (1993) and unpublished data of DAK. Compare the profiles shown here to those in Figures 3, 4 and 5. Photo in the center shows a bedding-concordant quartz–carbonate vein (carbonate is the whitish phase) in arsenopyrite-rich metasedimentary rocks of the Meguma Group at the Beaver Dam deposit. Scale for the vein fluid is based on measured and calculated concentrations of *REE* in geological fluids (*e.g.*, Michard 1989, Smedley 1991, Wood & Williams-Jones 1994).

to the signature for vein carbonate of magmatic affinity. We suggest, therefore, that the overall *REE* signature of the carbonates reflects precipitation from a metamorphic fluid.

However, two additional points are worthy of note: (1) the *REE* patterns deviate markedly from the *REE* patterns for the Meguma Group wallrock at the deposits (Kontak & Smith 1993, our unpubl. data); those patterns are identical to patterns typical of turbiditic sediments (*e.g.*, McLennan 1989). (2) The overall similarity of the *REE* patterns in the deposits is interpreted to reflect a common source-reservoir(s) or subsequent processes that singularly or collectively have generated similar abundances for *REE*; the exceptions to this generalization are discussed under second-order processes (*e.g.*, BD–87–100, 161A). This latter point reflects the fact that veins derived from metamorphic fluids represent the end product of large-scale events within the crust and tend to be characterized by chemical homogeneity rather than heterogeneity (Kerrich 1989, Holk & Taylor 1997). With these conditions stated, it is not surprising to see broadly similar *REE* patterns for *the majority of* *the carbonate data*, that is unfractionated to slightly fractionated, either slightly *LREE*- or *HREE*-enriched, regardless of vein type within and among deposits (Figs. 3, 4). The general restriction of the most intense alteration to narrow selvages around veins also suggests that *REE* patterns were not modified by wallrock–fluid interaction at the deposit site (see point 4 above). This finding explains the difference between the carbonate *REE* patterns, which includes characteristic Eu enrichment, and the Meguma Group wallrock.

The differences in absolute abundance of the *REE* among carbonate samples, as observed for example at Tangier, Caribou and Beaver Dam, may be a function of Σ*REE* in the vein-forming fluid (Zhong & Mucci 1995). This is best illustrated by the LAM data, where very similar chondritic patterns are obtained, but with a variation in chondritic abundance that covers nearly two orders of magnitude. Such variation requires changes in the fluid, as discussed below.

Secondary processes: The variations noted in terms of Σ*REE*, fractionation of *REE* and Eu/Eu* could be accounted for by secondary processes such rate of flow, changes in temperature, modification of intensive parameters of the fluid [*e.g.*, $f(O_2)$, pH, CH_4:CO_2 ratio), precipitation or dissolution of other *REE*-bearing phases, incursion of other fluids, and variable amounts of wallrock alteration (Mungall *et al.* 1987, Möller & Morteani 1983, Möller *et al.* 1984, 1991, Michard 1989, Erel & Katz 1990, Ayers & Watson 1993, Rubin *et al.* 1993). The LAM ICP–MS data can be used to illustrate the influence of such secondary processes. For example, in sample BD–87–161A, irregular patches of secondary magnesian calcite (6 to 16 wt.% MgO) replace earlier Mg-free calcite, and these later carbonates are characterized by *HREE* enrichment compared to earlier carbonate (Fig. 5); in addition, enrichment of Sr accompanied the *HREE* enrichment. Enrichment of the *HREE* in the later carbonate could be related to (1) preferential complexing of *HREE* by CO_2-bearing fluids, hence dissolution of earlier carbonate would lead to *HREE* enrichment of later carbonates, or (2) local dissolution of mineral phases enriched in *HREE* (garnet, zircon) in close proximity to growth of the new carbonate. Although such minerals do occur in the wallrock, no work has been done to demonstrate if such a process has occurred; we note, however, that trace element and *REE* data (unpubl. data of DJK) for veins near wall rocks do not indicate such mobility. In contrast to sample BD–87–161A, the other samples analyzed by the LAM technique contain only a single generation of carbonate which may account for internally consistent *REE* patterns despite variations in Σ*REE*.

The change in Σ*REE* observed in all four samples analyzed by LAM may relate to one or more of the following, given that it is not possible in this study to distinguish among enrichment, depletion or cyclicity of Σ*REE* with time: (1) temperature variation during precipitation, (2) depletion of the *REE* in a closed system, (3) influx of a new fluid, (4) dissolution or precipitation of the appropriate assemblage of *REE*-rich accessory minerals or mineral (*e.g.*, monazite, garnet, apatite), resulting in enrichment or depletion of *REE* in the vein fluid. The variation in the solution data (Figs. 3, 4) can be explained using the same processes.

Although a more thorough study of veins is required to properly assess the role of the above-mentioned processes, we tentatively conclude that the slight enrichment and depletion of the *LREE* and *HREE* and changes in Σ*REE* are best explained by a combination of such factors. The contribution of putative contaminants to the *REE* signature of the carbonate samples is not considered to be significant compared to the above processes.

Relationship between REE and isotopic signatures of the carbonates

In order to assess if the *REE* levels in the carbonates are related to either an overprinting fluid-circulation event involving mobilization of *REE* or are a direct function of the amount of interaction of the fluid with wallrock, the *REE* data are integrated with stable ($\delta^{18}O$) and radiogenic ($^{87}Sr/^{86}Sr$) isotope data collected during a companion study (Kontak & Kerrich 1997) (Fig. 8). The results indicate that there is no obvious relationship between the concentration of either the *HREE* and *LREE* contents of the carbonates and their isotopic composition. Even though the carbonates have clearly interacted with low-temperature fluids, as reflected by enriched $\delta^{18}O$ values (also negative Δquartz–carbonate $\delta^{18}O$ values for coexisting mineral pairs; Kontak & Kerrich 1997), their *REE* signatures have been retained.

Possible implications for source reservoirs

The *REE* are commonly used as petrogenetic indicators and tracers in geological processes (*e.g.*, Henderson 1984). The question of interest here is whether similar data from hydrothermal minerals can be used to infer source reservoirs given the potential complications discussed above. From the previous discussion, we have tentatively inferred that there is an overall *REE* pattern common to the carbonates from the various deposits, that is generally flat with moderate *LREE* or *HREE* enrichment or depletion (Figs. 3, 4), with superimposed complications arising from secondary processes operative at the site of vein formation. With the limitations and constraints of these conclusions and awareness of the many problems inherent in this approach (Cullers & Graf 1984), we attempt to use the *REE* patterns of the carbonates to address the question of source reservoir(s) for the fluid because of the relevance of this in studies of hydrothermal systems. Relevant to this argument, however, is the assumption that extrapolation of the experimental work of Zhong & Mucci (1995), conducted on seawater at 25°C, is valid to temperatures and chemical conditions typical of

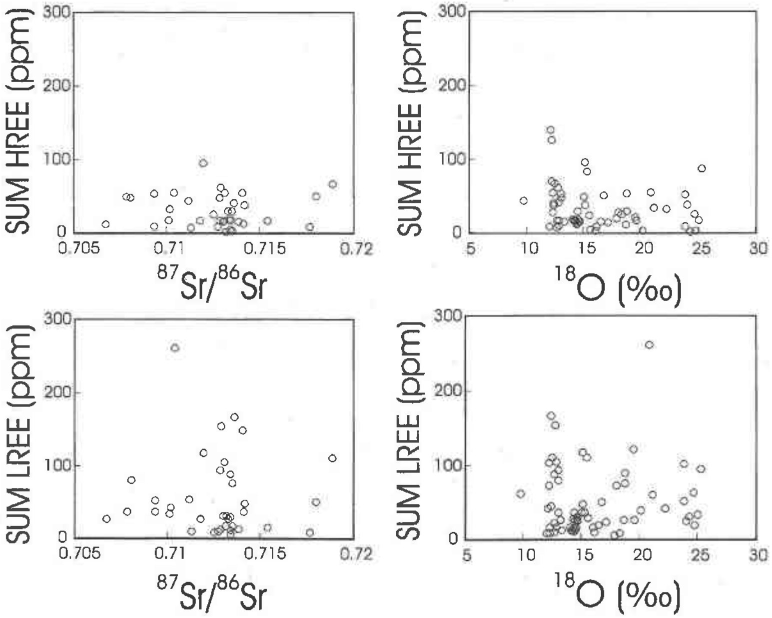

FIG. 8. Binary plots of rare-earth-element contents of carbonates *versus* their δ^{18}O and ^{87}Sr/^{86}Sr signatures (data from Kontak & Kerrich 1997). Note the lack of any apparent trends to the data and the fact that δ^{18}O values of the carbonates reflect the influence of a low-temperature thermal or fluid-circulation event.

mesothermal environments. Such extrapolations have been considered valid by previous workers for calculation of partitioning of the *REE* between minerals and fluids (Henderson 1984) and the aqueous behavior of *REE* (Wood 1990, Wood & Williams-Jones 1994).

With the above limitations stated, the *REE* data for the carbonates are interpreted to indicate that the source reservoir was characterized by an unfractionated *REE* pattern, or possibly even a *LREE*-depleted pattern, on the basis of the following: (1) the favored incorporation of the *LREE* by calcite, and presumably other carbonate phases, during precipitation, and (2) the facts that carbonic complexes favor the *HREE* over the *LREE* (Henderson 1984, Lee & Byrne 1993), and that such fluids are typical of the Meguma veins (*e.g.* Kontak *et al.* 1990a, 1991, 1996). In Figure 9, the *REE* signatures of the potential source-reservoirs identified within the Meguma Terrane are summarized. Solely on the basis of a comparison of the *REE* data for the carbonates in Figures 3, 4 and 5 to that in the potential reservoirs, it would appear that the metasedimentary and meta-igneous source-area of the Tangier xenoliths and the Liscomb gabbroic intrusive rocks are the most reasonable sources. However, integration of the *REE* data with additional information more firmly indicates that the metasedimentary and meta-igneous source area of the Tangier xenoliths is the most likely source, as summarized below.

1. The 370 Ma peraluminous granites are incompatible with the *REE* patterns of the carbonates. The following additional observations also are relevant: (1) stable and radiogenic isotope data eliminate this reservoir (Kontak & Smith 1989, Kontak & Kerrich 1997), (2) there is no spatial association of gold deposits and granites, (3) there is no consistent enrichment of granophile elements in the deposits, and (4) a fluid equilibrated with that reservoir and the vein fluids are incompatible in composition (*e.g.*, fluid inclusion and gas data of DJK).

2. The patterns of rocks of the Meguma Group are, like the granites, inconsistent with the *REE* patterns of the carbonates. The following points are relevant: (1) variable amounts of wallrock alteration indicate that the fluids were not in equilibrium with the Meguma Group, (2) radiogenic isotope data (Kontak & Kerrich 1997, Chatterjee *et al.* 1992) exclude the Meguma Group as the sole reservoir, (3) timing relationships indicate that the veins formed after the peak of metamorphism, hence much later than prograde metamorphism of the Meguma Group (Kontak *et al.* 1990b, 1993). It is also relevant to note that groundwater recharged through metasedimentary rocks in Cornwall (England), similar to the Meguma Group compositionally, has inherited the strongly fractionated, shale-like signature of the reservoir (Smedley 1991). Thus we might expect the same to

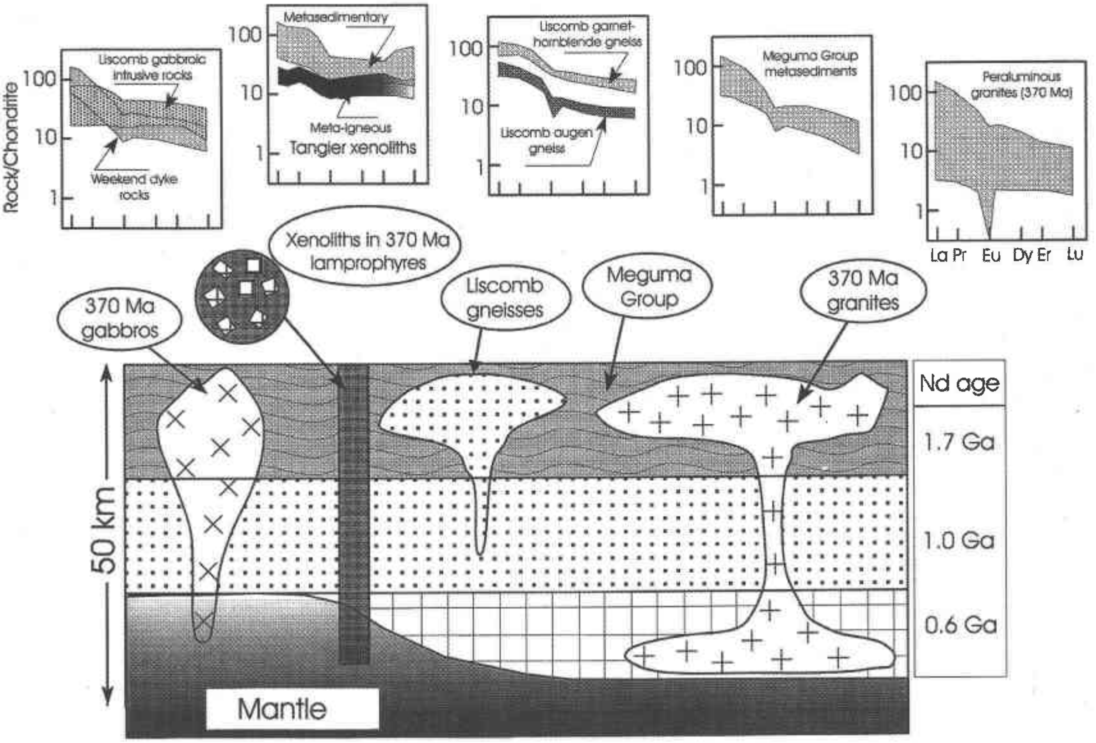

FIG. 9. Schematic diagram summarizing the geological relationships within the Meguma Terrane at *ca.* 370 Ma, the time inferred for gold mineralization [from Kontak & Kerrich (1997) and pers. commun. with A.K. Chatterjee, 1996]. The diagram identifies all the potential source-reservoirs present at that time. Note that there is an inverted stratigraphy within the terrane, such that the rocks with the greatest model Nd age (*i.e.*, Meguma Group) are at the highest structural level, whereas rocks with the youngest inferred age (*i.e.*, granulite-facies xenoliths in the Tangier dyke: Eberz *et al.* 1991) are deepest. The chondrite-normalized *REE* diagrams for the different reservoirs are also summarized for comparison to the carbonate data, as discussed in the text (data from Muecke & Clarke 1981, Eberz *et al.* 1991, Clarke *et al.* 1993, Tate & Clarke 1993, Greenough *et al.* 1993, Dostal & Chatterjee 1995; information about the Meguma Group rocks comes from the unpublished data of D.J. Kontak).

have happened if the vein fluids had originated within or equilibrated with the Meguma Group.

3. The Liscomb gabbroic rocks appear to have a suitable *REE* signature to satisfy the carbonate *REE* data, but the distribution of these rocks is very restricted within the Meguma Terrane (Clarke *et al.* 1993, Tate & Clarke 1993). It is also unlikely that such mafic rocks would have had the capacity to generate the fluids within all the gold-mineralized districts.

4. The Weekend swarm of lamprophyric dykes (Eberz *et al.* 1991, Ruffman & Greenough 1990) can be discounted both on the basis of their geochemical signatures and very restricted occurrence.

5. The Liscomb gneisses, with similar *REE* chondritic patterns as the Meguma Group metasediments, are also considered unlikely candidates as the primary source-reservoir, given the constraints of the *REE* patterns of the carbonates.

Although the Tangier xenoliths are obviously of restricted areal extent, Clarke *et al.* (1993) suggested that much of the Meguma Terrane was underlain by such rocks at *ca.* 370 Ma. However, the inferences based on the carbonate *REE* data in this study are in contrast to the findings of Chatterjee *et al.* (1992) and A.K. Chatterjee (pers. commun., 1996), who suggested on the basis of Pb isotopic analyses that the source of the auriferous vein-forming fluids are the Liscomb gneisses. An obvious compromise proposed here is that the *REE* data and the Pb isotope results merely reflect contributions from two different reservoirs.

CONCLUSIONS

A study of the trace and *REE* geochemistry of carbonates from 16 gold-mineralized districts in the Meguma Terrane of southern Nova Scotia indicates the following:

1. Except for Sr and the *REE*, the carbonates are characterized by low abundances of trace elements; some erratic anomalies (*e.g.*, Ba, W, Pb, Bi) relate to putative contaminants. The large range in Sr contents (to 15000 ppm) reflects variation in the Sr content of the vein fluid and may result from contamination of an originally homogeneous fluid either during ascent through the crust or at the site of vein formation. The variation in Sr also may reflect a regional enrichment of this element within the crust.

2. The *REE* elements in carbonate are variably enriched within and among deposits. Extreme modification of the *REE* or any other trace element at the site of deposition *via* wallrock alteration is considered unlikely, given that such a process requires exceptionally high water:rock ratios, and that wallrock alteration is generally cryptic or confined to the narrow selvages of veins. Variation of the *REE* in the vein carbonates from within the same deposit and sample (LAM analyses) reflects the interplay of several variables, including changing fluid composition, in particular *REE*/Ca^{2+}, change in fluid temperature, precipitation and dissolution of spatially associated *REE*-bearing phases, and recharging of the vein fluid.

3. The generally similar chondrite-normalized patterns of the *REE* within and among deposits is suggestive of a common source-reservoir. Consideration of the *REE* partitioning between carbonate and fluid permits a qualitative estimation of the *REE* signature of this reservoir. With the limitations of such extrapolations, the source reservoir is considered to be high-grade metamorphic rocks occurring as a layer in the crust within the Meguma Terrane at *ca.* 370 Ma, represented today by granulite-facies xenoliths within lamprophyric dykes. This potential association of the vein formation with granulite formation of parts of the Meguma Terrane at *ca.* 370 Ma indicates a temporal association of Meguma gold veins, granulite-facies metamorphism, emplacement of the peraluminous granites of this terrane and intrusion of mafic magma.

4. The lack of correlation of the carbonate *REE* and published stable ($\delta^{18}O$) and radiogenic ($^{87}Sr/^{86}Sr$) isotope data preclude any relationship between enrichment or depletion of the *REE* with wallrock alteration or with an overprint by later, low-temperature fluids.

ACKNOWLEDGEMENTS

This research was supported in part by the Canada – Nova Scotia Mineral Development Agreement (1984–1989). Operation of the analytical facilities at Memorial University is supported by NSERC funding. The project benefitted from the cooperation of Mr. Paul Smith, who provided some of the samples used in this study. The senior author acknowledges with pleasure the many fruitful discussions over the years with Mr. Paul Smith and Dr. A.K. Chatterjee concerning the genesis of Meguma gold deposits. Mr. Bob McKay, Dalhousie University, assisted with electron-microprobe work. Comments on the paper by journal reviewers and the editor led to substantial improvement and are sincerely appreciated. This paper is published with permission of the Director, Mineral Resources Division, Nova Scotia Department of Natural Resources.

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Received November 27, 1997, revised manuscript accepted February 15, 1999.