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LASER-ABLATION ICP–MS MICRO-ANALYSIS OF CALCITE CEMENT FROM A MISSISSIPPI-VALLEY-TYPE Zn–Pb DEPOSIT, NOVA SCOTIA: DRAMATIC VARIABILITY IN REE CONTENT ON MACRO- AND MICRO-SCALES

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ABSTRACT

Gays River is a Mississippi-Valley-type (MVT) Zn–Pb deposit in Nova Scotia, hosted by Visean-age dolomitized carbonates; the mineralization, formed at *ca.* 300 Ma, is due to infiltration and replacement of the host-rock dolostone by heated (to 250°C), saline (*ca.* 25 wt.% equivalent NaCl) brines. Isotopic data (Sr, C, O, Pb) indicate that the mineralizing fluids equilibrated with rocks of the Meguma Group, either as detritus within the Devono-Carboniferous Horton Group or in the underlying basement. The proportion of the *REE* of five different types of syn- to post-mineralization calcite cement has been determined *via* solution chemistry and a laser-ablation microanalysis (LAM) – inductively coupled plasma – mass spectrometry (ICP–MS) technique. The LAM–ICP–MS technique permits analysis on the scale of 40 μm and determination of zoning profiles by either vertical ablation or lateral traverses. The LAM results indicate a large variation in Σ*REE* (from 1000 to <1 times chondrite) and degree of fractionation, thus confirming the solution data and eliminating the possibility of putative contamination. Correlation of cathodoluminescence microscopy and LAM data indicate a systematic temporal decrease in Σ*REE* and degree of fractionation and a concomitant increase in Mn content of calcite cement with time. The data are explained by a combination of changing fluid:rock ratio and closed-system fractionation of the *REE*. Thus, the elevated *REE* contents of calcite are inherited from the infiltrating fluids that equilibrated with Meguma Group detritus in the Horton Group, whereas relatively depleted *REE* values reflect buffering by the wallrock. Closed-system fractionation of the *REE* can account for the variable $(La/Lu)_N$ values that characterize calcite with lower *REE* contents.

Keywords: calcite, rare-earth elements, laser-ablation microanalysis, inductively coupled plasma – mass spectrometry (ICP–MS), Gays River, Mississippi-Valley-type mineralization, Nova Scotia.

SOMMAIRE

Le gisement de Gays River (Nouvelle-Écosse) constitue un exemple de minéralisation à Zn–Pb du type "Mississippi Valley". Les roches hôtes sont des séquences à carbonate d'âge viséen. La minéralisation se serait formée il y a environ 300 Ma par infiltration et remplacement des dolomies encaissantes par des saumures (environ 25% de NaCl ou équivalent) chauffées (jusqu'à 250°C). Les données isotopiques (Sr, C, O, Pb) montrent que les fluides minéralisateurs ont atteint l'équilibre avec les roches du Groupe de Meguma, soit sous forme de détritus dans les roches dévono-carbonifères du Groupe de Horton, soit avec le socle sous-jacent. Nous avons analysé les cinq différents types de ciment calcitique syn- ou post-minéralisation pour leur teneur en éléments du groupe des terres rares (*TR*) par traitement de solutions ou par microanalyse par ablation avec rayon laser (LAM) et plasma avec couplage inductif et spectrométrie de masse (ICP–MS). La technique LAM–ICP–MS permet une analyse ponctuelle sur une échelle de 40 μm, et donc la détermination de profils de composition, soit par ablation verticale ou par traverses latérales. Les résultats de l'analyse par LAM indiquent une grande variation en teneurs totales des terres rares (entre 1000 et <1 fois les teneurs chondritiques) et en degré de fractionnement, confirmant ainsi les données obtenues sur solutions et éliminant du même coup la possibilité d'une contamination possible. Une corrélation entre les observations microscopiques en cathodoluminescence et les résultats obtenus par LAM indiquent une diminution systématique des concentrations des terres rares et du degré de fractionnement et une augmentation dans la teneur en Mn de la calcite dans les génerations de plus en plus tardives. Nous pensons que les données illustrent des changements dans le rapport du volume de fluide à quantité de roche, aussi bien que le fractionnement des terres rares en système fermé. C'est donc dire que les teneurs en terres rares de la calcite sont héritées de la phase fluide qui s'est infiltrée et qui avait atteint l'équilibre avec le détritus provenant du Groupe de Meguma et faisant partie du Groupe de Horton, tandis que les teneurs très faibles résultent du tamponnage dû aux roches encaissantes. Le fractionnement des terres rares en système fermé pourrait bien rendre compte des valeurs variables de $(La/Lu)_N$ qui caractérisent la calcite à faible teneur en terres rares.

(Traduit par la Rédaction)

Mots-clés: calcite, terres rares, microanalyse par ablation au laser, analyse par plasme avec couplage inductif et spectrométrie de masse (ICP–MS), Gays River, minéralisation de type "Mississippi Valley", Nouvelle-Écosse.

INTRODUCTION AND NATURE OF THE PROBLEM

The geochemical signature of hydrothermal ore deposits is generally examined *via* the study of fluid inclusions (Roedder 1984) or of emanating fluids in the case of active geothermal systems (Michard *et al.* 1983). Unfortunately, standard methods of fluid-inclusion analysis only provide information for the most concentrated species (*e.g.*, Na, Ca, K) unless very sensitive techniques are used (Rankin *et al.* 1993). In order to circumvent this problem, recent work has focused on the trace-element chemistry of hydrothermal minerals, and particularly their *REE* concentrations. With such data, it is possible to make inferences

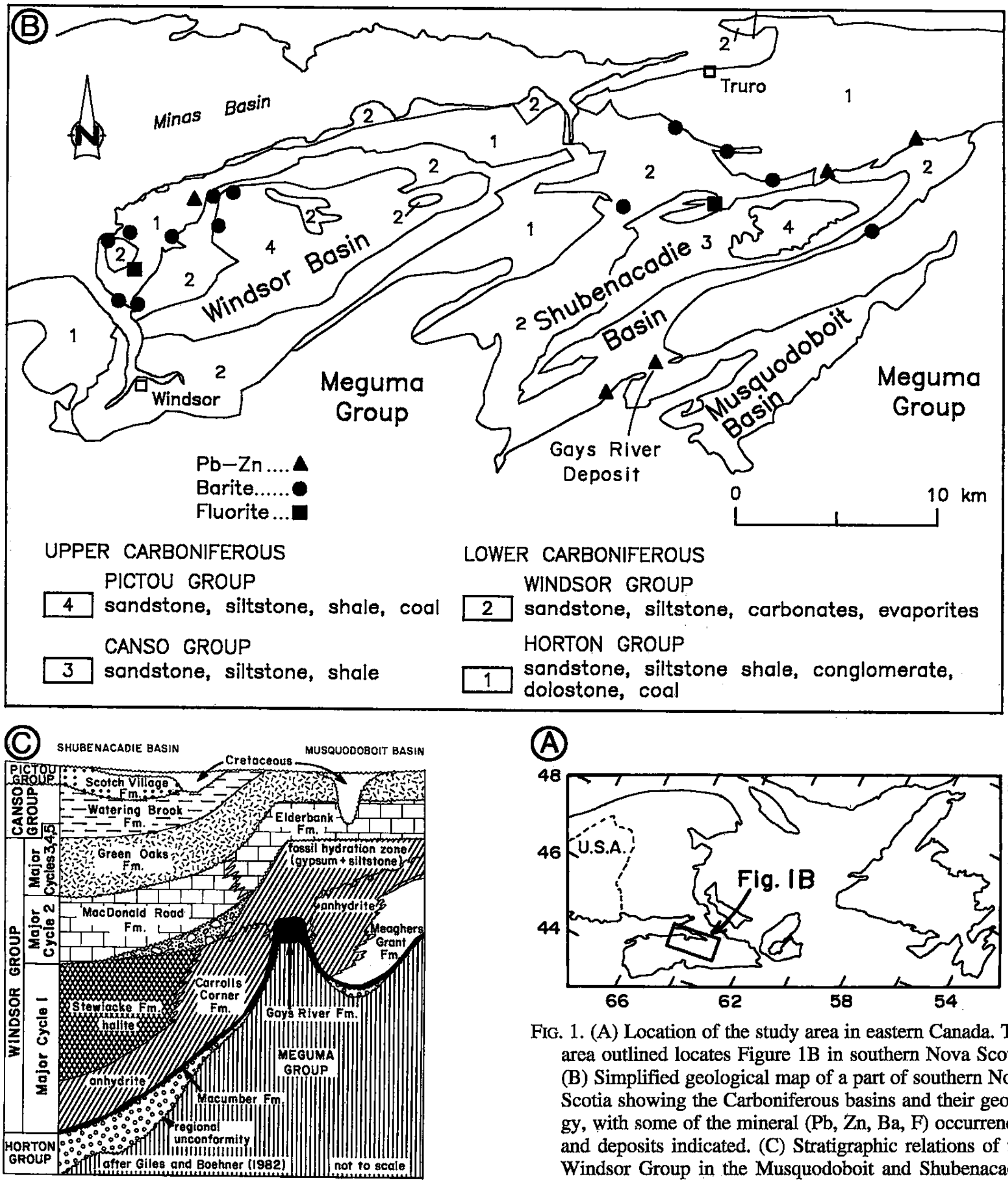

FIG. 1. (A) Location of the study area in eastern Canada. The area outlined locates Figure 1B in southern Nova Scotia. (B) Simplified geological map of a part of southern Nova Scotia showing the Carboniferous basins and their geology, with some of the mineral (Pb, Zn, Ba, F) occurrences and deposits indicated. (C) Stratigraphic relations of the Windsor Group in the Musquodoboit and Shubenacadie sub-basins (from Giles & Boehner 1982).

with respect to source reservoirs in equilibrium with the mineralizing fluids (Möller & Morteani 1983). Recent studies include: (1) carbonate phases in vein-type base- and precious-metal deposits (Möller *et al.* 1979, 1984, Kontak *et al.* 1991) and Mississippi-Valley-type (MVT) Pb–Zn deposits (Graf 1983, 1984, Grant & Bliss 1983); (2) fluorite from a variety of deposit types (Marchand *et al.* 1976, Collins & Strong 1985, 1992, Jébrak *et al.* 1985, Constantopoulos 1988, Hein *et al.* 1990; (3) tourmaline (King *et al.* 1988) and (4) scheelite from lode-gold deposits (Anglin *et al.* 1987). In such studies, it is difficult to assess the influence of various physical and chemical parameters on the distribution coefficients (Marchand *et al.* 1976, Morgan & Wandless 1980, Raimbault 1985, Michard 1989). The present data, for both experimental and natural systems, are considered insufficient, and more work is needed to determine the potential use of trace-element chemistry of hydrothermal minerals in ore-deposit studies.

In this paper, results of laser-ablation ICP–MS analysis of calcite cement in an MVT deposit are reported. Preliminary solution chemistry (ICP–MS) of calcite separates indicated extreme variation in *REE* chemistry for calcite of similar paragenesis and habit (Kontak 1992a, b, Kontak & Jackson 1993). These results contrast markedly with systematic geochemical patterns determined for calcite cement from other MVT deposits (Graf 1983, 1984) and carbonate strata (*e.g.*, Moldovanyi *et al.* 1990). In addition to documenting the nature of the *REE* variation within different types of calcite at Gays River, this study indicates the general application of the laser technique to: (1) determine K_d values for mineral phases, (2) document chemical homogeneity or heterogeneity in mineral phases, (3) determine the influence of various parameters on trace-element partitioning (Reeder & Grams 1987, Paquette & Reeder 1990, Paterson & Stephens 1992, Möller *et al.* 1991), and (4) evaluate trace elements as tracers in hydrothermal systems with implications for source reservoirs.

GEOLOGICAL SETTING

The Gays River Zn–Pb deposit, located in the Meguma Terrane of southern Nova Scotia, is hosted by Windsor Group (Visean) carbonates deposited in several sub-basins of the larger Maritimes Basin of eastern Canada (Giles & Boehner 1982; Fig. 1). A cross-section of the deposit (Fig. 2) and stratigraphic column (Fig. 1C) suffice to illustrate the salient geological features. The carbonate buildup developed on a substrate of Lower Paleozoic metaturbidites of the Meguma Group which, away from the deposit, are overlain by terrigenous clastic rocks of the Late Devonian – Early Carboniferous Horton Group (Fig. 1B). The basal unit of the buildup is a carbonate breccia containing fragments of Meguma Group lithologies in a carbonate matrix, whereas the main unit consists of interbank and bank facies, the latter being mollusc- and alga-rich. Onlapping the carbonate bank are evaporites. Locally, the carbonate–evaporite contact has been deeply incised and infilled by poorly consolidated sediments of Cretaceous and younger age. The laterally extensive equivalent of the Gays River Formation is the Macumber Formation, a generally thin (<1 m) laminated carbonate rock. Carbonate lithologies within the Musquodoboit and Shubenacadie

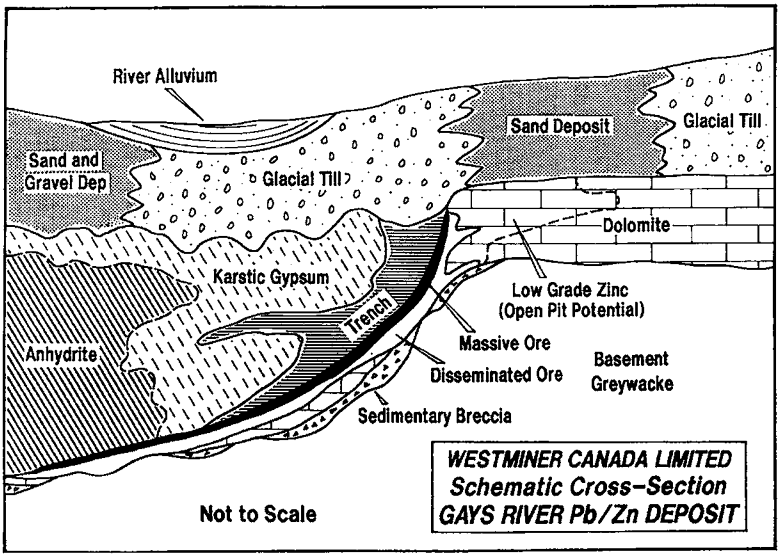

FIG. 2. Schematic cross-section (NW–SE) through the Gays River deposit area, showing the major rock types and distribution of the mineralized zone.

basins have been variably dolomitized *via* constant-volume replacement during diagenesis (Savard 1992a, b).

Mineralization (2.5 Mt of 15% combined Zn + Pb) consists of massive and disseminated ore and is confined to the carbonate host, with the massive ore preferentially located at the carbonate–evaporite contact (Fig. 2). The massive ore replaces the carbonate and consists of medium-grained galena and fine-grained (10–40 μm), Fe-poor, beige sphalerite. In contrast, disseminated mineralization occupies primary pore-space and tends to be coarser grained. Trace amounts of Fe and Cu sulfides, fluorite and barite also occur.

The deposit represents an example of MVT mineralization (Anderson & MacQueen 1982) in that the mineralization formed as a result of infiltration of heated (to 250°C), saline (23–35 wt.% equiv. NaCl) brines that replaced the host-rock carbonate (Akande & Zentilli 1984, Kontak 1992a, b). Mineralization formed at *ca.* 300 Ma, some 30 Ma after deposition of the host rocks (Pan *et al.* 1993, Kontak *et al.* 1994).

The mineral paragenesis for the deposit (Figs. 3, 4) is identical to that for carbonate samples of similar age within the Carboniferous basins of southern Nova Scotia (Savard 1992a, b). In general, mineralization postdates dolomitization of the host rock and growth of dolomite euhedra, but predates calcite cementation.

CALCITE TYPES AND PARAGENESIS

There are five types of calcite cement recognized in the deposit area: (1, 2) calcite infilling primary pore-space, either barren (Vb) or mineralized (Vm); (3) calcite cement in the matrix of the mineralized basal breccia (B); (4) calcite intergrown with massive ore (O); this type occupies pore-space in the galena-rich part of the massive ore; (5) calcite euhedra coating fracture surfaces (F); this type does not coexist with Pb or Zn sulfides and represents the latest stage of calcite deposition.

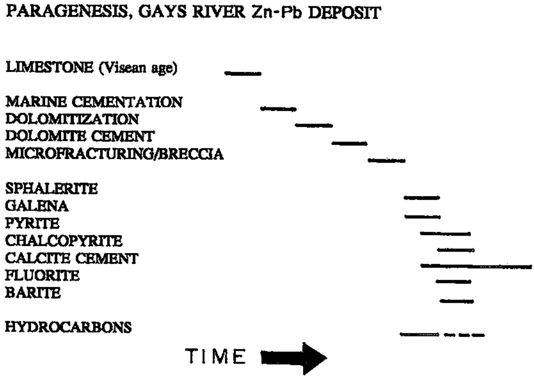

FIG. 3. Simplified mineral paragenesis for the Gays River Zn–Pb deposit. Note that the calcite cement overlaps much of the sulfide paragenesis and is poorly constrained with respect to the mineralization.

The calcite types are poorly constrained paragenetically, as calcite usually postdates galena and sphalerite (Figs. 3, 4). Even in the case of Vb and Vm types, it is not possible to tell if these groupings represent separate stages, as calcite invariably overgrows sphalerite euhedra lining these cavities, but not all cavities are lined with sphalerite (Figs. 4E *versus* 4F) even where cavities are separated by only 1 or 2 cm.

ANALYTICAL TECHNIQUES

Major- and minor-element compositions were determined with a JEOL 733 Superprobe equipped with an Oxford Link EXL energy-dispersion system (Dalhousie University), with the following operating conditions: accelerating voltage 15 kV, sample current 10 nA, beam diameter 1–3 μm, counting time 20 seconds. Instrument calibration was done on pure metal standards, and data reduction of raw counts was done using Link's ZAF matrix-correction program.

Trace-element contents were determined using inductively coupled plasma – mass spectrometry (ICP–MS) *via* solution chemistry or by laser-ablation microprobe (LAM). High-quality separates of calcite were prepared by pulverizing material to –35/+60 mesh and hand picking with the help of a binocular microscope. Calcite separates represent a single clot of cement infilling pore-space or coating a single fracture-surface. Calcite separates (*ca.* 100 mg) were dissolved in 8 M HNO_3, evaporated to dryness and taken to a final volume with 0.2 M HNO_3, and the solutions were analyzed on an Sciex Elan model 250 ICP–MS. The wallrock dolostone was analyzed in a similar manner, except that if the sample did not fully dissolve in HNO_3 alone, a second attack with a 2:1 ratio of 8 M HNO_3 + 6 N HCl was performed, after which HCl was removed with two HNO_3 evaporations before taking to a final volume. Further details of the analytical technique, precision and accuracy are given in Jenner *et al.* (1990).

Microanalysis of calcite, fluorite and dolostone was done on thick (150 μm), doubly polished sections (Figs. 4A, D) or hand-picked grains (Fig. 4B) using a Nd–YAG laser (Jackson *et al.* 1992, Longerich *et al.* 1993, Jenner *et al.* 1993). All samples were photographed prior to analysis, and examination of samples after each analysis allowed location of the ablation pit on the photograph (Figs. 4A, D). Because of the low absorptivity and poor ablation qualities of calcite at the laser's fundamental wavelength of 1064 nm, ablation was done using the frequency-quadrupled UV beam (λ 266 nm); UV radiation is

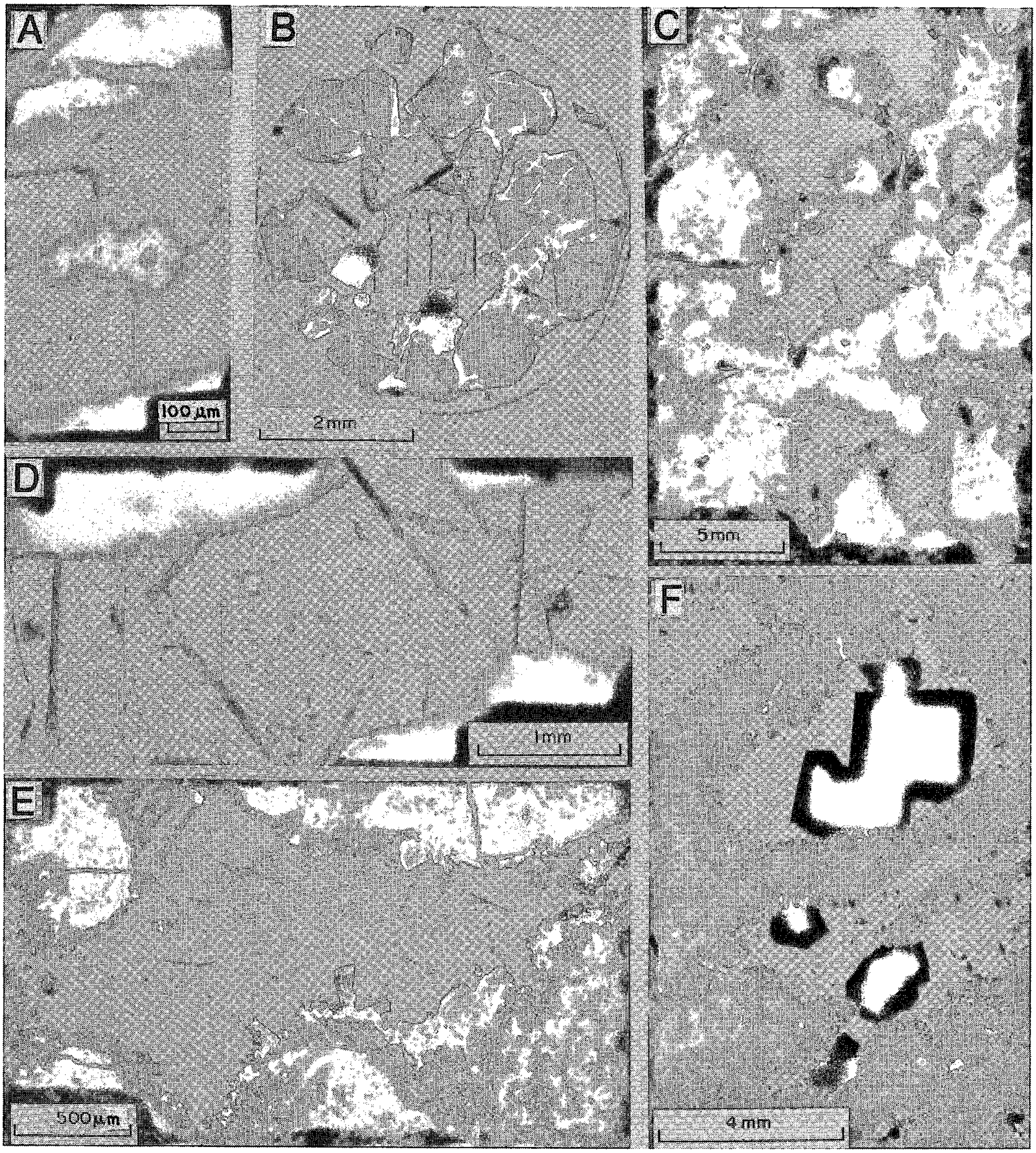

FIG. 4. Photomicrographs of various host-rocks, cements and mineralization at the Gays River Zn–Pb deposit. (A) Calcite cement (Vb) in dolostone with three laser-ablation pits illustrating the scale of analysis possible using the LAM technique. (B) Mount of hand-picked chips of calcite cement from a single pore-space; this material was used for LAM analysis. (C) Calcite cement (Vb) infilling primary pore-space in dolostone. Note the presence of fine-grained euhedra of dolomite (dog-tooth variety) lining the cavities and predating calcite cement. (D) Calcite cement containing three laser-ablation pits with adjacent wallrock dolostone. (E) Sample of dolostone illustrating the following mineral paragenesis: (1) marine cement; (2) pervasive dolomitization of rock; (3) cementation by fine-grained euhedra of dolomite; (4) sphalerite mineralization (*i.e.*, cement); (5) late-calcite cement infilling remaining pore-space. Note that in some places one passes immediately from stage 3 to 5. (F) Sample of dolostone illustrating again the mineral paragenesis as in Figure 4E, but here with galena mineralization. Note the well-developed marine cement stage, absence of sphalerite and presence of large euhedra of galena that overlap the calcite cement stage.

more strongly absorbed, and results in superior characteristics of ablation in transition-element-poor minerals (Jenner *et al.* 1993). LAM–ICP–MS procedures were as described by Jenner *et al.* (1993). Calcium was used as the internal standard to correct for differences in ablation yield between sample and calibration standard (NBS 610 silicate glass). A slightly defocused beam was used to produce ablation-pit diameters of *ca.* 40 μm (Figs. 4A, D), thereby significantly improving detection limits compared to operation at optimum focusing conditions (*i.e.*, 10 μm). For each analysis, ablation was continued until the laser bored through the mineral wafer (generally about 10–20 to a maximum of 40 seconds), as indicated by a sharp increase in Na from the underlying glass slide. The data were transmitted to a remote PC for processing using spreadsheet software. From graphical examination of the signals, the presence of spikes potentially related to ablation of microinclusions was assessed, and optimal background and signal time-intervals for integration were selected. Concentrations were calculated using the algorithm of Jenner *et al.* (1993). Detection limits (3σ) for most elements showed considerable ranges (>10 fold variation among samples). For the *REE*s, median values for the detection limits were all close to 0.14 ppm, corresponding to chondrite-normalized values ranging from approximately 0.5 for the light rare-earth elements (*LREE*) to 4.0 for the heavy rare-earth elements (*HREE*). Even after elimination of data below detection limits, many low-abundance compositions have extremely irregular chondrite-normalized patterns as a result of concentrations of some elements very close to detection limits (or errors in calculation of the detection limit inherent in techniques with near-zero background).

Complete analytical results are given in Kontak (1992a, in prep.) and are available from the senior author upon request. The chondrite-normalization values of Taylor & McLennan (1985) are used throughout.

ANALYTICAL RESULTS ON DOLOSTONE WALLROCK

Dolostone contains 16 to 24 wt.% MgO, up to 4.5 wt.% FeO and MnO, and 30 to 32 wt.% CaO (Table 1, Fig. 5). Comparison of trace-element data (Sr, Ba, Y, *REE*) from solution chemistry and LAM analyses (Table 2, Fig. 6) indicates similar results, which is remarkable given the contrast in sampling

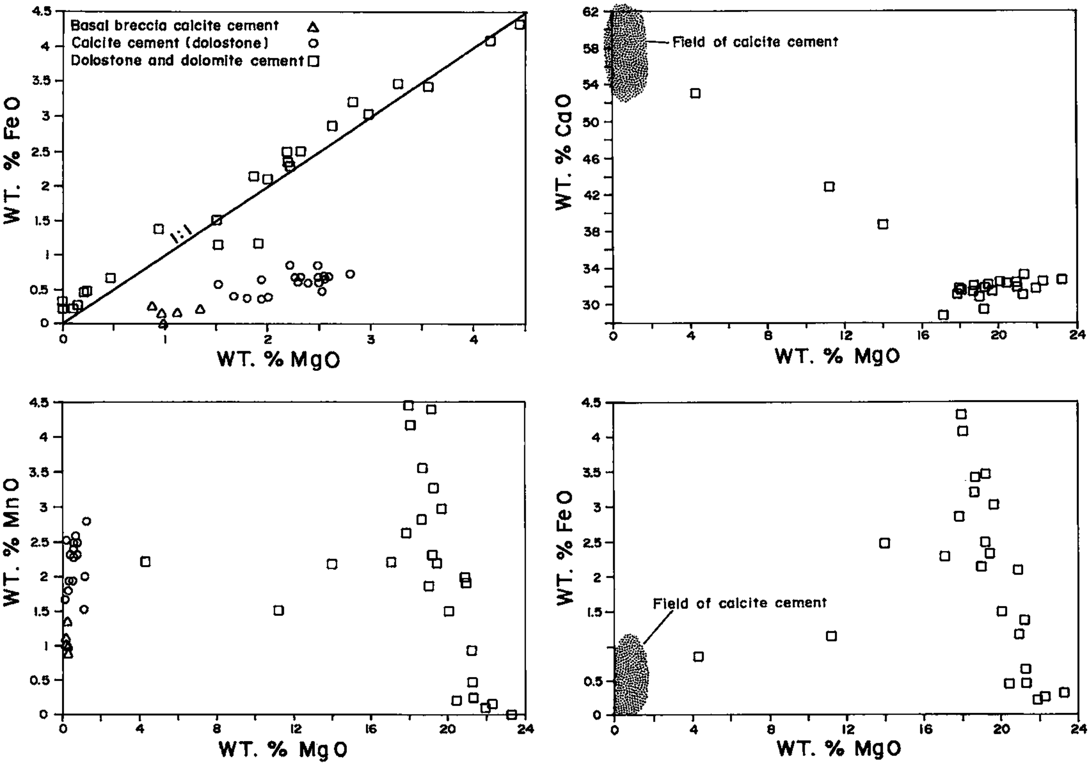

FIG. 5. Binary plots illustrating major- and minor-element chemistry (EMPA) for calcite cement (both in dolostone and basal breccia host), dolomite cement and dolostone host-rock.

TABLE 1. REPRESENTATIVE EMPA DATA OF DOLOSTONE AND CALCITE, GAYS RIVER, NOVA SCOTIA

Sample	Material	CaO	FeO	MgO	MnO	Σ wt.%
GR-91-13	calcite	57.86	0.62	0.51	2.30	61.29
	calcite	57.94	0.84	0.64	2.51	61.93
	dolostone	42.96	1.15	11.23	1.52	56.86
	dolostone	38.86	2.50	14.01	2.19	57.56
GR-91-6	dolostone	32.66	0.27	22.30	0.15	55.38
	dolostone	32.38	0.46	20.45	0.21	53.50
	dolostone	31.92	0.23	21.93	0.10	54.18
	calcite	57.11	0.38	0.29	1.80	59.58
GR-91-3	dolostone	31.40	3.21	18.66	2.83	56.10
	dolostone	31.95	1.18	20.96	1.91	56.00
	calcite	58.99	0.60	0.60	2.40	62.59
	calcite	58.79	0.68	0.58	2.27	62.32
	dolostone	31.80	4.33	18.01	4.46	58.60
GR-91-10	calcite	58.85	0.64	0.77	2.32	62.58
	calcite	58.19	0.26	0.31	0.88	59.64

Calcite cements in dolostone (Vb, Vm types) except GR-91-10, which is in basal breccia (B type).

volume of the two techniques. The elevated Ba contents for whole-rock material probably reflects trace amounts of barite that were not encountered with LAM analysis.

The chondrite-normalized plots (CNP) for the *REE* data of both barren and partially mineralized dolostones are typical of carbonate rocks in terms of Σ*REE*, degree of fractionation [(La/Lu_N) in the range 3 to 10] and negative Eu anomalies (*e.g.*, Jarvis *et al.* 1975, Schieber 1988). The slight see-saw pattern for the LAM data (Fig. 6B) indicates that concentrations approach detection limits; in addition, there seems to be a discernable difference in the *LREE* contents of the two samples analyzed, reflecting a difference in the degree of fractionation of the *REE*. A single composition of marine cement (see paragenesis in Fig. 3) also is shown in Figure 6B; such data could not be easily obtained using conventional techniques. The results indicate that the marine cement has *REE* abundances identical to those in the dolostone, which shows that the host rock buffered the fluids during diagenesis. This inheritance results from the fact that seawater has very low concentrations of *REE* compared to carbonates; hence even where there is a high fluid:rock ratio, the wallrock will buffer the fluid chemistry (Moldovanyi *et al.* 1990).

TABLE 2. ANALYTICAL DATA FOR DOLOSTONE MATERIAL DETERMINED BY LAM AND SOLUTION CHEMISTRY, GAYS RIVER, NOVA SCOTIA

Sample	Material	Technique	Sr (ppm)	Ba (ppn)	Y (ppm)
GR-91-92	dolostone	LAM	10.9	6.5	3.9
	dolostone	LAM	15.1	10.4	6.3
GR-91-84A	dolostone	LAM	13.1	6.3	6.6
	dolostone	LAM	14.9	6.7	4.5
	dolostone	LAM	14.4	25.7	3.8
	marine cement	LAM	24.0	14.2	6.3
GR-91-96	dolostone	Solution	9.6	38.3	4.1
GR-91-125	dolostone	Solution	10.3	46.9	5.2
GR-91-91, 92,93,98,164	mineralized dolostone	Solution	10.4 ± 3.6	42± 2.0	5.8± 1.5

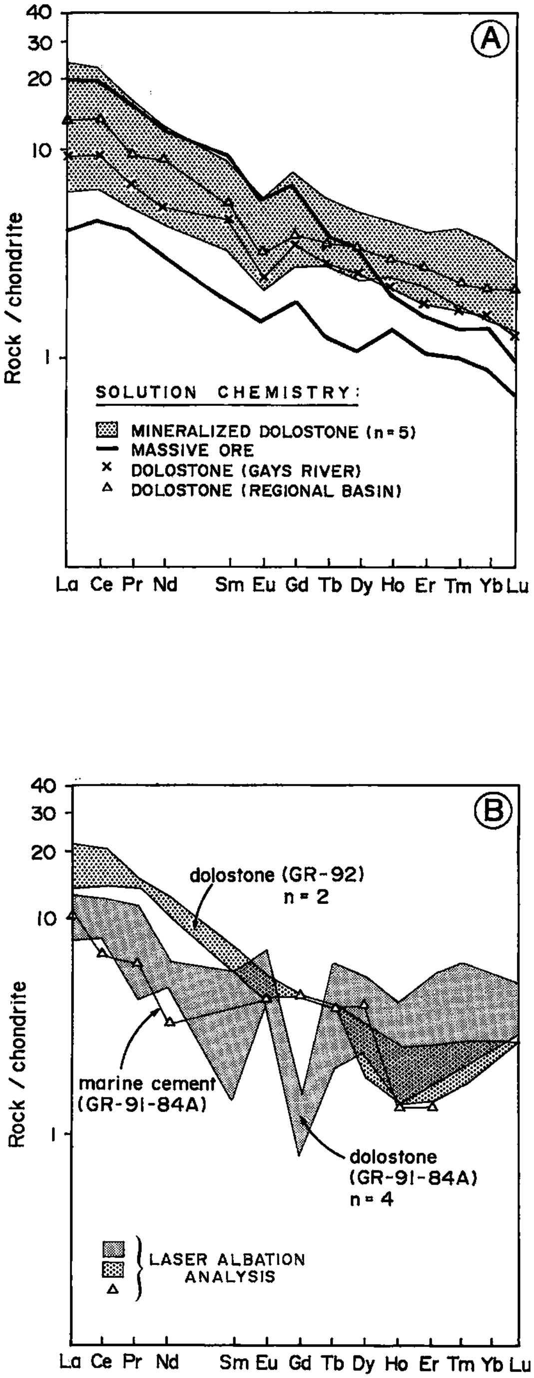

FIG. 6. Chondrite-normalized *REE* plots for dolostone host-rock (Gays River area and from within the regional Shubenacadie Basin), mineralized dolostone and massive ore. (A) Results for solution chemistry. (B) Results from LAM analyses.

ANALYTICAL RESULTS ON CALCITE CEMENT

Major- and minor-element chemistry

Chemical compositions of calcite cement (Table 1, Fig. 5) indicate between 1 and 3 wt.% MnO, with lesser concentrations of Mg (up to 2 wt.% MgO) and Fe (up to 1 wt.% FeO). There is a clear distinction between the calcite cement in the basal-breccia host (B) and the dolostone (Vb, Vm), the latter showing relative enrichment in Mn.

Trace-element chemistry: bulk separates

The level of strontium varies from *ca.* 50 to 250 ppm, with one sample at 500 ppm (Fig. 7); there is no consistent relationship between Sr content and calcite type. Extreme enrichment (to >3000 ppm) occurs in three samples, but the high Ba contents of these samples (*ca.* 2000 ppm) suggests the presence of barite as a contaminant. Although data were acquired for additional trace-elements (Li, Be, Sc, V, Cr, Rb, Zr, Nb, Mo, Cs, Hf, Ta, Tl, Bi, Th, U), abundances were found to be consistently below 1–2 ppm, the only exceptions being for Pb, Zn and Cu, which indicate trace amounts of sulfide (Kontak 1992a).

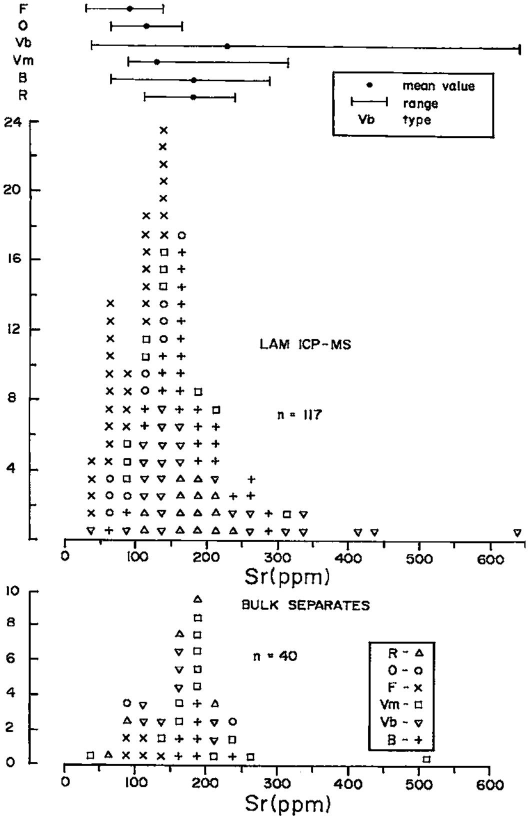

FIG. 7. Histogram plots of Sr contents (ppm) for calcite cements from Gays River determined by LAM–ICP–MS and bulk separates (ICP–MS). Data are also summarized in Table 5.

The CNP for different types of calcite (Fig. 8) indicate large variations in Σ*REE* and significant fractionation [*i.e.*, $(La/Lu)_N$], with the greatest variation for types Vb and Vm, both from the deposit area and regionally. Two patterns are distinguished: (1) an unfractionated CNP that is best represented by B and O types, and (2) a strongly fractionated CNP most prevalent in Vm and Vb types from the deposit area and regionally, although some unfractionated CNP occur for Vm calcite. Other features include: (1) F-type calcite is intermediate between these two broad categories (*i.e.*, Vm and Vb); (2) B-type calcite shows a positive Ce-anomaly; (3) a negative Eu-anomaly characterizes all types of calcite. The variation of *REE* data for calcite types is not related to analytical problems or impurities, as replicate analyses indicate similar results. Whereas the variability documented here contrasts with results of previous *REE* studies of carbonates from MVT-type deposits (*e.g.*, Graf 1983, 1984, Grant & Bliss 1983), comparable heterogeneity is noted in carbonates from other hydrothermal ore deposits (Kontak *et al.* 1991, Kontak & Smith 1993, Möller *et al.* 1979, 1984).

Trace-element chemistry: laser-ablation microanalysis (LAM)

Initial results of LAM analysis of calcite cement are summarized in Figure 9. Three important observations are noted: (1) spot analysis of a single grain (sample GR–91–41, Fig. 9C) indicates large variability in Σ*REE*, although the degree of fractionation (*i.e.*, CNP) recorded in different analyses is similar. Despite the apparent chemical heterogeneity of the sample, solution-chemistry data for the sample agree with the average of the five spot-analyses (Fig. 9C); (2) a vertical profile through a grain in the same sample discussed previously (GR–91–41, Figs. 9A, B) indicates pronounced zoning for the *LREE* (Ce, Nd), but relatively little zonation for other *REE* (Tm, Eu) or trace elements (Y, Sr); (3) where LAM data indicate a homogeneous composition, the results agree with solution chemistry for a bulk separate (sample GR–91–G, Fig. 9D). Collectively, these data thus offer an explanation for the large chemical variations recorded in the bulk analyses (Fig. 8).

LAM analyses of calcite types were done on an additional thirteen samples (representative samples in Figs. 10, 11, 13, 14) in order to fully characterize the nature and degree of trace-element variability in calcite cements, in an attempt to correlate this with their dif-

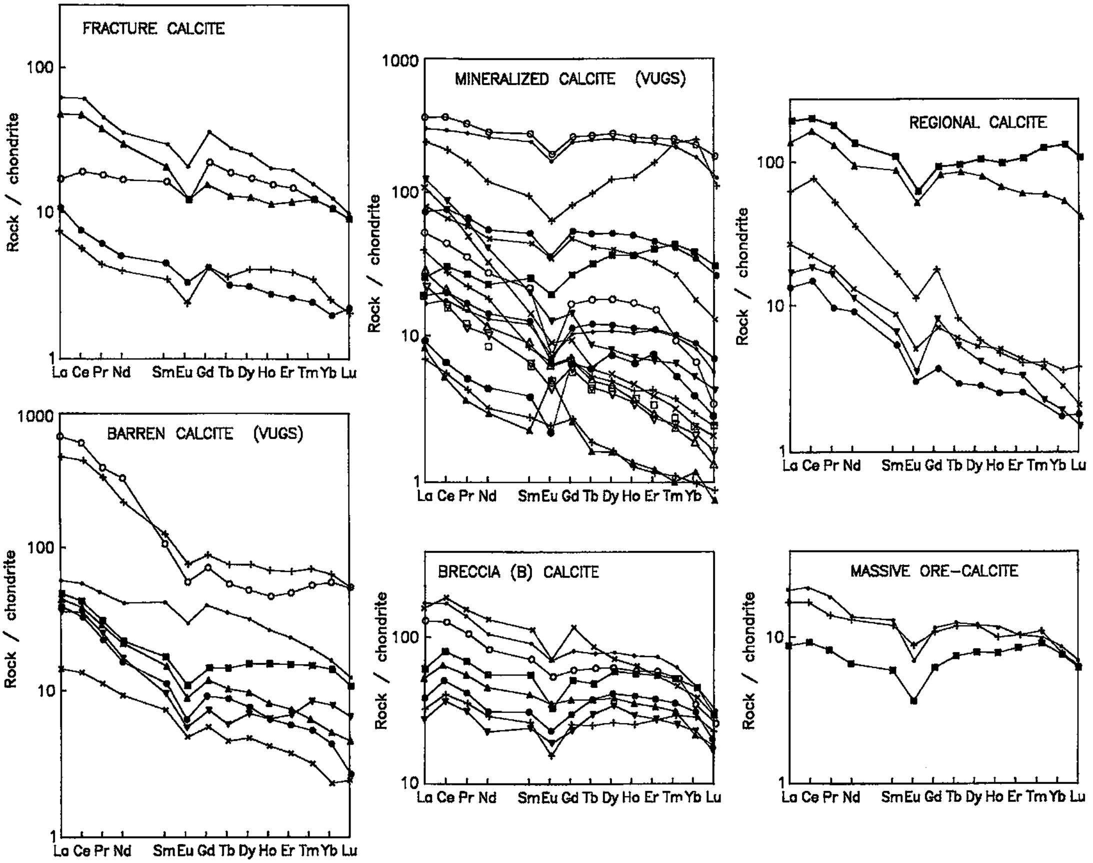

FIG. 8. Chondrite-normalized *REE* plots for calcite types from the Gays River deposit area and regional samples from the surrounding sub-basins. All samples represent solution chemistry on bulk separates of calcite cement.

ferent habits. As expected from the preliminary results, the analyses indicate a large range in Σ*REE* and degree of fractionation, although the least amount of variation is again noted for the B- and O-type calcite (Fig. 10). The LAM results also indicate that there is a large variation in the degree of the Eu anomaly developed, with Eu/Eu* ≤ 1.

Results of more detailed analyses for two samples of Vb-type calcite are presented in Figure 11 in order to assess intra- and intergrain variability. For sample GR–91–84A (Fig. 11A), results of *REE* analyses again indicate both a homogeneous (1, 2; 7, 8, 9; 10, 11) and highly variable (4, 5, 6) chemistry. Collectively, the CNP for these calcite samples representing the same type and, apparently, the same paragenesis (see sketch in Fig. 11A) indicate two groupings, one with elevated Σ*REE* and *LREE* enrichment, and the other with relative depletion in Σ*REE* and an unfractionated CNP. As with the previous sample, data for GR–92 (Fig. 11B) indicate both homogeneity (6,7; 2, 3, 5) and variability (9, 10, 11) on a inter- and intragrain scale with respect to *REE* chemistry. This particular sample comes from within the Musquodoboit basin (Fig. 1B) and was analyzed specifically for comparison to samples from Gays River. As with the bulk separates collected regionally, this sample indicates the same degree of variability and enrichment in Σ*REE* as observed for calcite cements from the deposit.

Correlation between compositions and cathodoluminescence in calcite

The calcite cements are strongly luminescent (Fig. 12), with a broad outer zone (*i.e.*, late stage) of uniform CL and a strongly zoned core (*i.e.*, early stage) characterized by numerous bands of variable CL. The CL results are similar to those observed by Savard (1991, 1992b) for calcite cements in the adjoining sub-basins.

The locations of analyzed spots are indicated in the

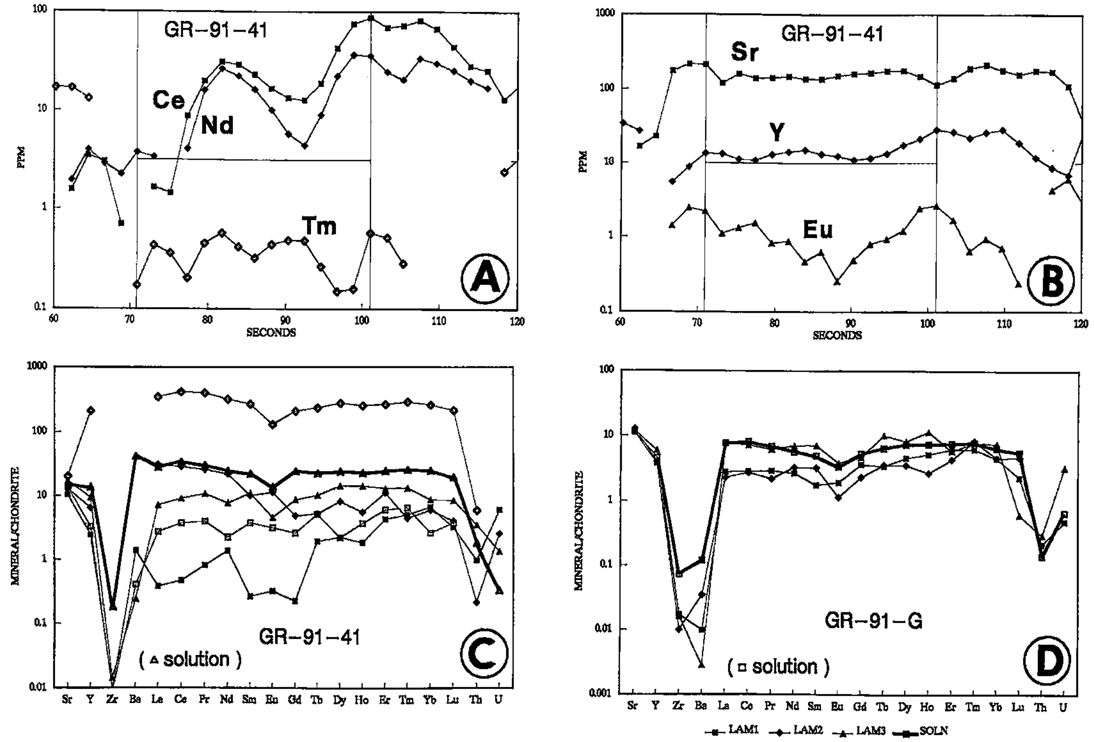

FIG. 9. Summary of the first results of LAM analyses of calcite cements from Gays River, which illustrate the presence of both homogeneous and heterogeneous *REE* chemistry. (A, B) Vertical chemical profile through calcite cement illustrating *LREE* enrichment with depth within the grain. Note that there is parallel behavior of all the *REE*, although best manifested by Ce and Nd because of their greater concentrations, whereas Sr concentration remains basically constant. (C, D) Comparison of LAM and solution-chemistry results for calcite cements, illustrating homogeneous and heterogeneous distributions of the *REE*.

CL photographs in Figure 12; the trace element (Mn, Fe, Sr, Y, La_N) and CNP for six grains of F-type calcite examined in detail are presented in Figures 13 (GR–91–27) and 14 (GR–91–67). In sample GR–91–67, three of the grains (E, G, T) have similar, generally flat CNP and Σ*REE*, and the fourth grain (H) has a distinct *LREE*-enriched pattern. Two grains with well-developed zonation in luminescence (Fig. 12, grains E, G) have relative enrichment of *REE* and Y in core areas. In sample GR–91–27 (Fig. 14), a similar pattern is developed, with enrichment of the Σ*REE* and *LREE* fractionation in grain cores. For grain B, a rim-to-rim profile (Fig. 14) indicates (1) a systematic decrease of La_N across the grain, (2) a symmetrical zonation of Y, and (3) an absence of zonation in Sr and Fe.

FIG. 10. Representative LAM analyses for different calcite cements from Gays River and regional samples. Note in particular the large range in Σ*REE* and the fractionation (*i.e.*, La/Lu_N). The results of solution chemistry on bulk separates from the same samples are illustrated where data are available.

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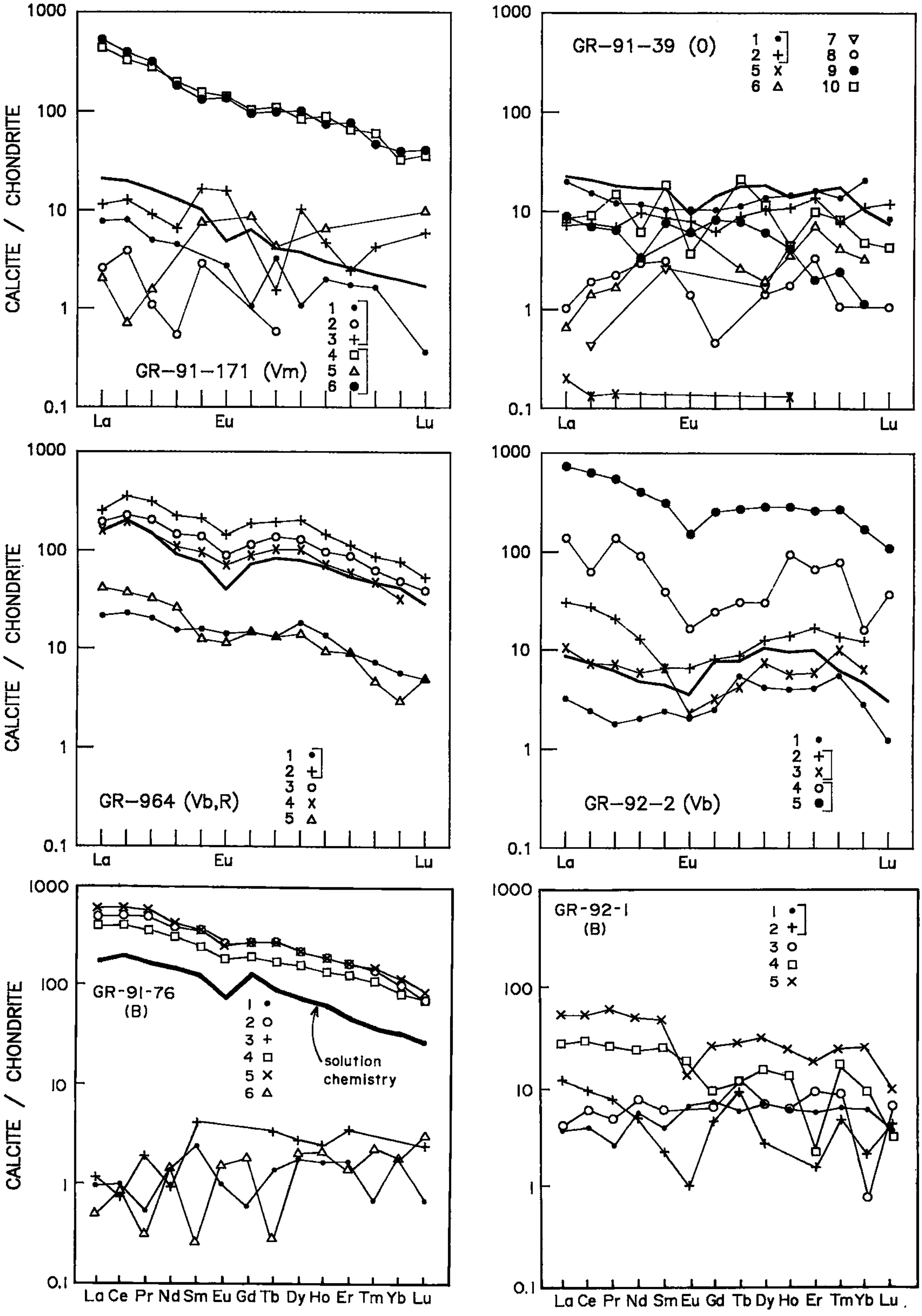
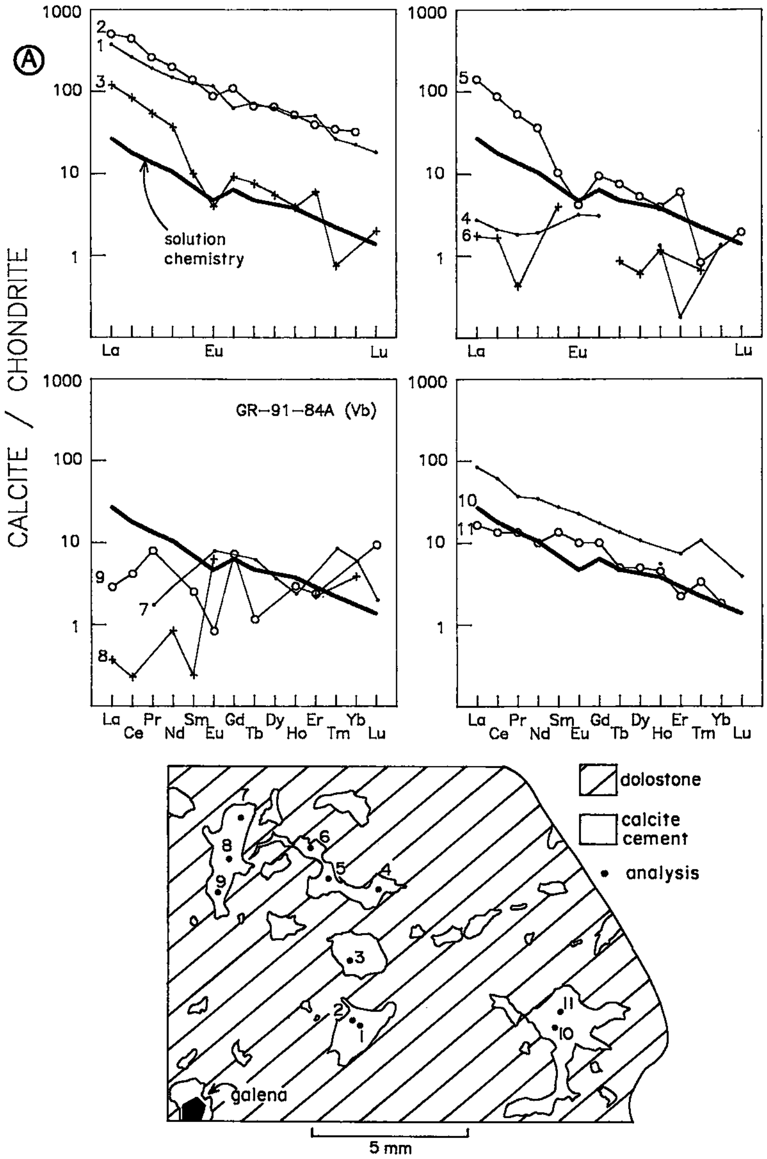

CALCITE / CHONDRITE
1000
100
10
1
0.1
La
Eu
Lu
GR-91-171 (Vm)
1 ●
2 ○
3 +
4 □
5 △
6 ●
GR-91-39 (0)
1 •
2 +
5 X
6 △
7 ▽
8 ○
9 ●
10 □
GR-964 (Vb,R)
1 •
2 +
3 ○
4 X
5 △
GR-92-2 (Vb)
1 •
2 +
3 X
4 ○
5 ●
GR-91-76 (B)
1 •
2 ○
3 +
4 □
5 X
6 △
solution chemistry
GR-92-1 (B)
1 •
2 +
3 ○
4 □
5 X
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu



The main activator element causing luminescence in the calcite is assumed to be Mn, given that it is the only element of sufficient abundance (0.5 to 1.5 wt.% Mn; Fig. 15); Fe contents are sufficiently low that Fe is not a suppressor of CL (Mason 1987). There is a strong negative correlation between *LREE* concentration and zones of Mn-depletion (Fig. 15), and the general enrichment of *LREE* in the cores of calcite cements correlates with depletion in Mn.

Comparison of solution chemistry versus LAM analyses

In cases where data on solution chemistry are available, *REE* concentrations have been compared to results of LAM analyses (Figs. 9, 10, 11, 13, 14). Examination of our findings indicates that results for the two techniques are only comparable in cases where LAM analyses indicate a relatively homogeneous trace-element chemistry. In contrast, where LAM analyses indicate heterogeneity in *REE* abundance, the solution data deviate considerably in terms of Σ*REE* and fractionation. However, where several separates of a single type of calcite have been analyzed (Fig. 8), the range in results generally coincide with the variation indicated from the LAM data. Therefore, these results, together with the observations from correlation of CL and LAM analyses,

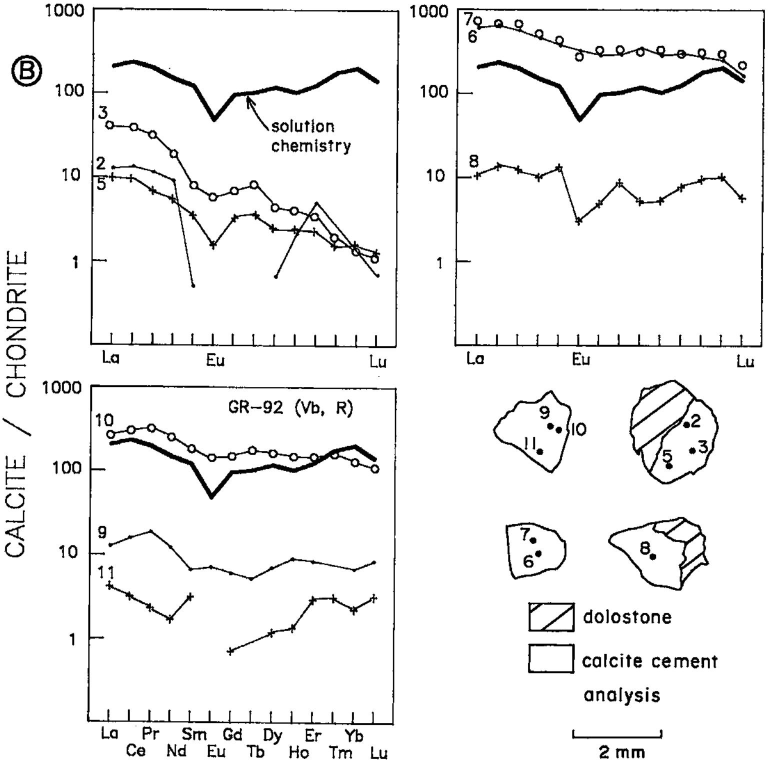


FIG. 11. Summary of LAM analyses for some detailed studies of calcite cements in two samples from Gays River. (A) sample GR–91–84a (Vb) from the deposit area; (B) sample GR–92 (Vb) from within the Shubenacadie basin.

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indicate that use of results of CL should permit one to preselect before hand samples for bulk analysis *versus* LAM analysis.

The results of Sr analyses obtained from solution chemistry and the LAM approach are compared in Figure 7. There is a good correlation of the results, although the modes occur at different concentrations, which may illustrate a sampling bias. However, whereas the deviation of a single sample in the case of the solution-chemistry data reflects contamination, as discussed previously, such variations in the LAM analyses are considered to reflect inherent chemical heterogeneities within the calcite.

Analytical Results on Fluorite Cement

A single sample of fluorite cement (GR–92–2) intergrown with calcite (Vm) has been analyzed (Fig. 16). Of the three separate grains analyzed, two grains (analyses 1, 2, 3) are similar in terms of both *ΣREE* and fractionation, with *LREE* depletion and *HREE* enrichment. In contrast, the third grain (analyses 4, 5) is relatively enriched in *ΣREE* and has the *LREE* enriched over the *HREE*; this grain is also relatively enriched in Sr (55 to 62 ppm) compared to the other grains (14 to 22 ppm). The variation in the *REE* noted here is not unique for hydrothermal fluorite (Möller & Morteani 1983, Hein *et al.* 1990, Constantopoulos

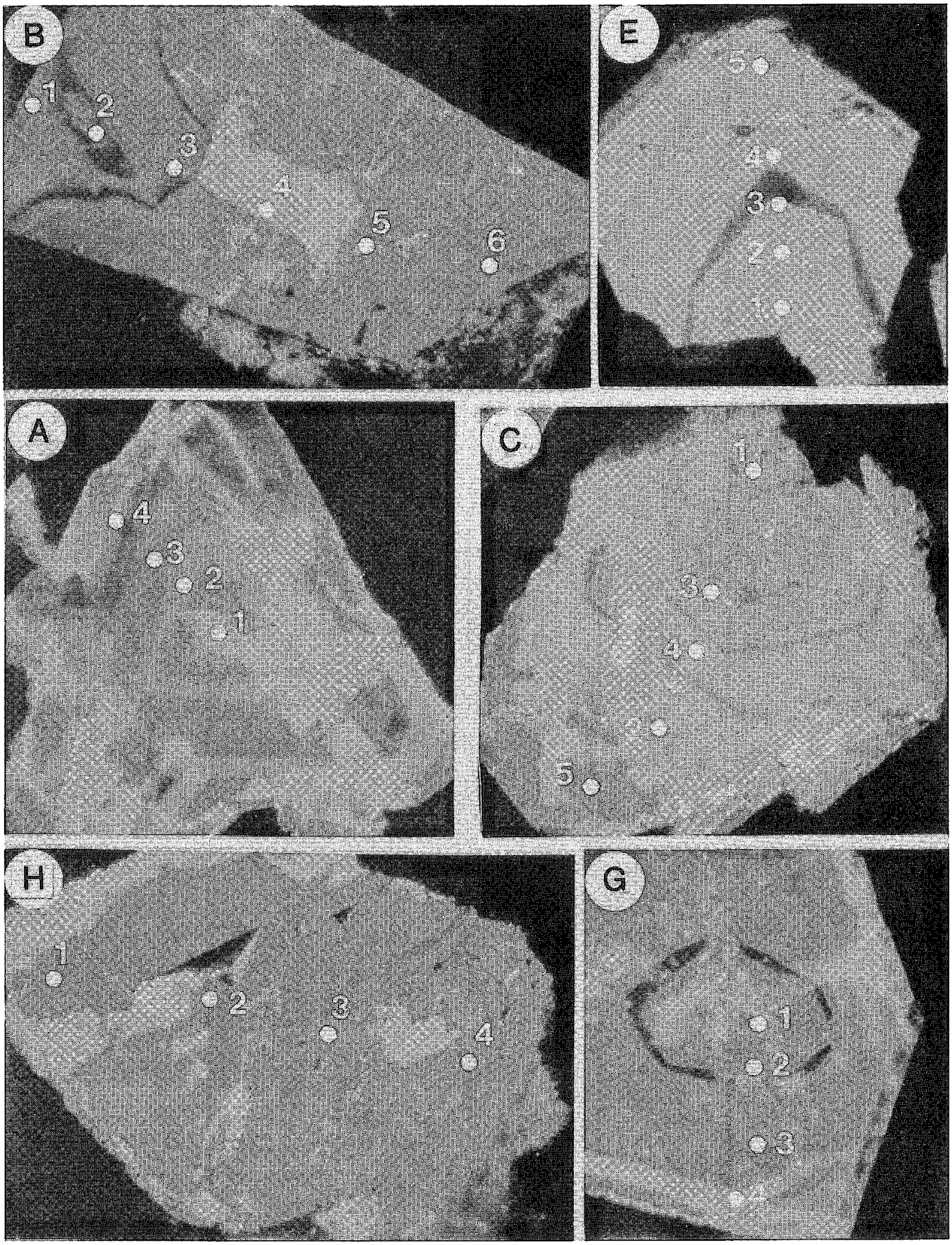

FIG. 12. Cathodoluminescence photomicrographs of calcite cements (F-type) with the location of LAM analyses (*REE* and trace-element data plotted in Figures 13 and 14). Note that there is a broad, dull outer zone and strongly zoned core areas in several grains of calcite.

1988), although a more homogeneous *REE* chemistry is normally the case (Marchand *et al.* 1976; Jébrak *et al.* 1985, Strong *et al.* 1984, Méary *et al.* 1985).

DISCUSSION

The data presented here for hydrothermal calcite and fluorite from the Gays River Zn–Pb deposit document the occurrence of dramatic chemical heterogeneity for the *REE* on both the macro- (*i.e.*, deposit) and micro-scale (*i.e.*, <100 μm in single grains). Such heterogeneity has previously been documented for hypogene phases from mineral deposits, for example tourmaline (King *et al.* 1988), calcite (Möller *et al.* 1979, 1984) and fluorite (Collins & Strong 1985, 1992), but the confirmation of this variability by spot analyses of individual grains using a laser-ablation technique provides corroborating evidence that variation in CNP by 1000 times does occur. Thus, the variability documented above is not related to potential contamination by micro-inclusions, a caveat that has been a problem with analyses of phases prepared using standard techniques of mineral separation [*e.g.*, Michael (1988) *versus* Mahood & Hildreth (1983)].

An assessment of REE variability in calcite cements at Gays River

The reasons for the *REE* variability in different types of calcite from the Gays River deposit may include: (1) variations in physicochemical parameters (T, P, solution chemistry), (2) wallrock reactions, (3) kinetics of mineral growth, and (4) chemical fractionation of the fluid. Morse (1985) and Reeder & Grams (1987) have reviewed several of these factors as they relate to growth of calcite. Fluid-inclusion studies (Kontak 1992a) indicate that, during the growth of calcite, temperatures varied from *ca.* 100 to 250°C, and salinities were 23–35 equiv. wt.% NaCl. Unfortunately, it is not possible to correlate between *REE* chemistry and temperature for the generations of calcite. However, this has been done for the St. Lawrence fluorite deposit in southeastern Newfoundland, where Collins & Strong (1985, 1992) have shown that fluorite precipitation was accompanied by a drop in temperature (*ca.* 400 to 100°C) and change in salinity (*ca.* 25 to 0 wt.% equiv. NaCl). Analysis of the fluorite indicates a systematic decrease in ΣREE (100 to 1 times chondrite), $(La/Lu)_N$ and Sr content (80 to 10 ppm). This contrasts with *REE* variations at Gays River of up to 1000 times chondrite within individual samples that show little correlation with depletion or enrichment in Sr. A similar magnitude of variation in CNP of *REE* to that observed at Gays River occurs in paragenetically similar calcite from base-metal deposits (Möller *et al.* 1984) characterized by only a small range in temperatures of fluid-inclusion homogenization. Thus, the large range in *REE* variation at Gays River is not unique and need not be related to fluctuations in physicochemical parameters such as temperature or solute chemistry.

Wallrock alteration can result in significant changes both in the chemistry of the precursor and hydrothermal fluid. However, alteration in the deposit consists only of replacement of the dolostone host and minimal modification of Meguma Group lithologies forming the local basement (Kontak 1992a). Thus, wallrock alteration is not considered a viable means of generating the changes in *REE* chemistry of the calcite.

Paterson & Stephens (1992) have documented large variations in trace-element abundance in sector-zoned grains of titanite, which the authors relate to rate of growth. In studies pertaining to calcite growth (Reeder & Prosky 1986, Reeder & Grams 1987, Paquette & Reeder 1990), it has been shown that compositional-sector zoning is an important factor for trace-element variation within single grains. However, the variation (to 100%) documented for Mg, Mn and Sr does not approach that observed for the *REE* in calcite cement from Gays River. More importantly, the *REE* variation does not correlate with Sr, suggesting, therefore, that these elements are geochemically decoupled.

Kinetic factors of possible importance with respect to trace-element partitioning in calcite are rates of fluid flow (Möller *et al.* 1991) and precipitation (Lorens 1981, Lahann & Siebert 1982). In the first case, variations by a factor of three in element/Ca ratios can be accounted for by changes in fluid-flow rates given isothermal and isobaric conditions. In terms of precipitation rates under equilibrium conditions, cation concentration was found to be proportional to the rate of precipitation from saturated solutions, with Sr having a trend opposite to that of Cd, Co and Mn. The CL studies (Fig. 12) indicate strong zonation and, hence, nonequilibrium growth during calcite precipitation. The narrow range in Sr content for calcite cement from Gays River suggests similar conditions during precipitation. Thus, whereas these kinetic factors may have been a factor, it seems that they cannot account for the magnitude of *REE* variation observed in the calcite fractions.

The potential for chemical fractionation of the fluid phase, specifically for the *REE*, is worth considering, as experimental studies indicate that the *HREE* form stronger carbonate complexes than the *LREE* (Dumonceau *et al.* 1978, Cantrell & Byrne 1987, Lee & Byrne 1993). Thus, simple precipitation of calcite will deplete the fluid in *LREE* and enrich it in *HREE*; this is the basis of the models proposed by Möller *et al.* (1979, 1984) in their studies of *REE* abundances in calcite from mineralized districts of the Harz Mountains, Germany. In this model, growth of calcite in a closed system would favor *LREE* depletion and *HREE* enrichment of the fluid; thus later-stage calcite will reflect this change in fluid chemistry. At Gays River, there is a trend of decreasing ΣREE and La_N

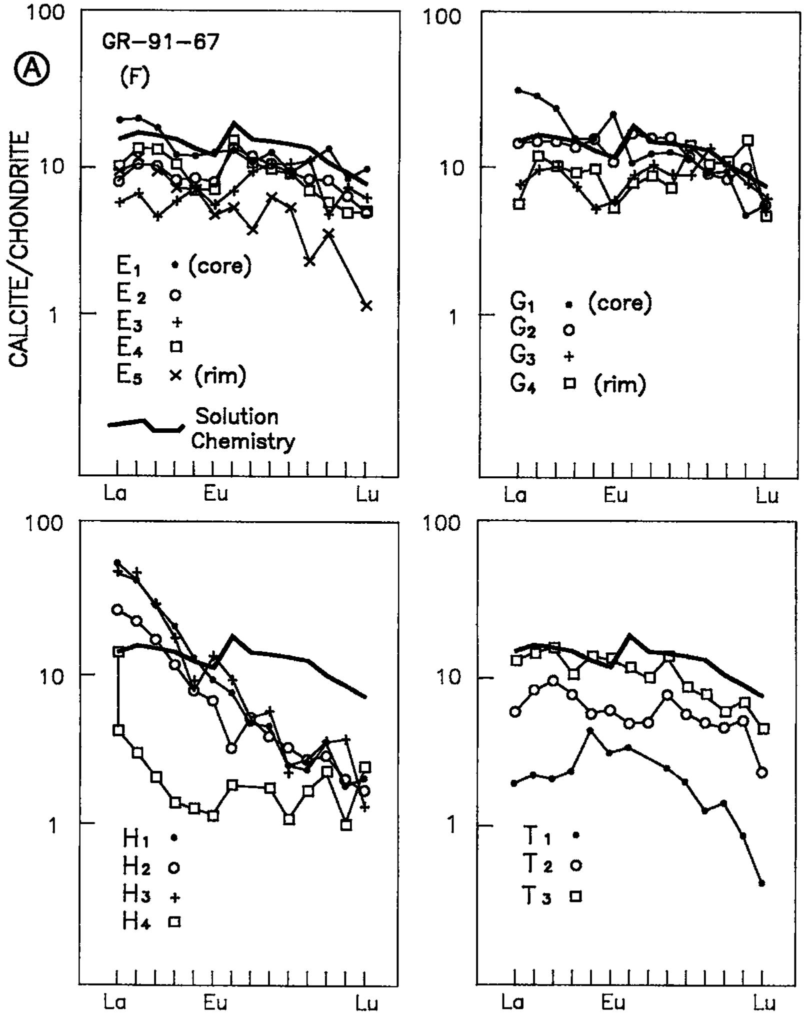

FIG. 13. LAM data for calcite cement (F-type) from sample GR–91–67. (A) Summary of detailed LAM analyses for three grains showing the chondrite-normalized *REE* plots for three grains; location of the ablation pits are shown in Figure 12. Note that there is a general increase in the *LREE* from the margin to the core of the grains. The results labeled T represent separate grains with 1 or 2 analyses. (B) Summary of the trace-element data for the grains analyzed plotted as function of their relative positions.

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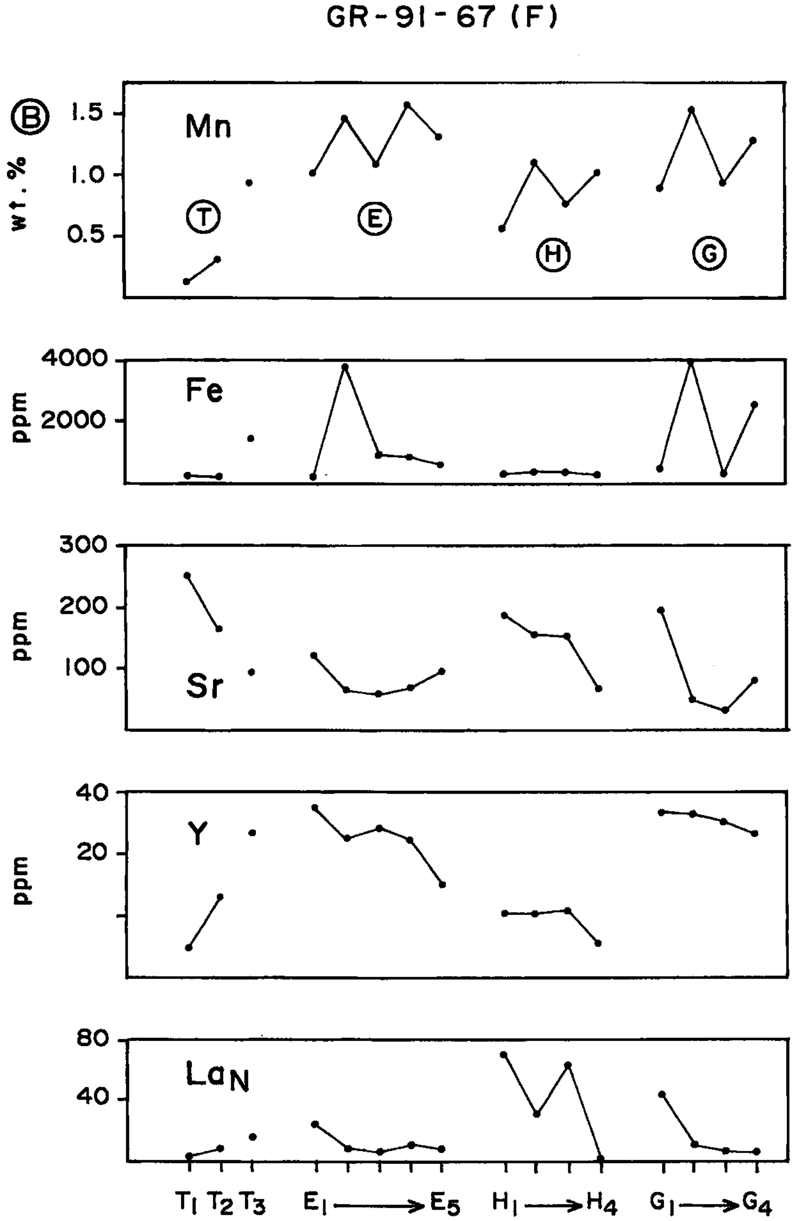
toward the margin of crystals (Figs. 13, 14), *i.e.*, in the later-stage growth zones.

Origin of the REE variation of calcite cements at Gays River

Potentially important in understanding *REE* variability are the results of C, O and Sr isotopic analysis of all types of calcite cement (Akande & Zentilli 1984, Ravenhurst *et al.* 1987, Kontak *et al.* 1993, Savard 1992a, b). These data show a continuum from a Carboniferous marine component having a $\delta^{13}C_{PDB}$ of +5‰, a $\delta^{18}O_{SMOW}$ of +25‰ and a $^{87}Sr/^{86}Sr$ of 0.708 to a $\delta^{13}C_{PDB}$ between 0 and –7‰, a $\delta^{18}O_{SMOW}$ between +12 and +16‰, and a $^{87}Sr/^{86}Sr$ of 0.712, the latter values having been obtained for calcite cements most closely related to mineralization (*i.e.*, O-, B- and Vm-types). This variation is explained in terms of increas-



ing fluid:rock ratio during infiltration of the carbonate bank by an external fluid; Ravenhurst *et al.* (1987), Kontak *et al.* (1993) and Savard (1992b) considered this external fluid to have equilibrated with rocks of the Meguma Group, either as detritus within the Horton Group or the underlying basement. A similar conclusion is supported by Pb isotopic analysis of galena (Ravenhurst *et al.* 1989, Kontak 1992a).

The *REE* data for the calcite cements can be explained in part by a temporal change in fluid:rock ratios based on the following: (1) the earliest stage of calcite growth, as represented by core regions, are closest paragenetically to mineralization, at which time fluid:rock ratios are inferred to have been the highest (see above); these fractions are the most enriched in *REE*; (2) core regions of calcite grains are relatively depleted in Mn compared to the margin of the grains, which grew under lower fluid:rock ratios (*i.e.*, buffered

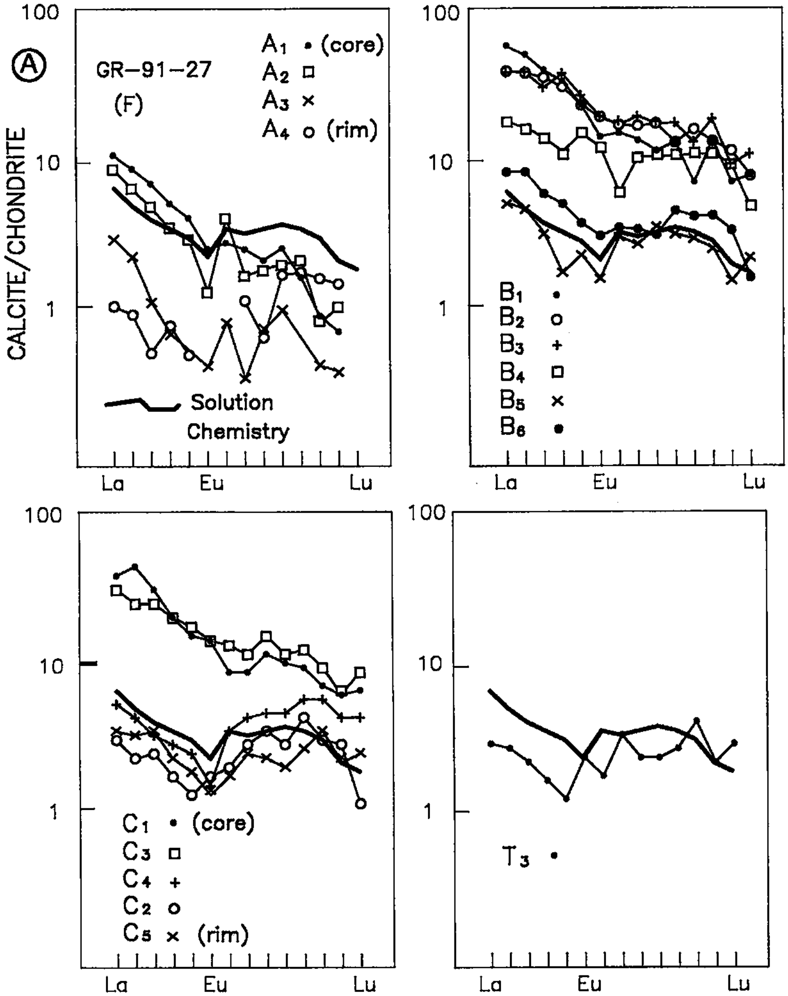


FIG. 14. LAM data for calcite cement (F-type) from sample GR–91–27. (A) Summary of detailed LAM analyses for three grains showing the chondrite-normalized *REE* plots for three grains; location of the ablation pits are shown in Figure 12. Note that there is a well-correlated increase in the *LREE* from the margin to the core of the grains. The results labeled T represent a single analysis of a grain. (B) Summary of the trace-element data for the grains analyzed plotted as function of their relative positions.

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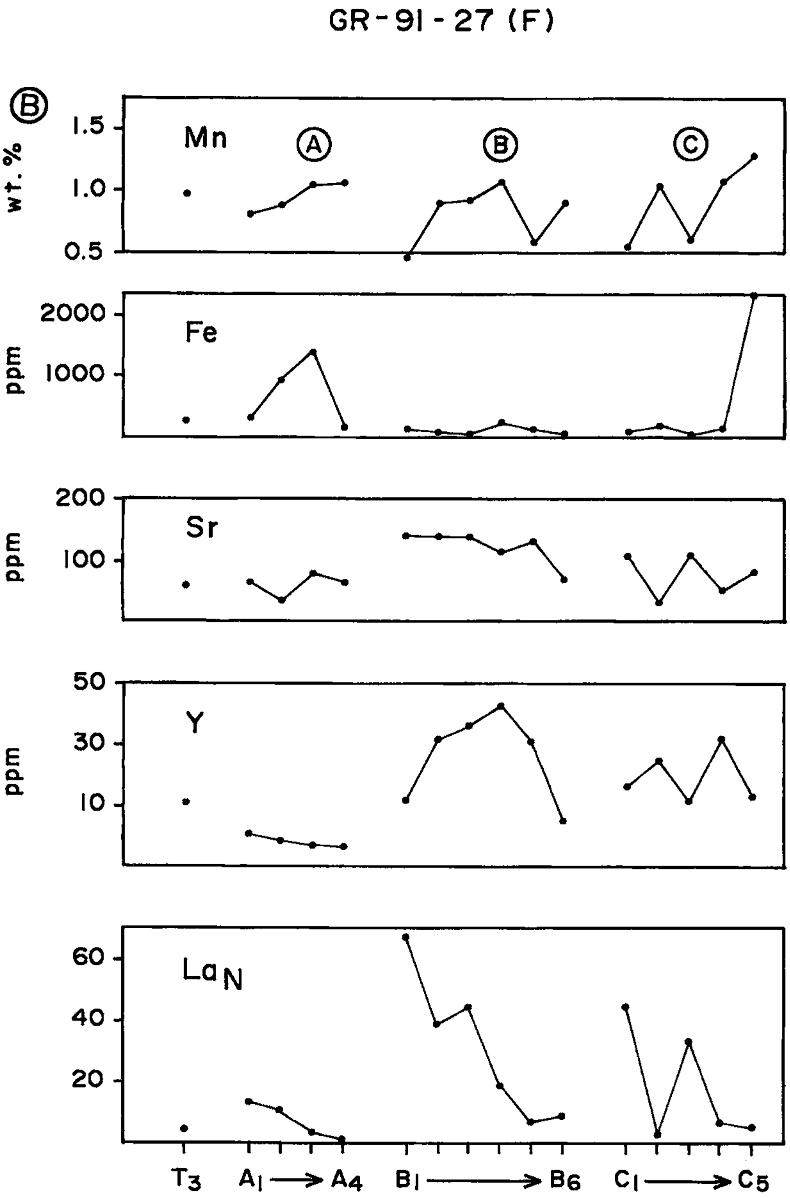
by wallrock). In this model, the external fluid is inferred to have been enriched in *REE*, as reflected by the data in Figures 13 and 14. However, interaction of the mineralizing fluids with rocks of the Meguma Group, which have CNP and Σ*REE* typical of shales (*i.e.*, NASC of Gromet *et al.* 1984) will not generate such *REE* enrichment. Such enrichment would occur, however, if an accessory phase within these metasedimentary rocks were to break down. Examination of the CNP of calcite with the highest *REE* indicate generally unfractionated patterns similar to those of apatite (*e.g.*, Hanson 1980), a phase present in Meguma Group rocks as a detrital component.

The subsequent decrease in the *REE* content of later-stage calcite cements can be explained by either (1) closed-system fractionation, as discussed by Möller & Morteani (1983), or (2) decreasing fluid:rock ratios such that calcite inherits the *REE* signature of the dolostone wallrock (Fig. 6), which is relatively depleted compared to paragenetically earlier calcite, or some



combination of these two mechanisms. The CNP for calcite with low Σ*REE* has a variable $(La/Lu)_N$ value either less than or greater than unity, suggesting therefore that both of the aforementioned processes participated, as neither one alone can account for variable fractionation.

CONCLUSIONS

Calcite cements from the Gays River Zn–Pb deposit show large ranges in both the abundance and fractionation of the *REE*. The variation was first determined using bulk methods, but use of a laser-ablation microprobe (LAM) confirms that this variability is real and not due to micro-inclusions. In addition, LAM analysis and cathodoluminescence microscopy show a systematic decrease in both Σ*REE* and La_N with time, concurrent with an increase in the Mn contents of later-stage calcite. The data reflect the following processes: (1) infiltration of the Gays River bank by an external fluid enriched in *REE* due to breakdown of apatite during fluid migration through the Horton Group, which is dominated by Meguma Group detritus (or the Meguna Group as basement proper), (2) decreasing fluid:rock ratio during calcite growth, and (3) closed-system fractionation of calcite. Whereas the first process accounts for the enrichment of *REE* (to 1000 times chondrite), the second and third can explain the decrease in Σ*REE* and variable $(La/Lu)_N$ values.

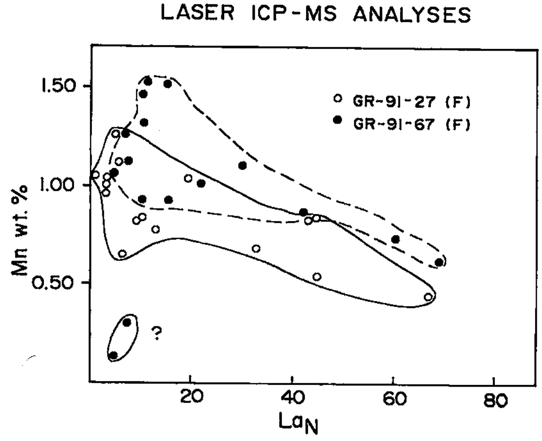


FIG. 15. Plot of wt.% Mn *versus* La_N for calcite samples GR–91–27 and GR–91–67. Note the strong negative correlation between the two parameters and the fact that two subparallel, but distinct trends are defined. The strong CL zonation in the core of the calcite grains (Fig. 12) mainly reflects increasing but fluctuating levels of Mn (the activator element).

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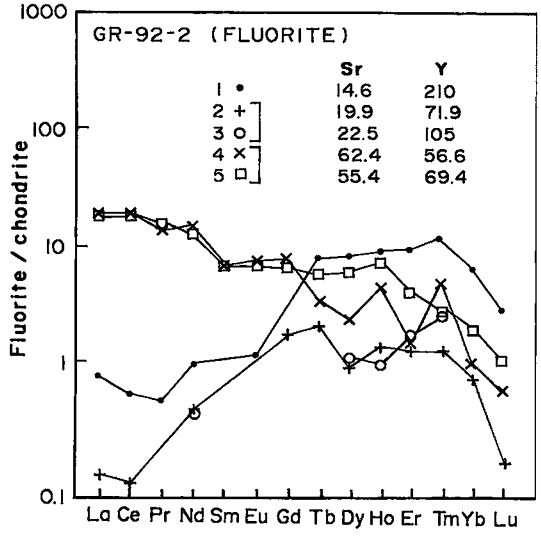

FIG. 16. Chondrite-normalized *REE* plot of LAM results for fluorite cement from the Gays River deposit. Note that of the three grains analyzed, there is an apparent consistency within a grain, but among grains two distinct and markedly different patterns are developed.

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