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FLUID-INCLUSION EVIDENCE OF COPPER REMOBILIZATION DURING RETROGRADE METAMORPHISM IN THE CENTRAL LABRADOR TROUGH

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ABSTRACT

Major-element compositions of decrepitates of individual fluid inclusions determined by scanning electron microscopy and energy-dispersion analysis of some representative Cu-sulfide-bearing quartz–dolomite veins in the Dunphy dolostone of the central Labrador Trough indicate mineral deposition at 350±50°C from highly saline (36–42 equivalent wt.% NaCl + $CaCl_2$) reduced solutions carrying 0.1 to 1.0 *m* total S and in excess of 300 ppm total Cu. The pH of these fluids has been calculated to be 4.4 ± 0.8, with oxygen fugacities ranging from 10^{-30} to 10^{-28}. Fluid pressures attending mineral growth in the veins (about 1 kbar) were considerably less than the 2.5–3.0 kbars proposed for peak greenschist-grade metamorphism. Early, diagenetic Cu-sulfide minerals within the Dunphy dolostone were leached by saline, retrograde metamorphic fluids. Sulfides (bornite + digenite + covellite ± chalcopyrite ± pyrite) were then reprecipitated in fractures within the same strata, perhaps during unloading of the region after the Hudsonian Orogeny.

Keywords: fluid inclusions, decrepitate, SEM–EDA, copper, remobilization, dolomite, vein, leaching, uplift, pressure–temperature–time path.

SOMMAIRE

Le dosage d'éléments majeurs a été déterminé par microscopie électronique à balayage et dispersion d'énergie sur les décrépitats d'inclusions fluides de quelques veines cuprifères quartzo-dolomitiques encaissées dans les dolomies de Dunphy (zone centrale de la Fosse du Labrador). Les résultats indiquent une déposition des minéraux à une température de 350°C ± 50°C à partir de solutions réduites fortement salines (36–42% poids équivalent NaCl + $CaCl_2$) transportant 0.1 à 1.0 *m* S total et au moins 300 ppm Cu. Le pH de ces fluides aurait été de 4.4 ± 0.8, avec une fugacité d'oxygène variant de 10^{-30} à 10^{-28}. La pression des fluides qui ont accompagné la croissance des minéraux dans les veines (environ 1 kbar) est considérablement inférieure aux 2.5–3.0 kbars proposés pour le paroxisme du faciès métamorphique des schistes verts. Les sulfures cuprifères de la minéralisation diagénétique précoce des dolomies de Dunphy auraient été lixiviés par les fluides salins issus d'un métamorphisme rétrograde, et reprécipités dans les fractures de la même unité, possiblement au cours du réajustement isostatique qui a suivi l'orogenèse hudsonienne.

Mots-clés: inclusion fluide, décrépitat, MEB–ADE, cuivre, remobilisation, dolomite, filon, lixiviation, soulèvement, cheminement *P–T–t*.

INTRODUCTION

Cryptalgal dolostones of the Aphebian Dunphy Formation of the Labrador Trough in northern Quebec (Dimroth 1978) host significant copper sulfide mineralization (Chevé *et al.* 1985, Schrijver *et al.* 1986). To date, four distinct stratabound zones have been recognized in a 10 km^2 area (Fig. 1). Zones A and B contain an estimated 20 Mt grading 0.14 to 1.48 wt.% copper (Russell 1963) and represent the largest known accumulation of copper in the sedimentary rocks of the Labrador Trough.

Copper mineralization occurs in association with sparry dolomite and quartz, both in fenestrae in the host dolostone and in discordant, anastomosing quartz–dolomite veins. Cathodoluminoscopy and electron microprobe analysis show that the stratabound, copper sulfide mineralization occurs as a diagenetic cement that filled remaining pore spaces after precipitation of several generations of dolomite cement (Chevé *et al.* 1985). These features, in conjunction with the lateral continuity of the cupriferous zones and their stratigraphic restriction to certain units of the Dunphy Formation, are considered evidence of an early diagenetic origin for the primary copper mineralization. The spatial association between these mineralized strata and copper-bearing veins led Chevé *et al.* (1985) to conclude that the discordant vein mineralization represents copper that was remobilized from early diagenetic disseminations during low-grade metamorphism, in the greenschist facies (350–400°C, 2.0–3.5 kbars: Dimroth & Dressler 1978).

Bornite, digenite, chalcopyrite and covellite are the principal sulfide minerals. Pyrite is a minor phase in dolostones and veins. In the limited occurrences where all of the Cu-bearing sulfides are present, the

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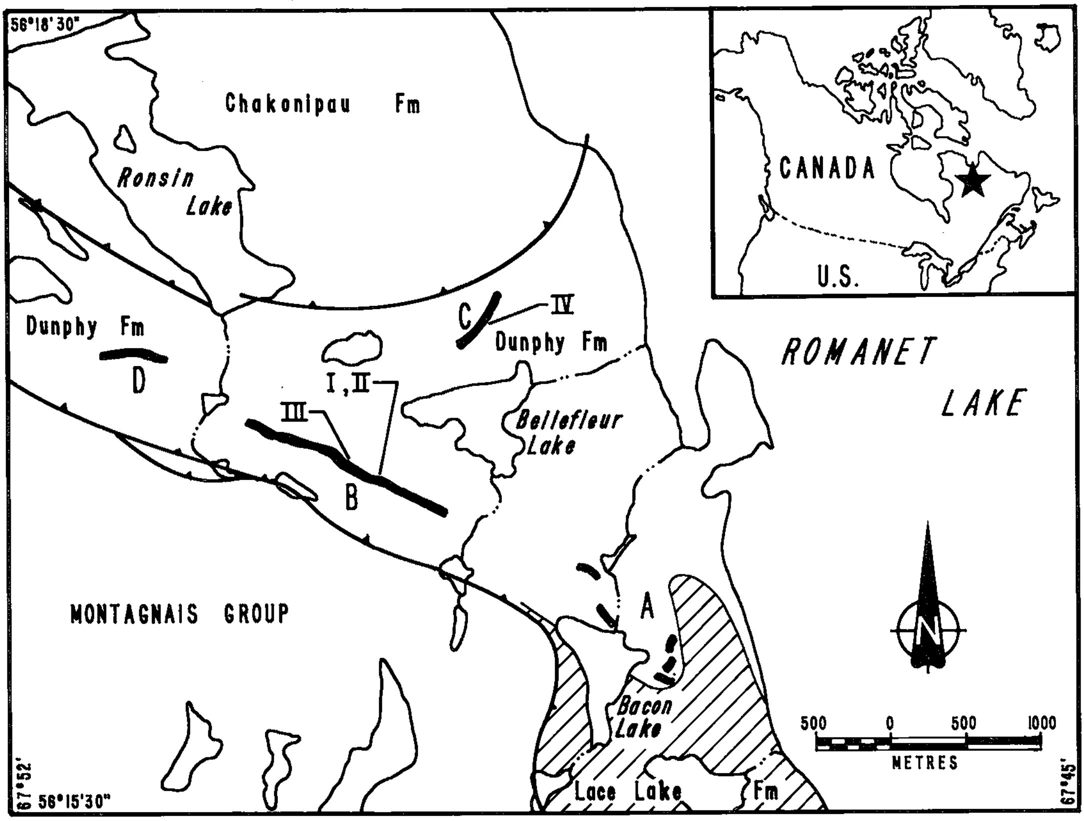

FIG. 1. Map showing cupriferous stratiform zones (A–D in black) of the Dunphy Formation with sample locations (I and II are veins; III and IV are dolostones). Simplified lithostratigraphy, from old to young: Chakonipau conglomerate and sandstones, Dunphy pelite (about 100 m thick) and dolostone (about 300 m thick), Lace Lake shale, Montagnais gabbro.

paragenetic sequence chalcopyrite → bornite + digenite → covellite is observed. The Cu–Fe sulfide assemblage is partly and locally replaced by aggregates of hematite at the fringes of the sulfide occurrences (Chevé *et al.* 1985).

Fluid-inclusion studies of sparry dolomite and quartz in both the dolostone and veins (Schrijver *et al.* 1986) support the above interpretation, as homogenization temperatures (*Th*) range from 225 to 290°C in the dolostones, and from 242 to 312°C in veins. Inclusions in vein quartz contain halite daughter crystals and exhibit salinities of 30–40 wt.% NaCl equivalent. All halite-bearing inclusions homogenize by vapor disappearance. Ice-melting temperatures range from -30 to -20°C, *i.e.*, consistently below the binary eutectic in the system H_2O–NaCl (-20.8°C), which suggests the presence of divalent cations (Ca, Mg, or both). No gas phases (CO_2 or CH_4) were observed in either the dolostones or veins. Primary, secondary, and pseudosecondary inclusions are present in all samples, and unambiguous assignment of individual inclusions to each type is difficult, but the agreement between the *Th* values and metamorphic conditions, and the elevated salinities, led Schrijver *et al.* (1986) to conclude that most of the inclusions are related to regional metamorphism.

These traditional heating and freezing, microthermometric observations fall short of providing the essential parameters for a complete evaluation of the nature of the metamorphism (prograde or retrograde, *P*, *T*) that might have led to the remobilization of copper. Homogenization temperatures provide minimum temperatures of formation, and temperatures of trapping cannot be determined without independent knowledge of pressure. In addition, the solubility of copper sulfides is controlled by ionic strength, through copper chloride complexing (Crerar & Barnes 1976, Barnes 1979) and by solution pH (Rose 1976, Sverjensky 1987). Estimates of ionic strength, based on values of freezing-point depression or halite melting temperatures (*Tm*), and their conversion to NaCl wt.% equivalent salinities (Potter *et al.* 1978), can be in error if divalent cations are present (Crawford 1981a). Furthermore, inclusion microthermometry does not permit estimation of solution pH.

In this paper, we employ a recently developed technique to obtain the major-element composition of individual fluid inclusions by scanning electron microscopy and energy-dispersion analysis (Eadington 1974, Chryssoulis & Wilkinson 1983, Haynes & Kesler 1987). Chemical data on representative cupriferous veins and fenestral cements in the Dunphy dolostones are integrated with traditional observations on inclusions and carbonate–silicate mineral equilibria to estimate ionic strength, solution pH, and the physicochemical conditions of metamorphism and inferred remobilization of copper.

METHOD OF ANALYSIS OF INCLUSIONS

Salt precipitates (herein called decrepitates) were produced by heating polished surfaces of quartz and dolomite until the inclusions decrepitated (about 400–425°C). Upon rupture, the inclusion content escaped to the mineral surface along microcracks where the non-volatile components precipitated in volcano-shaped mounds. Energy-dispersion analysis (EDA) of these decrepitates was performed at an operating voltage of 15 kV, beam current of 10 nA, count times of 100 seconds, and raster scan-speed of 1 second using a JEOL JSM-U3 scanning electron microscope (SEM). Rastered areas, rather than spot-mode analysis, were employed to reduce element volatility and the effects of chemical inhomogeneities in the decrepitates (Haynes & Kesler 1987). Because the volatile components (H_2O and CO_2) are lost, results are reported in cation – chloride ratios; total salinities must be evaluated independently. Standardization was accomplished with single-cation chloride salts evaporated on a mineral matrix.

Analyses on dolomite required subtraction of the Ca and Mg contributions from the matrix. This was accomplished by determining the Ca-to-Mg ratio in adjacent dolomite, assuming all Mg in the decrepitate was from the matrix (only trace amounts of Mg were present in decrepitates on coexisting quartz), and subtracting the appropriate Ca from the decrepitate analysis to balance the Mg (Haynes & Kesler 1987). Although this additional step augments the error involved in dolomite analysis, particularly with respect to Ca, decrepitates analyzed on dolomite showed good charge-balance (sum of cations equaling chloride), which suggests that errors in assigning Ca between matrix and decrepitate are not significant.

Experiments with decrepitates from synthetic inclusions of known composition grown in natural quartz using the method of Sterner & Bodnar (1984) indicate that cation ratios measured from decrepitates in excess of 5–10 μm in diameter in the NaCl–KCl–$CaCl_2$–H_2O system can be analyzed to ±6% using this technique (Haynes *et al.* 1988). All analytical results reported here pertain to decrepitates greater than 5 μm in diameter.

TABLE 1. RESULTS OF DECREPITATE ANALYSES IN DUNPHY-HOSTED VEINS AND FENESTRAL DOLOMITE

Sample[a]/ Mineral	(in wt.%) NaCl	$CaCl_2$	KCl	Sample[a]/ Mineral	(in wt.%) NaCl	$CaCl_2$	KCl	Sample[a]/ Mineral	(in wt.%) NaCl	$CaCl_2$	KCl	Sample[a]/ Mineral	(in wt.%) NaCl	$CaCl_2$	KCl
I/Qtz	51.6	30.6	17.7	I/Qtz	46.3	36.6	17.0	II/Qtz	61.9	25.9	12.2	II/Dol	65.3	23.6	11.1
I/Qtz	31.9	37.4	30.7	I/Qtz	48.5	37.5	14.0	II/Qtz	68.1	23.4	8.5	II/Dol	58.8	26.1	15.1
I/Qtz	42.7	30.2	27.0	I/Qtz	49.3	34.2	16.5	II/Dol	57.9	31.9	10.2	II/Dol	76.0	16.1	8.0
I/Qtz	22.4	47.0	30.6	I/Qtz	44.8	43.3	11.9	II/Dol	70.3	21.5	8.2	III/Dol	58.4	29.6	12.0
I/Qtz	44.4	43.5	12.1	I/Qtz	44.6	39.6	15.8	II/Dol	50.5	36.2	13.3	III/Dol	61.4	29.5	9.1
I/Qtz	44.1	41.3	14.6	I/Qtz	43.2	36.4	20.4	II/Dol	55.8	29.1	15.1	III/Dol	56.4	33.8	9.7
I/Qtz	45.7	43.8	10.5	II/Qtz	58.2	29.0	12.8	II/Dol	63.2	28.4	8.4	III/Dol	60.1	34.7	5.3
I/Qtz	45.2	29.7	25.1	II/Qtz	69.1	12.5	18.1	II/Dol	54.0	37.5	8.5	III/Dol	76.5	16.5	6.9
I/Qtz	43.7	36.3	20.0	II/Qtz	55.7	23.4	20.9	II/Dol	54.8	32.4	12.8	III/Dol	62.9	32.2	4.8
I/Qtz	59.4	28.8	11.8	II/Qtz	61.7	24.1	14.2	II/Dol	72.0	19.5	8.6	III/Dol	60.8	32.0	7.2
I/Qtz	42.4	40.5	17.2	II/Qtz	65.7	23.6	10.7	II/Dol	53.4	18.6	28.0	IV/Dol	59.5	33.7	6.8
I/Qtz	53.9	35.8	10.3	II/Qtz	48.5	40.0	11.5	II/Dol	64.4	26.4	10.2	IV/Dol	45.1	43.0	11.9
I/Qtz	44.9	41.4	13.7	II/Qtz	56.0	26.6	17.4	II/Dol	75.8	15.9	8.3				

Averages:

Sample/Mineral	n[b]	NaCl	s[c]	$CaCl_2$	s[c]	KCl	s[c]	Sample/Mineral	n[b]	NaCl	s[c]	$CaCl_2$	s[c]	KCl	s[c]
I/Qtz	19	44.7	7.5	37.6	5.1	17.7	6.2	All Qtz	28	49.8	10.3	33.7	8.0	16.5	5.8
II/Dol	14	62.2	8.3	26.0	6.8	11.8	6.0	All Dol	23	61.4	8.1	28.2	7.3	10.4	4.6
II/Qtz	9	60.5	6.3	25.4	6.7	14.1	3.8	II/Dol & Qtz	23	61.6	7.6	25.7	6.8	12.7	4.7
III/Dol	7	62.4	6.1	29.8	5.7	7.9	2.4	I & II/Dol & Qtz	42	53.9	11.3	31.1	8.5	15.0	6.0
IV/Dol	2	52.3		38.3		9.3		All analyses	51	55.0	11.0	31.2	8.2	13.8	6.1

a. Samples I. qtz-rich vein (sample 6, Schrijver et al. 1986)
II. qtz-dol vein (sample 7, Schrijver et al. 1986) (I and II are 5 m apart)
III. white dolostone with fenestral dolospar (sample 2, Schrijver et al. 1986)
IV. white dolostone with fenestral dolospar (sample 1, Schrijver et al. 1986)
b. n: number of decrepitates analyzed
c. s: standard deviation

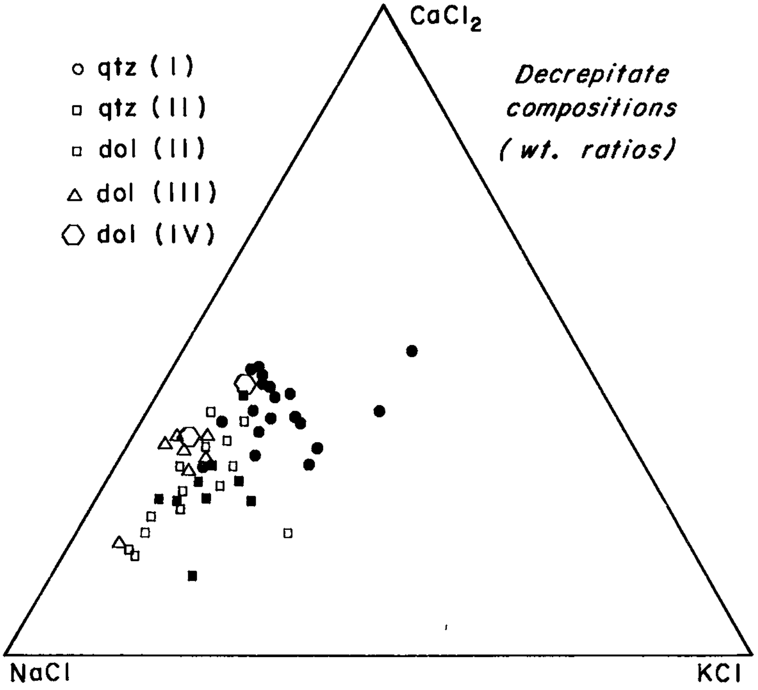

FIG. 2. Compositions of decrepitates from vein- (I and II) and dolostone-hosted (III and IV) samples in terms of the three abundant chloride salts (NaCl, $CaCl_2$, KCl), as compiled in Table 1.

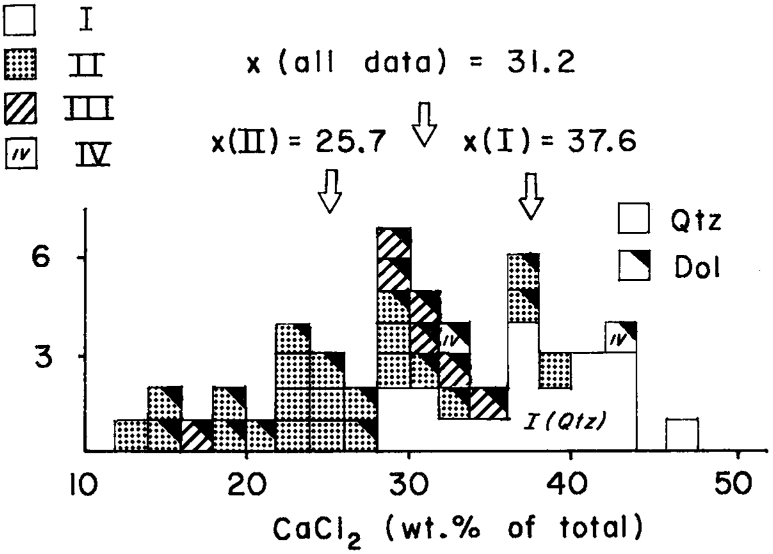

FIG. 3. $CaCl_2$ content of decrepitates (as wt.% of total chloride salt) in the Dunphy-hosted decrepitates from each of the four samples (depicted by patterns) and for both dolomite and quartz. The average $CaCl_2$ contents of the decrepitates from samples I and II and from the overall population are shown.

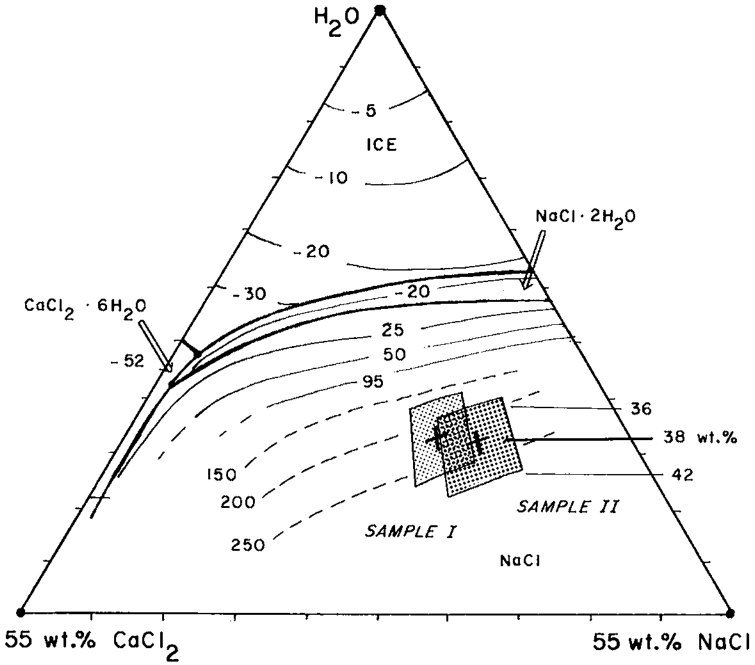

FIG. 4. Composition of Dunphy inclusion fluids in vein samples I and II (stippled boxes) in the three-component system H_2O-NaCl-$CaCl_2$. $CaCl_2$/NaCl ranges were determined by decrepitate compositions (Fig. 3), and total salinity ranges, by halite melting temperatures (Schrijver *et al.* 1986). Isotherms below 95°C are from Yanatieva (1946) and Assarsson (1950); 150°, 200°, and 250°C isotherms are extrapolations from the NaCl-H_2O binary system (Vanko *et al.* 1987).

RESULTS OF DECREPITATE ANALYSES IN THE DUNPHY FORMATION

Large (10–30 μm) inclusions in vein quartz from sample I, as well as smaller (< 10 μm) inclusions in vein quartz and dolomite from sample II, yielded numerous, large, charge-balanced decrepitates suitable for analysis (Table 1, Fig. 2). Vein samples I and II were collected from two discrete veins in the same trench in zone B, and are separated from each other by 5 m. A few decrepitates were analyzed in fenestral dolomite from samples III (zone B) and IV (zone C). The small size of the decrepitates (approximately 5 μm in diameter), irregular morphology and occurrence, and poor cation–anion balance suggest that analyses of decrepitates from these samples are likely to be less accurate than those from vein minerals. Subsequent calculations are based solely on the results from vein samples I and II.

The decrepitates from all four samples are dominated by Na–Ca chloride salts (Fig. 2). Values of the Na/Ca ratio in sample I are significantly different from those in sample II (Fig. 3), and the temporal relationship between these two adjacent vein samples is not clear. Subordinate but significant K is present in all the decrepitates (Fig. 2, Table 1). Aside from trace quantities of Mg (0.5 to 1.5% of the cations) and rare S (<2% of the anions), no other elements were detected by EDA.

Schrijver *et al.* (1986) reported halite melting temperatures in inclusions from vein quartz in the Dunphy Formation ranging from 143 to 250°C and averaging 210°C. A combination of their microthermetry with the Na–Ca–K compositional data from the decrepitates permits the average salinity for the inclu-

TABLE 2. ELEMENTAL AND IONIC MOLALITIES FOR INCLUSION FLUIDS IN VEIN SAMPLES

	(Molalities)		(Activity)^c
	elemental^a	ionic^b	ionic
Ca	1.72	0.8	0.002
Na	5.64	1.9	0.4
K	1.23	0.9	0.2
Cl	10.3	4.4	1.0
Avg. Ionic Strength =		5.2	

a. Averages from samples I and II (Table 1). b. NaCl° and KCl° equilibria from Helgeson (1969), $CaCl_2$° from Johnson & Pytkowicz (1968). c. Activity coefficients from extended Debye-Hückel theory (Helgeson 1969).

sion fluids in samples I and II to be estimated in the system $NaCl-CaCl_2-H_2O$ (Fig. 4). These calculations suggest an overall salinity of between 36 and 42 equivalent wt.% NaCl + $CaCl_2$, significantly higher than the 32 wt.% that would have been obtained had salinity been expressed in NaCl wt.% equivalence (Sourirajan & Kennedy 1962).

The occurrence of such high-salinity fluids in a metamorphic setting is not surprising. Sisson *et al.* (1981) encountered halite-saturated inclusions in the Grenville-age Lessard Formation, and Trommsdorff *et al.* (1985) and Trommsdorff & Skippen (1986) documented solid inclusions of halite and sylvite, which they interpreted as evidence of saturated metamorphic fluids. Nor is the presence of significant $CaCl_2$ in the Dunphy inclusions uncommon. Crawford *et al.* (1979b) found that nearly 50% of the total dissolved salt in inclusions associated with calc-silicate metamorphism in British Columbia is $CaCl_2$, and inclusion leachates from quartz in shear zones associated with the Doré Lake plutonic complex (Quebec) yielded a Ca/Na ratio betwen 0.5 and 1.5 (Guha *et al.* 1979). In a more recent study, Robert & Kelly (1987), working with gold-bearing quartz veins of the Abitibi greenstone belt, documented inclusion salinities of 25–34 wt.% and values of the $NaCl/CaCl_2$ ratio significantly less than 1.0.

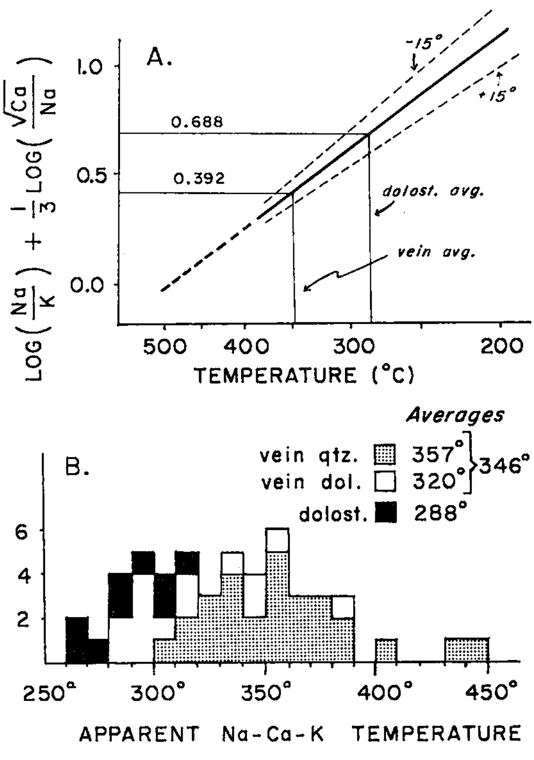

FIG. 5. Results of alkali geothermometry based on fluid composition in the Dunphy inclusions. A. Graphical depiction of the "best-fit" empirical relationship between Na–Ca–K fluid chemistry and temperature, as determined by Fournier & Truesdell (1973), and the average values calculated for the veins (samples I and II) and dolostones (samples III and IV) of this study. B. Histogram of "apparent" temperatures (see text) derived from the inclusion compositions with the averages from vein quartz (qtz), vein dolomite (dol), and dolostone (dolost.).

The total salinities obtained from the microthermometry can be combined with the average elemental ratios in the decrepitates to estimate free-cation molalities (Table 2), provided that ion pairing between each cation and chloride can be adequately modeled. Association constants for NaCl° and KCl° ion pairing (Helgeson 1969) suggest that 34% of the Na and 75% of the K would be present as free ion at 350°C. Reliable experimental data on the equilibrium constants for divalent cation – chlorite ion association are generally lacking (Pytkowicz 1983). Frantz & Marshall (1982) have suggested that significant pairing between Ca and Cl ions does not occur below 400°C, but Johnson & Pytkowicz (1978) have reported that 55% of the Ca in seawater is paired with chloride. We have assumed a similar value for the inclusion fluids in this study to obtain an average Ca^{2+} molality of 0.8 (Table 2).

Na–Ca–K GEOTHERMOMETRY AND INCLUSION GEOBAROMETRY

The calculation of Na, Ca, and K molalities (Table 2) enables application of the empirical Na–Ca–K geothermometer devised by Fournier & Truesdell (1973) for natural waters (Fig. 5A). It must be stressed, however, that this procedure deviates from the intended use of the geothermometer, which tacitly assumes that the fluid analyzed is in equilibrium with a Na–Ca–K silicate assemblage, an assumption that may not be true in carbonate-dominated terranes. In a system containing sufficient Ca and Mg to deposit dolomite, such as in the Dunphy veins, aqueous Na and K can be physically prevented from equilibrating with the host rock. Insofar as such a process would yield spuriously high estimates of temperature (Fournier & Truesdell 1973), it seems reasonable to consider that temperatures calculated from the Dunphy inclusion data are maximum temperatures existing during fluid entrapment.

Kelly *et al.* (1986) applied the Na–Ca–K geothermometer in a similar manner to compare Paleozoic basinal water chemistry with Precambrian-hosted mine waters from the Keweenaw copper district of northern Michigan. Although these waters were not buffered by a Na–Ca–K silicate assemblage, Kelly *et al.* (1986) documented systematic trends in the calculated temperatures and argued that these trends likely reflect partial re-equilibration of basinal fluids with basement lithology. They referred to the calculated temperatures as "apparent" Na-Ca-K temperatures, and we adopt that terminology here.

The apparent temperatures (*Ta*) obtained from the Na-Ca-K decrepitate data range from 280 to 390°C (Fig. 5B), and the average composition for the 42 decrepitates from the two vein samples yields a temperature of 346°C (Fig. 5). This temperature is in agreement with the published 350°C temperature of metamorphism (Dimroth & Dressler 1978), suggesting that the assumption of equilibrium between brine and silicate minerals may be justified. The three higher temperature points in Figure 5B correspond to the three solid circles plotting farthest from the NaCl apex in Figure 2. In our opinion, these anomalous compositions, and the resulting anomalous apparent temperatures, reflect incomplete dissolution and removal of NaCl daughter salts during decrepitation.

The variation in *Ta* (280-390°C) is similar to that exhibited in *Th* (230-310°C, Schrijver *et al.* 1986). Interpretation of the 50-80°C difference between the *Ta* and *Th* vein values as a pressure correction to the *Th* values yields a pressure estimate of about 1.0 kbar attending inclusion formation (Fig. 6). Decrepitates from the dolostone samples have a lower Na/K ratio and yield lower *Ta* values (average of 288°C, Fig. 5), consistent with the lower *Th* values of 225-290°C recorded for these samples by Schrijver *et al.* (1986).

Insofar as the geothermometer likely yields a maximum temperature, the agreement between *Ta* values and independent estimates of the peak metamorphic temperature (Dimroth & Dressler 1978) would seem to indicate that the calculated pressure of about 1 kbar provides a maximum for vein formation. There are two fundamental explanations for the difference between this estimate and the 2.0-3.5 kbar estimate by Dimroth & Dressler (1978) for metamorphism: a) one, or both, of the pressure estimates is in error; b) there is a geological process that permits regional metamorphism at one pressure and vein formation at a considerably lower pressure.

Uncertainties associated with pressure estimates

1) *The use of the Na-Ca-K geothermometer to obtain "apparent" temperatures and to "correct" Th values for pressure may be unjustified* for the Dunphy veins. The principal concern here is that the thermometer underestimates the true temperature, a problem that would most likely occur if carbonate dissolution added Ca to the fluid in amounts that could not re-equilibrate with the available silicates.

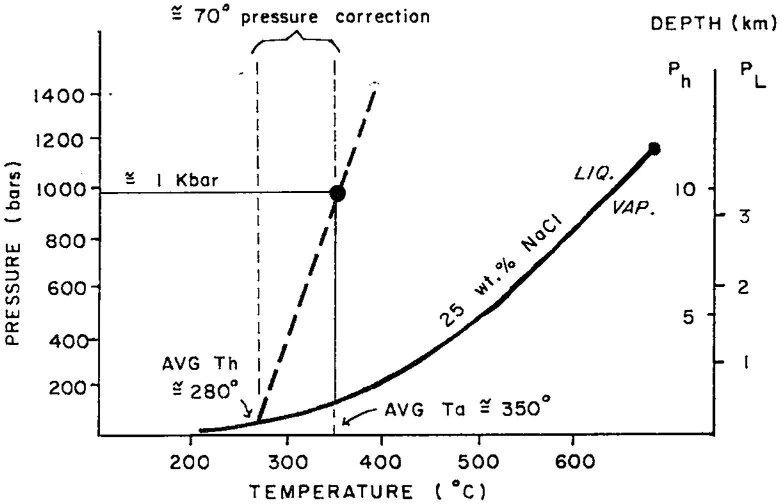

FIG. 6. Schematic *P–T* phase diagram for a 25 wt.% NaCl equivalent salinity solution (Potter & Brown 1977). Higher-salinity systems were not used because of the unknown effect of Ca on slope of isochores. The vertical axis is scaled in pressure units on the left and depth on the right, both under hydrostatic pressure (P_h) and lithostatic pressure (P_L) conditions. The estimate of a 1 kbar fluid pressure of formation of the Dunphy veins is obtained by "correcting" the average homogenization temperature (AVG *Th*) to agree with the average "apparent" temperature (AVG *Ta*) from the vein-hosted decrepitates.

The active precipitation of dolomite with quartz in the Dunphy veins suggests that carbonate dissolution did not occur at the site of mineralization, but it does not rule out the addition of Ca in the source areas of the brines. Nevertheless, the "apparent" Na–Ca–K temperatures are similar to those derived from the metamorphic mineral assemblages. To interpret *Ta* values as "low" would also require reinterpretation of the temperatures determined from the prehnite-pumpellyite assemblage in mafic units adjacent to the Dunphy Formation (discussed below).

2) *The use of isochores for 25 wt.% NaCl-equivalent solutions to define a pressure correction (Fig. 6) may be inappropriate.* The *Tm* and decrepitate compositions determined for the Dunphy veins indicate that the salinity of the inclusion fluids exceeds 25 wt.% and that they contain significant Ca. Data on molar volumes at high temperatures, used to define the slope of isochores for multicomponent chloride solutions, are not available (Bodnar & Sterner 1985), thus necessitating the use of NaCl-equivalent data. Additional solutes (both cation and anion) will alter the slope of isochores, and thus the interpreted pressure-corrections, but it is unlikely that slopes would be steepened sufficiently to alter pressure corrections by more than 100–200 bars. The experimental data of Potter & Brown (1977) show that a pressure correction obtained from the isochore of a 10 wt.% NaCl solution that intersects the liquid-vapor curve at 280°C would deviate by only 8% (or 80 bars per kbar) from that employed here using a 25 wt.% NaCl solution isochore.

3) *The determinations of metamorphic conditions from mineral assemblages led to an overestimate of pressure.* The principal reactions employed by Dimroth & Dressler (1978) to define a minimum pressure of 2 kbar for greenschist-facies metamorphism in the central Labrador Trough involved the formation of pumpellyite and actinolite at the expense of prehnite and chlorite:

prehnite + chlorite =
pumpellyite + actinolite + quartz (1)

Subsequent prograde breakdown of pumpellyite formed zoisite (Fig. 7) in the mafic units of the Trough:

pumpellyite + chlorite + quartz =
zoisite + actinolite (2)

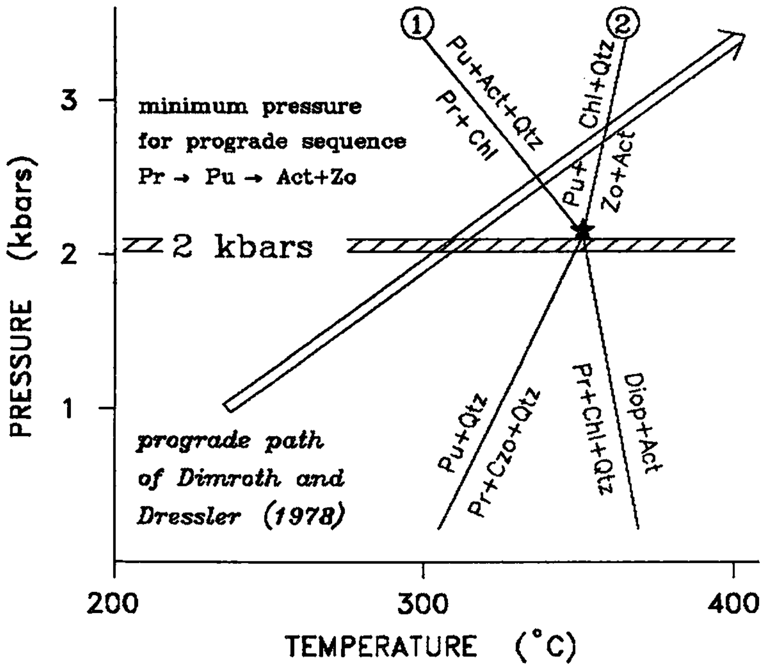

FIG. 7. Pressure-temperature plot depicting the univariant reactions and their invariant intersection used by Dimroth & Dressler (1978) to define a minimum peak metamorphic pressure of 2 kbars. Symbols: Pu pumpellyite, Pr prehnite, Chl chlorite, Act actinolite, Zo zoisite, Czo clinozoisite, Diop diopside, Qtz quartz.

Although Winkler (1974) defined the invariant point for this assemblage to be "near 2 kbar and at 345°C ± 20°", he also stated (p. 186) that its true position could fall anywhere within a pressure range of 1 – 4 kbar. The principal reactions that define the invariant point (Fig. 7) have steep slopes in *P–T* space (Brown 1977). Any small deviation in the position of these curves could lead to a significant change in the pressure of the invariant point, but would not likely cause a significant change in the temperature. The effect of solid solution in most of the minerals involved (particularly Fe in chlorite and actinolite), the lack of reliable data on the influence of buffered fluid composition, particularly $X(CO_2)$, and the difficulty of characterizing the products of experiments and deriving thermodynamic data for these silicates impart additional uncertainty to the calculated invariant point (Turner 1981).

Although the problems with the thermodynamic data for these phases could be significant, it does not seem likely that pressures determined from them could be in error by more than a kilobar. Furthermore, the geothermal gradient dictated by the mineral assemblage, assuming lithostatic pressure, is 30–50°C/km, a very reasonable geotherm for orogenic regions (Winkler 1974).

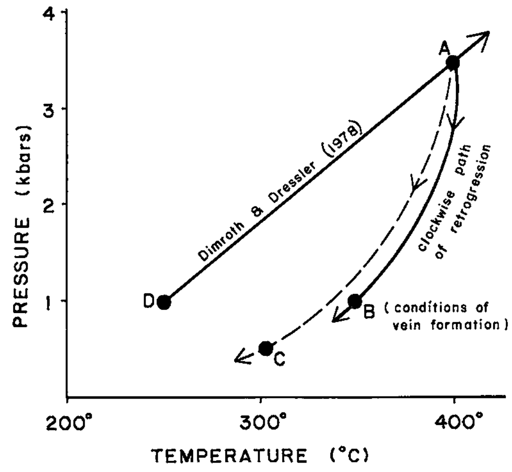

FIG. 8. Pressure–temperature plot depicting the generalized *P–T–t* path (AB) of retrograde metamorphism, as deduced from the inclusion data, and a second possible path (AC) if alkali geothermometry has overestimated the temperature of peak metamorphism. The linear prograde path proposed by Dimroth & Dressler (1978) is also shown.

Geological explanations of the pressure data

1) *The veins might not have formed under peak metamorphic conditions, but rather could record a retrograde event that occurred after significant unloading* (pressure drop) and perhaps after a moderate temperature drop. The formation of discordant quartz–carbonate veins during retrogression is common in low- to medium-grade metamorphic terranes (Crawford 1981b). Poty & Stalder (1970) documented greenschist-facies assemblages in veins hosted by amphibolite-facies rocks in the Pennines, and Mullis (1979) utilized CH_4-bearing fluid inclusions to document a similar phenomenon in the central Alps. Furthermore, it is not uncommon for retrograde metamorphic fluids to develop elevated salinities and for inclusions in these environments to contain daughter salts and elevated $CaCl_2$ contents (Crawford *et al.* 1979a). These authors suggested that salinity increased as a result of the removal of water through retrograde hydration reactions. Such a phenomenon could account for the systematic variation between homogenization and halite melting temperatures documented by Schrijver *et al.* (1986) in fluid inclusions from the Dunphy veins.

If the thermobaric data defined for the quartz–carbonate veins in the central Labrador Trough do record a retrograde event, then they may provide a valuable constraint on the pressure–temperature–time (*P–T–t*) path followed during uplift. Acceptance of the inclusion data (B in Fig. 8) as an indicator of a retrograde fluid would require a significant deviation from the linear geothermal gradient (path DA in Fig. 8) of Dimroth & Dressler (1978), and would imply a clockwise component to the P–T–t path (path AB in Fig. 8). Even if the Na–Ca–K geothermometer overestimates the temperature (discussed earlier) and, by inference, the pressure correction (Fig. 6), the qualitative sense of the path, toward a higher geothermal gradient, would persist. For example, reduction of the estimated true temperature by 40°, *i.e.*, 50% of the original *Ta* minus *Th*, would yield a pressure correction of 500 bars and path AC in Figure 8.

Most research involving the *P-T-t* evolution of metamorphism has been directed at amphibolite- and granulite-grade conditions (England & Thompson 1984, Thompson & England 1984) or to Archean settings (Groves *et al.* 1984), and at the use of growth (Thompson *et al.* 1977) and diffusional (Lasaga 1983) zoning in coexisting metamorphic minerals. Although the application of conclusions from studies of older or deeper crustal conditions to the shallower environment of greenschist metamorphism during the Proterozoic is somewhat speculative, it is noteworthy that the general path predicted by these investigators is consistent with that suggested by the inclusion data for the central Labrador Trough. Specifically, rocks buried during a period of thrusting, such as took place in northern Quebec during the Hudsonian Orogeny, are thought to remain near or

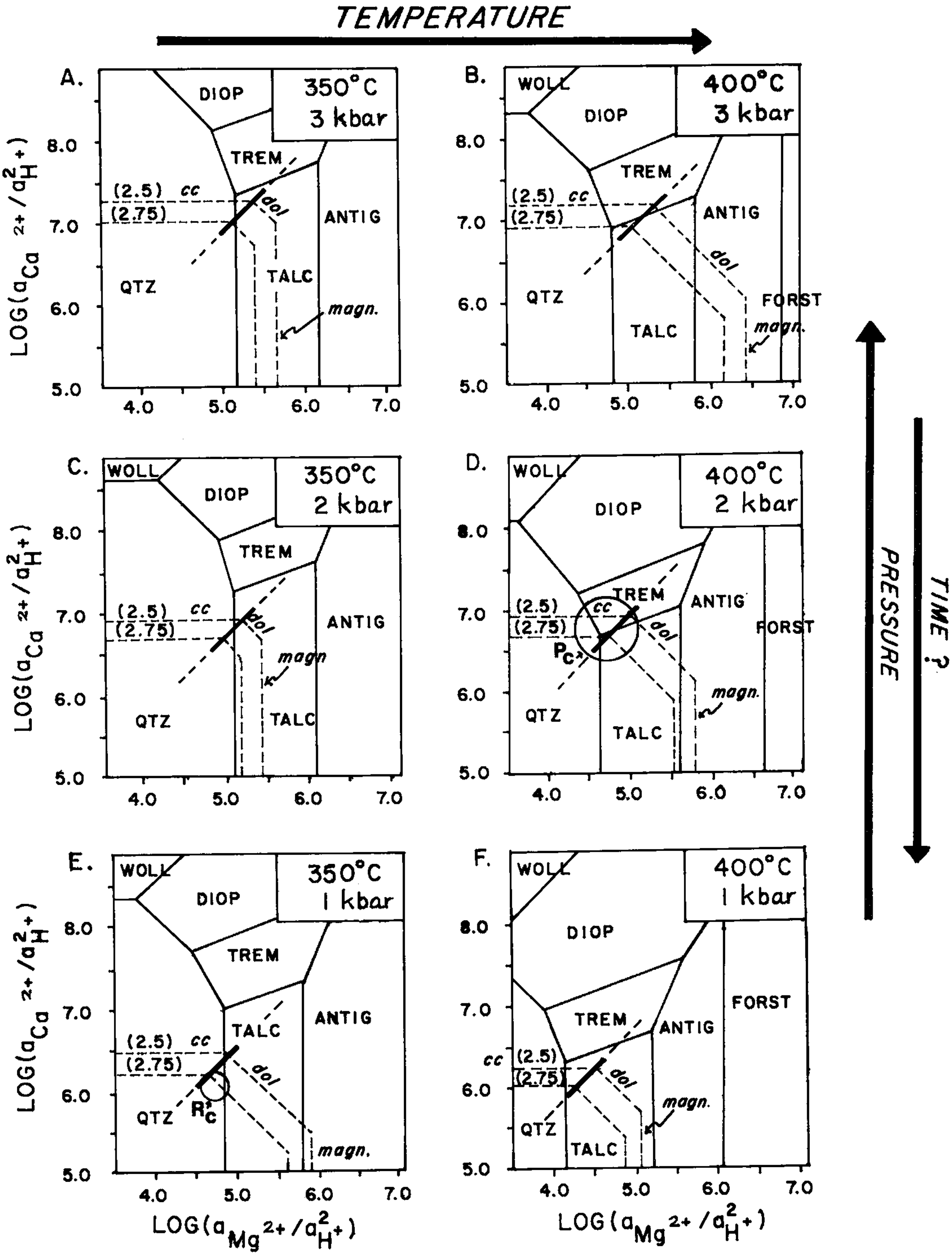

FIG. 9. Log activity ($[Ca^{2+}]/[H^+]^2$) *versus* log activity ($[Mg^{2+}]/[H^+]^2$) over the range of pressures and temperatures defined for metamorphism and vein formation in the Dunphy dolostone. Solid lines define stability regions for the calc-silicates phases. Symbols: diop diopside, trem tremolite, antig antigorite, forst forsterite, and qtz quartz). Dashed lines are saturation surfaces for carbonate phases (cc calcite, dol dolomite, magn magnesite) at variable log activities

at their maximum temperature upon uplift and erosion until 20-40% of the total uplift has occurred (England & Thompson 1984). If true, retrograde events associated with erosional unloading would be expected to record elevated geothermal gradients.

2) *The veins may have formed at peak conditions, but the inclusions analyzed could be secondary inclusions formed at lower pressure or temperature (or both).* Quartz and dolomite in the Dunphy veins contain abundant, small fluid inclusions of ambiguous origin. Schrijver *et al.* (1986) documented inclusions controlled by crystal-growth planes of apparently primary origin in dolomite, but noted that most of the halite-bearing inclusions in quartz occur in "complex arrays of indeterminate origin". As secondary and pseudosecondary inclusions are the rule, and not the exception, in metamorphic rocks (Crawford 1981b, Roedder 1984), it is plausible that some, if not all, of the decrepitates analyzed in this study came from secondary or pseudosecondary inclusions.

The issue of primary *versus* secondary origin of the inclusions is of paramount importance in discussions of copper remobilization, but it is less critical to the preceding discussion of retrograde metamorphic conditions. Whether the inclusions are primary and thus actually record conditions of vein growth, or secondary, they provide evidence of a presumed metamorphic fluid that once bathed the Dunphy Formation. As such, thermobaric data derived from their study provide constraints on the metamorphic history of the Labrador Trough.

3) *The fluid pressure (P_f) attending vein formation may have been significantly less than the geostatic pressure exerted by the rock column (P_{rk}).* In this case, pressure estimates from metamorphic assemblages in the host rock would record geostatic pressure gradients (250–300 bars/km), whereas those determined from fluid inclusions in the adjacent, and possibly coeval, veins could reflect lower gradients, perhaps as low as hydrostatic (P_h, 100 bars/km). The change from P_f equal to P_{rk} during peak metamorphism to P_f less than P_{rk} could be a single irreversible event during uplift, or the veins could act as locally underpressured domains (probably transient) within an otherwise geostatically pressured rock column.

Schrijver *et al.* (1986) documented a 23° lower average *Th* in inclusions in dolomite occluding fenestrae in the host Dunphy dolostone (average *Th* = 261°C) than in those from vein quartz and dolomite (average *Th* 284°C). They speculated that the higher *Th* values in the veins might result from strain-induced leakage in vein inclusions and subsequent resealing. A difference in the fluid pressures in the two settings provides an alternative explanation for this variation in the *Th* data. If P_f is less than P_{rk} during vein formation, and P_f equals P_{rk} in the adjacent Dunphy dolostones, then *Th* in vein inclusions would be expected to exceed that of contemporaneous growth of minerals in dolomite fenestrae. Given an isochore with a slope of 70°/kbar (Fig. 6), a 23° difference in average *Th* is equivalent to a 300 bar difference between P_f and P_{rk} if the trapping temperature in the two settings is the same.

In many studies of low-grade regional metamorphism (including that of Dimroth & Dressler 1978), it is assumed that P_f equals P_{rk}, so that dehydration and decarbonation equilibria require no adjustments for differences between P_f and P_{rk}. Documentation of fluid pressures below geostatic at depths of 6–10 km in many of the world's large sedimentary basins (Fertl 1976, Fyfe *et al.* 1978), and porosity and permeability measurements indicating the potential for significant fluid-flow in rocks buried up to 10 km (Norton & Knapp 1977, Walther & Orville 1982), suggest that P_f need not equal P_{rk} during upper crustal, low-grade metamorphism. Trommsdorff & Skippen (1986) speculated that pressures "less than lithostatic" may be maintained in fractured systems in rocks up to amphibolite grade. They further suggested that phase separation, with consequent removal of the vapor phase from the system, may be capable of generating saline inclusion fluids, and even solid halite and sylvite inclusions (Trommsdorff *et al.* 1985) observed in metamorphic veins.

The regional metamorphic conditions ascribed to the Dunphy rocks by Dimroth & Dressler (1978) project to burial depths of 8–12 km, within the range over which deviations from a P_f equal to P_{rk} have been postulated. The evidence for lower pressures reported in this study comes from fluid inclusions in veins, where increased permeability is likely and the opportunity for pressure release is maximized. Although physical evidence of phase separation is lacking in the samples of this study (no vapor-rich inclusions were found), it is certainly possible that the vein fluids represent a residual saline liquid phase, remaining after a gas-separation event, and that this gas had left the system prior to mineral deposition. We consider the pressure calculations from the inclusion data, though circumstantial, as evidence for the condition $P_f < P_{rk}$ during formation of the Dunphy quartz–dolomite veins.

of CO_2. The bold solid line with a positive slope and dashed extensions defines the stability of the univariant assemblage calcite–dolomite. The circle labeled P_c in D depicts the suspected *P, T,* and fluid composition during peak metamorphism; the circle labeled R_c reflects the proposed conditions of vein formation during retrograde metamorphism (see text). Thermodynamic data from Bowers *et al.* (1984).

CARBONATE–SILICATE MINERAL EQUILIBRIA

Talc and tremolite are the only calc-silicate phases in the impure Dunphy dolomites and marls of the central Labrador Trough (Dimroth & Dressler 1978). Diopside is encountered rarely in contact zones between the dolostones and Late Proterozoic gabbroic sills (Dimroth 1978); neither antigorite nor wollastonite has been documented. The calc-silicate minerals are accompanied by variable amounts of calcite ± dolomite ± quartz ± albite.

The activity–activity relationships in Figure 9 indicate that the regional metamorphic assemblage in the dolostones is consistent with the peak metamorphic conditions proposed by Dimroth & Dressler (1978). At these *P, T* conditions (Figs. 9B, D), the univariant curve marking the coexistence of calcite and dolomite with changing CO_2 (bold lines with +1 slope in Fig. 9) passes adjacent to the invariant point marking the coexistence of quartz, tremolite and talc. Although these five phases (trem–talc–qtz–dol–cc) were not documented in any one sample, the presence of all five within the same small zone is readily explained if only modest fluctuations in fluid composition, temperature, or pressure were required to reach all five stability regions (*i.e.,* within the circle labeled P_c in Fig. 9D). Significant changes in some aspect of fluid chemistry would be required at any of the lower temperature and pressure conditions (Figs. 9A, C, E, F).

It is also evident from Figure 9 that the quartz–dolomite vein assemblage is not possible under the peak metamorphic conditions without a significant increase in the activity of CO_2. Fluid-inclusion evidence of a separate CO_2 phase is lacking in the Dunphy vein samples (Schrijver *et al.* 1986). Thus, it does not seem reasonable to call upon a significant increase in CO_2 during vein formation. If, however, a retrograde *P–T* path involving an increase in geothermal gradient is postulated, or if P_f is reduced below P_{rk} (Fig. 7), then the assemblage quartz–dolomite would be stable at 350°C and 1 kbar without a change in CO_2 activity (Fig. 9E, circle labeled R_c).

In describing the chemical consequences of variable fluid pressure on calc-silicate carbonate mineral stability, Bruton & Helgeson (1983) noted the contrasting response of carbonate and quartz to reductions in fluid pressure. Whereas a drop in P_f can lead to the deposition of silica, it leads to undersaturation with respect to carbonate phases if pH is unchanged. A petrographic study of the Dunphy veins indicates that at least some of the vein quartz postdates vein dolomite (Schrijver *et al.* 1986). This change from carbonate-dominated filling to quartz filling may record the change in fluid pressure.

CHEMICAL CONDITIONS OF COPPER REMOBILIZATION

Solution pH

If the *T, P* and the circled region (R_c) depicted in Figure 9E do adequately record conditions of vein formation, then the diagram and the inclusion compositions can be used to estimate solution pH. Specifically, the relation, $\log [a_{Ca^{2+}}/(a_{H^+})^2] = 6.2$ (from Fig. 9E) reduces to $pH = 3.1 - ½ \log (m_{Ca^{2+}} \gamma_{Ca^{2+}})$, where *m* is modality and γ is an activity coefficient. Substituting a Ca^{2+} molality of 0.8 for the inclusion fluids and an activity coefficient of 0.002 (Table 2) leads to a pH estimate of 4.4 for the inclusion fluids in equilibrium with the quartz–dolomite vein assemblage. The largest single source of error in this calculation lies in the determination of an activity coefficient. After accounting for ion pairing, the mineralizing solutions have ionic strengths of 4.0 to 6.0 (Table 2). The use of extended Debye–Hückel theory (Helgeson 1969, Helgeson *et al.* 1981) for such high-ionic-strength solutions is tenuous (Anderson 1977, Harvie *et al.* 1984) and unwarranted in a rigorous sense. Nevertheless, an order of magnitude error in the calculated γ imparts an uncertainty of only 0.5 log units in the resultant pH. A 50% error in the calculated molality of Ca^{2+} (Table 2) translates into an additional uncertainty in pH of ±0.15 log units, and an error of ±0.3 in the log activity $[Ca^{2+}/(H^+)^2]$, as determined from Figure 9E, causes an additional ±0.15 uncertainty in the calculated pH. Even if all these errors were additive (which is unlikely), the total possible range of pH would still be only 1.6 log units or 4.4 ± 0.8.

This pH for sulfide formation is consistent with the K-phyllosilicate assemblage in the local dolostones. Coexisting muscovite and K-feldspar have been documented (Schrijver *et al.* 1986) in a few samples, including sample IV of this study. At the calculated activity of K^+ of 0.2 (Table 2), muscovite and K-feldspar would coexist at a pH of 4.7 (Fig. 10), well within the range defined by solution chemistry. The absence of kaolinite as a hypogene mineral provides an absolute minimum on solution pH of 2.8.

Oxygen fugacity and total sulfur

Sulfidation reactions in the Cu–Fe sulfide system (Fig. 10) indicate that over the pH range of 3.6 to 5.2, bornite and digenite have two regions of stability in $f(O_2)$–pH space, one under oxidized conditions, where aqueous S is predominantly present as $(Na, K)SO_4^-$, and a second in the reduced region, dominated by H_2S. In the case of the Dunphy veins, the high Ca content of the inclusion fluids and the lack of anhydrite limit the $f(O_2)$ to the reduced con-

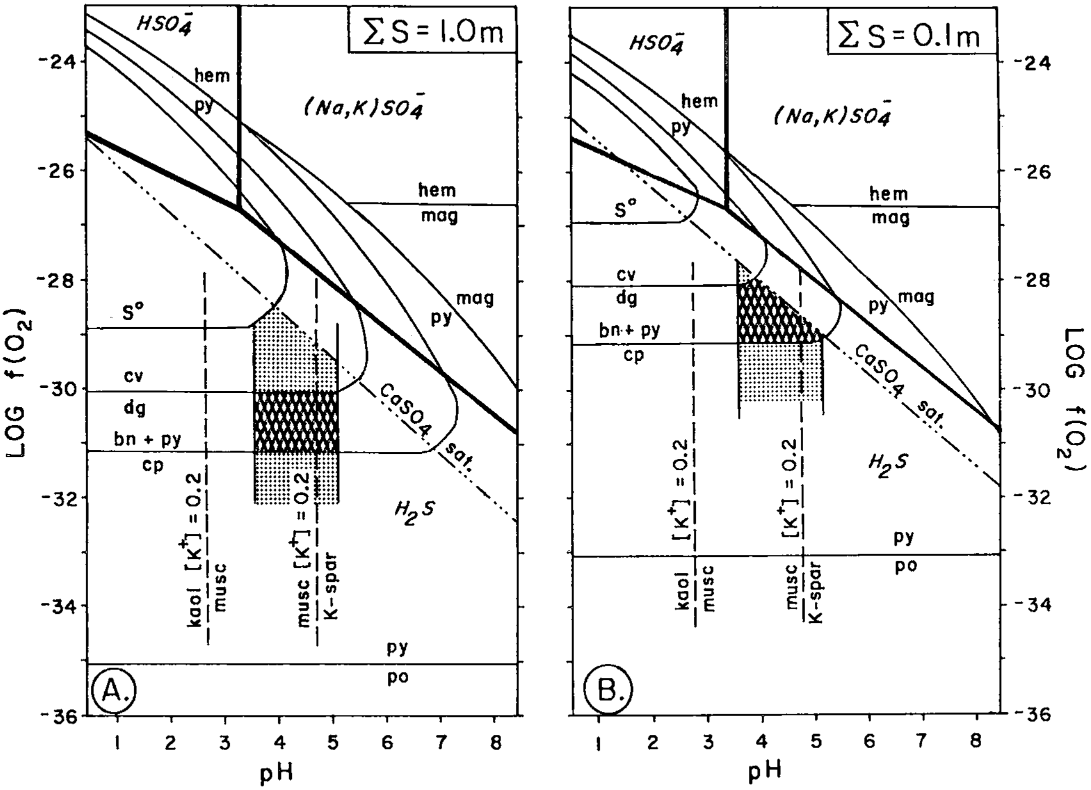

FIG. 10. Log $f(O_2)$-pH diagrams depicting the stability of Cu–Fe sulfides at 350°C and with H_2S activities of 10^{-1} and 10^0. The darker patterned areas define the stability region of the assemblage bornite + digenite over the calculated pH range of 4.4 ± 0.8. The lighter stippled areas include the stability regions of covellite and chalcopyrite. The fine lines define univariant mineral reaction [and are also lines of constant $f(S_2)$], whereas the bold lines delineate the dominant aqueous sulfur speciation. Anhydrite saturation is depicted by a dash–dot line. Univariant, pH-dependent reactions among the K-feldspar (K-spar), muscovite (musc), and kaolinite (kaol) are plotted as dashed lines. The diagrams were constructed using a BASIC version of the Ripley & Ohmoto (1979) FORTRAN program and the solution chemistry defined in Table 2. Thermodynamic data for aqueous speciation and Cu–Fe sulfides are from Helgeson (1969) and Ripley & Ohmoto (1977). Covellite–digenite stability and native sulfur saturation are taken from Barton & Skinner (1979). K-silicate equilibria are calculated from the data of Bowers *et al.* (1984) at the K^+ activity given in Table 2.

dition (Fig. 10), precluding deposition of copper sulfide by deeply circulating, oxidized groundwaters.

Cu–Fe activity–activity diagrams constructed for 350°C, 1 kbar and variable H_2S activities (Fig. 11) indicate that the presence of chalcopyrite in the Dunphy veins requires an activity of H_2S in excess of 10^{-1}. Chalcopyrite breaks down to bornite and magnetite, or to bornite and hematite, at lower activities of H_2S (Fig. 11C). Given the reduced nature of the solutions, H_2S would be the dominant aqueous species of S (Fig. 10) and H_2S molalities and total S in solution would be effectively equal. Thus, this minimum activity of H_2S, 10^{-1}, converts to a minimum total S of 0.1 *m*, if a unit activity coefficient is assumed for the uncharged H_2S molecule (Helgeson *et al.* 1981, Sverjensky 1984). A total S concentration as low as 0.01 *m* is possible in veins containing only bornite and digenite (represented by chalcocite in Fig. 11), but the presence of bornite in the mineralized veins (Chevé *et al.* 1985) precludes values of total S below 0.01 *m*, as the chalcocite–digenite saturation surface moves into the hematite field under lower total S, and the solution's composition would be unable to reach the bornite field.

With a total S content of 0.1–1.0 *m*, a pH of 3.6–5.2, and a temperature of 350°C, the absence of anhydrite fixes an upper limit of 10^{-30} to 10^{-28} on oxygen fugacity. The presence of bornite in the Dun-

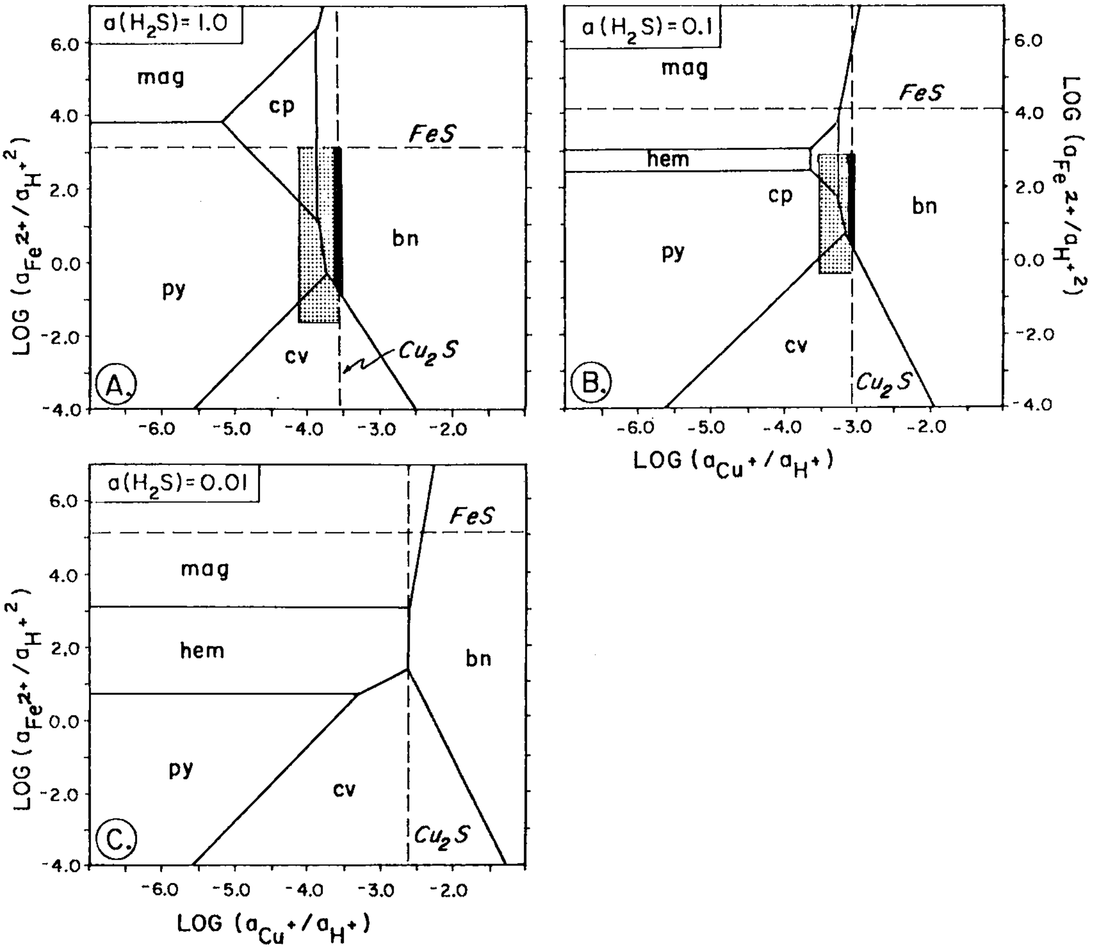

FIG. 11. Stability regions (bold lines) and saturation surfaces (dashed lines) for Cu–Fe sulfide and oxide phases in terms of the activities of Cu^+ and Fe^{2+} ratioed to H^+. Symbols: cp chalcopyrite, bn bornite, py pyrite, cv covellite, hem hematite, mag magnetite, FeS pyrrhotite, Cu_2S chalcocite). Diagrams are constructed for 350°C, 1 kbar, and three different activities (equal to molalities, see text) of H_2S. The bold dark vertical lines in A and B denote the region of bornite + chalcocite-digenite stability; lighter stippling marks the suspected range of fluid compositions that may have existed during vein formation, as deduced from the assemblage cp–bn–py–cv–Cu_2S. Thermodynamic data are from Bowers *et al.* 1984.

phy veins suggests a lower $f(O_2)$ limit of 10^{-30} to 10^{-29}, whereas the absence of pyrrhotite provides an absolute lower limit of 10^{-35} to 10^{-33} (Fig. 10A, B).

Limits on copper solubility

The dissociation constants of cuprous chloride complexes at temperatures above 200°C and their activity coefficients at elevated ionic strength are not known with certainty (Helgeson 1969, Crerar & Barnes 1976). Consequently, discussions of copper solubility in high-temperature, high-salinity solutions involve numerous assumptions and are generally qualitative. Nevertheless, the data acquired in this study do permit some calculations regarding the capacity of the Dunphy-hosted reduced brines to transport Cu and S.

Crerar & Barnes (1976) determined that NaCl solutions can carry appreciable amounts of Cu and S (Fig. 12). At 350°C, a pH of 4.4, and with a total S concentration of 0.1–1.0 *m*, their data indicate that reduced solutions with a Cl^- activity of 1.0 can carry a minimum of 900–3000 ppm Cu in equilibrium with chalcopyrite + bornite + pyrite, amounts similar to those proposed for ore-forming fluids in Cu-bearing hydrothermal systems (Czamanske *et al.*

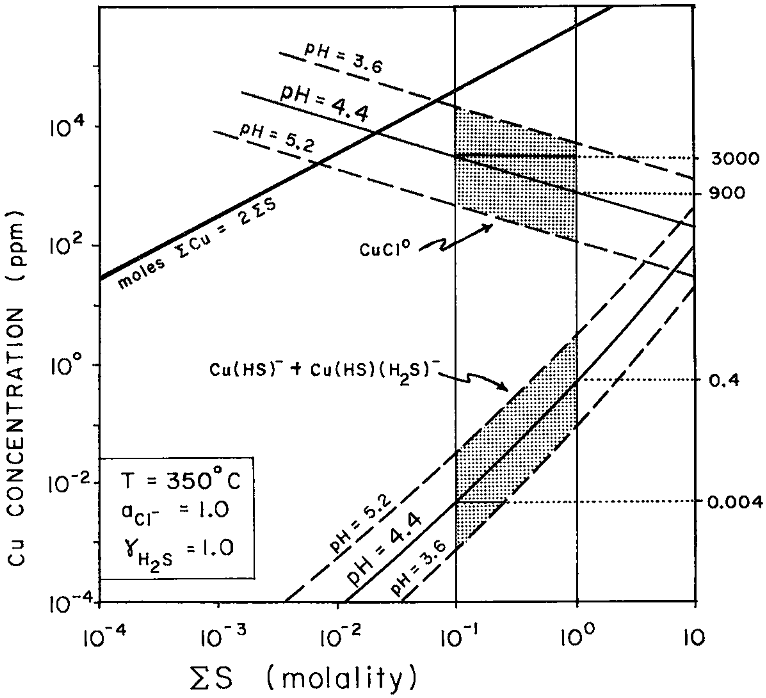

FIG. 12. Concentration of cuprous complexes $CuCl^0$ and $Cu(HS)^-$ + $Cu(HS)(H_2S)^-$ in a solution in equilibrium with pyrite + chalcopyrite + bornite as a function of pH and total S molality. Cl^- activity = 1.0 (Table 2). The stippled regions denote the pH - total S conditions defined by the inclusion fluids. The bold line labeled $\Sigma Cu = 2\Sigma S$ marks conditions of stoichiometric solubility of chalcocite, where the potential for chalcocite precipitation is maximized. Modified from Crerar & Barnes (1976).

1963, Rye & Haffty 1969, Hall *et al.* 1974). Although the Crerar & Barnes (1976) experiments are not directly applicable to systems sufficiently deficient in Fe such that digenite + bornite is the dominant sulfide assemblage, the presence of chalcopyrite and pyrite in the Dunphy veins indicates that some Fe is present and that fluid compositions were probably not too far removed from those used by Crerar & Barnes (1976). Their work also indicates that sulfide and bisulfide complexes are inadequate transporters of Cu under the Dunphy conditions. Even at the maximum total S content of 1.0 *m* and pH of 5.2 (the upper right corner of the lower stippled region in Fig. 12), only 3 ppm copper could be transported in S-bearing complexes.

Inspection of the *x*-axis values in Figure 12 confirms the necessity of chloride complexes in transporting Cu. Without chloride, the solubility of chalcocite in the Dunphy-hosted solutions can be calculated in a manner similar to the pH calculation involving the *y* axis of Figure 9. The chalcocite saturation surface for an H_2S activity of 10^{-1} (Fig. 11B) falls at a log activity (Cu^+/H^+) of -3.09, such that at a pH of 4.4 and an activity coefficient of 0.2 for Cu^+, only 2×10^{-7} *m* or 0.01 ppm Cu could be transported. However, if cuprous copper chloride complexes are considered using the data of Helgeson (1969), the total Cu solubility under these same conditions is 8×10^{-2} *m* or 4800 ppm.

SUMMARY AND CONCLUSIONS

Aqueous fluid inclusions in discordant quartz-dolomite-sulfide veins and in dolomite-filled fenestrae in the Dunphy dolostone of the central Labrador Trough contain 36–42 equivalent wt.% NaCl + $CaCl_2$. Values of the $CaCl_2/(CaCl_2 + NaCl)$ weight ratio determined by SEM–EDA of fluid-inclusion-derived decrepitates average 0.46 and 0.29 in two vein samples, and 0.34 for two dolostone samples; decrepitates from the vein samples have an average KCl content of 15 wt.%, whereas those in the dolostones average 8 wt.%. Carbonate–silicate mineral equilibria indicate that these saline solutions were moderately acidic (pH 4.4 ± 0.8) and therefore were capable of transporting several hundred to a few thousand ppm Cu. The sulfide assemblage (bornite + digenite + covellite ± chalcopyrite ± pyrite) indicates that the fluids were reduced, the $f(O_2)$ ranging from 10^{-28} to 10^{-30}, and the total S content was likely between 0.1 and 1.0 *m*. A 60–70° difference between fluid-inclusion homogenization temperature (242–312°C in veins) and temperatures calculated by Na–Ca–K thermometry using the inclusion compositions (300–390°C) suggests a fluid pressure of 1 kbar during vein formation, considerably less than the 2.0–3.5 kbars indicated by assemblages of metamorphic minerals in adjacent mafic units. This difference is interpreted to reflect the presence of pressures less than lithostatic during vein formation.

The inclusion chemistry, mineral assemblages, and geochemical calculations are consistent with veins originating from retrograde saline fluids. Early diagenetic, stratabound copper mineralization in the Dunphy dolostone would be leached by such fluids. Conditions permitting sublithostatic pressure gradients and the generation or (re-)opening of fractures hosting the remobilized sulfides were most likely attained during unloading of the region following peak metamorphism of the Hudsonian Orogeny.

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