ANALYSIS OF EVAPORATE MOUNDS AS A COMPLEMENT TO FLUID-INCLUSION THERMOMETRIC DATA: CASE STUDIES FROM GRANITIC ENVIRONMENTS IN NOVA SCOTIA AND PERU

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Abstract

The bulk composition of fluid inclusions is generally determined by using the temperature of ice melting (*i.e.,* freezing-point depression of H_2O–NaCl) and relating this to the ice-melting curve in the two-component system H_2O–NaCl. In reality, natural systems are more complex. Therefore, the bulk composition is referred to as equivalent wt.% NaCl to account for the presence of other, generally undetermined, cations (*e.g.,* K, Ca, Fe, Mn, Mg). Inferences of a more complex chemical composition are generally made on the basis of the depression of the eutectic temperature for the H_2O–NaCl system (–21.2°C), the other common solutes being $CaCl_2$, $MgCl_2$, and $FeCl_2$. Such an approach is qualitative at best, and the inherent problem of metastability invites caution. An alternative, relatively simple and cost-effective method among the many analytical methods available, is to artificially decrepitate fluid inclusions and analyze the resulting evaporate mounds with an electron microprobe equipped with an imaging system. To illustrate the potential of the method, three granitic environments, in Nova Scotia and in Peru, were chosen, two mineralized (Sn, Cu, Zn) and one barren (tourmaline pegmatite). Standard fluid-inclusion thermometric data have been integrated with compositions determined from evaporate mounds in the same suite of samples. The following points emerge: (1) the inclusions are invariably multi-component, being dominated by Na–K–Ca, but in consistently different proportion that reflect protracted fluid:rock interaction and mixing of reservoirs; (2) the low first-melting temperatures (*i.e.,* <–50°C) do not unequivocally indicate the presence of $CaCl_2$ in solution; (3) high concentrations of Fe and Mn are common within the mineralized systems examined, in addition to lesser amounts of Sr, Ba, P and Zn, and (4) the two methods complement each other, together providing a much more comprehensive account of the nature of the fluid and its evolution in space and time.

Keywords: fluid inclusions, evaporate mounds, granites, pegmatites, tin mineralization. Nova Scotia, Peru.

Sommaire

La composition globale de la phase fluide piégée dans les cristaux est généralement établie au moyen de la température de fusion de la glace, c'est-à-dire, l'abaissement du point de congélation de l'eutectique du système H_2O–NaCl, mis en relation avec la courbe décrivant la fusion de la phase solide dans le système binaire H_2O–NaCl. En fait, les systèmes naturels sont plus complexes. Pour cette raison, la composition globale du fluide est exprimée en termes d'équivalents de NaCl afin de rendre compte d'autres cations, non déterminés, par exemple K, Ca, Fe, Mn, Mg. Des conclusions à propos de la composition chimique plus complexe sont généralement faites pour rendre compte de l'abaissement de l'eutectique en dessous de –21.2°C, sa valeur dans le système H_2O–NaCl. Les autres solutés courants sont $CaCl_2$, $MgCl_2$, et $FeCl_2$. Une telle approche est définitivement qualitative, et le problème de métastabilité mérite une attention particulière. Une alternative relativement simple et peu couteuse, parmi les multiples méthodes analytiques qui sont disponibles, implique la décrépitation artificielle des inclusions fluides afin d'en analyser les amoncellements de matière évaporée avec une microsonde électronique munie d'un analyseur d'images. Afin d'illustrer le potentiel de la méthode, trois milieux granitiques ont été choisis, en Nouvelle-Écosse et au Pérou, deux de ceux-ci étant minéralisés (Sn, Cu, Zn) et un étant stérile (pegmatite à tourmaline). La thermométrie standard effectuée sur les inclusions fluides a été intégrée avec les compositions de ces amoncellements produits de la même suite d'échantillons. Il en ressort les points suivants: (1) les inclusions sont invariablement à multi-composantes, avec Na–K–Ca comme cations principaux, mais en proportions variables qui traduisent une longue interaction entre fluide et roche, et un mélange de réservoirs; (2) les faibles températures de fusion initiale (<–50°C) n'indiquent pas nécessairement la présence de $CaCl_2$ dans le système hydrothermal; (3) des concentrations élevées de Fe et de Mn sont courantes dans les systèmes minéralisés examinés, de même que des quantités moindres de Sr, Ba, P et Zn, et (4) les deux méthodes sont complémentaires, et ensemble contribuent à un meilleur aperçu de la nature de la phase fluide et son évolution dans l'espace et le temps.

(Traduit par la Rédaction)

Mots-clés: inclusions fluides, amoncellements de matière évaporée, granites, pegmatites, minéralisation en étain, Nouvelle-Écosse, Pérou.

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Introduction

Thermometric analyses of fluid inclusions, in particular temperatures of ice melting, provide a rapid means of obtaining bulk chemical compositions, in particular the frequently referred to wt.% equiv. NaCl term (*e.g.,* Crawford 1981, Roedder 1984, Goldstein & Reynolds 1994, Bodnar & Vityk 1994). As such, they provide a valuable non-destructive means of estimating fluid composition. However, this method assumes a simple binary system and treats all compositions equally, hence the equivalent wt.% value (Crawford 1981). More complicated compositions can, however, be determined by using the sequential freezing method (Haynes 1985, Goldstein & Reynolds 1994), in which hydrates (*e.g.,* hydrohalite, gas clathrates) can be identified and their melting temperatures determined. In these cases, use of the appropriate ternary system will provide an estimate of the bulk composition of the system, as has been demonstrated for the system H_2O–NaCl–$CaCl_2$ (Vanko *et al.* 1988, Oakes *et al.* 1990) and H_2O–NaCl–$MgCl_2$ (Dubois & Marignac 1997). However, the difficulty of discriminating between low- to moderate-salinity fluids dominated by NaCl or KCl, as well the difficulty in interpreting the phase changes in complex multicomponent systems, given the problems of metastability (*e.g.,* Samson & Walker 2000), limits the potential use of eutectic measurements to infer fluid composition. Although a variety of nondestructive and destructive methods are available to determine the major solute composition of single fluid-inclusions, trace and minor elements (*e.g.,* Heinrich *et al.* 1992, 1999, Audétat *et al.* 1998), a relatively simple, efficient, and underutilized method is the analysis of fluid-inclusion decrepitate mounds. This approach is tested here in case studies from Nova Scotia and Peru.

Background Information

The decrepitate method was first discussed and applied by Eadington (1974). It was the work of Haynes *et al.* (1988) on synthetic fluid inclusions, however, that demonstrated the reliability of this semiquantitative method to obtain cation and anion concentrations of fluid inclusions. Thus, Haynes & Kesler (1987) successfully applied decrepitate analysis to the study of MVT-style mineralization in the East Tennessee and Pine Point districts, and recognized the importance of reduced sulfur in these systems. In another study of MVT-type mineralization, Savard & Chi (1998) used the method to analyze mineralizing fluids in some carbonate-hosted Zn–Pb deposits of the Maritimes Basin of Eastern Canada. In yet another successful study, Chryssoulis & Wilkinson (1983) applied decrepitate analysis to show that quartz megacrysts in mineralized granite of San Luis Potosí, Mexico, contain fluid inclusions with several wt.% each of Na, K, Ca, Mn, Fe and Ag. Finally, Halter *et al.* (1998) integrated decrepitate

analysis with whole-rock chemistry to examine the alteration profile within a mineralized granite from East Kemptville, Nova Scotia. Other studies from a variety of mineralized environments where decrepitate analysis has been integrated with standard thermometric work include pegmatites (Kontak *et al.* 2001, 2002), base-metal vein-type mineralization (Kontak *et al.* 1999), greisens and veins in the South Mountain Batholith of Nova Scotia (Carruzzo *et al.* 2000), and fluorite mineralization hosted by a carbonatite (Palmer & Williams-Jones 1996).

The present study focuses on an integration of results of analyses of decrepitates with standard thermometric measurements in order to ascertain the nature of the cation proportions in fluids in a variety of granitic settings. These examples include greisen-type Sn – base-metal mineralization at East Kemptville, Nova Scotia, a pegmatite–aplite system in the South Mountain Batholith, Nova Scotia, and the San Rafael tin – base metal system of veins in southeastern Peru (Fig. 1). The results of this study confirm those of previous investigators and indicate that this rapid, relatively simple technique provides informative data that complement standard thermometric work. In addition, the results suggest a distinct fluid composition for mineralized *versus* barren systems in granitic environments that may have implications for exploration. Recently Roedder & Bodnar (1997) suggested that this method be referred to as evaporate analysis to distinguish it from nebulizate analysis, both of which require decrepitation of the fluid inclusion. This change in nomenclature is adopted herein.

Environments Studied

Peggys Cove, Nova Scotia

Flat-lying, layered pegmatite–aplite sheets occur within a biotite–muscovite leucomonzogranite of the Halifax pluton, part of the large, peraluminous South Mountain Batholith (SMB) of southern Nova Scotia (Figs. 1a, b). The similar ages of *ca.* 370 Ma for both host rock and the aplite–pegmatite sheets suggest a close petrogenetic association of the two granitic lithologies. Offshore from the coastal outcrops are metaturbiditic country-rocks of the Lower Paleozoic Meguma Group (MacDonald & Horne 1988), and this material accounts for the abundant xenoliths observed in the leucomonzogranite host. The pegmatite–aplite sheets are zoned, with a basal aplite, commonly with line-rock texture, that is overlain by coarse pegmatite with comb-textured K-feldspar. The boundary layer between these two zones is generally defined by coarse, intergrown quartz – K-feldspar – muscovite – tourmaline pegmatite with pocket zones. A detailed petrological and stable-isotope study of these rocks (Kontak *et al.* 2002) suggests an origin for the pegmatites involving local generation of volatile-rich melt *via* interaction of the
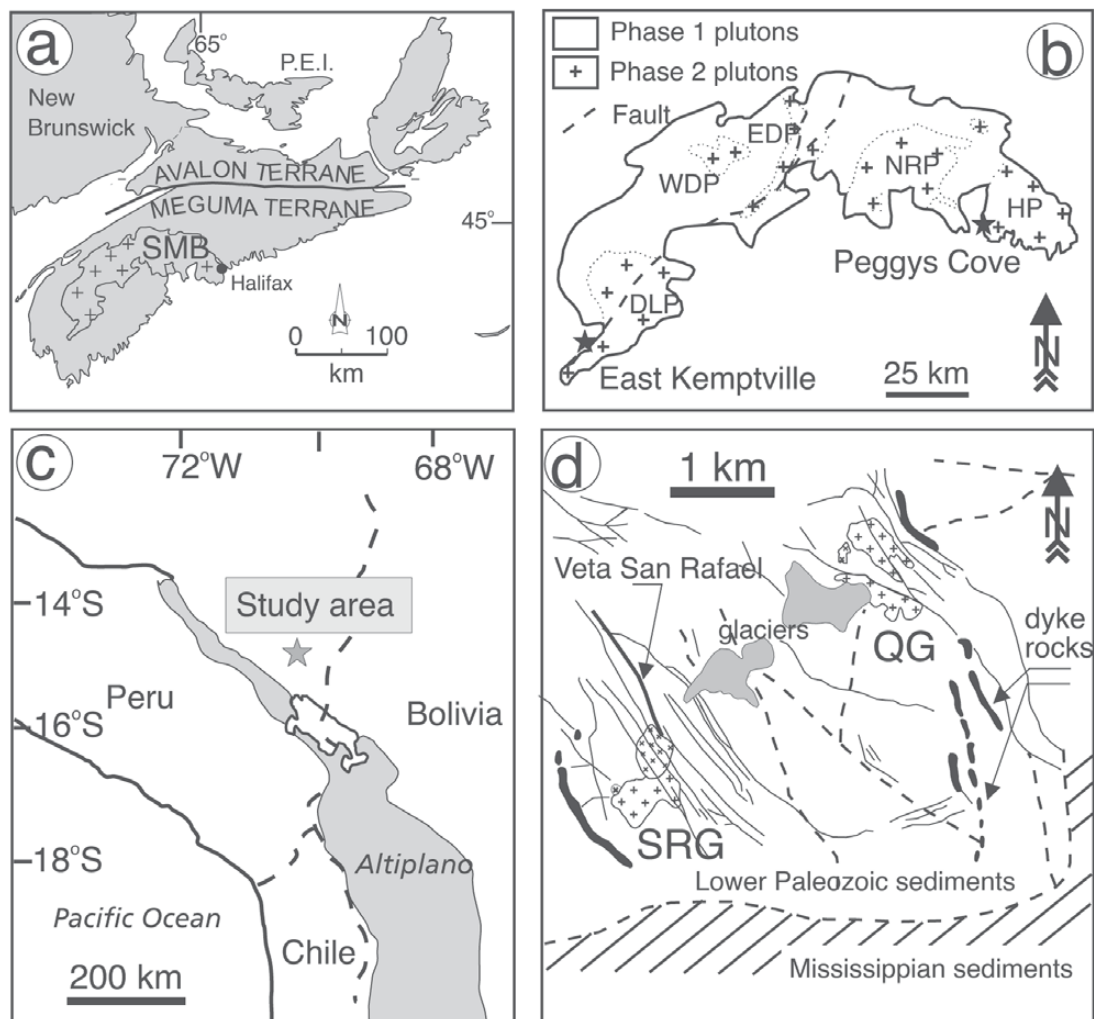
FIG. 1.   Location maps for the various areas studied. (a) Outline of Maritime Canada with location of the South Mountain Batholith (SMB) within the Meguma Terrane of southern Nova Scotia. (b) Outline of the SMB showing the distribution of early phase 1 and late phase 2 intrusions, and location of the two study areas, namely Peggys Cove (pegmatite–aplite sheets) and East Kemptville (Sn–Cu–Zn–Ag deposit). (c) Outline of the cental Andes showing location of San Rafael study area in southeastern Peru. (d) Simplified geology of San Rafael showing outline of the San Rafael (SRG) and Quenamari (QG) granites. Samples for the study come from within the SRG, both close to and away from mineralized veins (*e.g.,* Veta San Rafael).

xenoliths and magma, rather than formation from extreme fractional crystallization of a progenitor melt. Samples of the pegmatite, including the pocket zones, were used for the fluid-inclusion study.

East Kemptville, Nova Scotia (*Sn–Cu–Zn–Ag deposit*)

At the East Kemptville tin deposit, the host rock topaz–muscovite leucogranite represents the end product of protracted crystal–fluid fractionation of the Davis Lake pluton (Dostal & Chatterjee 1995), itself part of the large, peraluminous 370 Ma South Mountain Batholith of southern Nova Scotia (Fig. 1b). The deposit occurs at the contact between the leucogranite and metaturbidites of the Meguma Group. The upper contact of the leucogranite is marked by a chilled zoned with bodies of layered aplite–pegmatite containing unidirectional solidification textures (UST). Mineralization

consists of cassiterite-bearing pegmatites, quartz – topaz – cassiterite – sulfide greisens (*i.e.,* main mineralization), and quartz–sulfide veins (Kontak 1994, Halter *et al.* 1996). Similar ages and isotopic signatures indicate that this mineralization represents a single magmatic–hydrothermal event, and there is little evidence for incursion of another fluid or significant interaction of the mineralizing fluid with an exotic reservoir (Kontak 1994). Samples used in this study were collected from altered leucogranite, pegmatite, greisen and sulfide veins.

San Rafael, southeastern Peru (Sn–Cu deposit)

In southeastern Peru, that part lying at the northern termination of the Central Andean tin belt, a 25 Ma, high-level, biotite–cordierite monzogranite stock intruding Lower Paleozoic metasandstones and metasiltstones of the Sandia Formation contains a high-grade lode-tin deposit (*ca.* 36,685 t tin concentrate produced in 2000; Clark *et al.* 2000, Kontak & Clark 2002) (Figs. 1c, d). The mineralization occurs as vertically zoned (*i.e.,* Cu:Sn ratio decreases with depth), high-grade Sn–Cu chloritic lodes containing coarse cassiterite and chalcopyrite (Palma & Clark 1982). Within the granite occurs a pervasive, albeit cryptic, metasomatism reflecting widespread infiltration of a dominantly magma-derived, high-temperature (to *ca.* 550°C) brine, but mixing of this fluid with a low-salinity, probably meteoric fluid occurred (Kontak & Clark 2002). The metasomatic overprint is reflected by the presence of: (1) secondary, end-member albite and K-feldspar, (2) fluid-mediated ordering of originally disordered Al and Si in the alkali feldspar megacrysts (Kontak *et al.* 1984), and (3), most relevant to this study, abundant secondary fluid-inclusions in the quartz megacrysts. Samples of the metasomatized San Rafael granite were used for the present fluid-inclusion study.

ANALYTICAL TECHNIQUES

Samples used in this study formed part of previous petrological studies that documented the nature of mineralization, alteration and fluid composition in the areas of interest. Details of the thermometric work on these suites have been presented elsewhere. The reader is referred to these sources for more detailed descriptions of the fluid inclusions, phase behavior during cooling and heating runs, and results of thermometric measurements (Kontak *et al.* 2001, 2002, Kontak & Clark 2002).

Evaporate mounds were prepared in the following manner. (1) Chips of material used for fluid-inclusion thermometry were inserted into the same heating–cooling chamber previously used, *i.e.,* in this case a USGS-type gas-flow heating-freezing stage. (2) Samples were rapidly heated to artificially induce decrepitation, this generally occurring in the range 350–550°C, as samples dictated. (3) Samples were subsequently quenched by

immediately turning off the power supply to the heating stage. (4) Chips were transferred onto a glass slide and examined in reflected light microscopy to ensure that sufficient decrepitation of fluid inclusions had occurred. The presence of evaporate mounds is readily observable, as the surface of samples is generally covered with circular mound features, typically surrounded by an annulus of smaller debris (Figs. 2a, b). As noted below, where very-low-salinity inclusions are present (*i.e.,* ≤0.5 wt.% equiv. NaCl), mounds may not form. Instead, open inclusions without decrepitates will be observed. (5) The chip was then transferred to double-sided carbon tape attached to a petrographic glass slide (Fig. 3c) suitable for loading onto a mount for insertion into the electron-microprobe chamber, subsequent to the necessary coating with carbon. An important modification of this technique that others might consider where appropriate is to insert under the fluid-inclusion chip a silica plate, and decrepitate onto this substrate. This modification will permit analysis of a Ca-rich fluid inclusion hosted by, for example, a Ca-rich phase such as fluorite, which was done by Palmer & Williams-Jones (1996).

Imaging and analysis of carbon-coated mounds were done using a JEOL 733 Superprobe with a LINK EXL energy-dispersion system (EDS) system located in the Department of Earth Sciences, Dalhousie University, Halifax, Nova Scotia. Evaporate mounds were located using back-scattered (BSE) and secondary electron imaging (SEI). The analyses were done using the following operating conditions: 3–40 μm beam or rastering, accelerating voltage 15 kV, current 10 nA, and counting time 40 seconds. Other investigators have used an SEM setup with an EDS analyzing system (*e.g.,* Halter *et al.* 1998, Savard & Chi 1998).

For particular mounds, several analyses are made to ensure homogeneity. Where a large evaporate mound is present, either a defocused beam of electrons or a rastering technique is employed to prevent volatilization of light elements and also to provide a more homogeneous sampling size. If a complex composition is present, involving, for example, Fe, Mn and Mg, in addition to Na, K and Ca, then BSE imaging provides an indication of the homogeneity of the mounds, as discussed below. In general, however, similar compositions occur within mound groupings, and similar results are obtained regardless of beam size or point *versus* raster analysis, although exceptions do occur, as noted.

The initial dataset is screened for internal consistency by using the charge balance, the totals and homogeneity of results, as discussed above, to assess the reliability of the analysis. Since the power of this technique is its semiquantitative aspect, the screening need not be as rigorous as for chemical analysis of minerals. Thus, charge balance of ±10–15% and totals of 95 ± 10 wt.% are general guidelines that are employed. In general, these guidelines are considered flexible and can be modified for specific studies. As the results below indicate, the differences in the decrepitate compositions are
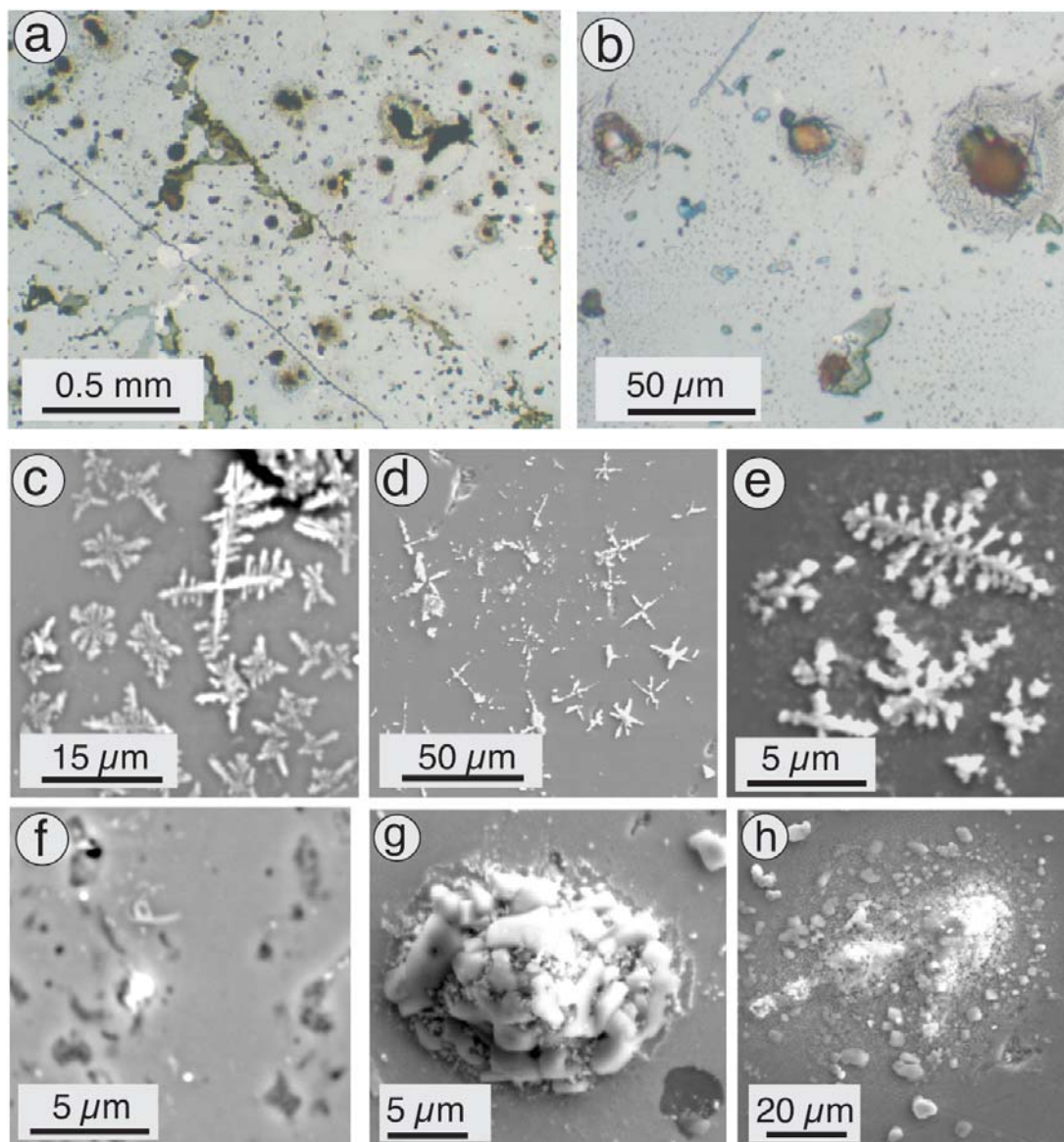
FIG. 2.   Photomicrographs of decrepitate mounds. (a) Reflected-light photomicrograph of decrepitate mounds on cassiterite substrate from East Kemptville tin – base-metal deposit, Nova Scotia. (b) Closeup of photo in 2a showing details of mounds. Note the regular round to subrounded outlines and annular array of decrepitate debris (*i.e.,* mound on the right side). (c) Back-scattered electron (BSE) image of K-rich mounds on quartz substrate. Sample is of vein quartz hosting base- and precious-metal mineralization from the Dunbrack vein deposit, Nova Scotia (Kontak *et al.* 1999). (d) BSE image of K-rich mounds on quartz substrate. Sample is of vein quartz from the Black Bull silica–clay deposit (Kontak & Kyser 2001) in the Davis Lake pluton of the SMB (Fig. 1b). (e) BSE image of Ca-rich mound on quartz substrate. The sample comes from an auriferous gold vein of the Caribou deposit, Nova Scotia. (f) BSE image of empty vugs (*i.e.,* evacuated fluid-inclusions) in quartz from the Dunbrack base– and precious-metal vein-type deposit, Nova Scotia. (g) BSE image of mixed Na–K mound on cassiterite substrate showing euhedra formed from recrystallized salt halides. Cassiterite-bearing pegmatite, East Kemptville tin deposit, Nova Scotia. (h) BSE image of decrepitate debris on quartz substrate from cassiterite-bearing pegmatite, East Kemptville tin deposit, Nova Scotia. Note that there is an asymmetrical distribution of mounds reflecting egression from a point to the upper right. The difference in brightness of the mound relates to higher concentrations of Fe and Mn in the upper right *versus* Na and K in the left part of image.

quite dramatic, and will be obvious even with less stringent guidelines.

Some comments regarding the application of this technique are also considered appropriate here. The modern use of digital imagery makes this technique even more applicable to fluid-inclusion studies. The author, therefore, emphasizes the following points for those interested in integrating this work into their fluid-inclusion studies. The initial step is to image the fluid-inclusion section to be studied (Fig. 3a), and map out the areas of potential use for thermometry, that is, areas of fluid inclusions with similar proportions of phases [*i.e.,* fluid-inclusion assemblages (FIAs) of Goldstein & Reynolds 1994]. By using digital images of planes of fluid inclusions (*e.g.,* Fig. 3b) and nearby marks that are easily located, it is possible to follow up on thermometric work with analyses of evaporate mounds of the same FIAs since the chip used can be subsequently mounted on double-side carbon tape and used for imaging and electron-microprobe analysis. Thus, a one-to-one correlation of compositions inferred from thermometry and decrepitate procedure is achievable. Although this was not done for the suite of samples discussed herein, such a procedure is currently being applied where suitable populations of fluid inclusions are present.

ANALYTICAL RESULTS: GENERAL CONSIDERATIONS

Before discussing the analytical results for individual study-areas, a few comments on the nature of the evaporate mounds based on the imaging and analyses of numerous mounds in a variety of mineralized environments are considered appropriate, as they may prove beneficial for subsequent investigators. Firstly, the textures of mounds are commonly, but not invariably, a reflection of their makeup, that is whether they are crystalline *versus* massive (Fig. 2g *versus* h). However, it is noted that these observations are not cast in stone and are offered as guidelines only. For example, the more irregular the shape of the mound, the more likely it is to be enriched in one or more of Fe, Mg and Mn (Fig. 2h). In contrast, the more regular the shape, the more likely the mounds are to be dominated by, if not solely composed of, Na or K chlorides, or both (Fig. 2g). Where the mounds are composed solely of Ca chloride, a millipede-type shape is commonly observed (Fig. 2e), and a dendritic pattern with a cross shape usually signifies K-chloride-dominated mounds (Figs. 2c, d).

Secondly, where complex compositions occur, *i.e.,* those containing Fe, Mg, Mn in addition to Na, K and Ca, the mounds may be zoned, with the ferromagnesian elements concentrated near the exit point and the alkalis enriched away from there. In this particular study, such inclusions were encountered for some of the East Kemptville (Fig. 2h) and San Rafael samples, as discussed in more detail below.

As a final point worth noting, inclusions containing very-low-salinity fluids may be identified by the ab-sence of mounds. For example, abundant empty cavities were noted in quartz (Fig. 2f) from a base- and precious-metal rich vein deposit in the Musquodoboit Batholith, Nova Scotia; these correlate with a population of low-salinity inclusions based on earlier thermometric studies (Kontak *et al.* 1999). Similar results have been obtained for quartz-hosted fluid inclusions from a hydrothermal silica–clay deposit within a fault zone along the southern margin of the Davis Lake pluton (Fig. 1b; Kontak & Kyser 2001, 2002).

In the ensuing discussion of analytical data, results of the decrepitate analyses are interpreted in the context of the thermometric measurements of fluid inclusions for each of the study areas. The results are then discussed collectively.

THE PEGGYS COVE
TOURMALINE-BEARING PEGMATITES, NOVA SCOTIA

Fluid-inclusion studies

The types of fluid inclusions observed in quartz from pegmatites in the aplite–pegmatite sheets, including the pocket zones, include liquid (L) – vapor (V) – halite (Hl) and L–V, but cooling runs indicate that the L–V population can be subdivided into aqueous and aqueous–carbonic types. In all cases, consistent proportions of phases indicate that a fluid inclusion assemblage (FIA) was being studied. The aqueous types are interpreted to be exsolved magmatic brine, whereas the carbonic type relate to the influx of exocontact fluids derived from metasedimentary rocks of the Meguma Group (Kontak *et al.* 2002). The results of low-temperature measurements (*i.e.,* freezing runs) indicate the following important compositional features about the inclusions. (1) A large range in temperatures of first melting (T_{fm}), with two broad peaks at –60° and –50°C (Fig. 4a), which suggests that cations in addition to Na and K are present in the fluid. (2) Because both hydrohalite and ice melting could be observed in many of the L–V-type inclusions, the data could be projected into the NaCl–CaCl$_2$–H$_2$O ternary system (Fig. 4b; note that data for L–V–Hl type inclusions are not plotted). This latter diagram indicates the presence of three compositional groups of fluid inclusions: (i) a Na fluid, (ii) a Na–Ca fluid, and (iii) a Ca-rich fluid. However, it is possible that additional cations (*e.g.,* K, Fe, Mg, Mn, *etc.*) exist within each of these types of inclusion, since the diagram is only appropriate for estimation of bulk compositions in the NaCl–CaCl$_2$–H$_2$O ternary system. Note also that these three different populations of inclusions could not be recognized petrographically.

Compositions of evaporate mounds

The two samples used for decrepitation are from a layered aplite–pegmatite zone (PCG–99–22) and the pocket zone of a pegmatite sheet (PCG–99–21a). The

analyses of these two samples indicate that the evaporate mounds consist solely of Na, K and Ca chlorides. These data are summarized in a Ca–Na–K plot in Figure 5. The notable features of the data follow: (1) three distinct populations are indicated, these being K–Na-rich, Na–Ca-rich, and Ca-rich (the three populations are shown in the inset in Fig. 5a); (2) an apparent lack of K-rich in mounds of sample PCG–99–21a, but with a Ca-rich population, and (3) low totals are recorded for the Ca-rich mounds, *i.e.,* there is insufficient Cl to provide charge balance, and in some cases sulfur is detected in these same mounds. Although Haynes *et al.* (1988) noted that variable volatility may occur at excessive temperatures (*i.e.,* above 450°C) and that preferential loss of chlorine and some alkalis may occur, this explanation is not considered appropriate, since the sample was not subjected to such high temperatures, and the Na–K mounds did not have this problem.
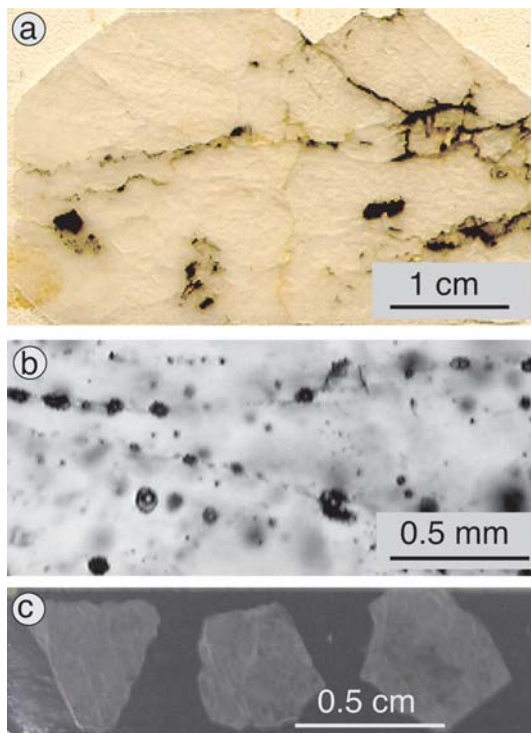
FIG. 3.   (a) Fluid-inclusion chip of auriferous quartz-vein material from Meguma gold deposit, Nova Scotia. (b) Photomicrograph of fluid-inclusion plane in quartz chip of Figure 3a. (c) Small fluid-inclusion chips mounted on double sided carbon tape adhered to petrographic slide. The sample is ready for carbon coating and analysis with an electron microprobe.

Comparison of decrepitate and thermometric data

A comparison of compositions of evaporate mounds and thermometric measurements indicate the following: (1) the mound compositions confirm the three compositional groups in terms of the proportions of Na–K–Ca; there is a correlation of the groupings I, II and III in Figure 4b *versus* the inset in Figure 5a. Whereas the thermometric data indicate three distinct compositions, it is the results of mound analyses that discriminate the true composition. (2) The K-deficient nature of the evaporate mounds in sample PCG–99–21a could not be determined on the basis of thermometric measurements alone given the difficulty of discriminating between binary and ternary eutectics with KCl, NaCl, $CaCl_2$ and H_2O (Hall *et al.* 1988, Oakes *et al.* 1990). This is an important observation; it suggests that there may be a petrogenetic relationship between the composition of the mounds and the fluid evolution of the aplite–pegmatite system. (3) The Ca-signature, along with trace amounts of S, reflect the incursion of an exotic fluid that may have equilibrated with an external reservoir, as discussed in detail by Kontak *et al.* (2002). These data support the interpretation that the carbonic component of the fluid also originated from equilibration of a fluid with the metasedimentary rocks of the Meguma Group (Kontak *et al.* 2002). (4) The eutectic measurements below –50°C (Fig. 4a) must relate to metastability or a recrystallization phenomenon (*cf.* Samson & Walker 2000), as such low eutectic temperatures cannot be explained by the cation proportions of these inclusions and known phase-relations.

THE EAST KEMPTVILLE Sn–Zn–Cu–Ag DEPOSIT, NOVA SCOTIA

Fluid-inclusion studies

Petrographic observations of the fluid inclusions in altered granite, pegmatites, greisens and veins indicate the following types of inclusions: (1) L–V–Hl–sylvite (Slv), (2) L–V–Hl, and (3) L–V. In addition, a solid phase considered to be a chloride of Fe has been noted in fluid inclusions in the greisens (Halter *et al.* 1998). The inclusions are well preserved and uniform proportions of phases occur; FIAs are thus easily identified. During freezing runs, hydrohalite is commonly the last phase to melt in L–V inclusions, which indicates compositions of 23–36 wt.% equiv. NaCl, whereas higher salinities are indicated from the melting of halite and sylvite (to 45 wt.% equiv. NaCl). The T_{fm} values cover a broad range from –70° to –20°C, but most of the data are in the range –40° to –25°C (Fig. 6). From the foregoing observations and temperature of last melting of ice and halides, the bulk composition of the fluid is inferred to be 20–45 wt.% equiv. NaCl . However, from the T_{fm} and presence of daughter minerals, the solute

composition is clearly variable and appears to contain Na, K, Fe and Mg, with lesser Ca, although the relative dominance of these cations is not constrained. On the basis of the homogenization temperatures, these fluids seem dominantly of magmatic nature, and were exsolved from a F-rich granitic melt at ≤550–600°C (Kontak *et al.* 2001).

Compositions of evaporate mounds

Compositions of evaporate mounds (Figs. 2g, h) were obtained for inclusions hosted by quartz and cassiterite from two pegmatites, quartz from a cassiterite-bearing miarolitic cavity, and quartz in a sulfide vein. The data indicate that the common cations, in descending order, are Na, K, Fe, Mn, Ca, Sr and Ba; Zn and P, in minor proportions, were mainly detected in the vein sample. The dominant anion is Cl, but minor sulfur occurs in the sulfide vein sample. Although discrete halite and sylvite occur in the evaporate mounds, most analyses indicate mixtures of Na–K–Fe–Mn–Ca salts. The most striking feature of the mounds at East Kemptville is the abundance of cations other than Na and K, in particular those elements that would otherwise go undetec-

ted (*i.e.,* Fe, Mn, Ca, Sr). These results agree with compositions of evaporate mounds and of fluid-inclusion leachate in samples of greisen and granite from East Kemptville by Halter *et al.* (1998). Finally, a most important observation is that the elevated Fe and Mn contents obtained for cassiterite-hosted decrepitate mounds are not related to the substrate for the following reasons: (1) the cassiterite is not enriched in either of these elements, and (2) similar results are obtained where quartz is the substrate.

In Figure 7, the Na–K–Ca data are subdivided on the basis of occurrence. The following points are noted: (1) The altered granite is dominated by Na and K, with very minor Ca. (2) The pegmatite contains two trends, one a Na–K and the other a Na–Ca trend, which is similar to the pattern observed at Peggys Cove (Fig. 5). (3) The quartz vein sample contains three distinct populations: (i) a Na-rich fluid, (ii) a mixed fluid of similar proportions of Ca–Na–K, and (iii) a Ca-rich fluid. The results for the different samples are plotted together in Figure 8, where the relative enrichment of several cations are examined. From these plots, one sees that: (1) the Na-rich fluid is preferentially enriched in Fe, Mn, and Sr compared to the K-bearing fluid, and (2) the fluid is depleted in Mg.
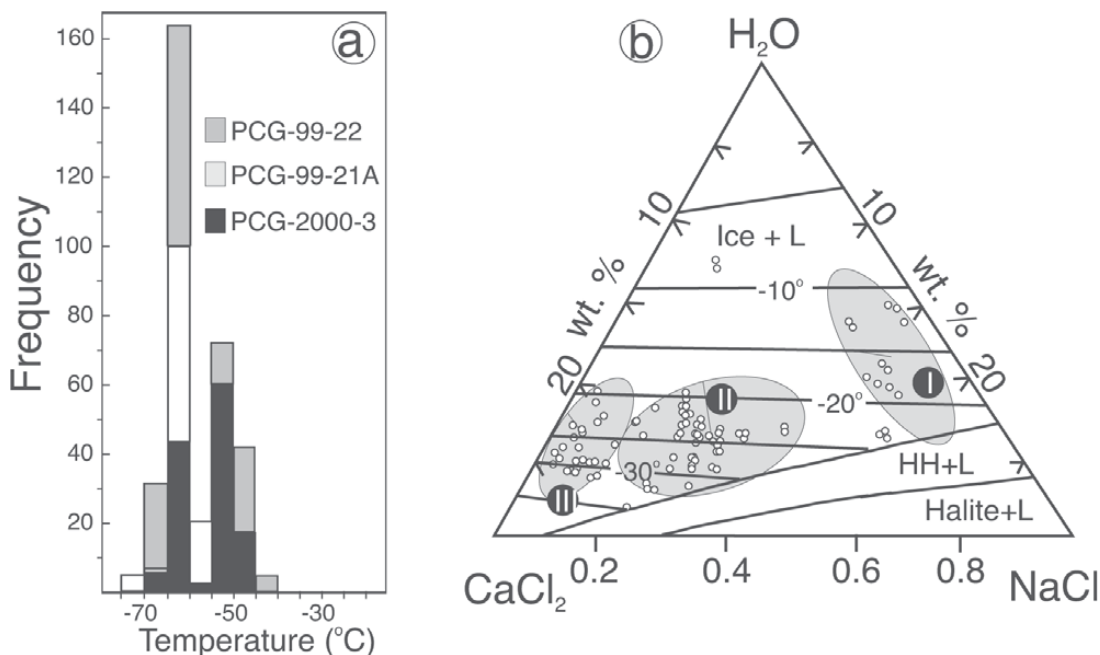

FIG. 4.   Thermometric data for quartz-hosted fluid inclusions from layered aplite–pegmatite sheets, Peggys Cove, Nova Scotia (from Kontak *et al.* 2002). (a) Histogram plot of temperatures of first melting for quartz-hosted inclusions in three samples. (b) Partial phase diagram for the ternary system $CaCl_2$–H_2O–NaCl (after Vanko *et al.* 1988) showing bulk compositions for fluid inclusions based on hydrohalite–ice melting relationships.

Comparison of decrepitate and thermometric data

The low temperatures of first melting, along with the presence of both halite and sylvite in the fluid inclusions of samples from East Kemptville, indicate that the composition of the system is complex. The low T_{fm} measurements indicate the presence of cations other than Na (*i.e.,* Ca, Fe, Mg; Borisenko 1977, Vanko *et al.* 1988, Dubois & Marignac 1997). The mound data confirm that a complex, multicomponent system exists and, furthermore, they provide important information regard-

ing the relative abundance of the components that could not be ascertained from the thermometric measurements. These results also indicate that Mg is absent in the fluid, although the temperatures of first melting might suggest its presence; instead, Fe chloride is evidently responsible for the low T_{fm} measurements in the –35° to –40°C range. The apparent enrichment of both of Fe and Mn in the fluids and their clear affinity for Na-rich *versus* K-rich fluids could not be determined with standard thermometric work.

Fluid-inclusion studies

The secondary fluid-inclusions in the magmatic quartz include the following types: L–V–Hl–Slv, L–V–Hl, L–V and V; a rare Fe chloride phase, confirmed from SEM analysis, occurs in some inclusions. The large range in T_{fm}, from –70° to near 0°C (Fig. 9a), indicates a complex composition of the fluid, with Ca, Mg and Fe probably present in addition to Na and K. Salinity, determined from dissolution of halite and sylvite, along with ice melting, cover a continuum from *ca.* 65 to 0 wt.% equiv. NaCl (Fig. 9b), generally commensurate with decreasing temperature. The range in salinity has been interpreted to reflect the incursion and mixing of meteoric water with a magma-derived brine from a felsic magmatic system undergoing intermittent boiling (Kontak & Clark 2002). A similar evolution of the fluid phase is recorded by fluid inclusions hosted by vein quartz and cassiterite (Palma & Clark 1982).
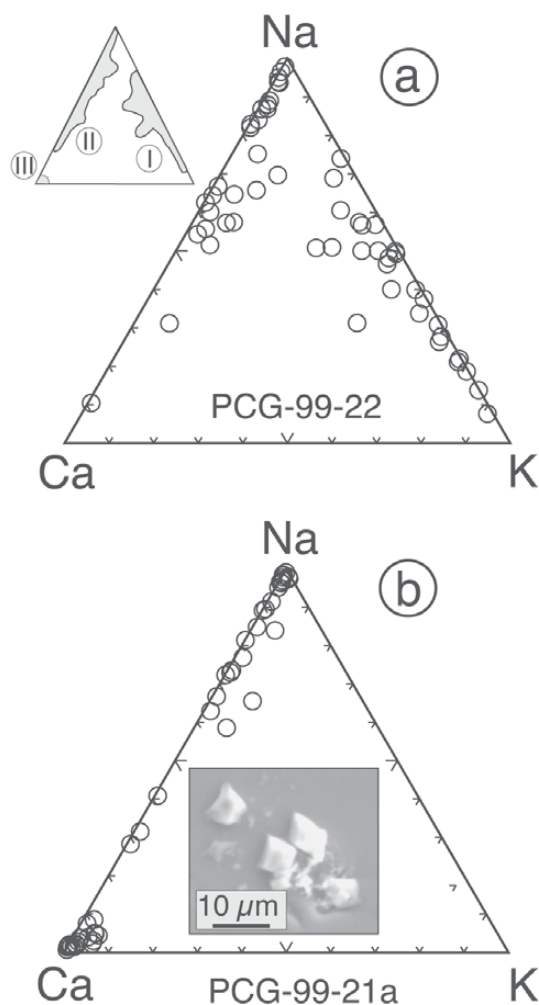

FIG. 5. Plots showing compositions of decrepitate mounds in pegmatitic quartz from aplite–pegmatite sheets, Peggys Cove, Nova Scotia, in Na–K–Ca space. (a) Sample PCG–99–22 is from a layered aplite. (b) Sample PCG–99–21 is from a coarse pocket of quartz – muscovite – tourmaline – K-feldspar. Inset is BSE image of typical Na-rich mound on quartz substrate from this sample.
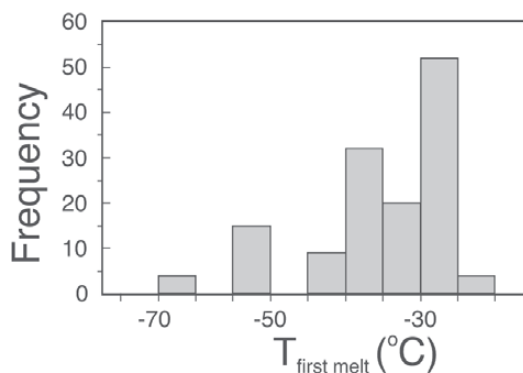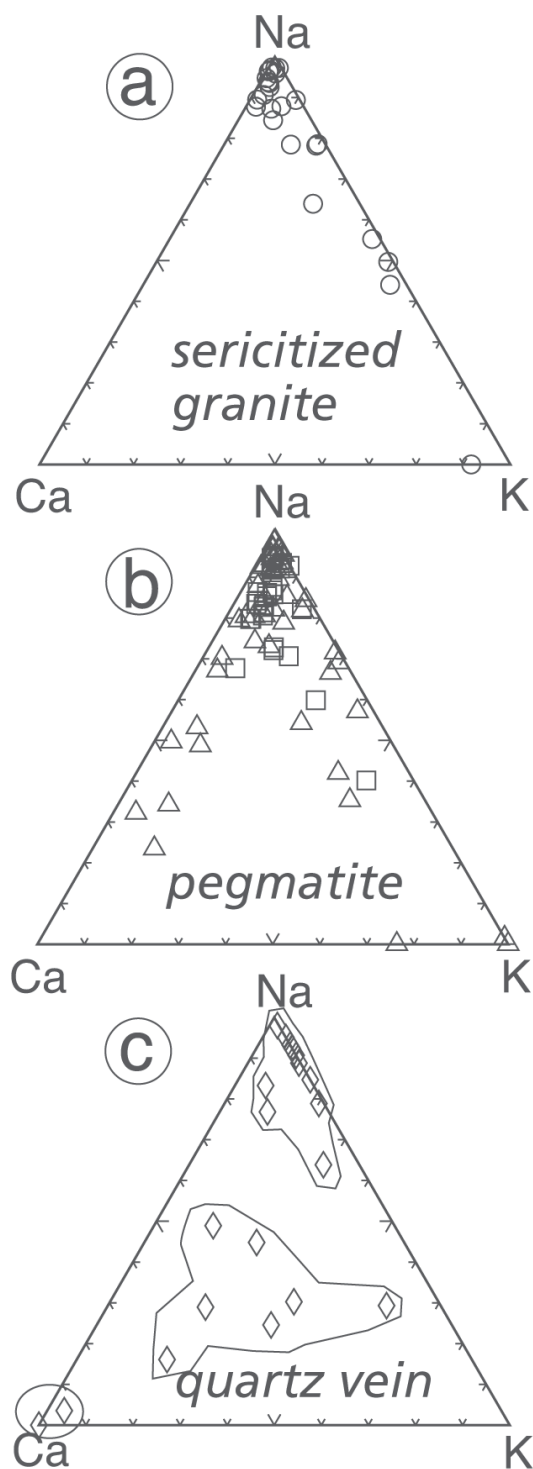

FIG. 6. Thermometric data summarizing temperatures of first melting for fluid inclusions in quartz from altered granite, pegmatite and vein from East Kemptville, Nova Scotia (from Kontak *et al.* 2001).

FIG. 7. Plots showing Ca–Na–K proportions of decrepitate mounds in (a) altered granite, (b) pegmatite and (c) vein quartz from East Kemptville tin – base-metal deposit, Nova Scotia. Note that in the sample of quartz vein, three populations of mounds are indicated.

Compositions of evaporate mounds

Compositional data have been obtained for evaporate mounds in the quartz megacrysts. The results are somewhat similar to those observed at East Kemptville, with high concentrations of Na, K, Fe, and Mn; Mg is present in trace to minor amounts. Mound shapes are also similar to those of East Kemptville, with both the regular, cube-like habit of the Na- and K-rich mounds and more massive form of those enriched in Fe, Mn and Mg (inset in Fig. 10a). In the Na–K–Ca plot (Fig. 10a), the data are concentrated along the Na–K limb and Na-rich part of the Na–Ca limb, whereas there Ca is depleted in the mounds (Figs. 10a, c, e). In other plots, it appears that both Fe and Mn are associated with Na rather than K (Figs. 10b, d), and Na, Fe and Mn are related (Fig. 10f). The results clearly indicate a complex, multi-component fluid with several distinct sub-groupings of the data (*i.e.,* Na–Mn–Fe fluid *versus* Na–K fluid).

Comparison of decrepitate and thermometric data

The analyses of the mounds confirm that the low T_{fm} values indicate the presence of significant Fe and Mn, rare Ca, and minor Mg in the fluid inclusions. In addition, the analyses suggest several distinct compositions of fluid that could not be discerned solely on the basis of thermometric results. The presence of a low-salinity fluid is also manifest by areas of evacuated inclusions lacking mounds.

DISCUSSION

There are several rather diverse aspects of this study that are worthy of discussion. These are addressed separately below. The protocol and validity of the technique, the applications to fluid-inclusion studies in general, and the implications for fluid:rock interaction in granitic environments specifically are discussed in turn.

Validity of technique and application to fluid-inclusion studies

The decrepitate technique that was pioneered by previous investigators has not been adopted as a routine procedure in fluid-inclusion studies despite the relative simplicity of the technique and the wealth of informa-
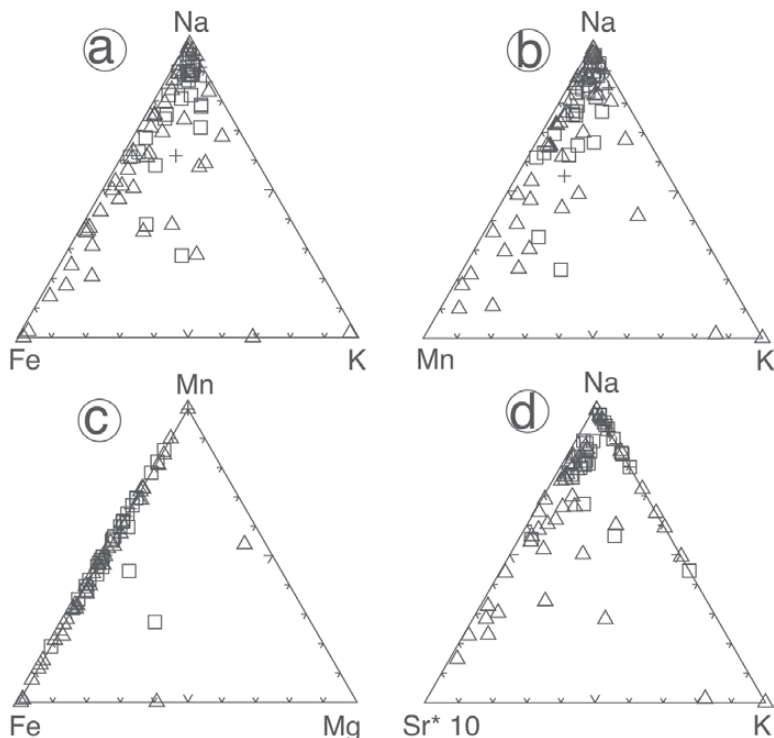
FIG. 8. Plots showing compositions of decrepitate mounds for quartz from altered granite, pegmatite and sulfide vein,East Kemptville, Nova Scotia. (a) Fe–Na–K plot, (b) Mn–Na–K plot, (c) Fe–Mn–Mg plot, and (d) Sr*10–Na–K plot. Symbols as in Figure 7.

tion that it can provide. There is no question that the method is not without analytical challenges, as discussed and addressed in some detail by Haynes *et al.* (1988) and briefly raised more recently Roedder & Bodnar (1997). Whereas most of the analytical details and protocol were the focus of Haynes *et al.*, the concern of Roedder & Bodnar is that there must be some fractionation of components between the nebulizate and evaporate during the decrepitation procedure. Although this aspect remains an unknown, it is the ratios of the solutes that are examined rather than absolute concentrations. The focus on ratios should minimize the importance of this factor.

More generally, it is noted that in recent reviews of fluid-inclusion procedures and applications, evaporate mounds are given little or no attention compared to a wide variety of other techniques (*e.g.,* Boiron & Dubessy 1994). Whereas more quantitative information may be obtained with other analytical techniques [*e.g.,* Anderson (2003) for review], it is emphasized that the decrepitate method has merit and can be applied to fluid inclusions in a variety of settings, as has been amply demonstrated by many investigators (*e.g.,* Haynes &

Kesler 1987, Halter *et al.* 1998, Savard & Chi 1998, Kontak *et al.* 2001). In addition, the foregoing presentation of data from a variety of granite-related settings has shown how this work can be integrated and, in fact, complements standard thermometric work. Thus, what is emphasized here is the relative ease of the technique and the wealth of information that is accessible in a relatively rapid and cost-effective manner.

The studies reported herein are specifically related to granitic environments. As noted in the introduction, however, this technique can easily be applied to a wide range of settings and, based on the writer's experience, a variety of minerals including silicates, sulfides, carbonates and oxides. Although the use of ICP atomic emission spectroscopy has been used to decrepitate mounds, the author is unaware of an application of the more common laser-ablation ICP–MS technique (Sylvester 2001), even though this method is used for *in situ* analysis of fluid inclusions (Audétat *et al.* 1998, Anderson 2003). Application of the laser-ablation ICP–MS technique should be feasible and would provide a more complete list of elements with, of course, information on abundances of the minor and trace elements.

Implications for fluid : rock interaction and mineral potential in granitic environments

The results from the three studies discussed above have some fundamental similarities that may, therefore, have implications for fluid : rock interaction in granitic environments. The first observation is that in all cases, there is a tendency for fluids to concentrate on the K–Na limb of the Ca–Na–K diagram, with one sole exception (PCG–99–21 in Fig. 5b). This enrichment of K may be linked to experimental studies, which have demonstrated that as temperature declines, the K/Na ratio of the fluid also declines in cases involving fluid – alkali feldspar interaction (Orville 1963, Lagache & Weisbrod 1977). Thus, for the case studies herein, the

decrepitate data may record the early formation of relatively K-rich fluids and gradual change over time to a more Na-rich fluid as temperature decreases. Relevant to this, therefore, is the fact that sample PCG–99–21a from Peggys Cove, a coarse quartz – K-feldspar – tourmaline – muscovite pocket of an aplite–pegmatite sheet, represents a late-stage product in terms of paragenetic evolution. As such, a fluid generated in this system would be expected to have a low K/Na ratio, which it does (Fig. 5b). In a similar manner, the paragenetically late-stage quartz vein at East Kemptville is deficient in K relative to the higher-temperature, earlier-crystallized pegmatite and altered granite (Fig. 7). Given the secondary nature of all the fluid inclusions in the quartz megacrysts at San Rafael, it is more difficult to interpret the data.

The second observation noted is that there is a distinct association of Fe and Mg with Na enrichment and a distinct lack of such a correlation with K for the decrepitates from East Kemptville and San Rafael. Assuming that the enrichment of the fluid records an evolution of the magmatic system with time, then the Fe and Mn enrichment is related to the same process and explains why there is a decoupling of K from these elements.

A third observation is that Ca appears to be coupled with Na, but, like Fe and Mn, decoupled from K. The best example of this is found in the Peggys Cove samples, where a distinct Ca-rich fluid is recognized from thermometric measurements (*i.e.,* fluid III in Fig. 4b). In this case, an exotic, non-magmatic source within the country rock has been suggested for the Ca (Kontak *et al.* 2002), which is consistent with the inferred late-stage paragenesis of this fluid. The general lack of Ca enrichment for the other two areas, East Kemptville and San Rafael, is consistent with other data suggesting that these systems were not infiltrated by an extraneous fluid that had equilibrated with the surrounding metasedimentary country-rock.

A final observation is that of the three systems examined, two are mineralized and one is barren. Although this is not a sufficiently large enough database from which to draw conclusions, the fact remains that the fluid compositions from the two mineralized systems are highly enriched in Fe and Mn. Detailed studies of fluid inclusions from Sn- and Cu–Au mineralized systems (*e.g.,* Heinrich *et al.* 1992, 1999, Rankin *et al.* 1992, Audétat *et al.* 1998) have shown that these metals, among many others, are enriched along with Na and K. Thus, at first hand it appears that perhaps the decrepitate method offers a rapid, easy method to quickly assess samples for their affinity to mineralization and also for subsequent work using laser-ablation ICP–MS and PIXE analyses employed in the aforementioned studies.

CONCLUSIONS

The analysis of evaporate mounds is a relatively easy and rapid method for the acquisition of compositional
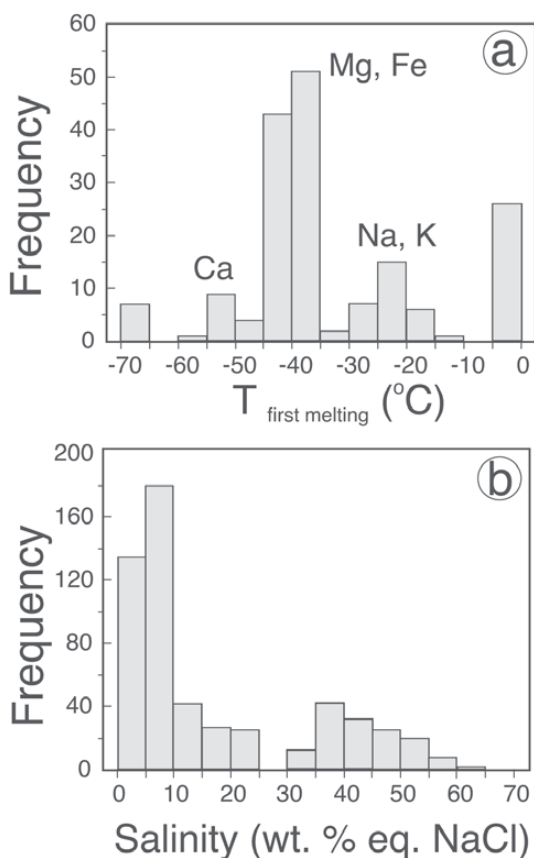

FIG. 9. Histogram plots of thermometric data for fluid inclusions hosted in quartz megacrysts, San Rafael granite, southeastern Peru (from Kontak & Clark 2002). (a) Temperatures of first melting. The chloride complexes (*e.g.,* $CaCl_2$, Oakes *et al.* 1990) most likely to be responsible for the eutectic temperatures are indicated (see text for discussion). (b) Salinity, expressed as wt. % equiv. NaCl, for fluid inclusions.
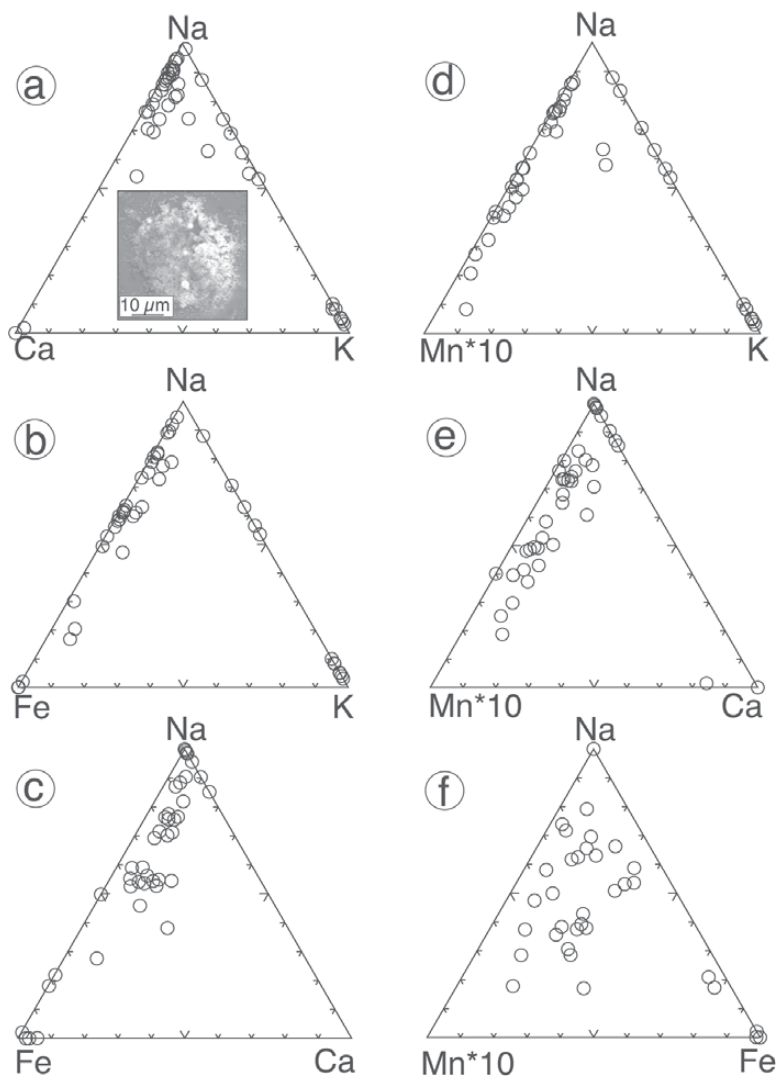
FIG. 10. Plots showing compositions of decrepitate mounds from quartz megacrysts in San Rafael granite, southeastern Peru. (a) Ca–Na–K plot with inset back-scattered electron image of mound enriched in Na–K–Fe–Mn. (b) Fe–Na–K plot. (c) Fe–Na–Ca plot. (d) Mn*10–Na–K plot. (e) Mn*10–Na–Ca plot. (f) Mn*10–Na–Fe plot.

information from fluid inclusions. Although the method was first employed nearly thirty years ago (Eadington 1974) and Haynes *et al.* (1988) provided a critical assessment of the technique, this relatively easy method of acquiring semiquantitative compositional data on fluid inclusions has not become widely applied. The application of the technique to three granitic environments has shown the following: (1) mound composition is consistent with and complements compositional information inferred from routine thermometric mea-

surements. (2) Compositional information not obtained from thermometry is easily obtained (*e.g.,* Mn, Fe contents). In some cases, the presence of minor elements (*i.e.,* Sr, Ba, P at East Kemptville) is also indicated. (3) Cationic proportions (*e.g.,* Ca–Na–K) of the important major and minor elements within most inclusions provide important information regarding fluid : rock interaction and fluid evolution within the granitic environment. (4) Specifically within granitic environments, the method may provide a valuable means of distin-

guishing between potentially mineralized *versus* barren environments.

The integration of information from decrepitate analysis with standard thermometric studies provides a rapid and effective means of elucidating the cation proportions in fluid inclusions, which has important implications in terms of the fluid reservoirs and fluid : rock interaction. Such work should become a standard part of fluid-inclusion studies.

ACKNOWLEDGEMENTS

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