

# Preliminary Fluid Inclusion and Oxygen Isotope Studies of the Flintstone Rock (NTS 21A/04) Silica-clay Deposit, Yarmouth County, Nova Scotia

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## Introduction and Previous Work

Drilling by Shell Canada Resources Ltd. in 1980 and 1982, part of a regional exploration program for tin and base metals in southwestern Nova Scotia, delineated several brittle-ductile deformation zones with associated intense silicification and kaolinite mineralization. One of these areas, Flintstone Rock, is now the site of Black Bull Resources' silica-clay deposit (Fig. 1). Smith (1985) noted that a 10 km long by ca. 1.5 km wide zone of intense deformation containing silica and kaolinite occurred along the southern contact of the South Mountain Batholith (SMB), both within granite and metasedimentary rock. Smith (1985) referred to this as the Rushmere Lake Shear Zone. Subsequently, Giles (1985) included the area in his Tobeatic Shear Zone, a structure proposed to accommodate some existing geological features in the SMB and Carboniferous basins in central mainland Nova Scotia. Ham and MacDonald (1994) showed the location of diamond-drill holes containing quartz-kaolinite and the strike extent of the shear zone in their regional map of the Wentworth Lake area. O'Reilly (personal communication, 1990) and O'Reilly *et al.* (1992) included the area in regional compilations of southwestern Nova Scotia, with an emphasis on the structural and metallogenetic significance of the zone. Finally, Corey and Graves (1996) compiled and described the presence of extensive breccia-hosted Pb-Zn-Ba-Au-Ag occurrences in the eastern extension of this silica-rich shear zone along Little Tobeatic Lake. In addition, these authors suggested an epithermal-type base- and precious-metal model for the shear zone environment.

Over the past two years Black Bull Resources has delineated a zone of 10 km length and 200 m width with a minimum of 100-150 m depth consisting of high-grade quartz-kaolinite. Initial sampling and testing of material has proven to be very promising and presently there are several tens of millions of tons of mineable product

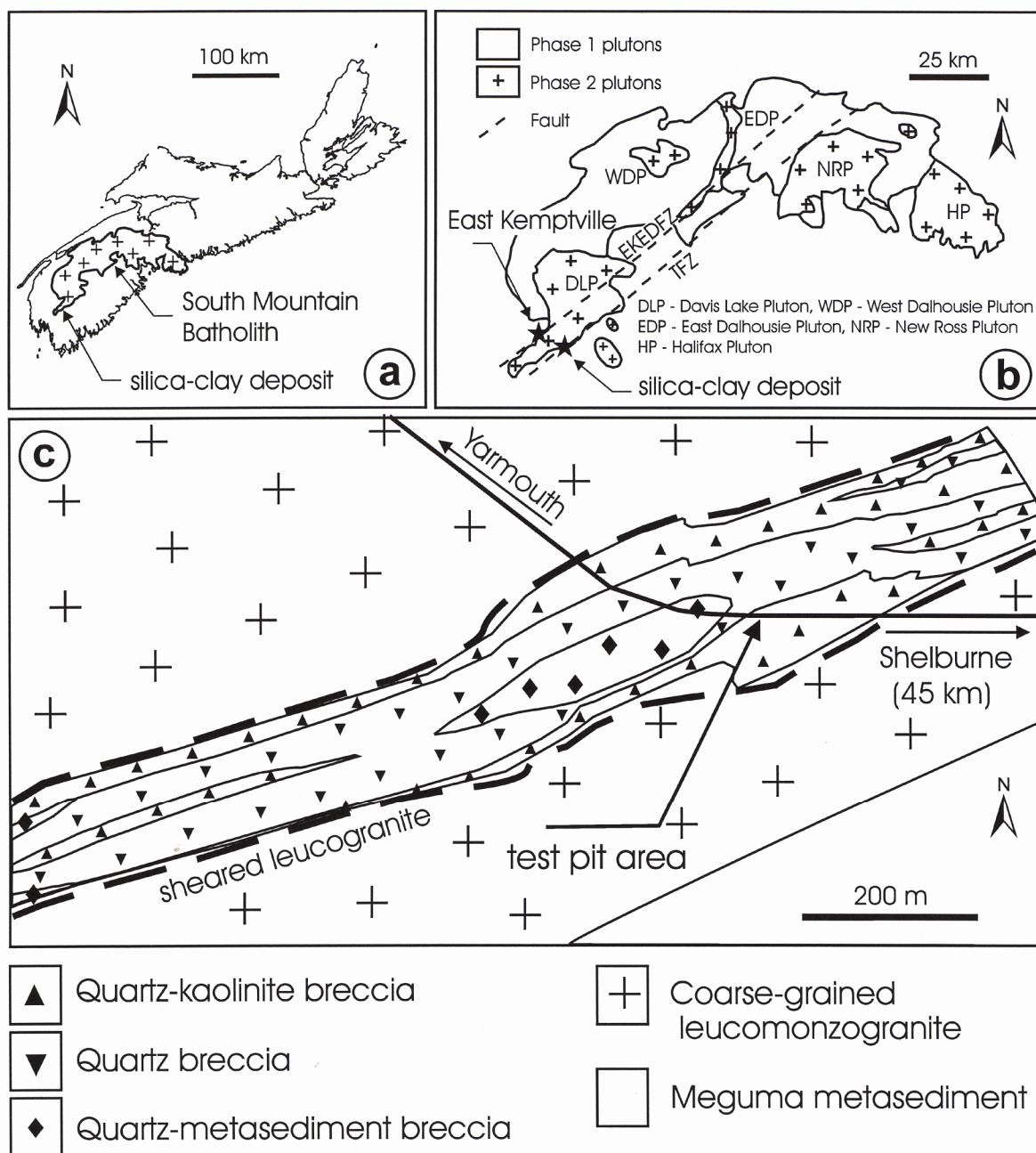
delineated (Black Bull Resources update, November 2000). Considering the presence of additional favourable zones along strike from Little Tobeatic Lake to the Rushmere-Moose Fly Lake area in the Tobeatic Fault Zone (Fig. 1), this environment must be considered to have great potential.

The presence of this quartz-kaolinite zone within a fault structure of considerable strike length has important metallogenetic implications for this part of southern Nova Scotia. The recent (1985-1992) production of Sn-Zn-Cu-Ag concentrate from greisen at the East Kemptville deposit, ca. 10 km from the Black Bull site (Fig. 1), established this area as an important granophile domain within the Appalachian region. Analogies to Sn-base metal and kaolinite mineralization in the Hercynian granites of western Europe (i.e. Cornwall, Brittany) are obvious and further indicate the highly favourable potential for more deposits in the area. Consequently, geological studies were undertaken to elucidate the genesis of the quartz-kaolinite and incorporate these results into the existing database for the southwestern Nova Scotia Sn-base metal domain (O'Reilly *et al.*, 1992). This paper reports the results of fluid inclusion and stable isotope studies conducted on materials collected from this site over the past year. Additional work is in progress and, thus, the data presented should be considered preliminary. The aim of the present work is to determine the nature and origin of the mineralizing fluids and interpret these data in the context of a genetic model with implications for the extent of mineralization within the immediate and surrounding area.

## Geological Setting

The study area occurs near the contact between granitic rocks of the Davis Lake Pluton (DLP) and metasedimentary rocks of the lower Paleozoic Meguma Group. The DLP, part of the large 370 Ma South Mountain Batholith, is one of several stage 2 intrusions emplaced following intrusion of the earlier granodiorite-

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**Figure 1.** Regional and local setting of the Black Bull silica-clay deposit, Yarmouth County, Nova Scotia. (a) Regional setting of the deposit area in southwestern Nova Scotia near the southern contact of the 370 Ma South Mountain Batholith (outlined with cross pattern). (b) Geology of the South Mountain Batholith with phase 2 plutons indicated. The silica-clay deposit is located at the southern contact of the Davis Lake Pluton. (c) Geology of the silica-clay deposit (after Black Bull Resources maps). Samples used in the present study come from the test pit area indicated on the map.

monzogranite phases of the batholith. Horne *et al.* (1992) have shown that granite emplacement was controlled by prominent northeast-southwest and northwest-southeast structures; hence, the regionally extensive Tobeatic Fault Zone (Fig. 1b) is considered an earlier structure (i.e. pre- or syn-granite intrusion) and important initially at defining the southern contact of the

DLP. In light of the present study it is relevant to note, therefore, that the East Kemptville deposit occurs within another prominent, regionally extensive northeast-trending fault zone (Fig. 1b) that was active at the time of emplacement of the host leucogranite and related greisen-style mineralization (Kontak, 1994; Kontak and Cormier, 1991; Halter *et al.*, 1996).

The Davis Lake Pluton is a zoned intrusion, with relatively primitive phases in the northeast and more evolved phases in the southwest (MacDonald *et al.*, 1992; Dostal and Chatterjee, 1995). The dominant rock type is light-grey to blue-white, coarse-grained, K-feldspar megacrystic leucomonzogranite. Toward the southern contact with quartzite of the Meguma Group, the pluton becomes intensely deformed, with early ductile fabrics overprinted by later brittle features. Within and proximal to this northeast-trending zone of deformation quartz-kaolinite and base metals occur, as noted on the most recent map of the area (Ham and MacDonald, 1994), and also summarized in Smith (1985) and Corey and Graves (1996), in addition to many exploration assessment reports.

The mineral deposit at Flintstone Rock occurs as a  $\leq 200$  m wide, northeast-trending fault zone in a strongly deformed part of the Davis Lake Pluton (Fig. 1c). Against the fault zone, coarse-grained leucomonzogranite of the DLP is reduced to ribbon-textured mylonite with C-S fabrics. Similar textures occur in rocks to the southwest (Smith, 1985) and northeast (Corey and Graves, 1996) of this locality. Within the mineralized structure, variably deformed fragments of granite are intensely silicified and/or replaced with bright white kaolinite (Fig. 2a, f). There is a progression from early, very fine-grained, beige to cloudy white silica to later, coarse-grained quartz euhedra (Fig. 2b,d). Quartz veins are common and, again, the early veins are fine-grained and the later ones consist of coarser quartz. Comb textures with vuggy interstitial space suggest that in some cases earlier kaolinite, or some other unknown phase, has been leached (Fig. 2c). Some samples show evidence of periods of brecciation, silicification and cementation. The central silica-rich breccia zone contains the most abundant and coarsest quartz with multi-centimetre size grains present (Fig. 2e). In the latter case, kaolinite may be present as a late stage phase between the coarse quartz euhedra. The mineralized zone consists essentially of quartz and kaolinite in addition to residual muscovite grains and remnant clasts of variably altered granite and metasedimentary rocks; no evidence of sulphides or other minerals (e.g. carbonate, barite) has yet been noted.

## Fluid Inclusion Studies

Doubly polished sections (150  $\mu\text{m}$  thick) of quartz-kaolinite material were prepared from eight samples for preliminary fluid inclusion study. Samples varied from very fine-grained quartz (i.e. grain size  $\leq 100\text{-}200$   $\mu\text{m}$ ) to aggregates of coarse euhedral grains. Although the former were inundated with fluid inclusions, in fact so many that they make the samples cloudy, the inclusions

were too small ( $\leq 1\text{-}3$   $\mu\text{m}$ ) for thermometric study. However, the coarser quartz grains contain abundant fluid inclusions suitable for thermometric study.

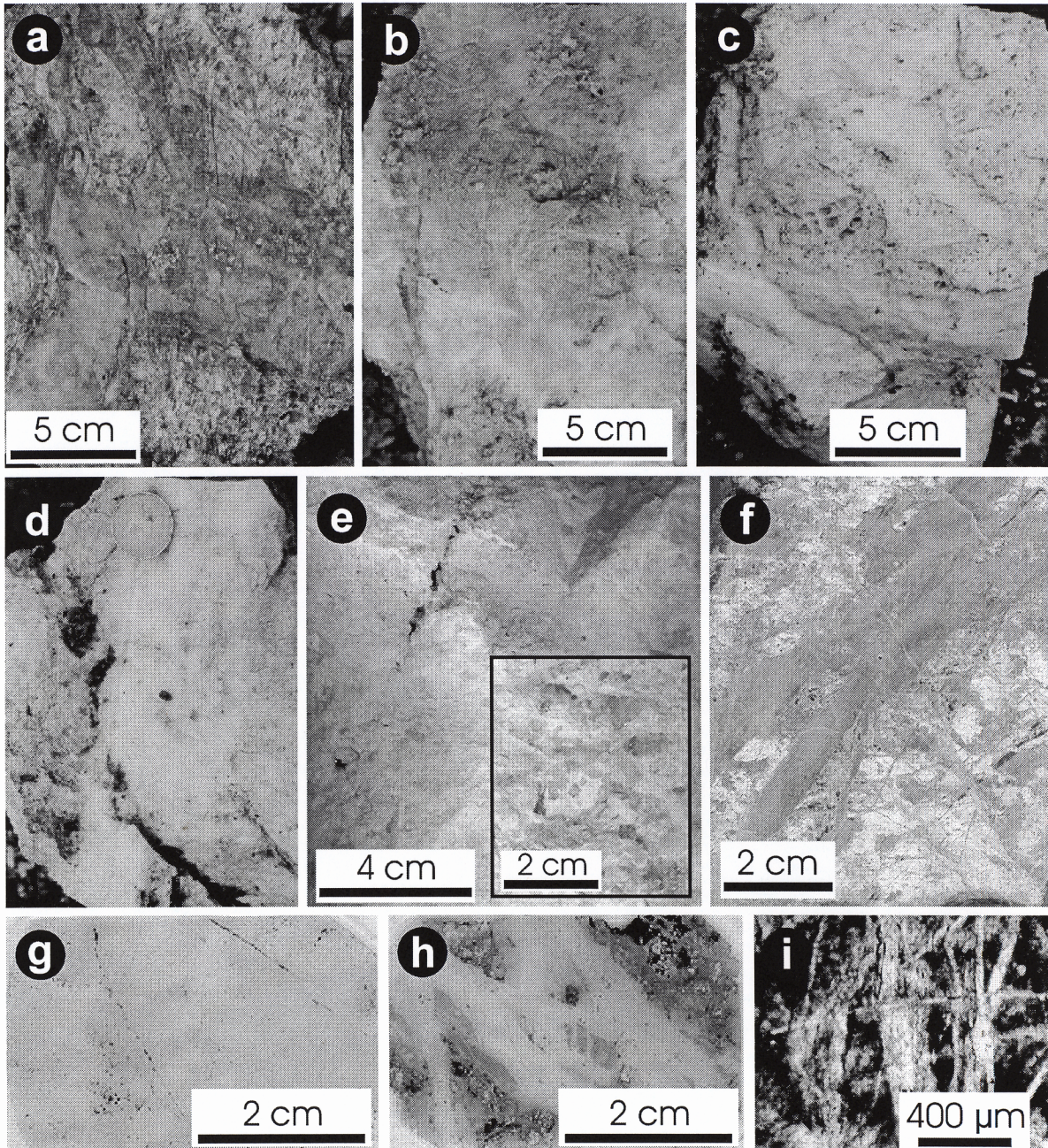
## Fluid Inclusion Petrography

Petrographic examination of quartz euhedra indicates the following types of inclusions: (1) L-V, (2) L-V-solids, (3) monophasic L- and V-rich (Fig. 3). Type 1 inclusions occur as isolated inclusions within quartz, along primary growth zones and healing fracture planes. They are highly variable in terms of size ( $\leq 10\text{-}30$   $\mu\text{m}$ ) and their shapes range from equant to irregular. Variable L:V ratios combined with the irregular shapes suggest necking was common, but areas dominated by equant- or regular-shaped inclusions occur rarely. Type 2 inclusions are rare and the solid phase, probably mica and feldspar (?), is considered to represent accidentally trapped inclusions of desegregated granite; no daughter phases (e.g. halite) were observed. Type 3 inclusions are similar to type 1 in terms of size and shape and are the most abundant inclusion type. A large proportion of these inclusions have clearly resulted from necking processes, but it is possible that some actually represent entrapment of L- and V-rich fluids. Further work is required to resolve the origin of these inclusions.

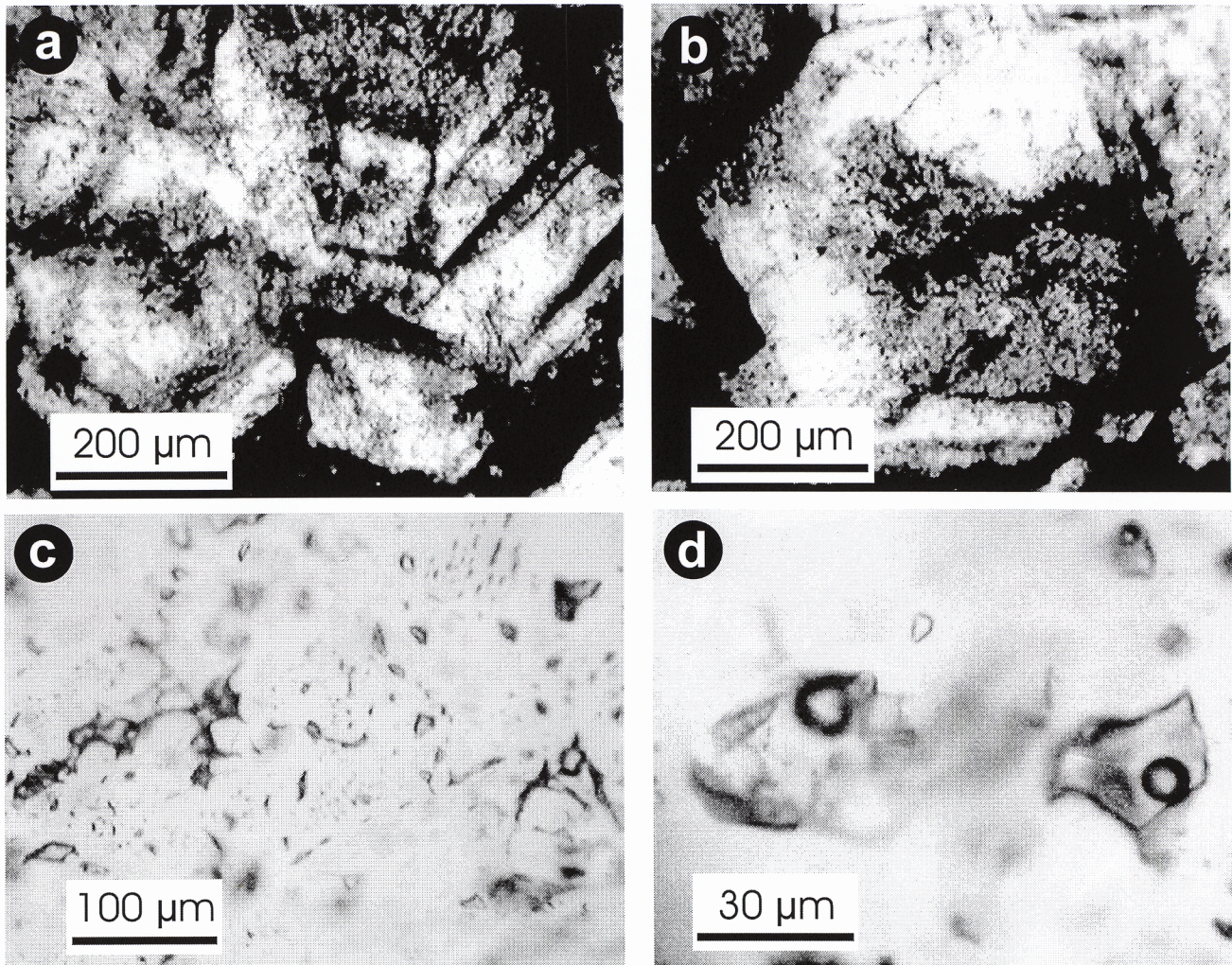
## Fluid Inclusion Thermometry

Thermometric measurements were made on two samples of quartz containing type 1 inclusions. Measurements were made with a United States Geological Survey gas flow heating-freezing stage (FLUID INC.) at the Nova Scotia Department of Natural Resources [see Kontak (1998) for details]. The equipment was initially calibrated and is routinely checked with synthetic fluid inclusions. Accuracy for the equipment is estimated at  $\pm 0.2^\circ\text{C}$  for low temperature runs and  $\pm 1.0^\circ\text{C}$  for high temperature runs, whereas precision determined from replicate runs is  $\pm 0.2^\circ\text{C}$  or better.

Inclusions were frozen to  $-100^\circ$  to  $-120^\circ\text{C}$  and heated at a controlled rate while observing the inclusions. During freezing, most inclusions suddenly froze, as recorded by a sudden shrinkage of the vapour bubble, at ca.  $-35^\circ\text{C}$ , but for some, cooling to  $-80^\circ\text{C}$  was required. During warming, most inclusions had apparent first melting of  $-15^\circ$  to  $-4^\circ\text{C}$ , but rarely some were near the  $\text{H}_2\text{O}\text{-NaCl}$  eutectic of  $-21^\circ\text{C}$  and others at  $-1^\circ\text{C}$ . The last melting of ice occurred between  $-0.5^\circ$  and  $+0.2^\circ\text{C}$ . In some inclusions where the vapour phase did not reappear during heating, ice melting temperatures above  $0.0^\circ\text{C}$  relate to metastability.



**Figure 2.** Rock and thin section photos of silica-clay material from Yarmouth deposit area. Note that the term granite in the following descriptions is only generalized and not *sensu stricto*. (a) Fragment of outcrop showing angular pieces of kaolinized granite (white areas) cut by multitude of quartz veins of various orientations and dimensions, but with the latest veins apparently the largest. (b) Remnant pieces of kaolinized and silicified granite (top of photo) but by paragenetically, later cloudy white, fine-grained quartz veins. (c) Remnant, ghost-like pieces of kaolinized and silicified granite with box work texture cut by later, cloudy white quartz veins. (d) Intensely silicified, fine-grained granite cut by later cloudy white quartz veins. Note loonie for scale. (e) A sample of white, fine-grained kaolinite-silica rock (i.e. altered granite) with coarser quartz euhedra throughout (see inset box for enlargement). (f) Multitude of quartz veins cutting kaolinized granite (white areas). Note the fine-grained nature of the quartz veins. (g) Thin section of silicified granite illustrating the very fine-grained nature of the rock and presence of fine veinlets cutting sample, as represented by hairline fractures. (h) Thin section of sample in Figure 2f illustrating the very fine-grained nature of vein quartz. Dark areas are silicified granite fragments with minor kaolinite. (i) Thin section of silicified granite showing the abundance of late quartz veins and the fine-grained nature of the quartz. Dark areas are quartz inundated with fluid inclusions.



**Figure 3.** Photomicrographs of quartz-rich material from silica-clay deposit in plane polarized light showing nature and distribution of fluid inclusions. (a, b) Euhedral quartz grains with zonally arranged fluid inclusions outlining growth zones and core areas. The quartz is dark because of the abundance of fluid inclusions. (c) Plane of necked fluid inclusions in quartz with highly variable L:V ratios. Note that the vapor-rich nature of the inclusions is not primary and relates to necking down. (d) Large, aqueous fluid inclusions with similar L:V ratios. Note the accidentally trapped solid phase (S) in the left inclusion.

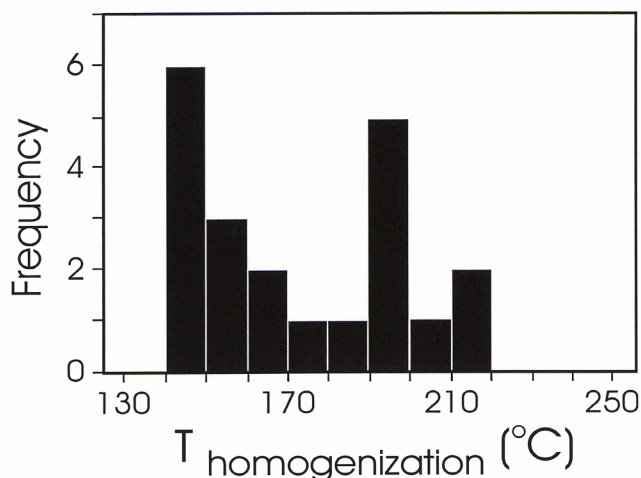
Homogenization temperatures (Fig. 4) of type 1 inclusions vary from 141° to 218°C; however, for a given fluid inclusion population a range of  $\leq 5^\circ\text{C}$  occurs. The large range indicates that fluids of different temperatures were trapped over time or, conversely, fluids were trapped at both varying pressures and uniform pressures.

### **Decrepitate Analysis**

A sample of quartz used for thermometric study was heated to 450 - 600°C to induce thermal decrepitation of fluid inclusions. This heating results in formation of precipitate mounds which may then be analyzed semi-

quantitatively via the electron microprobe (Haynes *et al.*, 1988). In addition, the evacuated inclusions may be examined for solid inclusions with use of the imaging facilities on the electron microprobe.

Examination of evacuated inclusions revealed the following features. (1) An abundance of empty or evacuated cavities were found without any precipitates in the surrounding areas (Fig. 5a). Whereas some of these cavities may represent inclusions that were opened during sample preparation (i.e. sawing and grinding), the abundance of such areas in the sample is unusual and suggests the former presence of very low-salinity fluids. (2) The occurrence of barite and kaolinite (Fig. 5b, c, d) was confirmed by microprobe analysis within evacuated



**Figure 4.** Histogram of homogenization temperatures for aqueous fluid inclusions where similar L:V ratios occur for individual groups or populations of inclusions. Note that the range of temperatures within a population of inclusions is  $\leq 5$ - $10^\circ\text{C}$ .

inclusions, with barite being common. In addition, it was noted that in several cases salt precipitates occurred near the inclusions containing barite (Fig. 5d, e).

The general paucity of precipitate mounds in the quartz sample studied is unusual, certainly compared to what is generally observed in our examination of hypogene quartz from veins and pegmatites that contain inclusions of moderate salinity (e.g. 10-20 wt. % eq. NaCl). In the present cases, two types of mounds were noted: those of equant shape and those of stellate shape (Fig. 5e and f, respectively). Analysis of these mounds, summarized in Figure 6, indicates that they are dominantly of  $\text{NaCl} \pm \text{K}$  and  $\text{KCl} \pm \text{Na}$  composition, respectively, with minor amounts of Ba consistently detected (Fig. 6). The Ba-rich analysis in Figure 6 corresponds to barite present within the inclusions. The only other cation noted was Ca, present in very minor amounts.

## Stable Isotopes

Three samples of quartz and two of kaolinite were analyzed for  $\delta^{18}\text{O}$  at the isotope laboratory, Department of Geological Sciences, Queen's University. Details of the analytical procedures are found in Kyser *et al.* (1998). The quartz samples are fine-grained, euhedral quartz infilling open space in silica-rich breccia and the kaolinite is a very fine-grained, white powdery material interstitial to silica-rich breccia. The measured  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values (in ‰) are shown in Table 1 along with the calculated  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta\text{D}_{\text{H}_2\text{O}}$  values for  $250^\circ$  and  $300^\circ\text{C}$ ,

using the appropriate fractionation equations [Zheng (1993) and Sheppard and Gilg (1996), respectively].

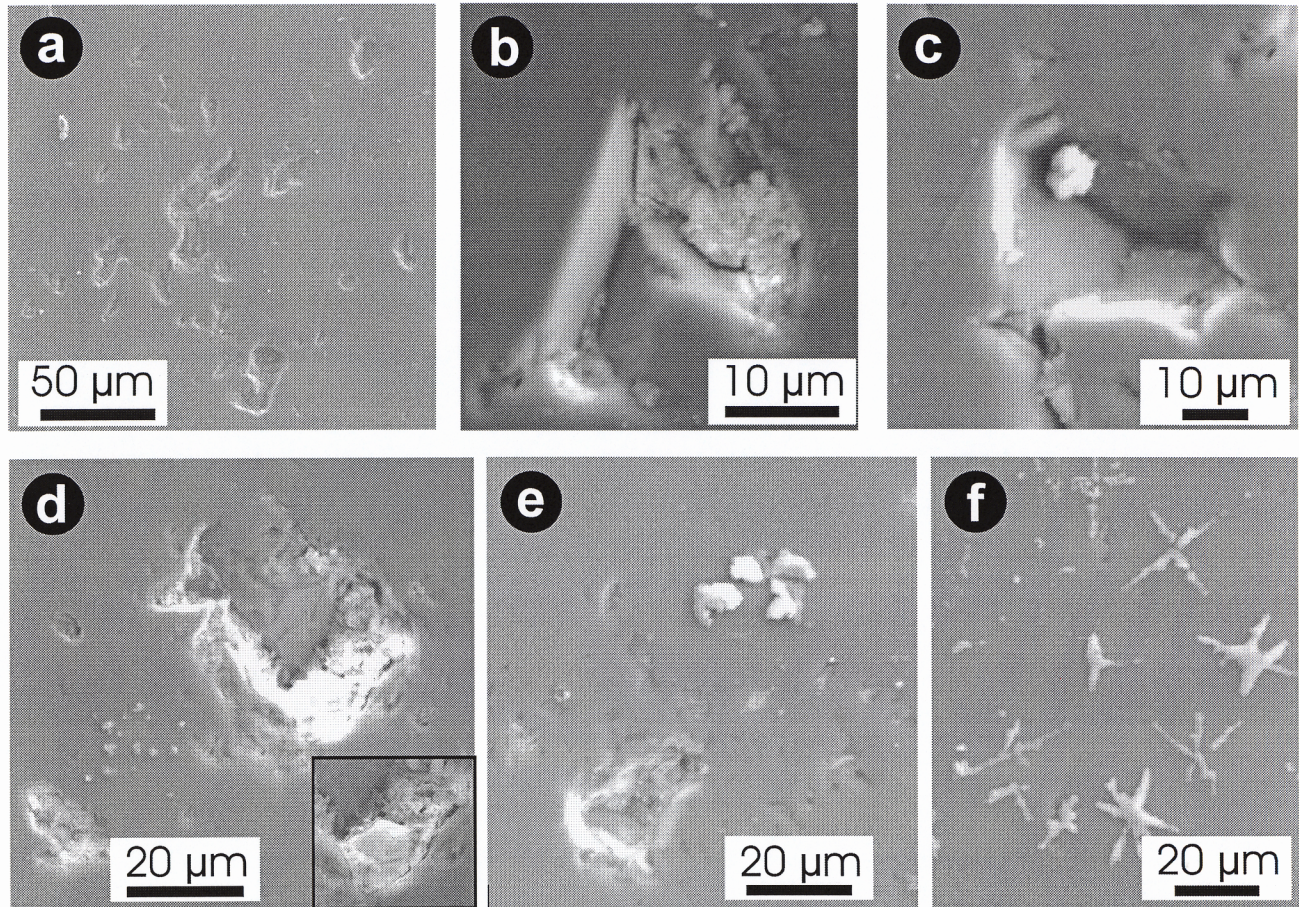
Measured  $\delta^{18}\text{O}$  values for quartz cover a large range for a mineral of apparently a single paragenesis, but the limited mineralogy does impede recognition of what might be a more complicated evolution. In Figure 7 the quartz data are compared to results for vein and pegmatitic quartz from a variety of occurrences in the South Mountain and Musquodoboit batholiths. The quartz samples in this study, albeit limited, appear to cover most of the range for the data set in Figure 7. It should be noted that for the Dunbrack vein Pb-Zn-Cu-Ag occurrence, the high  $\delta^{18}\text{O}$  values compared to the rest of the data set relate to the lower temperature of quartz deposition compared to the other occurrences, combined with the fact that at lower temperatures  $^{18}\text{O}$  is preferentially concentrated in quartz over water.

The two kaolinite  $\delta^{18}\text{O}$  levels are essentially similar at +14‰ and compare to  $\delta^{18}\text{O}$  levels of +13.8 and +17.1‰ for late-stage kaolinite at the East Kemptville Sn-base metal deposit (Kontak, 1994) and Dunbrack occurrence (Kontak *et al.*, 1999), respectively. The  $\delta\text{D}$  levels for the two kaolinite samples are also similar at -61 and -60‰, which compare to a level of -103‰ for kaolinite from Dunbrack, the only other kaolinite sample for which such data are available.

The levels of  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta\text{D}_{\text{H}_2\text{O}}$  in equilibrium with the quartz and kaolinite have been calculated for  $250^\circ$  and  $300^\circ\text{C}$  (Table 1), the former being constrained by fluid inclusion data and the latter being the temperature at which kaolinite converts to pyrophyllite. The quartz data indicate  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  levels of +0.9 to +7.6‰ and contrast with the +10.7 to +12.8‰ obtained for kaolinite. These levels in part overlap the range of  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values typical of magmatic water derived from metaluminous to peraluminous granites (Sheppard, 1986), but levels below ca. 5‰ indicate another fluid reservoir. The  $\delta\text{D}_{\text{H}_2\text{O}}$  levels of -45‰ are in the range for magmatic waters (Sheppard, 1986). It is important to note here that the presence of kaolinite in evacuated inclusions within quartz (Fig. 5c) indicates that at least some kaolinite formed at similar temperatures as quartz and is, therefore, also constrained by the fluid inclusion homogenization temperatures. However, it is possible that some kaolinite also formed at lower temperatures.

## Discussion

The results of fluid inclusion and stable isotope measurements permit some constraints to be made on the nature of the fluids responsible for mineralization at Flintstone Rock. In addition, the data are discussed in



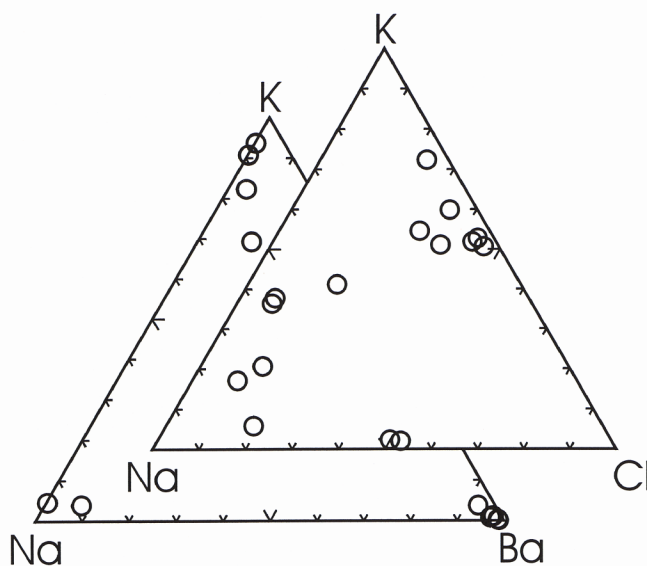
**Figure 5.** Combined back scattered and secondary electron images of thermally decrepitated sample of quartz showing the presence of evacuated inclusions and salt precipitates or mounds formed from decrepitation of fluid inclusions. (a) Multiple opened inclusions typical of many areas of quartz. Note the absence of any precipitate mounds in the area of the opened inclusions. (b) Opened inclusion with barite coating the bottom of the cavity. (c) Opened inclusion with small kaolinite grain resting in bottom of the negative-shaped cavity. (d) Opened inclusions with NaCl mounds present between the two larger cavities. The largest cavity has a euhedral barite crystal growing on its bottom wall (see inset). (e) Equant-shaped mounds of NaCl composition near an evacuated inclusion which contains small grains of barite coating the walls of the inclusion. (f) Area of quartz with abundant stellate-shaped mounds of KCl composition.

light of other mineral occurrences in the surrounding area, such as at Little Tobeatic Lake and East Kemptonville, in order to make some comments on the implications of the results to the regional metallogenetic evolution.

### **Nature of Mineralizing Fluids**

Fluid inclusion studies indicate that infiltration of a dilute (ca. 0 wt. % eq. NaCl) fluid with Na, K and Ba in solution was responsible for the mineralization. These solutes, albeit in low concentrations, are nevertheless consistent with the apparently widespread and pervasive dissolution of the feldspar component of the Davis Lake Pluton which would have liberated Na, K and Ba. However, the low salinity of the fluid is contrary to the nature of magmatic fluids (Roedder,

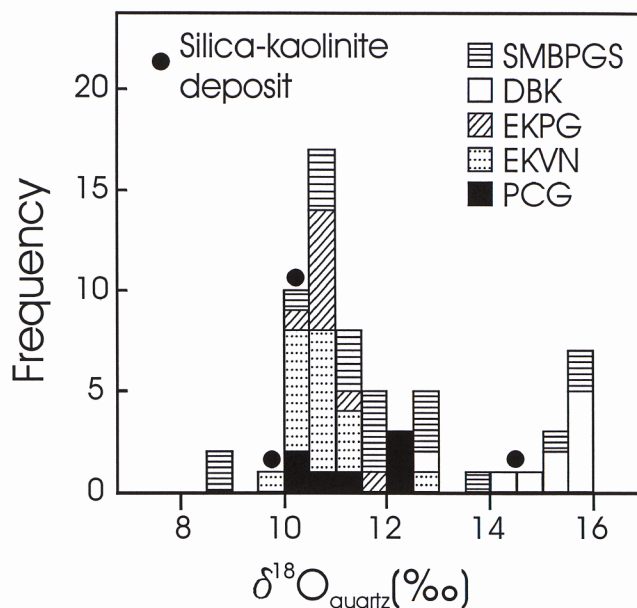
1984) and given the absence of any petrographic evidence of fluid unmixing or boiling, implicates another fluid type as being involved in the mineralization. The most likely source of a dilute fluid is surficial water, also known as meteoric water, which is commonly reported in high-level or epithermal environments (e.g. Bodnar *et al.*, 1985). If the fluid inclusion data for mineralization at Little Tobeatic Lake (Corey and Graves, 1996) are combined with the present data set, then a continuum is seen from high temperature fluids of 400°C and ca. 20-25 wt. % eq. NaCl to ca. 200°C and 0 wt. % eq. NaCl, as summarized in Figure 8. Also shown in the Figure 8 is the fluid responsible for greisen mineralization at the nearby East Kemptonville tin deposit, which is similar to the saline component of the fluid in the Tobeatic Fault Zone. The presence of barite, adularia and Zn-Fe-Pb-Cu sulphides in the veins at Little Tobeatic Lake is



**Figure 6.** Ternary plot of Na-K-Ca for decrepitate mounds analyzed on the electron microprobe.

consistent with a magmatic component in the fluid and, thus, explains the higher temperatures and salinities for vein material. The presence of barite in the fluid inclusions at Flintstone Rock also provides a geochemical link between the two areas in terms of their genesis.

Stable isotope data, although restricted to three quartz and two kaolinite samples, permit some important constraints. First, as noted above, the  $\delta^{18}\text{O}$  data for quartz indicate two contrasting values which translate into quite different  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values. These data can be interpreted in at least three different ways, as indicated by the models summarized in Figure 9. A two-fluid model would require fluids having  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values of ca. +7 and +3‰ to have been involved in mineralization, assuming quartz deposition at ca. 300°C. In the one-fluid model, quartz would have to be deposited at temperatures of ca. 300°C and ca. 150°C from a single fluid with a  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value of +7‰. And finally, a two-fluid mixing model would have a primary fluid with a  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value of +7‰ mixing with a fluid of much lower  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value (e.g.  $\leq 21$ ) to generate a second fluid with an intermediate  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value. The following constraints indicate that the two-fluid mixing model (#3 in Fig. 8) is the most likely. (1) Fluid inclusion data for the Flintstone Rock and Little Tobeatic areas indicate that mixing of two fluids occurred, these likely being of magmatic and meteoric origin. (2) Fluid inclusion thermometric data indicate that the quartz samples with the relatively lower  $\delta^{18}\text{O}$  values were not deposited at ca. 150°C, as required in the one-fluid model (#2 in Fig. 8), but instead at much higher temperatures. (3) Quartz with the  $\delta^{18}\text{O}$  level of +14‰ has a  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$



**Figure 7.** Summary of  $\delta^{18}\text{O}_{\text{quartz}}$  levels for quartz from the silica-clay deposit compared to  $\delta^{18}\text{O}_{\text{quartz}}$  levels for a variety of 370 Ma granite-related occurrences in the Meguma Terrane: SMBPGS-pegmatitic quartz from various localities in the South Mountain Batholith (e.g. Keddy's, Moreley's, Reeves, Walker; Kontak *et al.*, 1991), DBK-quartz vein material from Dunbrack Pb-Zn-Cu-Ag occurrence (Kontak *et al.*, 1999), EKPG-pegmatitic quartz from East Kemptville (Kontak *et al.*, 2001a), EKNV-vein quartz from East Kemptville (Kontak, 1994), PCG-pegmatitic quartz from Peggys Cove (Kontak *et al.*, 2001b). Note that the reason for the relative enrichment of Dunbrack vein quartz in  $\delta^{18}\text{O}$  is that they formed at relatively lower temperatures than the other occurrences sampled, combined with the fractionation for  $\delta^{18}\text{O}$  quartz- $\text{H}_2\text{O}$  which favors enrichment of  $^{18}\text{O}$  in quartz at low temperatures.

level of +7‰ at 300°C, which is similar to the magmatic signature of  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  for the South Mountain Batholith at this temperature. Thus, quartz with a +14‰ signature equates to quartz with  $\delta^{18}\text{O}$  levels of +10‰ from veins and pegmatites in the SMB (Fig. 7) that were deposited at ca. 500°C and suggests that this is a magmatic signature. Whereas points 1 and 2 eliminate the single-fluid model, the two-fluid model is ruled out as being unlikely since it cannot explain the mixing of two fluids, one with a magmatic signature and the other with a meteoric signature, based on fluid inclusions.

The  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  levels calculated using kaolinite are +8.6 to +10.6‰ for formation at 250-300°C (Table 1). These levels are higher than  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  levels calculated using quartz and suggest isotopic disequilibrium. Another way of examining this is to calculate the  $\delta^{18}\text{O}$  levels of kaolinite in equilibrium with the waters that

**Table 1.** Isotopic data for quartz and kaolinite samples from Yarmouth silica-kaolinite deposit.

Sample	Mineral	$\delta^{18}\text{O}$ (‰)	$\delta^{18}\text{O H}_2\text{O}$ (300°C) (‰)	$\delta^{18}\text{O H}_2\text{O}$ (250°C) (‰)	$\delta\text{D}$ (‰)	$\delta\text{D H}_2\text{O}$ (300°C) (‰)	$\delta\text{D H}_2\text{O}$ (250°C) (‰)
FR-99-01	quartz	9.8	2.9	0.9			
DK-99-A	quartz	14.5	7.6	5.6			
59	quartz	10.4	3.5	1.5			
99-39-1A	kaolinite	14	10.2	8.6	-61	-46.6	-45.2
99-39-1B	kaolinite	14.4	10.6	9.0	-60	-45.6	-44.2

deposited the quartz using the appropriate fractionation factors. When this is done, using a  $\delta^{18}\text{O}_{\text{quartz}}$  level of +14.5‰, it is determined that the kaolinite  $\delta^{18}\text{O}$  levels should be ca. +10.5 to +11.3‰ for deposition at 200-300°C. These levels compare to the ca. +14‰  $\delta^{18}\text{O}$  measured for kaolinite and again suggest that the two minerals are not in isotopic equilibrium. One possible interpretation of these data is that kaolinite may have exchanged at a lower temperature with another fluid after its initial formation, resulting in an increase in its  $\delta^{18}\text{O}$  level, as would happen if exchange with low temperature surficial water occurred in a supergene environment. A similar scenario has been reported for kaolinite in Hercynian granites in Brittany, France (Boulvais *et al.*, 2000). At this locality and also in Cornwall, England (Psyrillos *et al.*, 1998), upgrading of the granite-hosted kaolinite mineralization occurred during interaction with supergene fluids, with consequent generation of distinct morphologies for the different generations of kaolinite. Detailed mineralogical investigation is planned to evaluate this possible scenario. The similar  $\delta^{18}\text{O}$  level for kaolinite at Flintstone Rock and East Kemptville suggests a similar origin for kaolin formation at the two sites.

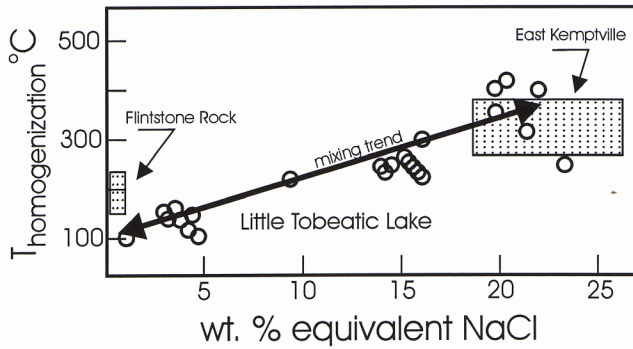
The  $\delta\text{D}$  data for the two kaolinite samples indicate  $\delta\text{D}_{\text{H}_2\text{O}}$  levels of ca. -45‰, which is within the range for magmatic fluids (Sheppard, 1986). However, the  $\delta\text{D}$  data are also consistent with a meteoric water influence, given that the moderate latitudes of Nova Scotia during the Late Devonian-Carboniferous equate to a similar range of  $\delta\text{D}$  levels.

In summary, the mineralizing fluid at Flintstone Rock appears to represent an end member of two fluids of magmatic and meteoric origin that mixed within the Tobeatic Fault Zone. Whereas the meteoric-dominant fluid gave rise to extensive silica-kaolinite mineralization, the magmatic component also contributed to deposition of base metals and precious metals in the Little Tobeatic Lake area.

### **Nature of the Mineralizing Environment at Flintstone Rock**

The nature of the mineralization at Flintstone Rock indicates that fluids penetrated a fault zone, and that internally conditions favored repeated brecciation of the vein fill. The structural fabrics of wallrock and fragments also indicate that initial ductile deformation occurred, subsequently followed by brittle conditions. The magnitude of this structure (i.e. strike length) suggests that it is part of a regional rather than localized event and, as discussed by Horne *et al.* (1992), this structure, the Tobeatic Fault Zone (Fig. 1), was active during emplacement of the South Mountain Batholith. The many similarities between the setting of the Flintstone Rock silica-clay deposit and the greisen-hosted Sn-base metal deposit at East Kemptville suggest that the two share a common origin, but with the nature of the fluids (i.e. magmatic- versus meteoric-dominant) relating to the differences in type of mineralization.

In Figure 10, a pressure-temperature plot, the salient aspects of the mineralization are shown. The field denoting the conditions of mineralization based on fluid inclusion data is shown along with extrapolation to higher P and T using the iso- $T_h$  lines. However, in order to better constrain the P-T conditions, an estimate of either temperature or pressure is required. Assuming that mineralization occurred shortly after emplacement and crystallization of the South Mountain Batholith, as suggested from geological arguments, and the fact that the only known source of magmatic fluid in the area relates to 370 Ma granitic magmatism, then the maximum pressure during formation is indicated by the contact aureole of the South Mountain Batholith at 3.2-3.5 kbar. However, fluid inclusion isochores for the fluids indicate a maximum P of ca. 1.2 to 2.7 kbar at 300°C, the upper limit of kaolinite stability. This pressure differential indicates that the confining pressure was somewhere between lithostatic and hydrostatic,



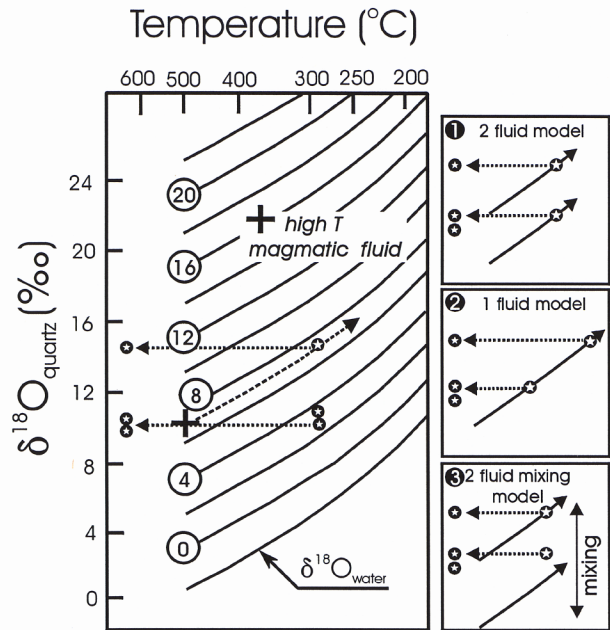
**Figure 8.** Plot of fluid inclusion homogenization temperature versus salinity for inclusions from the Flintstone Rock silica-clay deposit, mineralization at Little Tobeatic Lake (Corey and Graves, 1996), and East Kemptville (data of Kontak). Note that the salinities at East Kemptville extend to ca. 42 wt. % eq. NaCl.

which can be reconciled with the fact that large volumes of low-salinity fluid must have infiltrated the system via an open and connected network of fractures. Thus, the depth of mineralization may indeed have been ca. 10 km. Assuming this setting to be correct, the ambient temperatures, for a typical continental geotherm of 25°C/km, would have been 250°C. Given that this temperature is close to that inferred for mineralization, it indicates that descending fluids were heated by the adjacent granitic intrusion.

### Implications for Local and Regional Mineralization

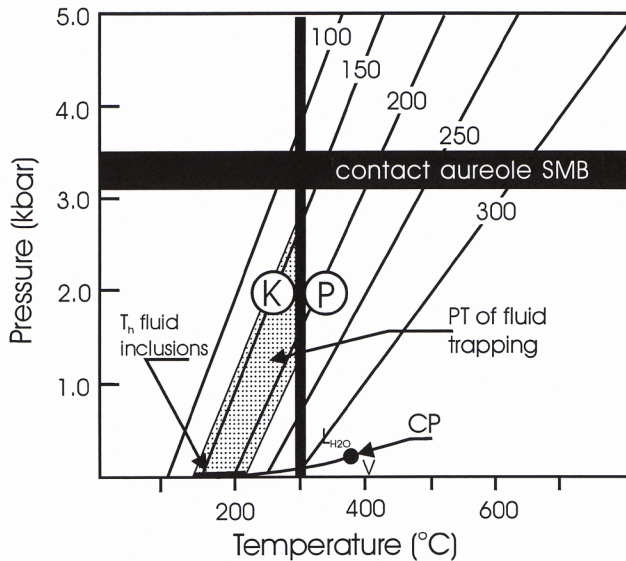
Integration of the results of the present study with the documentation of abundant silica ± clay occurrences along the strike length of the Tobeatic Fault Zone (e.g. Rushmere Lake, Little Tobeatic Lake, geophysical work of Black Bull) indicates high potential for lateral continuation of the Flintstone Rock deposit to the northeast and southwest. However, the potential for kaolinite would be confined to that part of the structure that lies within the Davis Lake Pluton, since the kaolinite originates from alteration of primary feldspar minerals.

The presence of a major, northeast-trending structure subparallel to the Tobeatic Fault Zone and within the DLP, this being the East Kemptville-East Dalhousie Fault Zone, also offers potential for similar occurrences. In fact, the presence of extensive hematite alteration, and U (e.g. Millet Brook) and Mn (e.g. New Ross area) proximal to fault and breccia zones along the middle and eastern extent of this fault (Horne *et al.*, 1992 and personal communication, 2001; O'Reilly,



**Figure 9.** Plot of Temperature versus  $\delta^{18}\text{O}_{\text{quartz}}$  for silica-clay deposit with calculated  $\delta^{18}\text{O}_{\text{water}}$  isopleths (circled numbers) for a fluid in equilibrium with quartz of known  $\delta^{18}\text{O}$  at a specific temperature. This diagram shows that based on the three quartz samples analyzed, three interpretations are possible, as shown in the boxes labeled 1, 2 and 3. In these boxes the arrows represent fluid evolution lines and the symbols the points where quartz is precipitated with a corresponding  $\delta^{18}\text{O}_{\text{quartz}}$  value indicated on the side. Models are: (1) Two distinct fluids with  $\delta^{18}\text{O}$  values of +3 to +7 ‰ assuming that quartz was deposited at similar temperatures of ca. 250–300°C. (2) A single fluid with initial  $\delta^{18}\text{O}$  values of ca. +3 ‰ with quartz deposition at ca. 250–300°C and subsequently at 200–150°C (3) Two fluids with  $\delta^{18}\text{O}$  values of 0 and +7 ‰ with some quartz deposited from the fluid of +7 ‰ and the rest from a fluid that represents mixing of the two such that its composition is +3 ‰, which would indicate roughly equal volumes of the two fluids mixed. Also note in the diagram that the cross (+) denotes a fluid of magmatic origin that would have deposited many of the pegmatitic and vein quartz occurrences in the South Mountain Batholith with  $\delta^{18}\text{O}$  levels of +10 to +11 ‰, as summarized in Figure 7. This fluid is of similar isotopic composition to one of the fluids mentioned in the above discussion and in the text.

1992) indicates infiltration of fluids. Recent fluid inclusion studies on some of this material have shown that mineralizing fluids were of variable salinity, including fluids of  $\leq 2$  wt. % eq. NaCl (Carruzzo *et al.*, 2001), in addition to magmatic fluids. Thus, a similar setting and origin of fluids is apparent along the two fault structures, which indicates similar potential of mineralization.



**Figure 10.** Pressure-Temperature plot showing the following: (1) iso- $T_h$  lines (i.e. homogenization temperatures for fluid of uniform composition) for fluid with salinity of 0 wt. % NaCl (from Bodnar and Vityk, 1994); (2) inferred pressure of contact aureole for the South Mountain Batholith (Raeside and Mahoney, 1996); (3) stability of kaolinite (K) and pyrophyllite (P); (4) range of fluid inclusion homogenization temperatures obtained in this study for quartz-hosted inclusions from the silica-clay deposit. The shaded area extending from the dark line delimits the inferred range of conditions for formation of the silica-clay deposit. (5) L-V curve for water, with critical point (CP) indicated.

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