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Contributions to Mineralogy and Petrology

A fluid inclusion study of vug minerals in dawsonite-altered phonolite sills, Montreal, Quebec: implications for HFSE mobility

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Abstract. Ordovician limestones in the Francon quarry on the island of Montreal, Quebec, are host to three sills of Cretaceous age composed of phonolite that has been extensively altered to dawsonite. An interesting feature of the sills is the presence of abundant vugs containing a wide variety of minerals, including several in which one or more high field strength elements (Zr, Hf, Nb, Ti) is a major component. The most important of these latter minerals is weloganite, a rare strontium zirconium hydrous carbonate, first identified in the Francon quarry. Four types of inclusions have been recognized in vug minerals: aqueous, aqueous-carbonic, carbonic and solid-bearing. Aqueous inclusions homogenize at temperatures mainly between 70° and 170 °C and between 230° and 390 °C. The homogenization temperatures of primary inclusions cluster around 350 °C. Aqueous inclusions and the aqueous phase in aqueous-carbonic inclusions have salinities ranging between 10 and 24 eq. wt.% NaCl equivalent. Primary aqueous-carbonic inclusions have low XCO_2 (< 0.03), whereas secondary aqueous-carbonic inclusions can have high XCO_2 (> 0.7); carbonic inclusions are all secondary. Nahcolite, dawsonite and weloganite occur as daughter minerals or trapped solids. Nahcolite and possibly natron or mirabilite appear to form in frozen inclusions. Analyses of fluid inclusion decrepitates detected high concentrations of Na, Cl, Al, S, and C. The extraordinarily high concentration of Al in the fluid (possibly exceeding 1 wt.%) suggests a pH of approximately 10. Pressure and temperature conditions, estimated from stratigraphic reconstruction and the isochores of primary aqueous fluid inclusions, were 450 bar and 360 to 400 °C, respectively. The relatively high temperatures and compositions of primary fluid inclusions suggest that vug filling was the result of mineral precipitation from an orthomagmatic fluid. A model is proposed in which a partially crystallized phonolite melt started exsolving a homogeneous low XCO_2 fluid immediately prior to or after intrusion. Sodium, aluminium, chlorine, fluorine, sulphur and HFSE elements such as Zr, Hf, Nb and Ti were partitioned into the hydrous phase, in the case of Zr, possibly to a concentration of 300 ppm. The near horizontal orientation of the sills and the chilled margins, produced by quenching of the magma, created a tight seal that inhibited escape of the fluids. As a result, the phonolite "stewed in its own juices" long after crystallization, giving rise to widespread replacement of primary igneous minerals by dawsonite, and precipitation of this and other minerals in vugs. Once the sills had cooled to temperatures between 200 and 300 °C, the aqueous fluid exsolved a high CO_2 fluid which was trapped as the secondary three-phase type II and type III inclusions. Decreasing temperature is considered to have been the principal control of mineralization, although in the case of the lower temperature minerals, decreased bicarbonate or carbonate ion activity, and a lower dielectric constant, as a result of CO_2 exsolution, may have played a role in the deposition of HFSE-bearing minerals.

Introduction

Montreal is the type locality for a rather unusual carbonate mineral, dawsonite [$NaAl(CO_3)(OH)_2$], which was discovered on the campus of McGill University and recognized in 1875 by Principal William Dawson as a probable new mineral (Stevenson and Stevenson 1965). Since that time several other occurrences of dawsonite have been reported from the Montreal area including the Francon quarry where it is a major mineral in three felsic sills. From a petrological viewpoint, the most interesting feature of the Francon occurrence and part of the motivation for the present study, is that the bulk of the dawsonite forms a pervasive metasomatic alteration of the primary sill mineralogy.

The petrology of the sills has been investigated by Jambor et al. (1976) who classified them as silicocarbonatites because of their high content of carbonate minerals. This classification is misleading because the bulk of the carbonate is of metasomatic origin. On chemical grounds and the nature of the relict primary mineralogy (discussed

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Correspondence to: A.E. Williams-Jones later), the sills are more appropriately classified as agpaitic phonolites. However, phonolites of this type are commonly associated with carbonatites and in some cases can be shown to represent the conjugate or evolved conjugate in the immiscible silicate-carbonatite pair (Freestone and Hamilton 1980; Le Bas 1987). It is therefore possible that the Francon magma, if not carbonatitic, was at least genetically linked to carbonatite.

The main focus of the paper is the fluid inclusions that are contained in secondary minerals, several of which are dominated by HFSE elements such as Zr, Hf, Nb and Ti. These minerals occur in vugs interpreted to have formed during or immediately after emplacement of the sills, and the case will be made that their deposition and the alteration of the sills was caused by aqueous-carbonic fluids which were released from the magma immediately prior to, or after intrusion. Our purpose is to furnish details on the nature of the fluids that can exsolve from phonolitic magmas, and to provide information that might be useful in trying to understand the unusual conditions under which Al and two of the most immobile elements, Zr and Nb, can undergo hydrothermal transport.

Regional setting

The sills in the Francon quarry are part of the Monteregian province of alkaline igneous rocks, Quebec, which were intruded during a Cretaceous episode of crustal extention (Gold 1967; Phillpotts 1974; Eby 1987). There are 10 major plutons plus numerous dykes and sills in the province, forming an arcuate trend extending from Oka in the west to Mt. Megantic in the southeast (Fig. 1). Within the Appalachian domain (southeast) the intrusives are largely felsic (granitic), in the centre of the trend they are dominantly gabbroic, and in the west they are silica-undersaturated and include carbonatites (Oka). Differences in the style of intrusion are also evident; intrusives in the southeast were emplaced passively, whereas, in the west, intrusion was commonly explosive, as is evident by the occurrence of a kimberlite on Ile Bizzard and diatreme breccias on Ile Ste Helene, both in the Montreal metropolitan area (Fig. 1).

Local geology

The three sills that are the subject of this study are hosted by flat-lying limestones of the Montreal formation and are exposed in the Francon quarry, 7 km north of Mt. Royal on the island of Montreal. As noted they are unusual in containing large concentrations of the carbonate mineral, dawsonite. They are also an important source for a variety of rare minerals, including the Zr-bearing mineral, weloganite [$Sr_5Zr_2(CO_3)_9.4H_2O$], which was first reported from this locality (Sabina et al. 1968).

The sills are 1–2 m thick, fine grained, porphyritic, and light grey to greenish in colour. Darker, chilled selvages, up to 6 cm thick, mark the contacts of each sill. The uppermost two sills (A and B, Fig. 2) are characterized by numerous mineralized vugs and cavities ranging from a few millimetres to in excess of 10 centimetres in diameter. Vugs are more concentrated near the tops of the sills and are generally flattened parallel to the sill margins (Doell and Chamberlin, personal communication 1990). With the exception of a few large cavities, which are irregularly oriented, this general alignment of vugs is maintained throughout. The limestone immediately adjacent to the sills has been relatively unaffected, the only evidence of intrusion being minor brecciation and a local yellowish discoloration of the limestone.

Sill petrography and chemistry

Jambor et al. (1976) have provided a detailed description of the sill petrography and presented preliminary chemical data. The summary that follows is based on their work.

The chilled selvages consist mainly of a microcrystalline intergrowth of dawsonite and feldspar and 5 to 10% by volume of phenocrysts measuring up to 1 cm in diameter, most of which have been pseudomorphed by dawsonite. The nature of the precursor to the pseudomorphs is unknown, but, based on a morphological

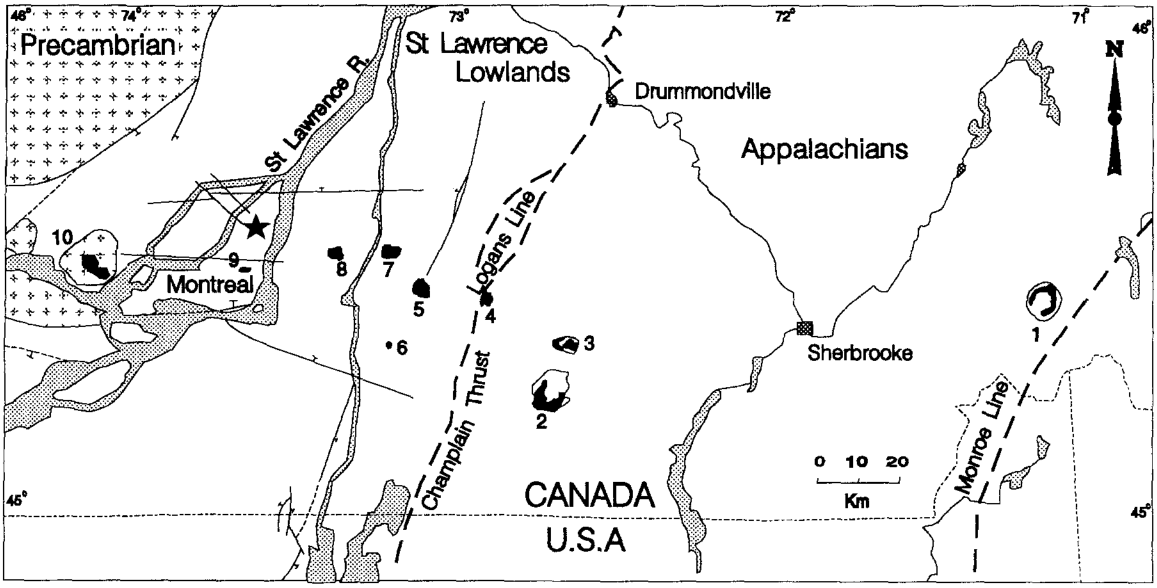

Fig. 1. Map showing the distribution of the main Monteregian plutons numbered *1*–*10*, major faults and the location of the Francon sills (*star*). The names of the Monteregian intrusions are: *1*, Mt. Megantic; *2*, Mt. Brome; *3*, Mt. Shefford; *4*, Mt. Yamaska; *5*, Mt. Rougemont; *6*, Mt. Johnson; *7*, Mt. St Hilaire; *8*, Mt. St Bruno; *9*, Mt. Royal; *10*, Oka; the *unshaded parts* of 1, 2 and 3 are granitic (after Gold 1967)

Fig. 2. Sills *A* and *B* in the Francon quarry, Montreal (courtesy of L. Stevenson)

Table 1. Chemical analyses of samples of altered (1) and least altered (2) sills in the Francon quarry taken from Jambor et al. (1976), an average agpaitic phonolite analysis for the Kenyan rift (3) from Baker (1987) and an average analysis for two samples of phonolite from the Oldoinyo Lengai carbonatite volcano in Tanzania (4) from Dawson (1989)

Wt.%	1	2	3	4
SiO_2	45.1	48.9	51.7	51.14
TiO_2	0.28	0.26	0.9	0.84
ZrO_2	0.11	0.17	0.11	0.08
Nb_2O_5	0.11	0.15	–	0.03
Al_2O_3	19.2	21.7	19.3	19.03
Fe_2O_3	0.5	1.1	3.9	3.88
FeO	1.8	1.0	2.4	1.26
MnO	0.25	0.27	0.2	0.18
MgO	1.0	0.9	1.1	0.60
CaO	2.3	2.0	4.1	3.66
SrO	0.16	0.16	0.14	0.22
BaO	0.20	0.20	0.14	0.20
Na_2O	8.5	9.8	8.9	9.38
K_2O	4.2	3.5	4.6	5.12
P_2O_5	0.12	0.10	0.3	0.27
H_2O_+	3.6	5.3	2.6	2.83
CO_2	11.9	2.9	–	1.37
Total	98.88	98.41	100.39	100.09

similarity to analcime phenocrysts, variably altered to analcime in the interior parts of the sills, the precursor was probably, in most cases, analcime. The remaining phenocrysts (a minor proportion) consist of unaltered albite laths up to 0.25 cm in length.

Phenocrysts are also common in the main body of each sill and, where they have not been pseudomorphed or only partly pseudomorphed by dawsonite, comprise primary albite and analcime. The latter mineral also fills small fractures and, in some cases, partly replaced albite phenocrysts. Aegirine-augite occurs locally as needles averaging less than 0.1 mm in length and, where present, imparts a greenish colour to the rock. The groundmass consists mainly of highly variable proportions of dawsonite and K-feldspar. Megascopically lighter parts of sills are enriched in K-feldspar, whereas darker parts contain mainly dawsonite. Dolomite and siderite are typically present in minor proportions and, with the dawsonite, form aggregates with somewhat rounded outlines. Locally, dolomite and siderite constitute the principal carbonate minerals in the groundmass. Zircon, apatite and pyrochlore are present as accessory minerals.

Chemical analyses of altered (average of 2 analyses) and least altered samples from Sill A, presented by Jambor et al. (1976), are reproduced in Table 1. From these it can be seen that the main effect of alteration was the addition of CO_2, 11.9 versus 2.9 wt.%. The silica and alumina contents of the altered sill samples are, as might be expected, a little lower than those of the least altered sample, reflecting the diluting effect on the former analyses of CO_2.

We have also compared the composition of the least altered sample with a wide variety of volcanic and hypabyssal igneous rock-types. This comparison and the petrographic characteristics described already, notably the presence of analcime phenocrysts, have led us to classify the sills as agpaitic phonolites. An average analysis for Kenyan rift agpaitic phonolites (Baker 1987) and the average of two analyses of agpaitic phonolite flows from the well-known and currently active carbonatite volcano at Oldoinyo Lengai, Tanzania (Dawson 1989), have been included in Table 1 to show the chemical similarity of the sills to these rock types. The reader's attention is drawn particularly to the high contents of alkalis, Zr, Sr, and Ba, which are some of principal chemical criteria by which agpaitic phonolites are distinguished from other similar rock types (Le Bas 1987).

Vug mineralogy

Mineralized vugs are most abundant in the central and upper parts of the two uppermost sills, A and B. The mineralogy of the vugs has been described by Sabina (1976, 1979) and varies somewhat between the two sills. According to Sabina the most common minerals are quartz, calcite, albite and dawsonite in Sill A and calcite, dawsonite, fluorite, quartz, analcime, and albite in Sill B. Other commonly found minerals are strontianite, celestite, barite, montmorillonite, hematite, marcasite, and pyrite. New minerals, include:- weloganite, dresserite $[BaAl_2(CO_3)_2(OH)_4 \cdot H_2O]$; hydrodresserite $[BaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O]$; strontiodresserite $[(Sr, Ca)\ Al_2(CO_3)_2(OH)_4 \cdot H_2O]$; franconite$[(NaCa)_2(NbTi)_4O_{11} \cdot 9H_2O]$ sabinaite $[Na_4(Zr\ Hf)\ (Ti\ Zr)\ O_4(CO_3)_4]$; hochelagaite $[(Ca, Na, Sr)(Nb, Ti, Si, Al)_4O_{11} \cdot nH_2O]$ (Jambor et al. 1969, 1977a, b, 1980, 1984, 1986), doyleite $[Al(OH)_3]$ (Chao et al. 1985) and montroyalite $[Sr_4Al_8(CO_3)_3\ [(OH), F]_{26}.10\text{-}11H_2O]$ (Roberts et al. 1986). These new minerals, with the exception of weloganite, all only occur in Sill A, and, apart from weloganite and dresserite, are comparatively rare. Calcite in Sill A, and quartz, calcite, albite, and analcime in Sill B typically line the vugs, forming a substrate on which the other minerals have grown. One of the most common of these latter minerals, particularly in sill A, is weloganite which typically occurs in calcite-lined vugs and appears to have co-precipitated with roughly equal volumes of quartz (Fig. 3a). Small quantities of dresserite are also commonly present in these vugs as are rare crystals of many of the other new HFSE-bearing minerals listed already.

The quartz forms clear prismatic crystals with hopper habit ranging in diameter from < 1 mm to 4 cm. Growth zones are visible even in hand specimen and, in thin section, show dense concentrations of both solid and fluid inclusions. The calcite occurs in two habits, as small anhedral grains (300 μm to 1 mm in diameter) intergrown with other minerals, and as early euhedral crystals (average diameter, 2 mm) lining fractures and vugs. Most of the albite forms a latticework of white or colourless plates intergrown with quartz and calcite in vug linings. Some weloganite is massive, but most occurs as poorly developed prisms roughly hexagonal in shape, the faces of which are striated and grooved parallel to the base (Figs. 3a). These crystals either terminate in a flat pedian or trigonal pyramids. Crystals up to 5 cms in length are common and vary in colour from white to yellowish green. A significant proportion show colour zonation, from yellowish green cores, containing dense concentrations of fluid inclusions, to white or pale yellow rims. The strontianite is typically represented by globular masses of

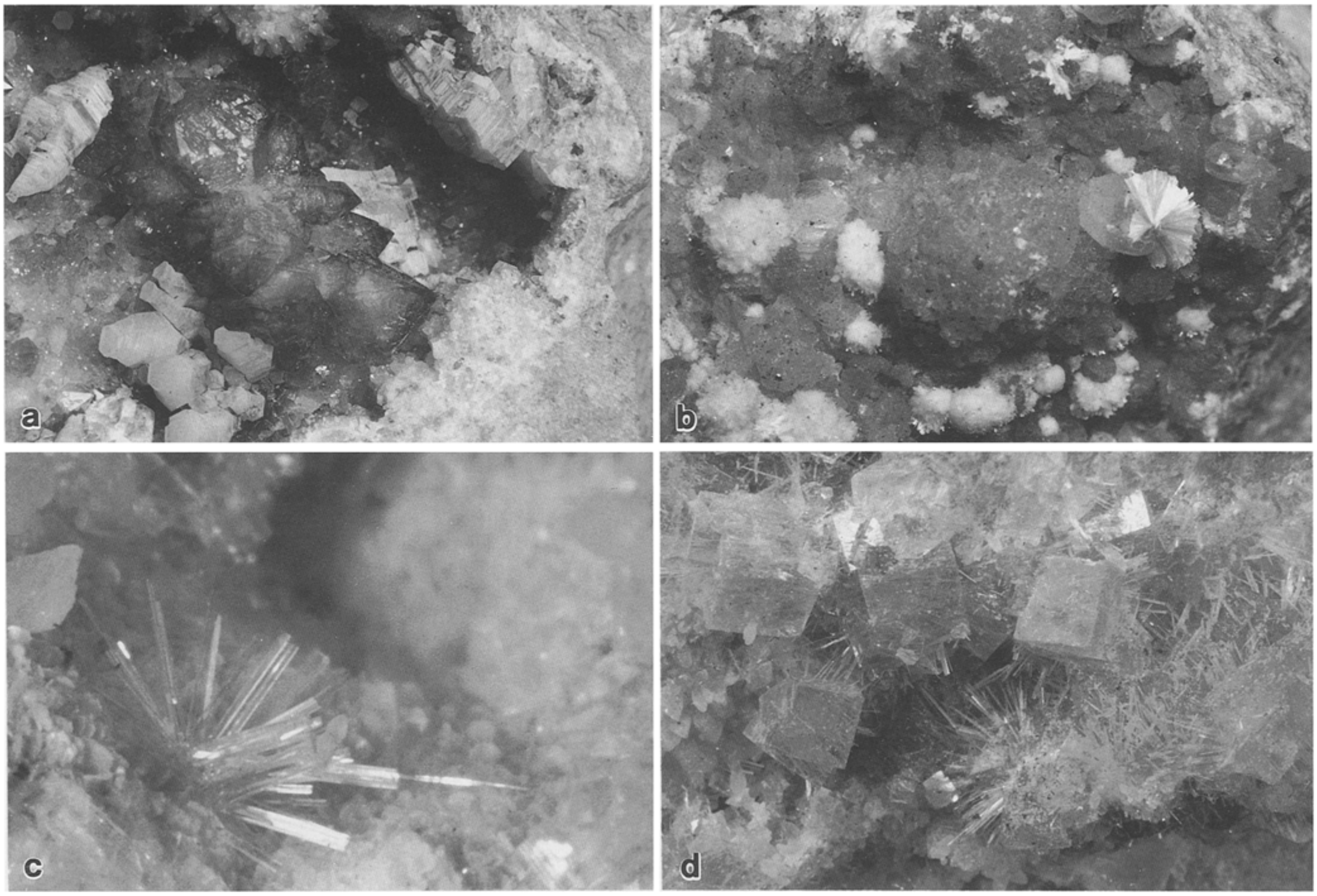

Fig. 3a–d. Vugs containing **a** striated and grooved crystals of weloganite (light colour) surrounding euhedral crystals of quartz (darker colour), field width = 5 cm; **b** a globular mass of acicular crystals of strontianite (dark colour) surrounded by small spheres of radiating dresserite fibres (light colour), field width = 2 cm; **c** a rosette of dawsonite, field width = 8mm; and **d** cubes of fluorite and rough rosettes or randomly oriented needles of dawsonite, field width = 15 mm

fibrous crystals (Fig. 3b), but some strontianite has developed composite crystals with a habit resembling that of weloganite. Dresserite occurs as spheres of radiating fibres up to 3mm in diameter (Fig. 3b) somewhat resembling the globular strontianite masses. It is most common in vugs containing weloganite, with which it appears to have been temporally associated. Dawsonite has several modes of occurrence, but is most spectacular as rosettes of radiating and randomly oriented acicular crystals up to 2 mm in length (Fig. 3c). Other modes of occurrence include composite bodies of acicular crystals, fibrous mats and scaly or botryoidal aggregates. Fluorite forms discrete colourless, blue and purple cubes (Fig. 3d) or purple encrustations on calcite, weloganite, and dawsonite.

Fluid inclusions

Petrography

Fluid inclusions were observed in quartz, calcite from vug linings, later anhedral calcite, weloganite, strontianite, dawsonite and fluorite. Four types of fluid inclusions have been distinguished: aqueous liquid-vapour (type I); aqueous-carbonic liquid-vapour and liquid-liquid-vapour (type II); carbonic liquid and liquid-vapour (type III); and solid-bearing (type IV).

Type I inclusions form the bulk of the fluid inclusion population and are most abundant in quartz, early calcite (vug lining) and weloganite, where they display evidence of both primary and secondary origin. Primary inclusions were identified by their occurrence along growth zones in each of these minerals. They are small ($< 10\ \mu m$ in diameter), regular to irregular in shape and typically have liquid-vapour volume ratios of approximately 2:1. Secondary inclusions and inclusions of indeterminate origin vary greatly in size (some up to 200 μm in diameter were observed), shape and liquid-vapour ratio (from 2-1 to 10-1). Fluid inclusions are relatively uncommon in strontianite and none were successfully analyzed microthermometrically. All are two-phase and liquid-rich and many are tubular and elongated parallel to the mineral fibres. These latter inclusions may be of primary origin. A few rounded two-phase inclusions were observed in the centres of spheroidal fibrous strontianite masses, and appear to have formed along fractures. Dawsonite and fluorite crystals were not suitable for sectioning. However, when examined in a liquid of suitable refractive index, sparse liquid-vapour inclusions were observed in dawsonite and numerous large liquid-rich two phase inclusions in fluorite.

Two-phase aqueous-carbonic inclusions (type II) were distinguished from type I inclusions by the formation of clathrate at low temperatures and were only recognized in quartz and calcite. We do not, however, exclude the possibility that these inclusions are also present in weloganite. Unfortunately microthermometric determinations on inclusions in this mineral were difficult to perform owing to its softness, brittleness and relative opacity. It is, thus, quite possible that clathrate formation was simply overlooked. A significant number of primary two-phase aqueous-carbonic inclusions were identified along growth zones in both quartz and early calcite. These inclusions are petrographically indistinguishable from the coexisting type I inclusions. The secondary inclusions and inclusions of indeterminate origin are quite variable in size, form and degree of fill, and are much more numerous in calcite than in quartz, although even in calcite, they are uncommon relative to type I inclusions. Some of these inclusions in calcite are quite large (up to 150 μm in diameter) and vapour-rich (up to 75% by volume vapour). Liquid-vapour-filled fractures, which interconnect inclusions, were also observed in this mineral. Three-phase type II inclusions are less common than those without carbonic liquid and were observed only along healed fractures in quartz; many of these inclusions contain two liquids at room temperature.

The majority of type III inclusions are uniphase at room temperature, but nucleate a vapour phase on being cooled. They are all secondary and are generally smaller in size than the type I or two-phase type II inclusions. Commonly type III inclusions occur along healed fractures with subordinate numbers of three-phase type II inclusions and, like the latter, they have been observed only in quartz.

Type IV inclusions can be either aqueous or aqueous-carbonic (liquid-vapour), and frequently occur along primary growth zones in both quartz and early calcite. Four solids have been observed repeatedly, and two of these solids "A" and "B" are particularly common. Solid "A" forms prismatic and irregularly shaped birefringent crystals, and was observed only in inclusions (aqueous and aqueous-carbonic) in quartz. The second solid, "B", is also found in both aqueous and aqueous-carbonic inclusions in quartz, and has been observed in inclusions containing solids "A" and "C". Solid "B" forms stumpy birefringent prismatic crystals, and some inclusions contain more than one crystal of solid "B", suggesting that it may represent a trapped mineral. Solid "C" forms irregularly shaped birefringent crystals, and was observed in aqueous inclusions in quartz. Solid "D" has an irregular shape rather similar to that of solid "C", and has one refractive index less than or equal to, and another greater than that of the fluid. As a result, it is generally difficult to see this solid clearly. Solid "D" is observed in aqueous and aqueous-carbonic inclusions in both quartz and calcite, but does not occur in inclusions containing solid "A".

Analytical techniques

Fluid inclusion microthermometry was carried out using a Fluid Inc. adapted/U.S.G.S. gas flow, freezing-heating stage (Werre et al. 1979). Temperatures of the various phase changes were measured using a chrome-alumel thermocouple, and were recorded on a digital trendicator. The thermocouple was calibrated for temperatures ranging from − 56.6 ° to + 374.1 °C using Fluid Inc. synthetic CO_2 and aqueous fluid inclusions. The temperatures of phase changes were reproducible to within ± 0.2 °C for subzero temperatures and ± 2.0 °C for higher temperatures.

A Yvon-Jobin Raman single channel spectrometer equipped with a Ramanor U-1000 monochrometer and a Spectra Physics 164 ionized 6 watt argon laser was used to analyze molecular species in fluid inclusions. The exciting frequency was 514.5 μm at a laser beam power of 200 to 400 mW. For further details of the analytical method see Salvi and Williams-Jones (1992). The host mineral in all cases was quartz. The strong fluorescence of calcite precluded analysis of fluid inclusions in this mineral.

Qualtitative/semi-quantitative elemental analyses of solids in opened fluid inclusions and residues of decrepitated inclusions were carried out using a JEM 840 scanning electron microscope, equipped with a Tracor Northern TN54 energy dispersive X-ray spectrometer (see Kelly and Burgio 1983). Samples opened for analyses of the solids were prepared by freezing them in liquid nitrogen, breaking them, and glueing the chips to glass slides. The analyses of the inclusion residues were carried out on carefully cleaned, doubly-polished sections that had been heated to cause decrepitation of the inclusions. Following the recommendation of Haynes et al. (1988), the temperature of decrepitation was kept below 450 °C. The analyses were performed with the spectrometer in raster-mode to ensure that a large part of each residue was analysed.

Microthermometry

Microthermometric data were collected mainly from inclusions in calcite and quartz. Fluid inclusions in weloganite generally leaked on both heating and freezing, but data for a few type I inclusions were obtained. Similar difficulties were encountered with strontianite, and no microthermometric data were collected for inclusions in this mineral. Owing to the tendency of fluid inclusions in calcite to stretch on freezing and decrepitate on heating, inclusions in this mineral were, in some cases, first heated and, in others, first frozen in an effort to reliably determine phase transition temperatures. In quartz, all inclusions were first frozen and then warmed.

Type I inclusions

Aqueous inclusions in calcite and quartz homogenize over a wide temperature range, from 70 to 390 °C (Fig. 4), however, there are two discernible populations. The majority of the inclusions and all primary Type I inclusions homogenized between 230 and 370 °C. A subordinate population group homogenized between 70 and 170 °C. All inclusions homogenized to the liquid phase and there were no significant differences in the distribution of homogenization temperatures as a function of host mineral. The type I fluid inclusions in weloganite all decrepitated at temperatures between 250 and 290 °C.

Freezing temperatures varied between − 38 and − 78 °C. At first the ice is generally dark brown in colour and then clears between − 23 and − 20 °C. In some inclusions, the vapour phase expands on cooling suggesting the presence of an incondensible gas. Estimates of the

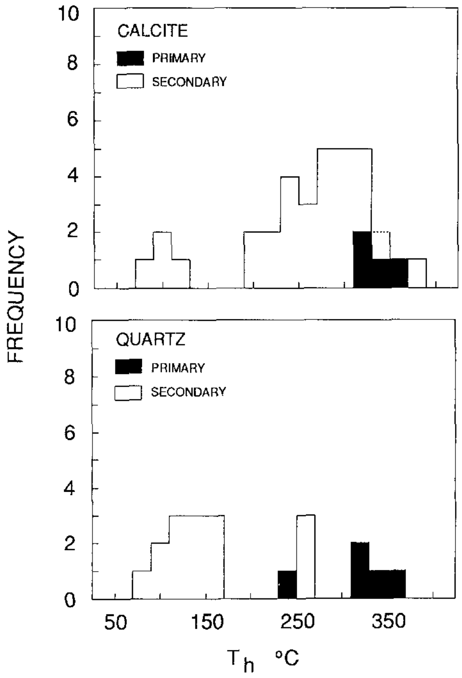

Fig. 4. Histograms of homogenization temperatures (T_h) for type I inclusions

initial melting temperatures range from − 54 to − 23 °C, indicating that these inclusions contain salts in addition to NaCl and KCl (the systems NaCl-H_2O and NaCl-KCl-H_2O have eutectic temperatures of − 20.8 and − 23.2 °C, respectively (Crawford 1981)). Although initial melting temperatures of the order of − 50 °C are commonly attributed to the presence of $CaCl_2$ (the eutectic temperature for the system H_2O-NaCl-$CaCl_2$ is − 52 °C; Crawford 1981), we do not believe this to be the explanation for these data. As has already been pointed out, the alteration of the sills was dominated by the replacement of primary minerals with dawsonite, a sodium aluminium hydrous carbonate (secondary calcium-bearing phases are conspicuously absent). Moreover, as will be shown later, SEM-EDS analyses of inclusion residues failed to detect Ca. These analyses did, however, reveal high Na and Cl and significant Al contents, and it is therefore possible that the low initial melting temperatures may be due to the presence of $AlCl_3$, given that the system H_2O-$AlCl_3$ has a eutectic temperature of − 55 °C (Linke 1958) and the ternary eutectic will be somewhat lower. Final ice melting temperatures ranged between − 22.9 and − 6.5 °C (Fig. 5), corresponding to salinities between 10 and 24 equivalent wt.% NaCl (Potter et al. 1978). Inclusions in quartz generally have salinities lower than 18 wt.% NaCl eq., whereas inclusions in calcite show a salinity range from 13 to 24 wt.% NaCl eq. The few inclusions analyzed in weloganite have salinities of about 20 wt.% NaCl eq. There is no indication that salinity varies with homogenization temperature (Fig. 6).

Several inclusions in quartz, on being frozen, crystallized a solid or solids in addition to ice, which persisted to temperatures higher than those of final ice melting. In some of these inclusions the solid consistently dissolved at a temperature of 22 ± 2 °C, whereas in others it dissolved at temperatures between 89 and 105 °C; one inclusion contained both solids, yielding dissolution temperatures of 19.8 and 93.8 °C, respectively. The final ice melting temperatures of these inclusions are, interestingly, not significantly different from those of the majority of type I inclusions. The solid with the higher dissolution temperature is probably nahcolite ($NaHCO_3$): it is optically similar to solid "A", which was identified as nahcolite (see later), and decomposes over approximately the same temperature range. The other solid could be either natron ($Na_2CO_3 \cdot 10H_2O$) or mirabilite ($Na_2SO_4 \cdot 10H_2O$), both of which have upper thermal stabilities of ≈30 °C. However, given that the first solid is probably nahcolite and evidence of high sulphur concentrations in the residues of decrepitated fluid inclusions (see later), we consider that the second solid is more likely to be mirabilite. If this interpretation is correct, its dissolution temperature (≈22 °C) would imply that the solution contained ≈20 wt.% Na_2SO_4 (Fig. 7).

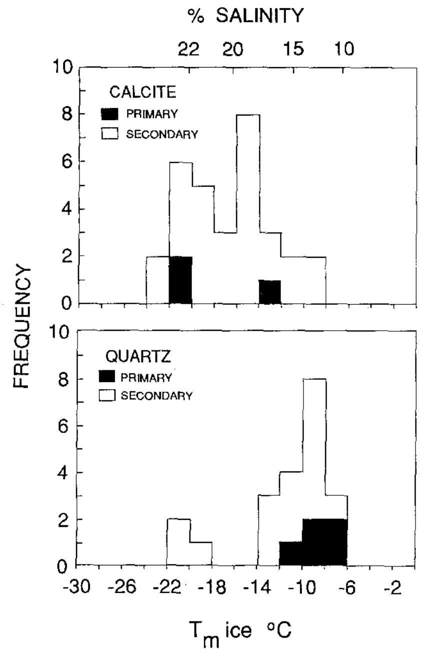

Fig. 5. Histograms showing the distribution of final ice melting temperatures ($T_m$ice) and salinities of type I inclusions

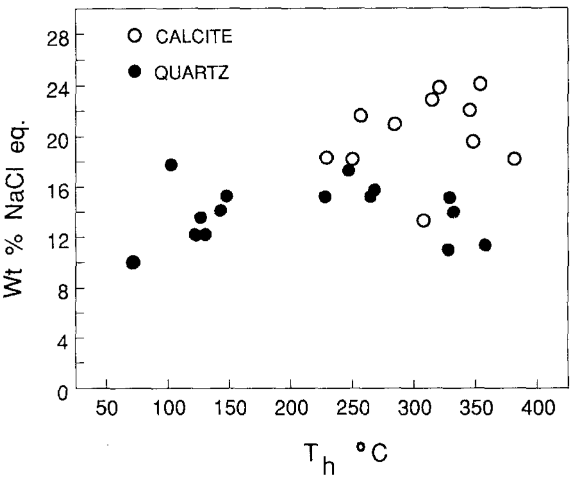

Fig. 6. Salinities (wt.% NaCl eq.) of type I inclusions as a function of homogenization temperature (T_h)

Type II inclusions

All aqueous-carbonic inclusions in calcite leaked and the three-phase variety in quartz all decrepitated before homogenization. Most two-phase type II inclusions in quartz homogenized and did so at temperatures between 254 and 338 °C.

The two-phase inclusions did not nucleate an observable second liquid on being cooled but crystals of clathrate were clearly observed to form along the margin of the vapour bubble. From consideration of the liquid-vapour ratio at room temperature and the minimum amount of CO_2 required to nucleate clathrate (Diamond 1992), we estimate the XCO_2 of these inclusions to be between 0.015 and 0.03. The clathrate melted at temperatures ranging from − 22.5 °C to + 4.2 °C (Fig. 8), which suggests that CH_4 is not a significant component of the carbonic phase (Burruss 1981). Salinities could not be determined from the clathrate melting temperature as there was no liquid CO_2. The initial ice melting temperature varied between

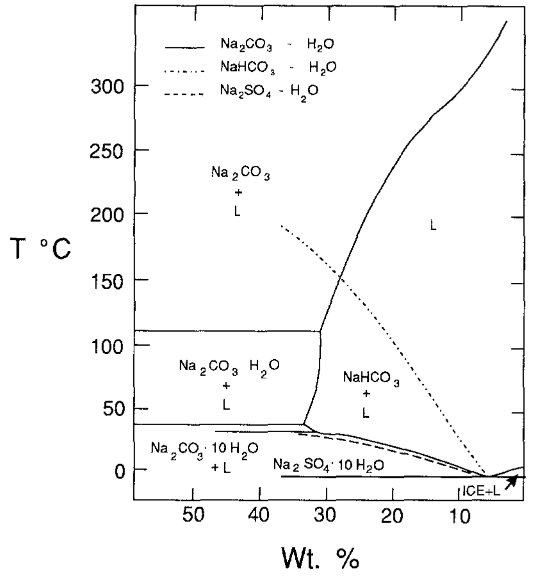

Fig. 7. A temperature-composition diagram showing phase relationships in the systems H_2O-Na_2CO_3, H_2O-$NaHCO_3$, and H_2O-Na_2SO_4 (after Crawford 1981)

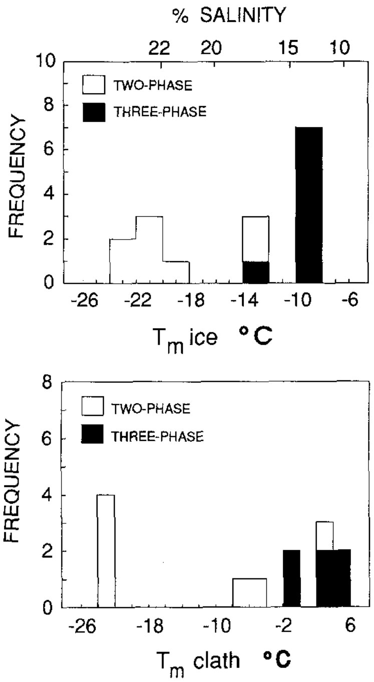

Fig. 8. Histograms showing the temperatures of final ice melting ($T_m$ice) and clathrate melting ($T_n$clath) in type II aqueous-carbonic inclusions

– 54 and – 30 °C, indicating that these inclusions, as is the case for type I inclusions, probably contain $AlCl_3$ in addition to NaCl. The ice finally melted at temperatures ranging from – 22.5 to – 13.2 °C, corresponding to a range in salinity from 17.5 to 24.5 wt.% NaCl eq. (Fig. 8). These values represent maximum estimates of salinity because clathrate formation removes H_2O but not salt from the aqueous liquid. Solids were formed, in addition to ice and clathrate, in most inclusions hosted by calcite. Some of these solids consistently reformed on repeated freezing, but others did not, and each freezing experiment gave rise to a solid with a different melting temperature, ranging from – 4 to + 6.4 °C. The reason for the inconsistent melting behaviour is not understood but may have something to do with the presence of clathrate. The solid could be natron or mirabilite (see Fig. 7).

The carbonic solid in three-phase type II inclusions disappears at temperatures between – 57.9 °C and – 56.6 °C and mainly above – 57.2 °C (Fig. 9), indicating that it consists largely of CO_2 and has very minor concentrations of CH_4 and/or N_2. The carbonic phases homogenize to liquid at temperatures mainly between 16 °C and 30.3 °C (Fig. 9). Other phase transition temperatures are similar to those for two-phase type II inclusions, except that the range for clathrate melting (– 2 to + 4.2 °C) does not go as low. These latter temperatures correspond to salinities in the range 10 to 17.5 wt.% NaCl eq. (Diamond 1992). The initial melting temperature of the ice was between – 40 and – 26 °C, and the final ice melting temperature between – 13 to – 9.2 °C. XCO_2 values, determined using the method of Burruss (1981), show that the three-phase fluid inclusions form two populations, one with values between 0.05 and 0.3 and the other with values > 0.7.

Type III inclusions

Frozen carbonic inclusions melt at temperatures ranging mainly from – 58 to – 56.6 °C (Fig. 9), indicating that they are CO_2-dominant. Most homogenize to liquid at temperatures between 16 and 22 °C (Fig. 9).

Type IV inclusions

Type IV inclusions, as noted earlier, are aqueous and aqueous-carbonic inclusions that contain solids. The phase changes, except those relating to the solids, are similar to those of inclusion types I and II.

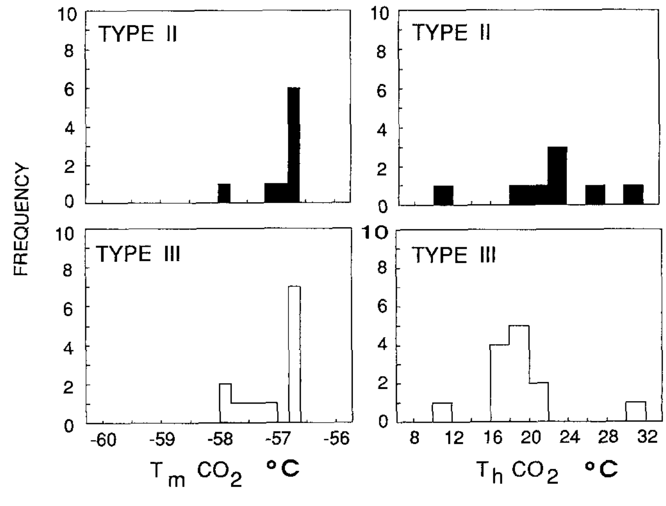

Fig. 9. Histograms showing the melting temperatures of CO_2 ice (T_mCO_2) and homogenization temperatures of the carbonic phases (T_hCO_2) in type II and type III inclusions

Solid “A”, dissolved readily at temperatures ranging from 82 to 112 °C and is particularly common in secondary aqueous inclusions that homogenized at temperatures < 150 °C. It is, however, also present in primary inclusions with homogenization temperatures up to 340 °C. With one exception (a secondary inclusion), dissolution occurred before filling. In contrast to solid “A”, solid “B” generally did not dissolve prior to decrepitation of the inclusion. Dissolution of this solid was only observed in two inclusions (primary) and occurred at temperatures of 275 and 305 °C; these inclusions decrepitated before filling at temperatures of 385 and 360 °C, respectively. In a third inclusion, solid “B” appeared to transform into another solid over a temperature interval ranging from 300 to 305 °C and then underwent no further change until decrepitation of the inclusion at 365 °C. The phase change involved the breakup of the solid into several rounded crystals. Solid “C” did not dissolve or give indication of any phase change prior to decrepitation of the inclusions hosting it. Solid “D” was generally observed only at elevated temperatures, and recognition of the mineral apparently coincided with the onset of its decomposition, which was recognized by the production of vapour, typically above 300 °C. In two aqueous inclusions, filling had occurred at lower temperatures and decomposition of the solid was heralded by the formation of a new vapour bubble. These two inclusions, which were in quartz, decrepitated before complete dissolution of the solid, at 379 °C and 389 °C, respectively. Solid “D” dissolved completely in only one inclusion; it began producing vapour at 335 °C and dissolved at 438 °C. Cooling caused reprecipitation of the solid which, on being reheated, dissolved at 443 °C. The production of a vapour phase suggests that the mineral may have a carbonate component.

Raman and SEM/EDS analyses

Raman spectra were gathered on the carbonic phase(s) in type II and III inclusions and confirmed the conclusions, drawn from microthermometry, that this phase(s) consists dominantly of CO_2. The spectra were gathered at wavenumber intervals corresponding to the principal frequencies of CO_2, CH_4, N_2 and H_2S, but only CO_2 was detected. The detection limit for these gas species was approximately 0.5 mol%. Raman spectra were also collected for each of solid phases A–D found in type IV inclusions and described already. Solid “A” was identified as nahcolite from comparisons of its spectrum (Fig. 10) with spectra for this mineral published by Dhamelincourt et al. (1979). Interestingly this mineral also occurs in vugs in sill B. Solid “B” was identified as dawsonite, both from comparisons of its spectrum with spectra in White (1974), and from comparisons with a spectrum for dawsonite from one of the vugs (Fig. 11). Solid “C” proved to be welogonite; its Raman spectrum is identical to that obtained from a weloganite crystal extracted from a vug (Fig. 12). The weloganite identified by Raman spectroscopy was in an aqueous inclusion which also contained dawsonite and nahcolite. The nahcolite in this inclusion dissolved at 100 °C and the dawsonite at 275 °C, whereas there was no change in the weloganite prior to decrepitation of the inclusion at 365 °C. As noted earlier, solid “D”, was difficult to see at room temperature and consequently no Raman spectra were collected for this mineral.

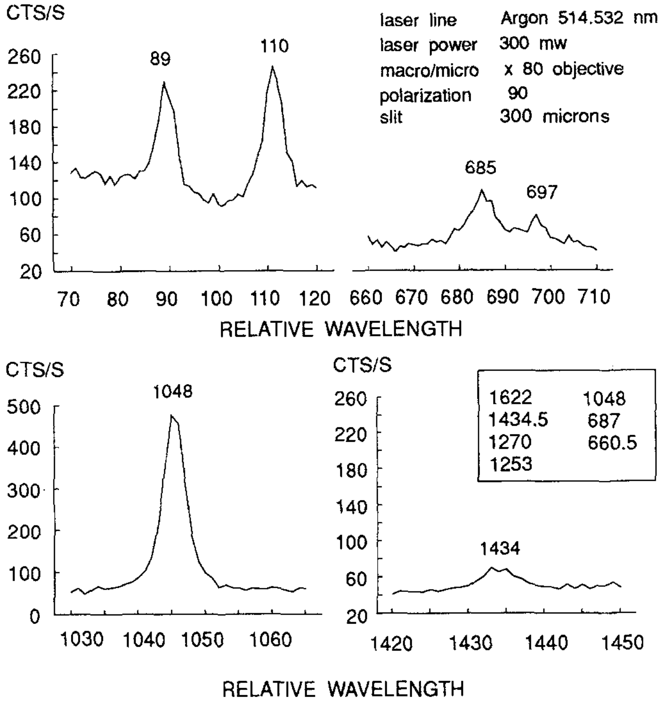

Fig. 10. A Raman spectrum for solid “A” in a type IV inclusion. The numbers in the *inset box* list the wavenumbers of the peaks for the spectrum of nahcolite reported by Dhamelincourt et al. (1979)

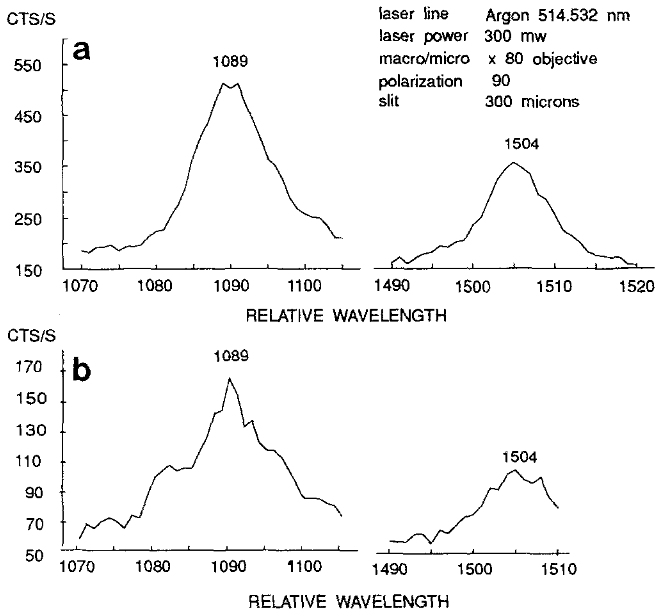

Fig. 11a, b. Raman spectra for **a** dawsonite from a vug, and **b** solid “B” in a type IV inclusion

The only primary solid that was found in opened inclusions during SEM imaging was a suhhedral to subrounded phase that was interpreted to be dawsonite from

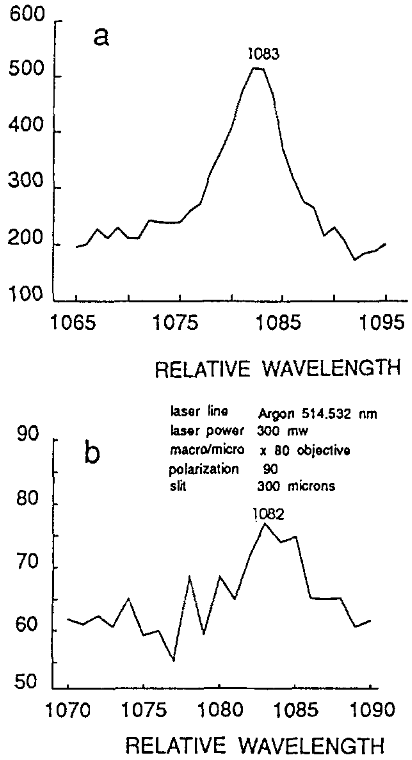

Fig. 12a, b. Raman spectra for **a** weloganite from a vug, and **b** solid "C" in a type IV inclusion

its EDS spectrum (peaks for Na, Al, and C). Several opened inclusions contained mats of crystallites in their interior which were shown to consist of Na and Cl. Such crystallite mats were also observed along fractures, and are interpreted to represent precipitates deposited as a result of evaporation when the inclusions were opened. Sulphur was detected in some of these mats and is assumed to represent another crystallite, possibly mirabilite.

Decrepitation of the fluid inclusions either yielded craters with evaporated salt residues within them, or mounds of salts representing fluids that had leaked to the surface from deeper fluid inclusions (Fig. 13). Most of the rims and mounds were compositionally similar, yielding EDS peaks for only Na, Cl, Al, S, and C. Representative semi-quantitative analyses using a ZAF correction procedure are presented in Table 2. These data indicate that Na and Cl are the principal ions at 7–15 and 23–30 wt.%, respectively. There are also important concentrations of Al and S, 0.5–5 and 0.9–5 wt.%, respectively. Unfortunately, it was not possible to analyze for C but, as seen in Fig. 13, its peak height is comparable to that of Al. If the data are normalized to 15 wt.% NaCl eq. on the basis of Cl concentrations, then it is apparent that the solutions contained up to 1.7 wt.% Al and up to 1.6 wt.% S. It should, however, be cautioned that the analyses are, at best, semi-quantitative, as can be seen from the fact that, in three of four of them, there is a significant deficiency in Na (probably because of preferential volatilization) with respect to that required to balance Cl and S in the components NaCl, $AlCl_3$, and Na_2SO_4. The deficiency would be even larger if C could be determined. Although the analytical data are very rough, they confirm earlier

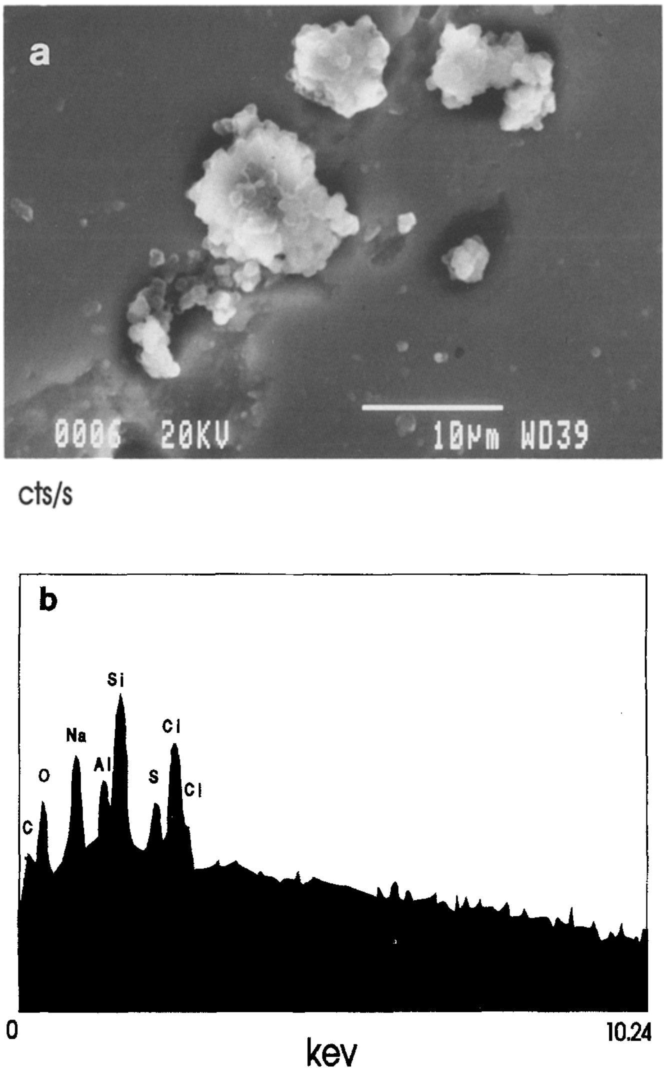

Fig. 13a, b. A SEM image of a typical salt residue from a decrepitated type I fluid inclusion and the corresponding EDS spectrum. The peak for *Si* and much of that for *O* is from the quartz host

Table 2. Representative SEM/EDS analyses of the salt residues of decrepitated fluid inclusions in quartz

	Wt.%			
Na	Cl	Al	S	Na Diff[a]
15.8	30.0	0.5	3.6	
14.7	25.6	4.9	4.6	
12.9	23.5	1.7	3.2	
7.3	23.4	2.4	0.9	
Wt.% normalized on basis of Cl to 15 wt.% NaCl eq.				
4.8	9.1	0.2	1.1	
5.2	9.1	1.7	1.6	
5.0	9.1	0.7	1.2	
2.9	9.1	0.9	0.4	
Ionic proportions				
1.34	2.54	0.04	0.31	− 0.99
1.46	2.54	0.48	0.46	+ 0.60
1.39	2.54	0.19	0.35	− 0.43
0.83	2.54	0.26	0.97	− 0.50

[a] The deficiency in Na was calculated by assuming that Na, Cl, Al, and S are partitioned amongst NaCl, $AlCl_3$, and Na_2SO_4, and first assigning Cl to $AlCl_3$ and Na to Na_2SO_4

conclusions, from microthermometry and the nature of the hydrothermal alteration, that the fluids were NaCl brines with high concentrations of alumina, sulfate, and carbonate or bicarbonate ions.

Pressure-temperature conditions

The relatively undeformed, flat-lying nature of the sedimentary succession hosting the Francon phonolite sills has permitted fairly reliable reconstruction of the stratigraphy, thereby providing an opportunity to estimate pressure from the thickness of the sedimentary cover. The principal uncertainty is the thickness of sedimentary rocks that was removed by erosion after emplacement of the sills during the early Cretaceous. This, fortunately, is qualitatively indicated by the presence of sedimentary blocks in the coeval Ile Ste Helene diatreme. These blocks include representatives from every formation in the Montreal area as well as from formations as young as middle Devonian, that have since been eroded. Using measured stratigraphic sections and borehole information from the Montreal area and, in the case of the eroded formations, from other parts of the Lower St. Lawrence Basin, the sedimentary cover at the time of emplacement of the Francon sills was estimated by Clark (1972) to have been approximately 1650 m. This corresponds to a lithostatic pressure of approximately 450 bar, which, for reasons discussed later, also probably represented the fluid pressure.

The trapping temperatures of the fluid can, in theory, be estimated from the isochores of the primary type I or type II inclusions. Limiting isochores for the primary type I inclusions, excluding one isolated inclusion in quartz which homogenized at 231 °C, were constructed using the computer program of P.H. Brown and the equation of state for H_2O-NaCl of Brown and Lamb (1989). These are shown on Fig. 14 and indicate trapping temperatures ranging from 360 to 400 °C at 450 bar. The isolated inclusion referred to already has a corresponding trapping temperature of 260 °C. Isochores cannot be accurately drawn for the primary type II inclusions because their XCO_2 values are not known. However, their isochore locations can be roughly approximated on the assumption that XCO_2 was < 0.03 (see earlier). Approximate isochores for these inclusions were accordingly calculated using the program of P.H. Brown, the equation of state of Bowers and Helgeson (1983), and an assumed XCO_2 value of 0.03; they plot in the same field as that delineated by the isochores of the type I inclusions. These data suggest that the crystallization of quartz and calcite probably commenced at about 400 °C and was largely complete by the time that the temperature had dropped to 360 °C. However, the existence of a large population of secondary inclusions with homogenization temperatures that overlap those of the primary inclusions, and extend down to about 220 °C, may indicate that other vug minerals crystallized at lower temperature.

In the case of dawsonite, nahcolite and weloganite, some information about possible crystallization temperatures can be gained from their microthermometric behaviour in fluid inclusions. Dawsonite, as noted already, dissolved in one inclusion at 275 °C and in another, appeared to decompose at about 300 °C, suggesting, therefore, that it probably crystallized below 300 °C. Nahcolite is clearly a very low temperature mineral, judging by the fact that it consistently dissolved at temperatures between 82 and 112 °C and was found predominantly in fluid inclusions that homogenized below 150 °C. Significantly, the homogenization temperature data for the type I inclusions show a bimodal distribution, with the lower temperature population clustering between 70 and 170 °C. Weloganite did not appear to undergo any change prior to decrepitation of the inclusions hosting it, and may therefore have crystallized at high temperature. It is also possible that its failure to dissolve was for kinetic reasons. On the other hand, the close spatial and apparent temporal association of weloganite with quartz suggest that it crystallized in the same temperature interval as this mineral, i.e. 360 to 400 °C. It is also worth noting that type I inclusions in weloganite decrepitated prior to homogenization, at temperatures up to 290 °C.

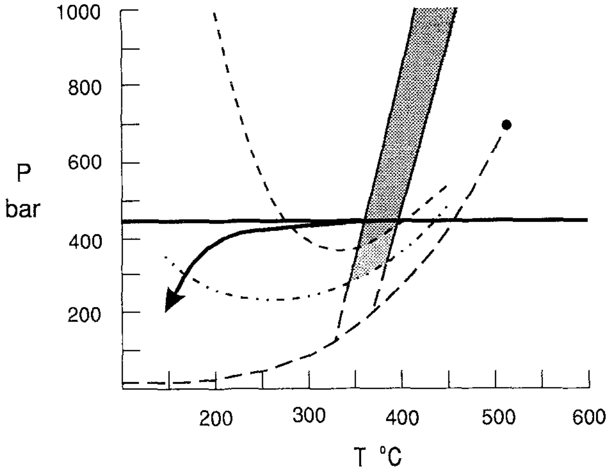

Fig. 14. A P-T diagram showing the region (*shaded*) of isochores for primary type I fluid inclusions calculated using the program FLINCOR developed by P.H. Brown. Also shown on the diagram are solvi for the system $NaCl_{15\,wt.\%}$-H_2O-CO_2 for XCO_2 values of 0.03 (– –) and 0.015 (– – · ·) calculated using the data of Takenouchi and Kennedy (1965), and the liquid-vapour boundary for the system $NaCl_{15\,wt.\%}$-H2O (– –) from Brown and Lamb (1989). The *horizontal line* indicates the lithostatic pressure estimated from stratigraphic reconstruction and *the arrow* depicts the possible cooling path of the fluid

Thus in summary, it would appear that quartz, calcite, and possibly weloganite crystallized at temperatures between 360 and 400 °C at a pressure of 450 bar, that dawsonite and probably some of the other minerals crystallized at temperatures between 250 °C and 300 °C, and that nahcolite crystallized at temperatures below 120 °C.

Origin of the fluids

The relatively high entrapment temperatures of most of the primary aqueous fluid inclusions (360–400 °C), suggest that the vug-filling fluid was of orthomagmatic origin, i.e. that it exsolved from the magma that produced the sills. If our interpretation of the petrology of the sills is correct, this magma was phonolitic. Unfortunately, as far as we are aware, there have been no previous studies of fluid inclusions in phonolites, and thus our only information on the possible nature of the fluids comes from rare sampling of gases during volcanic eruptions (e.g. Chaigneau et al. 1960) and gases extracted from glasses (see Bailey and Hampton 1990). These studies show that phonolitic magmas are gas-charged and have high contents of CO_2, SO_2, Cl, and F, but give little information on the nature of any dissolved aqueous species. Some inferences about the latter can be made from a number of studies that have been carried out on fluid inclusions in carbonatites. Agpaitic phonolites commonly show a close spatial association with carbonatites and, in the case of Oldoinyo Lengai, are thought to represent the parent from which the carbonatite liquid separated (Freestone and Hamilton 1980). It is thus reasonable to assume that fluid inclusions in agpaitic phonolites will be similar in some respects to those in carbonatites. Both aqueous (moderate to high salinity) and aqueous-carbonic fluid inclusions are observed (Haapala 1980; Andersen 1986). The aqueous fluids, on the basis of microthermometry, appear to be very low in Ca, being dominated by Na and possibly K (Andersen 1986). They commonly contain solids such as kalicinite ($KHCO_3$) and nahcolite (Rankin 1977) and a variety of sulphate minerals (Heinritzi et al. 1989), the latter underlining the importance of sulphur in these fluids. Indirectly, we can also infer that they must have high Al contents as shown by the fenitization (K-feldspar replacement) of pure quartz sandstones around the Amba Dongar carbonatite in India (Viladkar 1991). The carbonic fluids are essentially pure CO_2, which contrasts with other alkalic environments where reduced carbonic species are more important (Konnerup-Madsen et al. 1979; Salvi and Williams-Jones 1992). Thus, in summary, aqueous fluids exsolving from a phonolitic magma would be expected to be saline with a very high alkali to calcium ratio and have high contents of bicarbonate, chlorine, sulphur and alumina, i.e. the characteristics of the aqueous fluids in the Francon sills. The associated volatiles would include CO_2 and F, the presence of which, in the Francon sills, are indicated by aqueous-carbonic fluid inclusions and the common occurrence of several fluorine-bearing vug minerals, respectively. A final argument supporting the orthomagmatic nature of the vug fluids is the vug mineralogy, which is dominated by minerals with high contents of Sr, Zr, Nb, Ba, Ti, and F, elements that are typically enriched in agpaitic phonolites.

Although, in principle, the vugs could have been filled by external meteoric fluids that had interacted extensively with large unexposed bodies of alkaline rocks, this seems unlikely, as the fluids would also have had to interact with the limestone-dominated sedimentary succession, and would have inevitably dissolved significant Ca, an element that is below detection levels in the fluid inclusions. This, in turn, seems to eliminate the possibility that the CO_2 could have come from the limestone. We therefore conclude that the aqueous and carbonic fluids that filled the vugs in the Francon sills represent orthomagmatic fluids which exsolved from the magma.

The only concern with this interpretation is that the temperature of vug-filling is considerably lower than the solidus temperature of most magmas, although, interestingly, Piotrowski and Edgar (1970) report a solidus temperature for a nepheline syenite from the Ilimaussaq complex in Greenland, of 470 °C at 1 kb. We believe that the explanation for the existence of uncontaminated lower temperature orthomagmatic fluids lies in the observations that the sills are thin and flat-lying, display chilled margins, and are hosted by sedimentary rocks that were at shallow depth. If we assume that the thickness of the sedimentary cover was 1650 m (see earlier), the geothermal gradient was 30 °C/km, and the ambient temperature was 20 °C, the temperature of the limestones prior to intrusion would have been 70 °C. Even if the geothermal gradient was as high as 80 °C/km, because of the Cretaceous plutonism, the pre-intrusion temperature would only have been 150 °C. These features indicate that cooling would have been rapid and fluid escape slow because of the sealing provided by the chilled margins. Under such circumstances it is possible to envisage cooling of the order of several hundred degrees below the solidus before complete loss of the exsolved orthomagmatic fluid.

Fluid evolution

The abundance of vugs in the Francon sills leaves little doubt that there was major degassing of the magma and that this was significant even after intrusion. The nature of the fluid initially responsible for vug formation is unknown. However, the composition of the primary fluid inclusions, aqueous and aqueous-carbonic with $XCO_2 < 0.03$, suggests that the orthomagmatic fluids that precipitated the early vug minerals were dominantly aqueous. It thus seems likely that aqueous fluids were also responsible for vug formation. This interpretation of an agpaitic phonolite exsolving dominantly aqueous fluids conflicts with the finding of Bailey and Hampton (1990) that the gases extracted from phonolite glasses consist mainly of CO_2 and SO_2, and contain only minor H_2O. Nevertheless, the interpretation is consistent with the observation, from fluid inclusion studies, that the fluids exsolved in the late stages of carbonatite crystallization are aqueous (Andersen 1986).

The wide range of fluid inclusion compositions, from aqueous with no detectable CO_2 to carbonic with no detectable H_2O, suggests that the subsequent evolution of the vug fluids involved exsolution of separate aqueous- and carbonic-rich phases. Whether or not this had already started at the time of vug formation is less clear. The absence of CO_2-rich primary inclusions would suggest that it had not started; according to diagrams presented in Bowers and Helgeson (1983) and data in Takenouchi and Kennedy (1965) the coexisting immiscible fluids, would, at the conditions estimated for vug-filling, have had XCO_2 values of 0.03 and 0.6. Our preferred explanation for the separate primary aqueous and aqueous-carbonic fluid inclusion populations is that they represent a continuum of compositions arbitrarily subdivided into two sets by the limits of our ability to see clathrate. Significantly the highest XCO_2 value inferred for a primary type II inclusion is 0.03, i.e. that of the aqueous member of a possible immiscible pair. In order to further investigate the question of subsequent fluid immiscibility we have plotted solvi representing the probable range of XCO_2 values of the primary type II fluid inclusions on the P-T diagram introduced earlier (Fig. 14). Also shown on this diagram is a possible cooling path. From this diagram it can be inferred that the immiscibility limit would only have been reached after the fluid had cooled to about 300 °C and perhaps as low as 200 °C. At these conditions the XCO_2 values of the exsolved carbonic fluid would have been 0.85 and > 0.95, respectively (Bowers and Helgeson 1983). We intrepet the secondary three phase type II inclusions and type III inclusions to have been trapped at these or possibly even lower temperatures and consider that their compositions are a natural consequence of low temperature immiscibility. The ranges in XCO_2 values for the two populations of three phase type II inclusions, 0.05 to 0.3 and > 0.7, we attribute to heterogeneous entrapment of the immiscible fluids.

Fluid pressure during much of this period of cooling and crystallization of vug minerals would have remained at or close to lithostatic pressure, and may actually have initially increased as a result of continued degassing after intrusion. Eventually, however, fluid pressure would have declined as a result of the reduced volume demands (on the vugs) of the cooler fluids.

It, thus, appears reasonable to conclude that the vugs were filled at near lithostatic pressure conditions by dominantly aqueous orthomagmatic fluids containing up to 3 mol% CO_2 and that, on cooling, these fluids exsolved their CO_2, preserving it as high XCO_2 type II and ultimately, at lower pressure, as type III fluid inclusions.

The solubility of HFSE

It is well known that elements such as Al, Ti, Nb, and Zr have very low solubility in most hydrothermal fluids, although there are rare cases reported in the literature where even the most immobile of these elements, Zr and Nb, have been transported hydrothermally in significant quantities (e.g. Hynes 1980; Gieré 1986). The mineralogy of the vugs shows that all these elements were highly mobile during alteration and that, in the case of Al, the concentration in the fluid was extraordinary, possibly in excess of 1 wt.%.

To our knowledge Al concentrations as high as 1% have not previously been reported from natural fluids, but appear to be theoretically possible. For example, using the equations presented in the experimental study of Castet (1991), it can be shown that that an aqueous solution, containing 1 wt.% Al, can be produced by equilibrating the solution with boehmite (AlOOH) at a temperature of 350 °C and a pH of 10.1. Although such a pH is extremely high it may not be unusual for a fluid originating from a highly alkalic magma.

We were not able to directly estimate the concentrations, in the fluids, of the other elements mentioned earlier, nor are we aware of published experimental data that could help us in this regard. However, some insight into the probable concentration of Zr can be gleaned from the fact that weloganite appears to have co-precipitated in roughly equal volumes with quartz. The solubility of this latter mineral has been extensively investigated and is predicted to be approximately 1680 ppm/kg H_2O in aqueous solutions containing 15 wt.% NaCl at 400 °C and 450 bar (Fournier 1983). More importantly quartz solubility decreases to 1330 ppm/kg H_2O at 360 °C, the temperature by which most of the quartz and, by extention, the weloganite had precipitated. From this change in quartz solubility (350 ppm) and an assumption that quartz and weloganite were precipitated from the solutions in equal amounts, it can be calculated that the change in Zr concentration was approximately 60 ppm. If the integrated solubilities of the quartz and weloganite were similar this could indicate an initial concentration of Zr in the fluid of nearly 300 ppm. The concentrations of Ti and Nb were undoubtedly also significant, but were probably lower than that of Zr, judging by the much smaller volumes of vug minerals containing them.

The reason for the high concentration of the HFSE elements, Zr, Nb, and Ti is unclear. In part, it may reflect the high pH, but it is also possible that high concentrations of bicarbonate/carbonate and fluoride may have led to the formation of soluble complexes of these elements. Another unresolved problem, given the relatively high content of SiO_2 in the fluid, is why Zr was precipitated as weloganite rather than zircon. A clue to this is, however, provided by the hydrothermal experiments of Caruba (1975) on zirconsilicate synthesis; these were only successful in very alkaline fluids and otherwise produced zircon. It is thus possible that the very high pH conditions of the fluids may likewise have played a role in controlling the nature of the zirconium mineralogy in the Francon sills.

A model for the late stage evolution of the phonolite

The pervasive nature of the alteration of the Francon sills by dawsonite and the wide variety of exotic minerals preserved in them is the direct consequence of the intrusion of a gas-charged phonolitic magma. Prior to and immediately after intrusion, this magma underwent major degassing, as is shown by the presence of numerous vugs, some of which are flattened against the top contacts of the sills. A high level of emplacement into cold sedimentary rocks ensured the rapid quenching required for vug preservation, and also produced the thick chilled-margins which provided the tight seals necessary for retention of the fluids. In contrast to the conclusions of Bailey and Hampton (1990) that the gases exsolving from phonolites are mainly carbonic, those which exsolved from the Francon magma were dominantly aqueous. At the onset of degassing, Na, Al, Cl, S, C, and incompatible elements such as Zr, Ba, Sr, Nb and Ti, which were present in the magma, were partitioned into the aqueous phase, and subsequently deposited as vug minerals. Deposition of the latter commenced after the fluids had cooled to about 400 °C and became saturated with calcite, quartz, and weloganite. This process was largely complete by 250 °C, although there is some evidence, namely the occurrence of nahcolite as both a vug mineral and a daughter mineral in the fluid inclusions, that some precipitation continued to temperatures below 120 °C. The principal cause of deposition was the precipitous fall in temperature, assisted perhaps, in the case of lower temperature minerals by H_2O and CO_2 immiscibility and consequent decrease in concentration of carbonate or bicarbonate ligands and the dielectric constant of the fluid. Fluid pressure remained at, or close to, lithostatic pressure during much of the mineral deposition, and initially may actually have exceeded lithostatic pressure as a result of the continued degassing. These high fluid pressures helped promote diffusion and infiltration of the fluids into the main body of the sills where they caused pervasive alteration of the primary minerals to dawsonite. Apart from the addition of CO_2 this alteration left the chemistry of the sills unchanged, as would be expected for a rock that stewed in its own juices.

Conclusion

The results of this study provide some information on the nature of the fluids that may accompany emplacement of phonolitic intrusions. Such fluids may, in some cases, be dominantly aqueous, and if so will have unusually high pH, moderately high contents of alkalis, Cl and S, and remarkably elevated levels of Al and HFSE. The implication of the latter is that the normally immobile HFSE elements (Ti, Nb, Zr, and Hf) and Al may be comparatively mobile in environments where there are intrusions of alkaline silicate magmas and carbonatites.

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