## FLUIDS IN THE SIILINJÄRVI CARBONATITE COMPLEX, EASTERN FINLAND

# Fluid inclusion evidence for the formation conditions of zircon and apatite

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POUTIAINEN, MATTI, 1995. Fluids in the Siilinjärvi carbonatite complex, eastern Finland: Fluid inclusion evidence for the formation conditions of zircon and apatite. *Bull. Geol. Soc. Finland* 67, *Part 1*, 3-18.

In the studied zircon and apatite crystals, data recorded two different compositional types of fluid inclusions: Type 1  $H_2O-CO_2$  low salinity inclusions (XCO<sub>2</sub>=0.42 to 0.87; XNaCl=0.001 to 0.005) with bulk densities of 0.73 to 0.87 g/cm<sup>3</sup>, and Type 2  $H_2O$  moderate salinity (XNaCl=0.03 to 0.06) inclusions with densities of 0.83 to 1.02 g/cm<sup>3</sup>. The Type 1 inclusions are not present in apatite. In zircon, the observed fluid inclusion types occur in separate domains: around (Type 1) and outside (Type 2) the apparent core. Fluid inclusions are further subdivided into pseudosecondary and secondary inclusions. Using a combination of SEM-EDS, optical characteristics and crushing-stage, various daughter and captive minerals were identified.

The fluid inclusion data suggest that the pseudosecondary Type 1 and Type 2 inclusions in zircon and apatite were trapped during the pre-emplacement evolution of the carbonatite at mid-crustal conditions ( $P \ge 4$  kbar,  $T \ge 625^{\circ}$ C). The Type 1 fluid was depleted in CO<sub>2</sub> during crystal fractionation and cooling leading to a fluid phase enriched in water and alkalies. Fenitization was obviously induced by these saline aqueous fluids. During emplacement of the carbonatite to the present level, zircon phenocrysts were intensively fractured, some Type 1 inclusions were re-equilibrated, and multiphase Type 2 inclusions were trapped. It is assumed that all these inclusions in zircon and the pseudosecondary Type 2 inclusions in apatite have a magmatic origin.

In apatite, calcite inclusions occur side-by-side with the secondary Type 2 inclusions. These calcites co-existed with the aqueous fluid during fracturing and metamorphic re-crystallization of apatites. Probably, this metamorphic fluid also is responsible for the transport and deposition of at least some of the calcite at low temperatures (200-350°C).

Key words: carbonatites, fluid inclusions, zircon, apatite, microthermometry, Siilinjärvi, Finland.

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#### INTRODUCTION

Carbonatites are enigmatic magmatic rocks whose origin has been discussed extensively (e.g., Tuttle and Gittins, 1966; Bell, 1989). Based on experimental data, the crystallization of carbonatite magma is strongly dependent on the composition of the co-existing fluid phase (Wyllie, 1966 and 1989). The early magmatic features of carbonatites, however, are easily destroyed and disturbed by post-magmatic re-equilibration processes (e.g., Andersen, 1984). Thus, the early formed crystals (i.e., zircon and apatite) probably carry the best evidence for early processes and associated fluids in carbonatites. Various studies on fluid inclusions in minerals from carbonatites and rocks closely associated with them are reported in the literature (see reviews by Roedder, 1984 and 1992). Compositions of fluid inclusions range from hydrous saline melts to simple gas/liquid aqueous and apparently pure CO, inclusions. This paper gives a description of fluid inclusions found in zircon and apatite from the Siilinjärvi carbonatite complex, eastern Finland. The aim is to establish their status (pre- to post-emplacement) during the evolution of the complex and to characterize the PTX-conditions in which they formed. To the author's knowledge, this is the first paper in which fluid inclusion evidence from the early phase of carbonatite magma evolution is based on a detailed study of fluid inclusions in zircon.

## **GEOLOGIC SETTING**

The geology of the Siilinjärvi carbonatite complex has been described by Puustinen (1971, 1972, 1973 and 1974) and Härmälä (1981), so that only a few pertinent features are discussed here. It is located ca. 20 km N of the city of Kuopio, eastern Finland. The carbonatite intruded into the southern Archean terrain (Fig. 1a) soon after its consolidation. The sequence of intrusion of the complex began with an ultramafic phase (glimmerite). The carbonatite (sövite) was emplaced, probably in several intrusion phases, into pre-existing ultramafic rocks giving a U-Pb zircon age of ca. 2.6 Ga (published by the Geological Survey of Finland 1978). The Hf and Sr-Pb isotopic ratios from zircon plot close to the chondritic growth curve (Patchett et al., 1981) and very close to the model bulk Earth ratio (Tilton and Bell, 1994), respectively. This implies rapid intrusion of the rocks through the sialic crust to the surface - probably along a large fissure - with neglible contamination. The complex forms a N-S running subvertical and tabular body in the surrounding granite gneiss. It consists of glimmerite and a series of mixed rocks together with carbonatite, carbonatite, diabase and various dike rocks (Fig. 1b). The margins of the complex are fenitized, and fenitized granite gneiss xenoliths are found in the glimmerite-carbonatite rocks. The low metamorphic grade of the glimmerite-carbonatite rocks is indicated by the preservation of dolomite exsolution textures in calcite and the lack of carbonate-silicate reactions. The composition of dolomite-calcite pairs suggests an average minimum equilibration temperature of 450°C (Puustinen, 1974). The complex was deformed by the 1.9 Ga Svecofennian orogeny. The characteristic features of the complex are briefly: elongated form, age, composition of the ultramafic phase (i.e., glimmerite), presence of mixed rocks and the absence of rare minerals.

#### ZIRCON AND APATITE

Zircon phenocrysts occur mostly in the alkali amphibole-rich parts of the glimmerite. They are rare in the carbonatite. The zircon crystals contain 1.21% hafnium (Puustinen, 1971). They are euhedral in form, brownish-red in colour and up to several centimeters in the longest dimension. In ultraviolet light, they have an orange fluoresence. In the studied zircon crystal from glimmerite (Fig. 2), there is an apparent rounded core possibly of older zircon, inherited either from a mantle magma source region or from a crustal source. The crystal is also intensively fractured, especially in the core region.

Apatite is not associated with any specific rock type of the glimmerite-carbonatite series. However, the apatite content is highest in the carbonate-rich



Fig.1. A. Location of the Siilinjärvi carbonatite complex in relation to the Svecofennian (SD), Archean (AD), and to the Raahe-Ladoga tectonic zone (TZ, modified after Kinnunen, 1991). B. General geology of the complex (modified after Puustinen, 1971).



Fig. 2. Euhedral zircon crystal, sectioned parallel to the crystallographic  $\underline{c}$ -axis, showing intense fracturing and a rounded apparent core of possibly older zircon.

sövites. Apatite phenocrysts occur as green or yellowish-green prisms (up to several centimeters long), single euhedral crystals (up to 56 cm in diameter) or as light green irregular grains and grain aggregates in the glimmerite-carbonatite rocks. The mineral is a cerian-type fluor-apatite, which contains an average of 0.4% lanthanides (Puustinen, 1971). The studied apatite crystals come from sövite.

## **METHODS**

Microthermometric measurements were made using Linkam THMSG 600 programmable heating-freezing stage and Linkam TH 1500 high temperature stage. Both stages were calibrated with a set of synthetic fluid inclusion standards (see Sterner and Bodnar, 1984). All measurements were made on doubly-polished thin sections of 0.2 to 0.5

Table 1. Fluid inclusion characteristics.

Inclusion type	Туре 1		Type 2		
Paragenetic classification	Pseudosecondary (1a)	Secondary (1b)	Pseudosecondary (2a)	Secondary (2b)	Secondary (2c)
Mineral	Zircon	Zircon	Zircon and apatite	Zircon	Apatite
Phases at Troom	$H_2O+CO_2(1)$ ±solids	$H_2O+CO_2(1)+CO_2(v)$	H <sub>2</sub> O+vapour bubble	H <sub>2</sub> O+vapour bubble+solids	H <sub>2</sub> O+vapour bubble
Shape	Negative crystal to tubular	Rounded to negative crystal	Negative crystal to tubular	Tubular or irregular	Irregular
Occurrence	Near the core	Near the core	Outside the core in zircon	Randomly orientaded healed fractures	With carbonate inclusions
Daughter (captive?) minerals	Rare apatite and other solids			Carbonate, apatite, Na-K chlorides, baryte, magnetite	

mm thickness. In the temperature interval of -60 to 400°C, the recorded temperatures of phase transitions have a precision of  $\pm 0.2$  to 2.0°C, respectively. The crushing-stage test (see Roedder, 1970) using glycerol and acidified (HCl) glycerol as a mounting medium was used in order to detect possible non-condensable gases and carbonate daughter minerals in aqueous inclusions. Some fluid inclusions in zircon were cracked open to allow daughter minerals to be identified using SEM-EDS (see e.g., Metzger et al., 1977).

#### FLUID AND SOLID INCLUSIONS

In the studied crystals, data recorded at least two compositional types of fluid inclusions in zircon, only one compositional type in apatite and some solid inclusions in both minerals. A distinction is made between  $CO_2$ -bearing (Type 1) and pure aqueous inclusions (Type 2). This classification does not carry any genetic implications. Fluid inclusions are further subdivided into pseudosecondary and secondary inclusions (Table 1). The criteria used for distinguishing pseudosecondary and secondary inclusions were those given by Roedder (1984).

Zircon

*Type 1.* Two or three visible phases are present at room temperature: water, liquid CO<sub>2</sub> and vapour

CO<sub>2</sub>. The longest dimension of the inclusions ranges from 5 to 30 µm. The visually estimated volume of the CO, phase varies from approximately 70 to 90 vol.%. Pseudosecondary Type 1a inclusions occur sparsely, oriented in small, almost regular, isolated groups and show negative crystal shapes (Fig. 3a). In some inclusions, hexagonal apatite (diameter 2-5 µm) occurs as a rare daughter mineral. Secondary Type 1b inclusions occur either isolated (Fig. 3b) or in small groups (Fig. 3c), with rounded to negative crystal shapes. The thin water film is sometimes difficult to see due to the black borders of the inclusions. Some inclusions exhibit post-entrapment re-equilibration features (i.e., decrepitation, fractures). No daughter minerals were observed. Very rare multiphase Type 1 inclusions (Fig. 3d) with variable phase ratios were also recorded. The inclusions of this type have an aqueous fraction with a CO<sub>2</sub>-liquid bubble (ca. 5 to 70 vol.%) but are characterized by numerous daughter and captive (?) minerals of colorless birefringent and non-birefringent solids. The inclusions occur in small groups and range in size from 5 to 60 µm. The shape is usually rounded, but some larger inclusions are tubular and aligned parallel to the c-axis of the zircon. This suggests their pseudosecondary origin. The distribution of the inclusions in zircon is transitional between the pseudosecondary Type 1a and Type 2a inclusions. Only a few measurements were carried out on this type.

*Type 2*. Two visible phases are present at room temperature: H<sub>2</sub>O-rich aqueous liquid and vapour.



Fig. 3. Fluid inclusions in zircon. A. Pseudosecondary Type 1a  $H_2O$ - $CO_2$  inclusions. B. Secondary Type 1b  $H_2O$ - $CO_2$  inclusions. C. A group of secondary Type 1b  $H_2O$ - $CO_2$  inclusions. D. Multiphase Type 1  $H_2O$ - $CO_2$  inclusions. E. Pseudosecondary Type 2a aqueous inclusions. F. Secondary multiphase Type 2b inclusion. The scale bar is 50µm.

The vapour phase occupies ca. 10 vol.% of the inclusion volume. The longest dimension of the inclusions is  $3-70 \,\mu\text{m}$ . The mode of occurrence of pseudosecondary Type 2a inclusions (Fig. 3e) is

similar to that of Type 1a inclusions. No daughter minerals were encountered. Secondary Type 2b inclusions occur in regular planes and healed fractures with tubular to rounded and irregular



Fig. 4. The SEM-EDS produced spectra for apatite (A) and Na-K chlorides (B). They occur as daughter minerals in secondary Type 2b aqueous inclusions in zircon.



Fig. 5. Spatial relationship of Type 1  $H_2O$ - $CO_2$  and Type 2  $H_2O$  inclusions in the studied zircon crystal.

shapes. They may contain various daughter and captive minerals (Fig. 3f). Using a combination of SEM-EDS, optical characteristics and crushing-stage, calcite, apatite, phlogopite, baryte,

halite, sylvite and magnetite were identified. The SEM-EDS produced spectra for apatite and Na-K-chlorides are shown in Fig. 4. Usually, the size of daughter minerals range from ca. 2 to 5  $\mu$ m. On some inclusion walls, non-crystalline Na-K-Cl precipitates were recorded.

In the studied zircon crystal, the distribution of Type 1 and Type 2 inclusions is shown in Fig. 5. The observed fluid inclusion types occur mainly in separate domains: around (Type 1) and outside (Type 2) the apparent core. The Type 2b inclusions form a network of healed fractures, some of which transect the core.

Zircon contains very little solid inclusions: single apatite crystal (diameter ca. 1 mm), calcite as irregular inclusions and as fracture filling together with minor baryte.

#### Apatite

*Type 2.* Two visible phases are present at room temperature:  $H_2O$ -rich aqueous liquid and vapour. The vapour phase occupies 5 to 10 vol.% of the inclusion volume. Pseudosecondary Type 2a inclusions are extremely rare and only two isolated

groups showing tubular and negative crystal shapes were found. The longest dimension of the inclusions ranges between 3 and 20  $\mu$ m. No daughter minerals were found. Thus, they are similar to Type 2a inclusions encountered in zircon. Secondary Type 2c inclusions are associated with minute carbonate inclusions. They are irregular in shape and have diameters from 5 to 60  $\mu$ m. No daughter minerals were observed.

Solid inclusion content of apatite varies greatly. It depends on the size and the degree of deformation of the host rock. In the sheared host rock, long apatite prisms contain more solid inclusions than the smaller apatite grains and grain aggregates in the less deformed rocks. Most of them are almost completely devoid of any kind of inclusions (fluid or solid). Single inclusions of carbonates occur in the apatite as rounded and elongated crystals of ca. 5 to 100  $\mu$ m in size. They are oriented either with their longest axis parallel to the apatite's crystallographic <u>c</u>-axis, parallel to the 0001-cleavage, or more or less randomly. Sometimes, carbonate inclusions form a halo around the <u>c</u>-axis. The most common carbonate solid

inclusion is dolomite (Härmälä, 1981). Calcite and opaques occur as minor inclusions.

#### **MICROTHERMOMETRY**

The microthermometric measurements summarized in Table 2 are based on several polished plates made from zircon and apatite. A total of 157 fluid inclusions were studied in the temperature range of -196 to 1000°C. The reduction of laboratory microthermometric data was made using the computer program FLINCOR (Brown, 1989).

## Zircon

*Type 1.* Melting of the carbonic phase  $(T_mCO_2)$  occurred in the range of -56.6 to -57.6°C (Fig. 6a). These temperatures indicate virtually pure CO<sub>2</sub>, possibly with minor CH<sub>4</sub> or N<sub>2</sub>. Homogenization of the carbonic phases  $(T_hCO_2)$  to liquid was observed between +10.8 and +27.5 °C (Fig. 6b). The clathrate melting  $(T_mCla)$  temperatures vary from +8.1 to +9.4°C (Fig. 6c), which is equivalent to 1.2 -3.7

Table 2. Microthermometric data (C°),	composition and density	of fluid inclusions in	n zircon (z) and apatite (a	1).

Inclusion typ	e Type 1a (z)	Type 1b (z)	Type 2a (z)	Type 2b (z)	Type 2a (a)	Type 2c (a)
T <sub>m</sub> CO <sub>2</sub>	-57.1 to -57.6	-56.6 to -56.8				
T <sub>m</sub> Cla	8.1 to 8.6	9.1 to 9.4				
T <sub>h</sub> CO <sub>2</sub>	10.8 to 19.1 (L)	17.7 to 27.5 (L)				
Th H2O-CO	2 244 to 269 (V)	234 to 277 (V)				
Te			-25 to -30	-24 to -31	-30	-23 to -35
T <sub>m</sub> H <sub>2</sub> O			-8.9 to -14.5	-8.7 to -12.7	-12.2 to -14.4	-5.5 to -11.8
T <sub>h</sub> H <sub>2</sub> O			302 to 367 (L)	234 to 287 (L	.) 322 to 344 (L)	148 to 221 (L)
eq.wt.%NaCl	2.8 to 3.7	1.2 to 1.8	12.7 to 18.2	12.5 to 16.6	16.1 to 18.1	8.5 to 15.8
dCO <sub>2</sub>	0.78 to 0.86	0.67 to 0.80				
dH <sub>2</sub> O-CO <sub>2</sub>	0.79 to 0.87	0.73 to 0.86				
dH <sub>2</sub> O			0.83 to 0.89	0.89 to 0.95	0.86 to 0.88	0.93 to 1.02
Mole fraction	IS					0.00 10 1.02
X <sub>H2O</sub>	0.125 to 0.558	0.146 to 0.579	0.94 to 0.96	0.94 to 0.96	0.94	0.95 to 0.97
X <sub>NaCl</sub>	0.002 to 0.005	0.001 to 0.004	0.04 to 0.06	0.04 to 0.06	0.06	0.03 to 0.05
X <sub>CO2</sub>	0.44 to 0.87	0.42 to 0.85				
Abbreviations	used:					
TmCO2	Melting of CO2			Te Tem	perature of eutectic melt	ing
TmCla	Melting of clathrate			Tm H <sub>2</sub> O Melt	ting of ice	
ThCO2	Homogenization of CO	2 to liquid (L)		Th H <sub>2</sub> O Hon	nogenization of H <sub>2</sub> O to	liquid (L)
T <sub>h</sub> H <sub>2</sub> O-CO <sub>2</sub>	Total homogenization	of $H_2O$ and $CO_2$ to v	apour (V)	d fluid	l density g/cm <sup>3</sup>	

eq.wt.% NaCl. Total homogenization ( $T_h$ Tot) of the inclusions to gas was measured between 232 and 283°C (Fig. 7).

The pseudosecondary Type 1a inclusions have lower  $T_mCO_2$ ,  $T_hCO_2$  and  $T_mCla$  than the secondary Type 1b inclusions. This indicates some minor impurities in the  $CO_2$  phase, higher  $CO_2$  density and slightly more saline fluid for the Type 1a inclusions.

Type 2. The apparent eutectic  $(T_{a})$  temperature (i.e., first melting) was observed between -24 and -31°C (Fig. 8a). These low temperatures require other dissolved salt components (e.g., K, Mg and Ca) besides NaCl. Melting temperatures of ice (T<sub>m</sub>ice) range between -8.7 to -14.5°C (Fig. 8b), corresponding to salinities from 12.5 to 18.2 eq.wt.% NaCl. On an average, the salinity of Type 2b inclusions is somewhat lower than that of Type 2a inclusions. The lack of a visible CO, phase and the inability to nucleate clathrate phase on cooling suggest the presence of <0.85 molal CO<sub>2</sub> or CH<sub>4</sub> (Hedenquist and Henley, 1985). It should be noted, however, that in spite of the absence of free CO<sub>2</sub>, the presence of solid carbonates as daughter minerals in the Type 2b inclusions indicates that the fluid was saturated or nearly saturated with ionic carbonate species at the time of trapping. Homogenization (T, H<sub>2</sub>O) of the Type 2a and Type 2b inclusions to liquid took place at temperatures from 302 to 367°C and from 234 to 287°C (Fig. 7), respectively.

#### Apatite

*Type 2.* The first melting ( $T_e$ ) of the inclusions was observed between -23 and -35°C. The  $T_m$  ice of the Type 2a and Type 2c inclusions varies from -12.2 to -14.4°C and from -5.5 to -11.8°C (Fig. 9a), corresponding to salinities from 16.1 to 18.1 and from 8.5 to 15.8 eq.wt.% NaCl, respectively. The  $T_hH_2O$  to liquid ranges from 322 to 344°C (Type 1a) and from 148 to 221°C (Type 2c, Fig. 9b).

In the apatite and zircon, the pseudosecondary Type 2a inclusions have a similar range of salinity and  $T_hH_2O$ , whereas the secondary Type 2b and Type 2c inclusions do not. The Type 2c inclusions have a clearly lower range of  $T_hH_2O$  and salinity



Fig. 6. Frequency-temperature histograms of fluid inclusion microthermometric data (zircon). A. Carbonic phase melting temperature. B. Carbonic phase homogenization temperature. C. Clathrate dissociation temperature.



Fig. 7. Frequency-temperature histogram of total fluid homogenization temperature (Type 1) and liquid-vapour to liquid homogenization temperature of Type 2 inclusions in zircon.



Fig. 8. Frequency-temperature histograms of apparent eutectic (A) and ice melting temperatures (B) of Type 2 inclusions in zircon. The eutectic temperatures of the NaCl-KCl-H<sub>2</sub>O (-22.9 °C) and NaCl-MgCl<sub>2</sub>-H<sub>2</sub>O (-35 °C) are shown for reference (Crawford, 1981).

than those of Type 2b inclusions in zircon.

The compiled homogenization and density versus salinity plots for the Type 1 and Type 2 inclusions in both zircon and apatite are presented in Figs. 10 and 11.

## High temperature heating studies

High temperature heating studies were only

conducted on pseudosecondary Type 1 multiphase inclusions (Fig. 3d) in zircon. The chosen inclusions did not contain any extremely large solid phases which were obviously trapped. A chip (1.0x1.5mm) from a normal doubly polished zircon plate was used for the study. Heating was done using the Linkam TH 1500 stage. The inclusions were heated stepwise up to 1000°C at 50 and 100°C intervals and held at the pre-determined temperature for



Fig. 9. Frequency-temperature histograms of ice melting (A) and liquid-vapour to liquid homogenization temperatures (B) of pseudosecondary Type 2a and secondary Type 2c inclusions in apatite.

between ten minutes and one hour. These times are obviously insufficient for complete equilibration of the contents at any given temperature. Heating rates from 5 to  $2^{\circ}$ C/min were used.

The sequence of phase changes during heating is given in Fig. 12. The vapour bubble disappeared at 360°C. The bulk of the solids dissolved before that temperature. During further slow heating, almost complete homogenization and sudden re-crystallization on the inclusion walls occurred at 970°C. Only one solid phase remained undissolved. In other inclusions, some solids disappeared between 580 and 680°C. When cooled to room temperature, the fluid phase consisted of CO<sub>2</sub> vapour with no visible amount of water. Thus, preferential leakage of water must have occurred, though there is not any visible sign of it. Some inclusions decrepitated between 600 and 700°C. A group of new minute inclusions developed away from the leaked inclusion.

## DISCUSSION OF RESULTS

#### Pressure and temperature of trapping

The composition and density relations summarized in Fig. 11 were used to calculate isochores for the fluid inclusions using the program FLINCOR (Brown, 1989). The resulting isochores are illustrated in Fig. 13. The isochores for the pseudosecondary Type 1a and Type 2a inclusions pass through the P-T field limited by the eutectic temperature of calcite carbonatite melt ( $625^{\circ}$ C), and the minimum pressure (4 kbar) for the liquidus assemblage calcite+dolomite+H<sub>2</sub>O-CO<sub>2</sub> fluid



Fig. 10. Diagram showing homogenization temperature  $(T_h)$  versus salinity in Type 1 and Type 2 inclusions of both zircon and apatite. Salinity of Type 2 inclusions decreases with decrease in  $T_h$ , corresponding to pseudosecondary (2a) and secondary (2b and 2c) inclusions.



Fig. 11. Diagram showing fluid density versus salinity derived from the microthermometric data presented in Figs. 6-9. Density of Type 2 inclusions in both zircon and apatite increases with decrease in salinity, corresponding to pseudosecondary (2a) and secondary (2b and 2c) inclusions.



Fig. 12. Heating study of multiphase Type 1 inclusion in zircon. The sequence of phase changes drawn at different temperatures (A-J), has been reproduced from images captured by a Mitsubishi video copy processor. Abbreviations: cp = captivemineral, dm= daughter mineral, lq= liquid, v=vapour, rs= re-crystallized solid, s =solid.

Fig. 13. P-T diagram showing sets of isochores for the Type 1 and Type 2 pseudosecondary (1a and 2a) and secondary (2b and 2c) inclusions encountered in zircon and apatite. A P-T field limited by the carbonatite eutectic ( $625 \,^{\circ}$ C) and the minimum pressure (4 kbar) for the liquidus assemblage calcite+dolomite +H<sub>2</sub>O-CO<sub>2</sub> (Wyllie, 1966), is shown for reference (see text for further explanation).



(Wyllie, 1966). In zircon and apatite, the isochores of the Type 2a inclusions fall within the same sector. None of the isochores cross the P-T field of the final, obviously shallow crustal emplacement of the carbonatite (1 to 2 kbar) at temperatures above the experimental solidus (625°C). The fluid inclusion data thus suggest that the pseudosecondary Type 1a and Type 2a inclusions in zircon and apatite were trapped during the pre-emplacement evolution of the carbonatite at mid-crustal conditions ( $P \ge 4$  kbar,  $T \ge 625^{\circ}$ C). This is also supported by the high liquidus temperature (970°C) of multiphase Type 1 inclusions in zircon. The minimum pressure of 4 kbar would correspond to a crustal depth of at least 14 km. Fluid inclusion evidence for the Fen carbonatite complex (Norway) also demonstrates the mid-crustal origin for the apatite (Andersen, 1986). Haapala (1980) obtained evidence for high

P-T conditions (ca. 4.5 kbar and 600°C) for the apatite from the Sokli carbonatite.

The Type 1 H<sub>2</sub>O-CO<sub>2</sub> inclusions pre-date the Type 2 aqueous inclusions, as indicated by their mode of occurrence in zircon. This implies a change in fluid composition. According to experimental data (Wyllie, 1966), a fluid phase in equilibrium with a cooling carbonatite melt crystallizing solid carbonates would be greatly enriched in water (98-99% H<sub>2</sub>O at the CaCO<sub>3</sub>-MgCO<sub>3</sub>-H<sub>2</sub>O eutectic). This explains the lack of Type 1 inclusions in apatite. Furthermore, apatite crystallized later than zircon. The occurrence of minute apatite daughter crystal in some of the Type 1 H<sub>2</sub>O-CO<sub>2</sub> inclusions indicates beginning of apatite crystallization before calcite. During the early stage of crystal fractionation, multiphase Type 1 inclusions were trapped in zircon. They represent heterogeneous trapping of crystallized solids and enclosing fluid. Apatite and calcite co-exist in the secondary Type 2b inclusions. They were trapped during emplacement of the carbonatite into the pre-existing glimmerite, causing intense fracturing of zircon and re-equilibration of some Type 1a inclusions (now Type 1b). Thus, during crystal fractionation and subsequent compositional change in the cooling carbonatite magma, the Type 1 fluid was depleted in CO, and enriched in water and alkalies (i.e., towards higher salinity). The alkalies were partitioned into the aqueous phase interacting with the carbonatite melt because of their higher solubilities in water. Fenitization of the country rock and the country rock xenoliths was obviously induced by these saline aqueous fluids. This is supported by the presence of Type 2 inclusions. It is assumed that all these inclusions in zircon and the very few pseudosecondary inclusions in apatite have a magmatic origin.

Phlogopite-apatite geothermometer (Stormer and Carmichael, 1971) yields a crystallization temperature range of ca. 300 to 420°C for the apatite, calculated from the chemical composition of apatite and phlogopite from glimmerite (Puustinen, 1971). This temperature range is well below the experimental eutectic temperature of 635°C for the system calcite+apatite+H<sub>2</sub>O (Biggar, 1969).

However, apatite and calcite may co-crystallize over a wide range of temperatures and pressures, and they may also co-exist with liquid at temperatures below 600°C. There is also a possibility that this temperature range (i.e., 300 to 420°C) refers to the post-crystallization re-equilibration conditions of apatite during the regional metamorphism ca. 1.9 Ga ago. Late-stage fluorine and hydroxyl exchange may have occurred at low metamorphic temperatures with an aqueous fluid, mainly affecting the mica.

Single crystals and trails of calcite inclusions completely sealed within the apatites are thought to result from the trapping of already precipitated crystals of calcite. They often occur side-by-side with the secondary Type 2c aqueous inclusions in the same apatite crystal. It is concluded from these observations that these calcites co-existed with the aqueous fluid during fracturing and re-crystallization of the apatites. This fluid may also be responsible for the transport and deposition of at least some of the calcite. Malinin and Dernov-Pegarev (1974) showed that appreciable quantities of calcite can be transported by alkali-carbonate solutions, even at low temperatures (200-350°C). Unfortunately, it was not possible to obtain direct fluid inclusion evidence for the formation conditions of calcite. Obviously, these secondary Type 2c inclusions in apatite have a metamorphic origin.

Re-crystallization of apatite to granular aggregates took place either during emplacement of the magma to their present position, or more probably during the later metamorphism. This together with deformation would explain the scarcity of fluid inclusions in apatite.

ACKNOWLEDGEMENTS: I wish to thank H. Kauppinen for providing the zircon samples and especially O. Härmälä for guiding me in the Siilinjärvi open pit and for help in locating additional proper apatite samples for the study. Excellent polished sections were prepared by L. Rämö. I am grateful also to J. Juhanoja of the Department of Electronmicroscopy for his genereous technical help with the SEM-EDS. P. Salonsaari assisted me in the geothermometric calculations of apatite. The paper also benefited from reviews by S. Lindblom, K. A. Kinnunen and I. Haapala.

## REFERENCES

- *Andersen, T.*, 1984. Secondary processes in carbonatites: petrology of "rödberg" (hematite-calcite-dolomite carbonatite) in the Fen central complex, Telemark (South Norway). Lithos 7, 227-245.
- Andersen, T., 1986. Magmatic fluids in the Fen carbonatite complex, S.E. Norway. Evidence of mid-crustal fractionation from solid and fluid inclusions in apatite. Contributions to Mineralogy and Petrology 93, 491-503.
- *Bell, K.* (ed.)., 1989. Carbonatites-Genesis and Evolution. Unwin Hyman. 618pp.
- Biggar, G.M., 1969. Phase relationships in the join  $Ca(OH)_2$ - $CaCO_3$ - $Ca_3(PO_4)_2$ - $H_2O$  at 1000 bars. Mineralogical Magazine 37, 75-82.
- Brown, P.E., 1989. FLINCOR: A microcomputer program for the reduction and investigation of fluid inclusion data. American Mineralogist 74, 1390-1393.
- *Crawford, M.L.*, 1981. Phase equilibria in aqueous inclusions. Mineralogical Association of Canada Short Course Handbook 6, 75-100.
- *Geological Survey of Finland*, 1978. Annual Report on the Activities for the Year 1977, 76pp.
- *Hedenquist, J.W. and Henley, R.W.* 1985. The importance of CO<sub>2</sub> on freezing point measurements of fluid inclusions: Evidence from active geothermal systems and implications for epithermal ore deposition. Economic Geology 80, 1379-1406.
- *Haapala, I.*, 1980. Fluid inclusions in the apatite of the Sokli carbonatite, Finland A preliminary report. Geologi 32, 83-87.
- Härmälä, O., 1981. Siilinjärvi apatite mine: Mineralogy and concentration properties of the ore. Unpublished MSc-thesis. Department of Geology, University of Turku. 121pp. (in Finnish).
- *Kinnunen, K.*, 1991. Fluorescent minerals in Finland. Geological Survey of Finland, Special Paper 12, 225-229.
- *Malinin, S.D. and Dernov-Pegarev, V.F.* 1974. Investigation of calcite solubility in K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions at temperatures of 200-350°C. Geokhimiya 3, 454-455.
- Metzger, F.M., Kelly, W.C., Nesbitt, B.E. and Essene, E.J., 1977. Scanning electron microscopy of daughter minerals in fluid inclusions. Economic Geology 72, 141-152.

- Patchett, P.J., Kouvo, O., Hedge, C.E. and Tatsumoto, M., 1981. Evolution of continental crust and mantle heterogeneity: Evidence from Hf isotopes. Contributions to Mineralogy Petrology 78, 279-297.
- Puustinen, K., 1971. Geology of the Siilinjärvi carbonatite complex, eastern Finland. Bulletin de la Commission Géologique de Finlande 249, 43pp.
- *Puustinen, K.*, 1972. Richterite and actinolite from the Siilinjärvi carbonatite complex, Finland. Bulletin of the Geological Society of Finland 44, 83-86.
- *Puustinen, K.*, 1973. Tetraferriphlogopite from the Siilinjärvi carbonatite complex, Finland. Bulletin of the Geological Society of Finland 45, 35-42.
- *Puustinen, K.*, 1974. Dolomite exsolution textures in calcite from the Siilinjärvi carbonatite complex, Finland. Bulletin of the Geological Society of Finland 46, 151-159.
- *Roedder, E.*, 1970. Application of an improved crushing microscope stage to studies of the gases in fluid inclusions. Schweizerische Mineralogische und Petrographische Mitteilungen 50, 41-58.
- *Roedder, E.*, 1984. Fluid inclusions. Reviews in Mineralogy 12. Mineralogical Society of America. 644pp.
- *Roedder, E.*, 1992. Fluid inclusions evidence for immiscibility in magmatic differentiation. Geochimica et Cosmochimica Acta 56, 5-20.
- Stormer, J.C. and Carmichael, S.E., 1971. Fluorinehydroxyl exchange in apatite and biotite: A potential igneous geothermometer. Contributions to Mineralogy and Petrology 31, 121-131.
- *Tilton, G.R. and Bell, K.*, 1994. Sr-Nd-Pb isotope relationships in Late Archean carbonatites and alkaline complexes: Applications to the geochemical evolution of Archean mantle. Geochimica et Cosmochimica Acta 58, 3145-3154.
- *Tuttle, O.F. and Gittins, J.* (eds.) 1966. Carbonatites. Interscience. 591pp.
- Wyllie, P.J., 1966. Experimental studies of carbonatite problems: The origin and differentiation of carbonatite magmas. In: Tuttle, O.F. and Gittins J. (eds), Carbonatites. Interscience, New York, 311-352.
- *Wyllie, P.J.*, 1989. Origin of carbonatites: evidence from phase equilibrium studies. In: Bell, K. (ed.), Carbonatites-Genesis and Evolution, Unwin Hyman, 500-545.