Roger H. Mitchell · Bruce A. Kjarsgaard

# Solubility of niobium in the system CaCO$_3$–Ca(OH)$_2$–NaNbO$_3$ at 0.1 GPa pressure

**Abstract** Experimental data are presented for the solubility of NaNbO$_3$ in the ternary system CaCO$_3$–Ca(OH)$_2$–NaNbO$_3$ (or calcite–portlandite–lueshite) over the temperature range 500–950 °C at 0.1 GPa pressure. Near-liquidus phase relationships are given for the pseudo-binary join ([CaCO$_3$]$_{45}$[Ca(OH)$_2$]$_{55}$)$_{100-x}$–(NaNbO$_3$)$_x$; (0 < $x$ < 70 wt%). These data show the presence of a large field of calcite plus liquid and the absence of NaNbO$_3$ as a primary liquidus phase until the melts contain greater than 60 wt% NaNbO$_3$. The primary crystallization fields of calcite and NaNbO$_3$ are separated by a steep thermal valley located at about 55 wt% NaNbO$_3$. Quenched liquids contain calcite, portlandite, sodium carbonates and perovskite-structured calcium niobates. The maximum solubility of Nb$_2$O$_5$ in this system is estimated to be on the order of 48 wt% at 650 °C at 0.1 GPa pressure. The experiments show that perovskite-structured compounds rather than pyrochlore crystallize from these fluorine-free, water-rich melts.

## Introduction

Carbonatites and genetically-related silicate–carbonate rocks are the principal sources of niobium. Within these rocks niobium is sequestered principally in oxide minerals such as niobian perovskite (Ca,Na)(Ti,Nb)O$_3$ and latrappite (Ca,Na)(Ti,Nb,Fe)O$_3$ (Mitchell et al. 1998) or the pyrochlore–microlite solid solution series

R.H. Mitchell (✉)
Department of Geology, Lakehead University,
955 Oliver Road, Thunder Bay,
Ontario P7B 5E1, Canada
E-mail: rmitchel@gale.lakeheadu.ca

B.A. Kjarsgaard
Geological Survey of Canada, 601 Booth St.,
Ottawa, Ontario K1A 0E8, Canada

Editorial responsibility: I. Parsons

(Ca,Na)$_2$(Nb,Ta)$_2$O$_6$(OH,F). In some carbonatites, e.g. Prairie Lake (Ontario), Oka (Quebec), Nb-bearing silicates such as wöhlerite [NaCa$_2$(Zr,Nb)Si$_2$O$_7$] and niocalite [Ca$_{14}$Nb$_2$(Si$_2$O$_7$)$_4$O$_6$F$_2$] are common and may coexist, though not necessarily in equilibrium, with pyrochlore or perovskite (Mariano 1989). The perovskite group mineral lueshite (NaNbO$_3$) is known from late-stage carbothermal veins at the Lueshe complex, Democratic Republic of Congo (Safiannikoff 1959). Lueshite is also rarely observed in a primary magmatic carbonatite association, e.g. apatite dolomite carbonatite at Lesnaya Varaka (Russia), and in the Kovdor, Sallanlatvi and Gem Park complexes (Chakhmouradian and Mitchell 1998). The paragenesis of lueshite in the magmatic association is not well documented, although at Lesnaya Varaka, lueshite is replaced by late-stage pyrochlore.

Outstanding problems in understanding niobium mineralization in carbonatites include determination of the factors controlling the crystallization of Nb-bearing perovskite versus pyrochlore and explaining why lueshite is not a typical primary mineral. Some advances in understanding these factors have been made by experimental studies of the Nb-bearing synthetic or haplocarbonatite systems described below. The experimental data reported in this paper for the join ([CaCO$_3$]$_{45}$[Ca(OH)$_2$]$_{55}$)$_{100-x}$–(NaNbO$_3$)$_x$, (0 < $x$ < 70 wt%) build upon the earlier work of Jago and Gittins (1993), and Mitchell (1997), and represent the first of a series of studies of joins in the quaternary system calcite–portlandite–fluorite–lueshite. The objective is to determine the solubility of Nb and understand the control that composition and temperature have upon the character of the niobium-bearing phases crystallizing from haplocarbonatite liquids. Of particular interest is the effect of F and H$_2$O in the melt on Nb solubility.

## Previous experimental work

Initial studies of the systems CaCO$_3$–Ca(OH)$_2$–Nb$_2$O$_5$ by Watkinson (1970) and CaO–Nb$_2$O$_5$ (Ibrahim et al.

1962) suggested that up to 5 wt% $Nb_2O_5$ was soluble in Ca-rich liquids. Subsequently, Beckett (1987) determined that the solubility of pyrochlore is extremely low in melts at the binary eutectic in $CaCO_3$–$Ca(OH)_2$ and in alkali-rich carbonate liquids in the system $Na_2CO_3$–$CaCO_3$–pyrochlore. A maximum solubility of pyrochlore ($<1$ wt%) was found only for a $CaF_2$-rich (–30 wt%) composition near the ternary eutectic in the system $CaCO_3$–$Ca(OH)_2$–$CaF_2$. Jago and Gittins (1993), in an attempt to resolve these discrepancies, investigated parts of the systems $CaCO_3$–$Ca(OH)_2$–$Nb_2O_5$, $Na_2CO_3$–pyrochlore, $Na_2CO_3$–$CaCO_3$–pyrochlore–F, and nyerereite [$CaNa_2(CO_3)_2$]–pyrochlore–F. Jago and Gittins (1993) concluded that up to 7.5 wt% $Nb_2O_5$ might be soluble in melts in the system $CaCO_3$–$Ca(OH)_2$–$Nb_2O_5$. They further noted that in anhydrous systems containing $Na_2CO_3$, increasing alkalies result in a drastic decrease in Nb solubility to $<0.75$ wt% because of the enhanced stability of lueshite. Jago and Gittins (1993) conclude that in fluorine-free anhydrous systems Nb in not very soluble and precipitates as lueshite or niobian perovskite. Preliminary experiments in the system $CaCO_3$–$Ca(OH)_2$–$NaNbO_3$ (Mitchell 1997) indicated that lueshite is not a stable liquidus phase at 700 °C at 0.1 GPa pressure in compositions containing up to 60 wt% $NaNbO_3$. Diverse Na–Ca-niobates were encountered amongst the phases forming from quenched liquids. These data suggested that the solubility of Nb in Na-bearing haplocarbonatites might be much higher than determined by Jago and Gittins (1993).

## Experimental procedures

All starting compositions were prepared by mixing dried (110 °C) analytical grade compounds under alcohol in an agate mortar. Experimental charges were made by adding various amounts of $NaNbO_3$ to the 0.1-GPa eutectic composition, $CC_{45}CH_{55}$ (Wyllie and Tuttle 1960), in the binary system $CaCO_3$–$Ca(OH)_2$ or [CC–CH]. All experiments were conducted in 3-mm-diameter Au tubes, which had been previously degreased with alcohol, cleaned in HCl and annealed.

Approximately, 0.05–0.10 g of the starting mixture was loaded into the gold tubes, which were sealed by arc-welding. Experiments were performed at a pressure of 0.1 GPa, over the temperature interval 950–500 °C. The experimental charges were run in Tuttle-type, externally-heated pressure vessels in the experimental laboratory of the Geological Survey of Canada, Ottawa. A few additional experiments at 950 and 900 °C were performed in a rapid-quench, externally-heated vessel. Argon was used as pressure medium for all experiments. Run times varied from 4 to 144 h. Temperature was measured with a thermocouple located in a well at the base of the pressure vessel. A temperature correction was employed based on calibration with an internal thermocouple. Reported temperatures are considered to be accurate to $\pm 5$ °C. Pressure was measured using a Bourdon tube gauge (Astrogauge), calibrated against a Heise laboratory standard gauge and is thought to be accurate to $\pm 0.02$ GPa. Samples were quenched at the end of the run by a jet of compressed air. Quenching rates for the Tuttle-type vessels were on average 300 °C/min for the first minute.

Experimental products were characterized at Lakehead University by back-scattered electron imagery and X-ray energy dispersion spectrometry using a JEOL 5900 LV scanning electron microscope equipped with a LINK ISIS analytical system incorporating a Super ATW Light Element Detector. All polished sections were prepared using kerosene.

## Experimental results

Experimental data for the compositions in the join $(CC_{45}CH_{55})_{100-x}(NaNbO_3)_x$ ($0 < x$ 70 wt%) are given in Table 1. The experiments were designed to determine the primary liquidus phases and assess the solubility of Nb in water-bearing carbonate melts. Near-solidus assemblages were not investigated. Liquids in this join do not quench to a glass, but instead form an extremely fine-grained intergrowth of calcite, portlandite and Na–Ca-carbonates. Large (10–25 μm) primary liquidus phases are absent in all supra-liquidus experiments. Figure 1 illustrates a typical liquidus assemblage in the field of calcite plus liquid, which is characterized by large sub-hedral calcite crystals set in a groundmass of very fine grained calcite, portlandite, Na–Ca carbonate and calcium niobates. Figure 2 shows that the latter phases are actually very small crystals ($<1{\times}10$ μm) exhibiting a plate-like morphology. Figure 3 shows the phase assemblage calcite plus portlandite, plus liquid encountered in experiments with low $NaNbO_3$ contents. Figures 4 and 5 illustrate the character of melts quenched in the primary phase field of $NaNbO_3$. Note that, up to approximately 900 °C, the crystals of $NaNbO_3$ are typically subhedral to anhedral and small ($<10$ μm) relative to crystals of liquidus calcite (Fig. 4). In some of

**Table 1.** Experimental data for the join ($CC_{45}$–$CH_{55}$)–$NaNbO_3$ at 0.1 GPa pressure. $CC$ $CaCO_3$; $CH$ $Ca(OH)_2$; $LU$ $NaNbO_3$; $L$ liquid consisting of quench crystals of calcium niobates, Na–Ca carbonates, calcite and portlandite; *Time* duration of the experiment in hours. All LU contents are in wt%

| %LU | T (°C) | Time | Products | %LU | T (°C) | Time | Products |
|---|---|---|---|---|---|---|---|
| 70 | 950 | 8 | LU+L | 70 | 600 | 12 | LU+L |
| 70 | 900 | 24 | LU+L | 60 | 600 | 12 | LU+L |
| 70 | 850 | 5 | LU+L | 55 | 600 | 14 | L |
| 70 | 800 | 5 | LU+L | 50 | 600 | 12 | CC+L |
| 70 | 750 | 16 | LU+L | 45 | 600 | 14 | CC+L |
| 70 | 700 | 6 | LU+L | 35 | 600 | 4 | CC+L |
| 60 | 700 | 6 | L | 25 | 600 | 4 | CC+L |
| 55 | 700 | 144 | L | 15 | 600 | 12 | CC+L |
| 45 | 700 | 144 | L | 5 | 600 | 12 | CC+CH+L |
| 35 | 700 | 144 | L | 70 | 550 | 12 | LU+L |
| 25 | 700 | 144 | L | 60 | 550 | 12 | LU+L |
| 15 | 700 | 144 | L | 55 | 550 | 8 | L |
| 5 | 700 | 144 | L | 50 | 550 | 12 | CC+L |
| 5 | 675 | 10 | CC+L | 45 | 550 | 8 | CC+L |
| 25 | 675 | 10 | CC+L | 35 | 550 | 6.5 | CC+L |
| 70 | 650 | 16 | LU+L | 25 | 550 | 6.5 | CC+L |
| 60 | 650 | 14 | LU+L | 15 | 550 | 14 | CC+CH+L |
| 55 | 650 | 14 | L | 5 | 550 | 14 | CC+CH+L |
| 45 | 650 | 14 | CC+L | 55 | 525 | 14 | CC+LU+L |
| 35 | 650 | 4 | CC+L | 45 | 525 | 7.5 | CC+L |
| 25 | 650 | 4 | CC+L | 35 | 525 | 7.5 | CC+L |
| 15 | 650 | 12 | CC+L | 25 | 525 | 14 | CC+L |
| 5 | 650 | 17 | CC+L | 70 | 500 | 16 | LU+L |
| | | | | 50 | 500 | 16 | CC+LU+L |
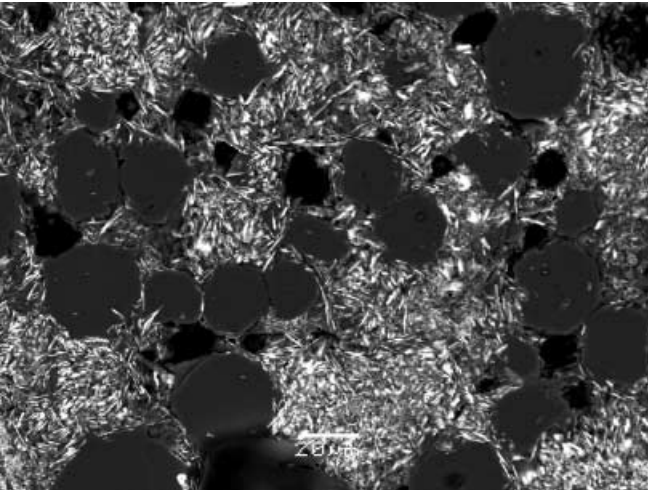
**Fig. 1.** Back-scattered electron image of subrounded crystals (20–40 μm) of liquidus calcite (*grey*) set in a fine grained, quenched-liquid matrix consisting of calcite, sodium carbonates, portlandite and plate-like crystals of calcium niobates (*white*). Composition $CC_{45}CH_{55}$ plus 25 wt% $NaNbO_3$ at 600 °C and 0.1 GPa. Magnification ×550; field of view approx. 160×200 μm
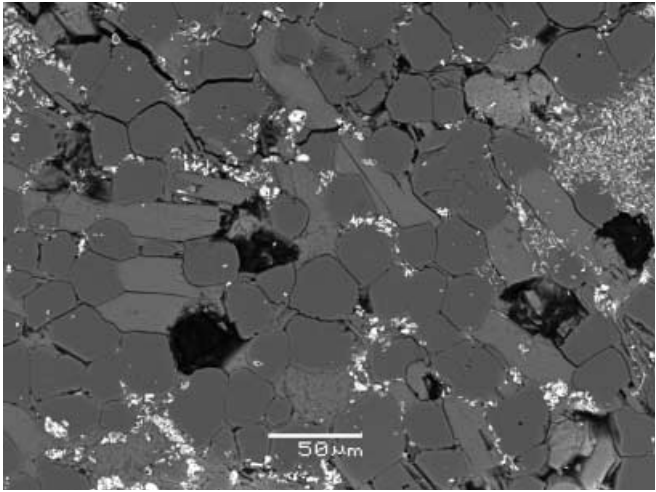


**Fig. 3.** Back-scattered electron image of liquidus calcite (*dark grey*, subrounded) and portlandite (*light grey*, prismatic) crystals with interstitial quench calcium niobates (*white*), calcite, portlandite and Na–Ca carbonates. Composition $CC_{45}CH_{55}$ plus 5 wt% $NaNbO_3$ at 650 °C and 0.1 GPa. Magnification ×370; field of view approx. 230×325 μm
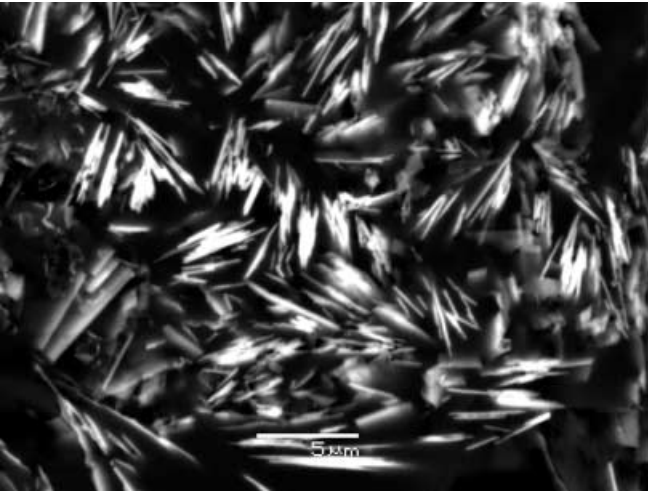


**Fig. 2.** Back-scattered electron image of quench plate-like crystals of calcium niobates. Composition $CC_{45}CH_{55}$ plus 25 wt% $NaNbO_3$ at 600 °C and 0.1 GPa. Magnification ×4,000; field of view approx. 20×30 μm
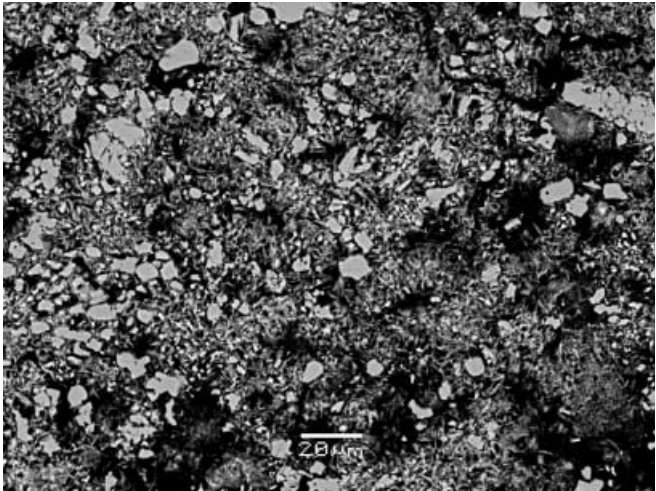


**Fig. 4.** Back-scattered electron image of liquidus $NaNbO_3$ (rounded 'phenocrysts') set in a quenched liquid matrix of calcite, sodium carbonates, portlandite and calcium niobates. Composition $CC_{45}CH_{55}$ plus 70 wt% $NaNbO_3$ at 750 °C and 0.1 GPa. Magnification ×600; field of view approx. 145×200 μm

the lower temperature experiments small (<15 μm) euhedral prismatic crystals of $NaNbO_3$ are present. Large euhedral crystals of calcian lueshite occur as the liquidus phase at temperatures above 900 °C (Fig. 5).

Figure 6 illustrates the near-liquidus phase relations established for this join. Particularly noteworthy aspects of these data are the presence of a large field of calcite plus liquid and the absence of primary $NaNbO_3$ as a primary liquidus phase until the melts contain greater than 60 wt% $NaNbO_3$ at 650 °C. These data show that the solubility of $Nb_2O_5$ in this system is on the order of 48 wt% at 650 °C at 0.1 GPa pressure. The primary crystallization fields of calcite and $NaNbO_3$ are

separated by a steep thermal valley located at about 55 wt% $NaNbO_3$. The steep liquidus surface for $NaNbO_3$ extends towards the melting point of this compound at 1,422 °C. Melts lying in this thermal valley crystallize along a cotectic precipitating calcite and $NaNbO_3$.

The liquidus surface for calcite is relatively flat and slopes from about 675 °C at 10 wt% $NaNbO_3$ to 650 °C at 45 wt% $NaNbO_3$ (Fig. 6). The investigated join originates at the binary eutectic (637 °C; Jago and Gittins 1993) in the system CC–CH. Based on our experiments, in which the liquidus is defined by the appearance of calcite, it follows that the CC–CH cotectic
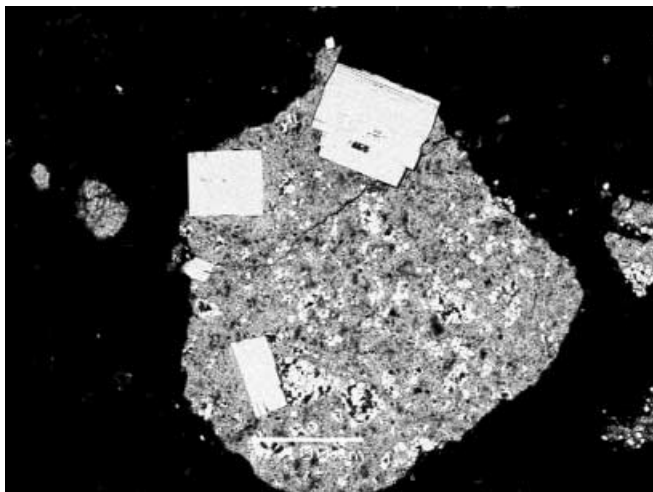
**Fig. 5.** Back-scattered electron image of large (50–100 μm) liquidus calcian NaNbO₃ crystals (*white*) together with smaller (< 25 μm) crystals of calcium-free NaNbO₃, set in a matrix of calcite, sodium carbonates, portlandite and calcium niobates. Composition CC₄₅CH₅₅ plus 70 wt% NaNbO₃ at 900 °C and 0.1 GPa. Magnification ×220; field of view approx. 375×550 μm
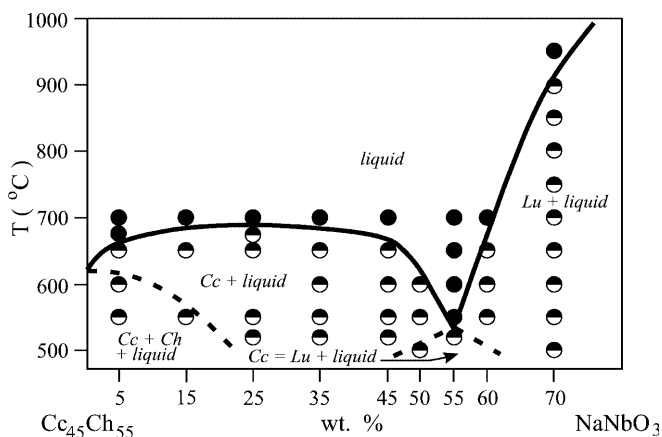


**Fig. 6.** Phase relationships on the join Cc₄₅Ch₅₅–NaNbO₃ at 0.1 GPa pressure. *Cc* Calcite; *Ch* portlandite; *Lu* NaNbO3

in the ternary system CC–CH–NaNbO₃ must lie at more CH-rich compositions than the join studied. The (CC–CH)–NaNbO₃ join must lie approximately subparallel to isotherms on the calcite liquidus surface, up to about 50 wt% NaNbO₃, at which point the thermal valley associated with the calcite–lueshite cotectic is encountered. The ternary liquidus phase assemblage CC–CH–NaNbO₃ was not encountered in our experiments. Thus, the CC plus CH cotectic probably curves away from the investigated join towards more CH-rich compositions. (Note: determination of the location of either the CC–CH cotectic or the CC–CH–NaNbO₃ ternary eutectic were not objectives of this study.)

The compositions of the primary phases CaCO₃ and Ca(OH)₂ do not deviate from stoichiometry. NaNbO₃ crystallizing below 900 °C is stoichiometric. NaNbO₃ forming above 900 °C contains significant amounts of

CaO (11.5–13.0 wt%) in solid solution. A typical composition of 12.75 wt% Na₂O, 11.54 wt% CaO and 76.36 wt% Nb₂O₅ is represented by the structural formula Na₀.₆₇Ca₀.₃₃Nb₀.₉₃O₃. Compositions of quench phases are very difficult to determine because of the small size and irregular habit of the crystals. Stoichiometric CaCO₃ and Ca(OH)₂ are present together with Na–Ca carbonates and Na₂CO₃. The Na–Ca carbonate has a composition similar to that of nyerereite [Ca-Na₂(CO₃)₂]. Quench niobates exhibit a range of compositions, none of which correspond with those of pyrochlore. Although many crystals contain small amounts of Na₂O (< 3 wt%) it is not possible to determine whether or not this results from excitation of the matrix carbonates. Niobates in which Nb < Ca and Nb > Ca are present. Quantitative analysis is not possible because of the small size and poor surface character of the grains. Semi-quantitative data obtained from the coarsest crystals (< 5 μm) suggest that the majority of compositions correspond to (Ca,Na)₄Nb₂O₉ and (Ca, Na)₂Nb₂O₇, with (Ca,Na)₅Nb₄O₁₅ possibly being present. All of these compounds have been prepared by solid-state synthesis and have been shown to be derivatives of the ideal $ABX_3$ perovskite structure. Ca₄Nb₂O₉ is a complex perovskite, which forms three polymorphs with 1:1 and 2:1 cation ordering (Levin et al. 2000), and Ca₂Nb₂O₇ is a layered derivative of the perovskite structure (Scheunemann and Muller-Buschbaum 1974). Thus, Watkinson (1970) and Jago and Gittins (1993) are incorrect in stating that Ca₂Nb₂O₇ is analogous to pyrochlore. Our data suggest that perovskite-structured compounds rather than pyrochlores will form during the later stages of crystallization of water-bearing, F-free carbonatite melts.

## Discussion

Our study has shown that Nb is extremely soluble in water-bearing melts in the system CC–CH–NaNbO₃ at 0.1 GPa pressure. This conclusion differs significantly from that of Jago and Gittins (1993) for the Na-free join CC₄₅CH₅₅–Nb₂O₅ which indicate a maximum solubility of Nb₂O₅ of approximately 7.5 wt%. Our near-liquidus experiments show clearly that the contribution of Na to the melt as consequence of breakdown of NaNbO₃ significantly enhances Nb solubility. This must be because of complex formation in the water-bearing carbonated melt. Unfortunately, nothing is known of the structure of such melts. We are confident that Nb is taken into the melt because relict NaNbO₃ is not present, Nb₂O₅ or NbO₂ are not precipitated, and quench material contains Na–Ca niobates. The latter are concentrated interstitially to calcite or portlandite crystals in the 5 wt% (Fig. 3) and 15 wt% NaNbO₃ experiments, showing clearly that the melt is undersaturated with respect to Nb-bearing phases in the primary liquidus field of calcite or calcite plus portlandite. Although near-solidus phase relations were not investigated it is apparent that

perovskite-structured compounds will form in the final stages of crystallization of these melts. Note that we are confident that these data are applicable to real carbonatite magmas as the bulk compositions of our experimental charges with 20–40 wt% $NaNbO_3$ represent realistic carbonatite liquids with 3.8–7.6 wt% $Na_2O$.

$NaNbO_3$, analogous to lueshite, is the only perovskite-structured compound to appear as a near-liquidus primary phase. As high concentrations of Nb in the melt are required to stabilize this phase it is suggested that, in water-bearing F-free carbonatites, lueshite must occur only as a late stage mineral in carbothermal veins in accord with its paragenesis at Lueshe. The typical absence of lueshite in other carbonatites might indicate that depletion of the magma in Nb by pyrochlore crystallization prevents its formation or that $H_2O/F$ ratios are low. The low solubility of $NaNbO_3$ in the anhydrous system $CaCO_3$–$Na_2CO_3$–pyrochlore, observed by Jago and Gittins (1993), is not directly comparable to the water-bearing system studied by us, although these data suggest that $H_2O$ has a significant effect on Nb solubility and that the presence of Na alone is insufficient to enhance the solubility.

Pyrochlore was not encountered as a primary liquidus mineral in this system. It is also apparently absent as a quench phase. These observations are consistent with the observations of Jago and Gittins (1993) that fluorine must be present to stabilize pyrochlore as a primary liquidus phase.

## Conclusions

Our data suggest that water-bearing, fluorine-free melts will crystallize perovskite-structured compounds rather than pyrochlore, and that lueshite is a mineral that crystallizes from late-stage carbothermal residual melts. The addition of $Na_2O$ to fluorine-absent hydrous haplocarbonatite melt increases $Nb_2O_5$ solubility sixfold, i.e. from approximately 7 to 44 wt% $Nb_2O_5$. We also conclude that, in agreement with the data of Jago and Gittins (1993), the $H_2O/F$ ratio of the melt and not the presence of alkalies alone determines whether or not perovskite- or pyrochlore-structured minerals are precipitated from carbonatite magmas. To address this question, further experiments in the systems CC–$CaF_2$–$NaNbO_3$ and CC–CH–$CaF_2$–$NaNbO_3$ are being undertaken.

## References

Beckett MF (1987) Phase relations in synthetic alkali-bearing dolomite carbonates and the effect of alkalinity and fluorine content on the solubility of pyrochlore and the formation of niobium deposits in carbonatites. MSc Thesis, University of Toronto, Toronto

Chakhmouradian AR, Mitchell RH (1998) Lueshite, pyrochlore and monazite-(Ce) from apatite–dolomite carbonatite, Lesnaya Varaka complex, Kola Peninsula, Russia. Mineral Mag 62:769–782

Ibrahim M, Bright NFH, Rowland IF (1962) The binary system $CaO$–$Nb_2O_5$. J Am Ceram Soc 45:329–334

Jago BC, Gittins J (1993) Pyrochlore crystallization in carbonatites: the role of fluorine. S Afr J Geol 96:149–159

Levin I, Bendersky LA, Cline JP, Roth RS, Vanderah TA (2000) Octahedral tilting and cation ordering in perovskite-like $Ca_4Nb_2O_9 = 3 \cdot Ca(Ca_{1/3}Nb_{2/3})O_3$ polymorphs. J Solid State Chem 150:43–61

Mariano AN (1989) Nature of economic mineralization in carbonatites and related rocks. In: Bell K (ed) Carbonatite: genesis and evolution. Unwin Hyman, London, pp 149–176

Mitchell RH (1997) Preliminary studies of the solubility and stability of perovskite group compounds in the synthetic carbonatite system calcite–portlandite. J Afr Earth Sci 25:147–158

Mitchell RH, Choi JB, Hawthorne FC, McCammon CA, Burns PC (1998) Latrappite: a re-investigation. Can Mineral 36:107–116

Safiannikoff A (1959) Un nouveau mineral de niobium. Acad R Sci Outre Mer Bull 5:1251–1255

Scheunemann K, Müller-Büschbaum HK (1974) Zur kristallstruktur von $Ca_2Nb_2O_7$. J Inorg Nucl Chem 36:1965–1970

Watkinson DH (1970) Experimental studies bearing on the origin of the alkaline rock–carbonatite complex and niobium mineralisation at Oka, Quebec. Can Mineral 10:350–361

Wyllie PJ, Tuttle OF (1960) The system $CaO$–$CO_2$–$H_2O$ and the origin of carbonatites. J Petrol 1:1–46