

Na-rich carbonate inclusions in perovskite and calzirtite from the Guli intrusive Ca-carbonatite, polar Siberia

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Abstract. Carbonate phases, some rich in Na₂O and comparatively rich in SrO and BaO, occur as inclusions in perovskite and calzirtite (Ca₂Zr₃Ti₂O₁₆) in the carbonatite of the Guli complex, Siberia. This is the first record of alkali carbonates, akin to 'nyerereite' [Na₂Ca(CO₃)₂], in plutonic igneous rocks. The inclusion populations suggest that the parental magma of the complex was Ca-rich but developed Na-rich differentiates during the latest stages. This points to the dominant calcic carbonatites of the complex not being derivatives of alkali-rich parental carbonatites. These alkali-rich carbonate inclusions (and rare inclusions of djerfisherite) have been preserved due to the resistance of perovskite and calzirtite to processes of leaching, hydrothermal alteration and weathering.

Introduction

The role of alkali carbonates in the genesis of carbonatite complexes, particularly related to the processes of fenitization and fractionation of hypothetical parental carbonatite magmas, is a vigorous, continuing debate (e.g. Gittins 1989). Calcium carbonate liquids undoubtedly exist, having been extruded as lavas and tuffs at several localities (e.g. Keller 1989; Ngwenya and Bailey 1990), whereas, hitherto, alkali carbonate lavas have been proved to exist only at Oldoinyo Lengai, Tanzania (Dawson 1962). Evidence for alkali carbonate in other, non-calcic carbonatites, is based on textural evidence together with the suggestion that its high solubility has led to the pre-existing alkali components being leached from all but the most recent extrusions. We report here the presence of Na-rich carbonate inclusions in perovskite and calzirtite from a calcic-carbonatite intrusion in which fenites have not been identified at the present exposure level. In this paper we present the significant

data and consider the implications of the results to the Guli intrusion and to calcic-carbonatites in general.

Petrography and analytical results

The Guli complex (Maimecha-Kotui province, polar Siberia) is of Triassic age (240 Ma) and based on geological and geophysical evidence covers an area of 1500–1600 km². It is a polyphase pluton consisting of a variety of rock types intruded in the order: dunites – titanomagnetite pyroxenites – melilitic rocks – melteigites/jacupirangites – melanephelinites – syenites – carbonatites; the carbonatites occur in northern (3 km²) and southern (5 km²) units (Kapustin 1980). The sample studied in the present work is a sövite (1985-I34) from a drill hole in the southern unit. In this rock the most abundant minerals are calcite (up to 3 mm) and apatite (exceptionally up to 4 mm long and 0.5 mm across but usually <1 mm long and up to 250 µm across) with smaller amounts of phlogopite (up to 10 mm long), monticellite (3 mm × 1 mm), diopside, calzirtite and perovskite. The apatites are often well-aligned forming clusters and 'mats' of grains with small amounts of interstitial calcite. Monticellite and phlogopite often enclose apatite grains. The perovskite forms small (up to 400 µm), rectangular, euhedral crystals sometimes associated with, and partly enclosing, equant, euhedral grains of calzirtite (up to 100 µm). Calzirtite also occurs as inclusions in phlogopite, monticellite and apatite, but perovskite is never enclosed by these phases. Thus textural relations are consistent with calzirtite being of significantly earlier crystallization than perovskite.

Both calzirtite and perovskite contain numerous minute (<30 µm) inclusions of carbonates and, more rarely, apatite (Fig. 1). Somewhat similar inclusions have been described in apatites from silicate-carbonatite complexes, usually in association with condensed aqueous fluids and CO₂-rich vapours (see e.g. Rankin 1977; Aspden 1981; Le Bas and Aspden 1981) and in monticellite from the Magnet Cove carbonatite, Arkansas (Nesbitt and Kelly 1977). Although the apatites in the Guli car-

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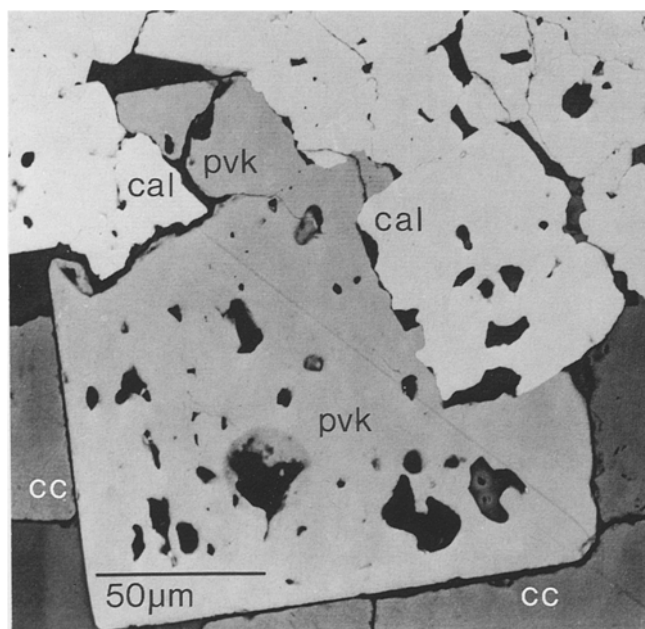


Fig. 1. Back-scattered electron image of perovskite (pvk), calzirtite (cal) and matrix calcite (cc) in the Guli calcio-carbonatite. Some of the calzirtites are partly enclosed by perovskite. The inclusions are mainly of carbonate phases

bonatite frequently contain primary fluid inclusions (up to 10 μm diameter), often forming negative crystals with vapour bubbles and small amounts of solid daughter phases, as well as trains of secondary fluid inclusions, many of the carbonate inclusions in perovskite and calzirtite show no obvious associated fluid phases. The optical opacity of their host phases makes it difficult to be categorical about this, however, Le Bas and Aspden (1981) have pointed out that inclusions containing much gas or liquid usually disgorge their solid contents during the polishing of probe mounts. Thus, these Guli carbonate inclusions are believed to be primary and formed by incorporation of solid and/or melt phases rather than of hydrothermal fluids; note that the carbonate inclusions in monticellite (Nesbitt and Kelly 1977) were also interpreted in this way.

Table 1 contains the wet chemical analysis for the bulk rock carbonatite; the high P_2O_5 content reflects the high modal content of apatite, but note in particular the low alkali contents. Microprobe analyses of the main minerals (EDS and combined WDS/EDS with a Cameca Camebax microprobe using a Link AN10000 analysis system with ZAF4/SPECTA software) are also shown in Table 1. The phlogopite, diopside and monticellite have very high $\text{Mg}/(\text{Mg} + \text{Fe} + \text{Mn})$ ratios of 0.93, 0.98 and 0.84 (atomic proportions), respectively; note that the ratio for phlogopite is similar to those for micas from the Jacupiranga carbonatite complex, Brazil and from mantle peridotite nodules (Gaspar and Wyllie 1982). The phlogopite has a moderately high Ba content, slightly higher than that for primary phlogopites from mantle nodules, and at the lower end of the range for the Jacupiranga complex micas (Gaspar and Wyllie 1982). The perovskite contains a relatively high Nb con-

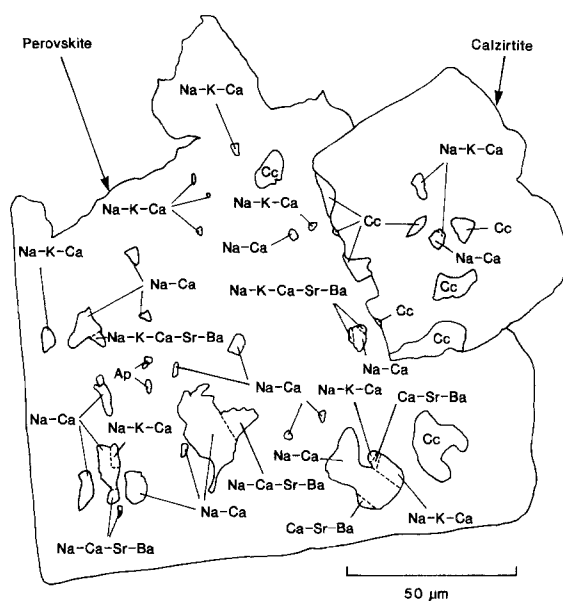


Fig. 2. Reconstruction of inclusion species based on secondary X-ray images for Ca, Na, K, Sr and Ba (Cc = calcite; Ap = apatite). Note that Figs. 1 and 2 have the same scale. This reconstruction does not include all the features shown in Fig. 1, some of which are holes where the inclusion has been lost, possibly by leaching during sample preparation

tent (12.5 wt.% Nb_2O_5) similar to niobian perovskites reported from Oka, Quebec (15.8%) (Gold 1966). The calzirtite has compositions similar to those reported from various Russian carbonatites (Kapustin 1980). We originally identified it as an exceptionally Zr-rich zirconolite similar to that reported in the Mothae kimberlite, Lesotho (Raber and Haggerty 1979); it seems likely that the latter phase is also calzirtite. It should be noted that the perovskite has a deficiency of Na to Nb relative to that required by lueshite (NaNbO_3); this is presumably due to the presence of REE (Ce and La detected but not quantified) replacing Na, and Fe^{3+} replacing Ti and Nb to maintain electrical neutrality. Apatite is essentially the same composition whether it occurs as a matrix phase or as minute inclusions in perovskite (cf. analyses 7 and 8, Table 1). Apatite is moderately F-rich (2 wt.% F) with a much higher content than the coexisting phlogopite (0.4 wt.% F). This relationship is at variance with the results of Dawson and Fuge (1980) but is consistent with those of Chernysheva et al. (1976). The relatively high Si content in apatite coupled with the low P suggests some replacement for the phosphate anion. Table 1 also includes an analysis for a K-rich sulphide inclusion in perovskite (analysis 9). This phase has a composition similar to djerfisherites reported from alkaline rocks [$\text{K}_6\text{Na}(\text{Fe}, \text{Cu}, \text{Ni})_{24}\text{S}_{26}\text{Cl}$] (Czamanske et al. 1979) except that it is close to an Fe end-member and contains Ca rather than Na; the relatively low analytical total (Table 1) may indicate the presence of small amounts of Cu and/or Ni which were not analysed for. Until now such an Fe-rich variety was only known as a synthetic phase (Clarke 1979).

Analyses of the carbonate inclusions occurring in the perovskite and calzirtite are given in Table 2 and the

Table 1. Analysis of sövite bulk rock and mineral phases

	1.	2.	3.	4.	5.	6.	7.	8.	9.
SiO ₂	6.29	40.5 ^a	55.2	37.2	n.d.	n.a.	1.07 ^a	1.20 ^a	
TiO ₂	0.20	0.27	n.d.	n.d.	43.5	12.6	n.d. ^a	n.d. ^a	
Al ₂ O ₃	0.40	13.2	n.d.	n.d.	0.40	n.a.	n.d.	n.d.	
Fe ₂ O ₃	1.17	—	—	—	—	—	—	—	Fe 53.1
FeO	1.27	3.46	0.58	6.40	3.88	1.12	n.d.	n.d.	
MnO	0.14	0.12	0.12	1.04	n.a.	n.a.	n.d.	n.d.	
MgO	3.44	24.9	18.4	21.3	n.a.	n.a.	n.d.	n.d.	
CaO	53.25	n.d.	25.5	33.5	34.0	12.0	54.4	56.2	Ca 0.6
Na ₂ O	0.21	0.83	0.11	n.d.	1.83	n.d.	n.d.	n.d.	
K ₂ O	0.44	9.68	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.	K 9.1
P ₂ O ₅	18.02	n.d.	n.a.	n.a.	n.a.	n.a.	37.2	37.7	
ZrO ₂	n.a.	n.a.	0.07	n.a.	1.36	69.1	n.a.	n.a.	
Nb ₂ O ₅	n.a.	n.a.	n.a.	n.a.	12.4	4.73	n.a.	n.a.	
SrO	n.a.	0.11 ^a	n.a.	n.a.	1.02	n.a.	0.43 ^a	0.47 ^a	
BaO	n.a.	0.94 ^a	n.a.	n.a.	n.a.	n.a.	n.d. ^a	n.d. ^a	
F	n.a.	0.37 ^a	n.a.	n.a.	n.a.	n.a.	2.01 ^a	2.00 ^a	
Cl	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
CO ₂	14.66	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	Cl 1.3
H ₂ O	0.45	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
Less O≡F	—	0.16	—	—	—	—	0.85	0.84	S 31.9
Total	99.94	94.32	99.98	99.44	98.39	99.55	94.26	96.73	96.0

Cell formulae (number of oxygens or sulphurs)

	(22(0))	(6(0))	(4(0))	(3(0))	(16(0))	(25(0))	(25(0))	(26(S))
Si	5.846	1.995	1.003	—	—	0.192	0.210	K 6.036
Al	2.250	—	—	0.011	—	—	—	Ca 0.392
Ti	0.030	—	—	0.799	1.442	—	—	Fe 24.850
Nb	—	—	—	0.137	0.325	—	—	S 26.000
Zr	—	0.001	—	0.016	5.102	—	—	Cl 0.993
Fe	0.418	0.016	0.144	0.079	0.142	—	—	
Mn	0.015	0.004	0.024	—	—	—	—	
Mg	5.371	0.992	0.857	—	—	—	—	
Ca	—	0.989	0.969	0.888	3.959	10.438	10.553	
Na	0.229	0.008	—	0.086	—	—	—	
K	1.782	—	—	—	—	—	—	
Sr	0.010	—	—	0.014	—	0.044	0.047	
Ba	0.053	—	—	—	—	—	—	
P	—	—	—	—	—	5.650	5.592	
F	0.169	—	—	—	—	1.139	1.107	

1. Chemical analysis of sövite bulk rock (1985 –I34); 2. Phlogopite; 3. Diopside; 4. Monticellite; 5. Perovskite; 6. Calzirtite; 7. Apatite from calciocarbonatite rock matrix; 8. Apatite inclusion

from perovskite containing Na-rich carbonate inclusions (see Table 2); 9. Djerfisherite inclusion in perovskite, elemental analysis.

^a Analysed by WDS methods (others by EDS); n.d. = not detected; n.a. = not analysed

high Na contents for some of these are readily apparent. As sulphur and halides were generally below detection we will assume that these inclusions are of carbonate-rich phases. Analysis of the alkali-rich carbonate inclusions was extremely difficult as, due to their small size, the beam could neither be sufficiently defocused, nor rastered over the sample, to reduce alkali volatilisation. In fact, microprobe analysis of the carbonates resulted in extreme beam damage with the Ti (or Zr and Ti) contents progressively increasing with time as the beam sampled more of the host perovskite (or calzirtite) below the inclusion. For the inclusions in perovskite this effect was monitored from the Ti contents of the resultant analysis with analyses having >2 wt.% TiO₂ being dis-

carded. The generally small sizes of the alkali-rich carbonate inclusions in calzirtite (<5 µm) led invariably to very high Zr (and Ti) contamination (Table 2, analyses 8 and 9); thus the carbonate compositions of these analyses were calculated after subtracting Ca present as calzirtite components based on the contaminant ZrO₂ in the analyses. The most reliable Na analyses were obtained with 10 or 15 s counts using EDS methods with a beam current of 3.0 nA. A few analyses were obtained using a cooling stage at liquid nitrogen temperature and an even weaker electron beam (current 1.5 nA) on a JEOL 6400 Analytical SEM. Analyses for Sr and Ba by WDS methods involved using a more intense beam (15 nA) and resulted in extreme Na loss (cf. Table 2,

Table 2. Analyses of carbonate phases in sövite I34 with some comparative data

	1	2	3	4	5	6	7	8	9	10	11	12	13
Na ₂ O	27.9	27.7	24.5	16.8	16.9	6.42 ^a	n.d. ^a	10.2	3.01	n.d. ^a	24.68	30.30	26.3
K ₂ O	n.d.	n.d.	0.22	3.87	0.47	0.18	n.d.	1.93	3.11	n.d.	0.68	6.55	6.1
CaO	25.0	27.6	29.3	29.1	32.3	22.1	54.6	28.6	36.5	54.0	25.29	13.93	19.1
MgO	n.d.	n.d.	n.d.	n.d.	n.d.	0.74	n.d.	n.d.	n.d.	n.d.	0.49	0.26	—
MnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.55	0.25	—
FeO	n.d.	n.d.	n.d.	n.d.	0.42	0.26	n.d.	n.d.	0.60	n.d.	0.99	0.26	0.9
SrO	0.51	0.31	n.d.	0.19	2.59 ^a	10.1 ^a	0.94 ^a	n.d.	0.55	0.80 ^a	1.49	1.41	0.5
BaO	n.a.	n.a.	n.a.	n.a.	0.84 ^a	7.21 ^a	n.d.	n.a.	0.21	0.08 ^a	0.92	0.99	4.4
Cl	n.a.	n.a.	n.d.	n.a.	0.13	n.d.	n.d.	n.a.	0.38	n.d.	0.20	2.45	6.9
SO ₃	n.d.	n.a.	n.d.	n.d.	0.30	0.67	0.27	n.a.	n.a.	n.d.	0.20	3.23	4.4
CO ₂ (calc)	39.6	41.5	40.1	36.8	38.9	28.4	44.9	27.0	31.6	42.8	32.71	33.90	29.2
TiO ₂	0.19	2.04	5.46	0.68	0.89	4.65 ^a	0.25 ^a	5.28	1.53	n.d.	0.03	0.01	—
ZrO ₂	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	27.8	9.48	n.a.	—	—	—
Total	93.20	99.15	99.58	87.44	93.74	80.73	100.96	100.81	86.97	97.68	99.76	99.45	100.0
wt. % carbonates													
Na ₂ CO ₃	51.7	49.0	44.1	33.2	33.0	21.6	—	27.9	7.2	—	47.8	60.1	49.8
K ₂ CO ₃	0.1	—	0.3	6.6	0.8	0.5	—	4.5	6.3	—	1.1	11.1	4.6
CaCO ₃	48.2	51.0	55.6	60.2	66.2	77.8	100.0	67.6	86.5	100.0	51.1	28.8	45.7

1–7. Carbonate inclusions in perovskite: 1–3 low-K, Na–Ca, 4 high-K, Na–Ca, 5, 6 Sr,Ba-rich, Na–Ca, 7 calcite; 8, 9 Carbonate inclusions in calzirtite; 10 Calcite in calcite-carbonatite rock matrix; 11, 12. Oldoinyo Lengai lavas (Dawson et al. 1987), 11: altered natrocarbonatite, GA47 (total includes SiO₂ 0.73, Al₂O₃ 0.25, P₂O₅ 0.64, F 1.06, H₂O⁺ 9.33); 12: fresh natrocarbonatite, BD118 (total includes SiO₂ <0.10, Al₂O₃ 0.03, P₂O₅ 1.13, F 1.20,

H₂O⁺ 4.51); 13. fluid/melt inclusion in apatite from ijolite (Le Bas 1981) (total includes SiO₂ 2.0, Al₂O₃ 1.0, F 1.4 and is recalculated less O = F, Cl).

^a Analyses by WDS methods (others by EDS).

Microprobe detection limits (EDS, wt.%) Na₂O, MnO, FeO 0.2%; K₂O, MgO, Cl 0.15%; SO₃, P₂O₅ 0.25%

analysis 6). An overall impression of the spatial distribution of carbonate inclusions is shown in Fig. 2 which is a composite drawing based on X-ray images for Ca-, Na-, K-, Sr-, and Ba. It is clear that the Ca-rich areas (usually calcite but occasionally apatite) are distinct from the other carbonate inclusions which tend to be Na-rich or to have both Na-rich and Na- and K-rich patches in the same inclusion. Sr and Ba rich areas seem to form distinct regions of large alkali rich inclusions.

Analyses for the Ca-rich inclusions in perovskite and calzirtite are very similar to those for the rock matrix calcite (Table 2, analyses 7 and 10, respectively); note that close to 1 wt.% SrO is present but that alkalis are undetected. The totals for the alkali-rich carbonate inclusions, after including recalculated CO₂, tend to be rather low which could be due to a combination of factors: alkali loss not totally eliminated; inappropriate standards (silicates used rather than carbonates); the presence of some hydrated phases such as nahcolite (NaHCO₃) or pirssonite (NaCa_{0.5}CO₃·2H₂O); irregularities on the 'polished' surface. Most of our microprobe analyses were obtained on a sample prepared using water rather than paraffin, thus hydration effects or alkali loss from the carbonate inclusions could have occurred during sample preparation. A possible analogy may be seen in the compositions of pristine and partially altered Oldoinyo Lengai natrocarbonatite lavas (Dawson et al. 1987) (cf. Table 2, analyses 12 and 11, respectively). However, another sample of Guli carbonatite I34 was prepared in paraffin and provided similarly Na-

rich carbonate-inclusion analyses commonly with somewhat higher analytical totals (cf. Table 2, analyses 1 and 3).

Discussion

The alkali-rich inclusion analyses can be divided into low-K (Fig. 3, solid and open diamonds) and comparatively high-K (Fig. 3, solid and open triangles) groups. Na-rich compositions in the low-K group (Table 2, analyses 1–3) approach that of a K-free phase close to nyerereite in composition. It is noteworthy that nyerereite [(Na_{0.82}K_{0.18})₂Ca(CO₃)₂] is a major mineral in quenched carbonatite lavas from the Oldoinyo Lengai volcano and we believe that the Guli 'nyerereite' is the first plutonic occurrence of this mineral, albeit less potassic than the Oldoinyo Lengai specimens. Other low-K analyses fall between 'nyerereite' and shortite (Na₂Ca₂(CO₃)₃); note that shortite inclusions in apatite have been reported for the Tororo carbonatite complex, Uganda (Aspden 1981). It is possible that both these phases occur in the present sample but it seems more likely that the analyses represent different degrees of Na loss from 'nyerereite' (see later). Only one Na-rich, low-K inclusion from calzirtite is plotted in Fig. 3 which reflects their rarity relative to the inclusion population in perovskite. The group of relatively-high-K analyses define a trend of increasing Ca with decreasing Na (Fig. 3). Although this trend is likely to be influenced

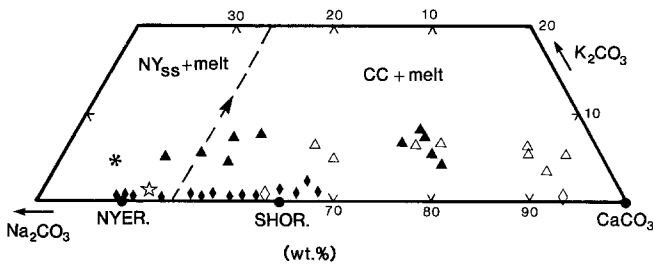


Fig. 3. CaCO_3 -rich corner of the CaCO_3 - Na_2CO_3 - K_2CO_3 system (wt.%). Solid diamonds and triangles mark the compositions of Na-rich and Na,K-rich carbonate inclusions, respectively, in perovskite; open diamonds and triangles those in calzirtite; calcite inclusions plot at the CaCO_3 corner. NYER 'nyerereite' ($\text{Na}_2\text{Ca}(\text{CO}_3)_2$); SHOR shortite ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$). The dashed line marks the position of the field boundary between the liquidus phase fields of nyerereite solid solution (NY_{ss}) and calcite (CC) (Cooper et al. 1975); the arrow marks falling temperature, Open star is a partially altered lava composition (GA47) from Oldoinyo Lengai (Dawson et al. 1987) and the asterisk marks the composition of a magmatic melt inclusion in papatite from an ijolite (Le Bas and Aspden 1981)

by different amounts of Na loss during analysis (as discussed already), note that the inclusions in calzirtite (Fig. 3, open triangles) tend to be generally less Na-rich, for similar analytical totals, than those in perovskite (Fig. 3, solid triangles) (also cf. Table 2, analyses 8 and 4). The highest Na analysis for the higher-K group falls fairly close to the field boundary between nyerereite and calcite in the system CaCO_3 - Na_2CO_3 - K_2CO_3 (Cooper et al. 1975). The analysis with the highest Sr and Ba concentrations (Table 2, analysis 6) has low alkali contents but detectable S (calculated as SO_3 in Table 2) suggesting that some sulphate-bearing phases may be present in small amounts in this inclusion. However, the generally low amounts of sulphate-bearing phases is consistent with the magma having a very low oxygen fugacity as reflected by the presence of inclusions of djerfisherite.

The overall lack of halide and sulphate solid phases in comparison to inclusions formed in aqueous-fluid-rich environments (Nesbitt and Kelly 1977; Rankin 1977; Le Bas and Aspden 1981) suggests that the Guli inclusions represent entrapped solid and/or melt phases. We suggest that the relative lack of hydrous components limited the possibilities for transport of carbonate components subsequent to trapping (the inclusions were effectively in closed systems) so that the analysed compositions are likely to represent those of the primary phases. Thus we conclude that the analyses for K-poor, Na-Ca-carbonate inclusions and for Ca-carbonate inclusions represent the compositions of 'nyerereite' and calcite crystalline phases, respectively. A liquid coexisting with both of these phases must therefore lie on the field boundary between the stability fields for these two minerals (Fig. 3). The more K-rich inclusions could represent possible quenched carbonatite melt compositions, although this is speculative. If this assumption is correct, the presence of quenched 'liquids' in perovskite which are richer in Na-components compared to 'liquids' in calzirtite, combined with the textural evidence suggesting that perovskite is a somewhat later-crystallizing phase

than calzirtite, points to the K-rich trend (Fig. 3) representing progressive magmatic evolution from Ca-rich to Na-rich compositions. In addition, the paucity of inclusions in calzirtite with compositions close to 'nyerereite' (Fig. 3) points to the liquid having reached the field boundary between calcite and nyerereite after the main growth stage of calzirtite. By contrast, the ubiquitous occurrence of 'nyerereite' and Na-rich melt inclusions in perovskite points to the continued growth of this mineral after the liquid reached this field boundary. As apatite inclusions occur in both calzirtite and perovskite it seems that the carbonatite liquids fractionated along a calcite-apatite field boundary before reaching the nyerereite stability field. Indeed, it is conceivable that the linear trend defined by the K-rich inclusions at about 6 wt.% K_2CO_3 , marks the projected position of the calcite-apatite field boundary in the carbonate system. The status of the Sr and Ba rich inclusions is unclear but we favour the possibility that most represent crystalline inclusions, possibly of benstonite ($\text{Ca}_7(\text{Ba},\text{Sr})_6(\text{CO}_3)_{13}$) (cf. analysis 6, Table 2). However, some are definitely Na- or Na,K-bearing (analysis 5, Table 2) and may represent liquid compositions.

To the best of our knowledge, no experimental data are available on the stability relations of perovskite and calzirtite in carbonate melts. Earlier petrographic studies have indicated that Nb-rich perovskite varieties and calzirtite may be 'early' liquidus phases (Kapustin 1980). Textural evidence for the Guli sample is consistent with calzirtite being an early phase. However, based on its inclusion population, it seems that the Guli perovskite began to precipitate after calcite, 'nyerereite' and apatite appeared on the liquidus. It seems therefore, that the perovskite most likely nucleated after the carbonate liquid intersected the calcite-nyerereite-apatite field boundary, i.e. relatively late in the cooling history. The relative modal abundance of carbonate inclusions in perovskite is: 'nyerereite' 85 vol.%; calcite 10% quenched K-rich, Na-Ca 'liquid' 5%. These modal ratios of 'nyerereite' to calcite (89.5:10.5) are very similar to the amount of solid phases precipitated by a carbonate liquid on the nyerereite-calcite cotectic (94:6) in the system NC-KC-CC (Cooper et al. 1975). Similar evidence for the existence of alkali-rich carbonate liquid compositions comes from the study of fluid and carbonate solid inclusions in apatites from ijolites, urtites and calcio-carbonatites (Rankin 1977; Le Bas 1981; Aspden 1980, 1981; Le Bas and Aspden 1981). For example, the composition of an alkali-rich magmatic inclusion from an ijolite (Le Bas and Aspden 1981) is shown as analysis 13, Table 2. Although this composition is enriched in Cl, F and sulphate relative to our analyses (indicating the presence of an aqueous component) the analyses are broadly similar (Fig. 3).

The textural, chemical and phase equilibrium lines of evidence presented above can be combined to deduce the crystallization history schematically shown in Fig. 4. The Guli sövite is not obviously associated with effects of fernetization, suggesting that the parent magma originally had a relatively low alkali content. This would be consistent with our interpretation that a high degree

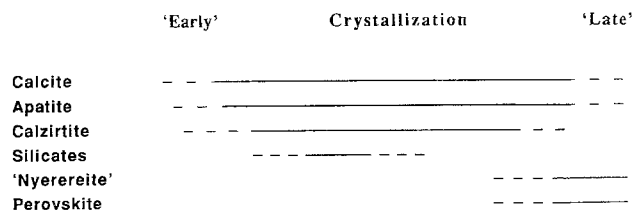


Fig. 4. Inferred crystallization sequence for the Guli sövite. Silicates correspond to monticellite, phlogopite and diopside

of crystallization must have occurred before 'nyerereite' became a stable liquidus phase. Even though the Guli carbonatite studied was from a drill core sample, which had not been exposed to normal surface weathering processes, any alkali-rich phases which developed in the carbonate matrix late in the differentiation process, appear to have been eliminated. Because perovskite and calzirtite are dense, essentially uncleaved minerals, they should be resistant to alteration or leaching by hydrothermal fluids or weathering, thus accounting for the alkalis in the Guli inclusions having been retained, perhaps quantitatively. It is precisely these properties that makes perovskite a suitable site for disposal of radioactive elements (Ringwood et al. 1979).

Conclusions

It seems that the microprobe study of inclusions in perovskite and calzirtite can provide important insights into the relationships between carbonatite fractionation and alkali enrichment. In the Guli sample at least, this alkali enrichment seems to be a relatively late-stage process from a calcic parent. If our interpretation is correct we would expect that alkali-rich inclusions should certainly occur in perovskites from calcic-carbonatites associated with fenites, perhaps in even greater abundance than in the Guli carbonatite. We await reports of further discoveries.

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