Origin of carbonatites—liquid immiscibility caught in the act

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Carbonatites are rare but worldwide occurring igneous rocks and their genesis remains enigmatic. Field studies show a close spatial but controversially debated genetic relationship with alkaline silicate rocks, and petrological and experimental studies indicate liquid immiscibility from mantle-derived magmas being one viable model for the generation of carbonatites. However, unaltered carbonatitic melts are rare and the composition of primary carbonate liquids and their silicate conjugates is poorly constrained. Here we show an example of primary Ca-carbonatitic melt formed by liquid immiscibility from a phonolitic magma of the Laacher See volcano (Eifel, Germany). The conjugate blebs of carbonate-silicate liquids are found in hauyne-hosted melt inclusions. The Ca-carbonatite melts are moderately alkali-rich and contain high F and Cl at elevated SiO₂ and Al₂O₃ concentrations. Such carbonatite liquids are viable parental magmas to the globally dominating intrusive Ca-carbonatite complexes and may provide the missing link to extrusive Na-carbonatitic magmas.
Carbonatites are igneous rocks with significant amounts of magmatic carbonate (>50 vol%), only little silica, and their origin remains uncertain. Field observations often show a close spatial relationship with alkaline silicate rocks. However, the genetic link between carbonate and silicate rocks as well as the petrological evolution of carbonate melts has been a matter of debate for decades (e.g.3,4) and several hypothesis have been proposed. These models include extreme differentiation by fractional crystallization (e.g.5,6) and/or separation of a carbonate from an immiscible (e.g.7-15). CO2-rich parental silicate melt or primary mantle-derived carbonate melts (e.g.16,17).

Many carbonatites associated with silica-undersaturated alkaline rocks are thought to form by liquid immiscibility from mantle-derived alkaline silicate magmas, as proposed from field evidence for numerous locations (e.g. Oldoinyo Lengai18-20, Kerimasi21-23, Shombole24, Gronnedal-Ika25, Gardiner complex26).

In order to assess the nature of the physical processes and petrogenetic relationships leading to carbonatites, genuine high volume compositions of primary carbonate would be required, as well as the textural setting in which they may occur with conjugating alkaline silicates. Such knowledge could also contribute to the longstanding question why the majority of carbonatitic rocks worldwide are Ca-carbonatites while the only active carbonatite volcano (Oldoinyo Lengai, East African Rift, Tanzania) is Na-carbonatitic.27

As most carbonatites are plutonic, usually coarse grained and mostly cumulates from carbonatitic magmas, such rocks cannot represent primary carbonate quenched liquids and clear textural evidence of petrogenetic processes such as liquid immiscibility is largely lost with some notable exceptions (e.g. 29,30). Therefore, extrusive carbonatites may be better suited to determine primary carbonate melt compositions, but the latter are rare (~10% of known carbonate occurrences worldwide31) and often heavily altered.

Melt inclusions offer a better way to understand the petrogenesis of carbonatites, as demonstrated by numerous studies (e.g.30-32,36) indicating liquid immiscibility is a key process in the formation of carbonatites. However, data from unaltered consanguine silicate-carbonate liquids are rare as many carbonatite-silicate melt inclusions underwent at least partial recrystallization and/or alteration.

Brooker and Kjarsgaard showed experimentally that low to moderately alkaline carbonatites can be produced at crustal pressures by liquid immiscibility from a silica-undersaturated alkaline-magma. Such carbonate liquids contain ~5 wt% Na2O + K2O, significant amounts of SiO2 + Al2O3 (>10 wt%), and may be parental to common Ca-carbonatites (e.g.9,37) by accumulation and fractionation processes. However, such moderately alkaline Ca-carbonatite liquids with significant amounts of SiO2 + Al2O3 have not been found in nature, yet.

Here we present results from a study of hauyne-hosted conjugate silicate-carbonate melt inclusions from the phonolitic Laacher See volcano (13,006 ± 9 years BP38), located in the alkaline continental intraplate East Eifel Volcanic Field, Germany. The crystal-free liquids are rapidly quenched by the volcanic eruption and due to their young age unaltered. Furthermore, the pre-eruptive conditions of the Laacher See volcanic system are well investigated allowing accurate constraints of pressure, temperature, and compositional parameters at which silicate–carbonate liquid immiscibility in mantle-derived alkaline magmas can take place, thus allowing a new insight into the origin of carbonatites.

**Results**

**Geological setting.** The Laacher See volcano erupted 13,006 ± 9 years BP (BP as AD 1950)38 in less than 10 days39 about 5.3 km3 phonolitic magma, with eruption types alternating mainly between phreatomagmatic activity and plinian eruptions40,41. The Laacher See Tephras (LST) deposits are well preserved and allow a detailed reconstruction of magma chamber conditions. The single magma reservoir was chemically and mineralogically zoned, ranging from crystal-rich mafic phonolites at the bottom towards highly differentiated, volatile-rich and phenocryst-poor phonolites at the top.40 Temperatures varied from 880 °C in the lower parts to 720 °C in the uppermost section11,12,14,2. The depth of the magma chamber is estimated at 3–6 km with pressures between 100 and 200 MPa42,43. The basanitic parental magma of the LST differentiated over 100 kyr in the deeper crust to a mafic phonolitic melt, during which it continuously fractionated and ascended into shallow crustal levels11,14,45. U-Th zircon ages44,45 indicate that a highly evolved phonolitic magma had already existed 10–20 kyr prior eruption.

Laacher See phonolites are silica-rich (54.4–58.2 wt% SiO2), Mg-poor (0.09–1.1 wt% MgO) and are characterized by high alkali concentrations (11.6–17.3 wt% Na2O + K2O).46 The most important phenocrysts are sanidine, plagioclase, hauyne, amphibole, clinopyroxene, titanite, magnetite, phlogopite, apatite, and zircon. The LST is high in incompatible trace elements and volatiles like F (690–4060 ppm), Cl (1770–4400 ppm), and S (150–1490 ppm).46 Melt inclusions occur in all phenocrysts present in the LST47 and are not significantly modified after entrainment.46 Crustal contamination or secondary alteration of the LST in general are negligible as constrained from strontium- and oxygen isotope studies48,49.

Carbonatitic syenites, enclosing the Laacher See magma chamber as a mostly crystalline carbapac50,51, occur as clasts in the middle and late erupted LST, and are consanguine to Laacher See phonolite magma as concluded from conjugate phonolite–carbonatite trace element patterns50,52 as well as carbon- and oxygen isotope50,52. While the exact mechanism of carbonate melt formation remains unclear, Schmitt et al.45 and Rout and Wörner suggest liquid immiscibility between carbonate and phonolite liquids with subsequent fast segregation of the carbonate melt forming a carbonate-syenite intrusive complex at the magma chamber margin.53 Three different groups of the Laacher See Carbonatites (LSC) can be distinguished: LSC 1, which is a nosean-syenite with sővite droplets indicating liquid immiscibility. LSC 2 is a hybrid sővite-syenite that may have formed by either remixing of carbonatite and syenite or represent co-crystallized conjugate silicate and carbonate melts that were not completely separated after unmixing. LSC 3 is a residual calcite-bearing nosean-syenite. Major components of the LSC are calcite, nosean, and sandidine as well as less abundant clinoptyroxene, albite, and garnet. Accessory phases are magnetite, biotite, zircon, apatite, and pyrochlore. Rhodochrosite, cencrinite, allanite, and fluorite occur sporadically.45,52. Overall, the association of alkaline silicate rocks with Ca-carbonatites in the LST is typical, albeit at larger scales, for many intrusive carbonatite complexes worldwide (e.g.53).

**Immiscible carbonate-silicate liquid compositions.** Here we show conjugate blebs of quenched carbonate-silicate liquids in hauyne-hosted melt inclusions (<1–20 μm in diameter) from the LST deposits (Fig. 1). The mm-sized euhedral hauynes are embedded in highly vesicular phonolitic pumice lapilli from the middle Laacher See Tephra (MLST; Layer 10340). Those hauynes might be phenocrysts, or they may have been derived from a crystal-rich carbonatitic syenite carapace that surrounded the erupted phonolite melt. The presence of such carapace-derived crystals in the main magma body has been demonstrated by44,34,55.
While most of the melt inclusions consist of phonolitic glass (Ls) only, about 5% exhibit additional globular carbonate melt droplets (Lc) (<1–5 µm). High-resolution BSE images show that the phonolitic part of those melt inclusions also contain nm-sized carbonate liquid droplets which are less abundant in the close proximity of larger carbonate blebs (Fig. 2) as a result of coarsening driven by decrease in interfacial free energy. Some of the melt inclusions contain bubbles indicating the presence of a vapour phase. Modal abundance of carbonate and phonolitic melt entrapped in the melt inclusions is ~4% and ~96%, respectively (see "Methods" and Fig. 1 in the Supplementary Notes). 36 conjugate silicocarbonate to carbonate-silicate liquid pairs were sufficiently large enough to be analyzed with field-emission electron microprobe (EPMA) techniques. Furthermore, we measured 23 melt inclusions with only phonolitic liquids (Ls*) and 13 carbonate melts, where the conjugating phonolitic part was too small to perform quantitative analyses (Lc*). Representative compositions are given in Table 1, all microprobe analyses are presented in the Supplementary Data 1.

The compositional trend of conjugate immiscible melts indicates a two-liquid field (Fig. 3). The two-liquid field expands depending on the degree of separation of the immiscible carbonate-silicate melts, while the carbonatic melts show a wider compositional range than conjugating silicate liquids. The silicocarbonate to carbonate liquids have Na2O + K2O concentrations ranging from 1.7–7.8 wt% (average 4.2 wt%), SiO2 + Al2O3 vary between 16.2–68.8 wt%, CaO and CO2 range from 12.7–52.4 and 5.4–24.9 wt%, respectively. Consanguine phonolite melts show SiO2 + Al2O3 concentrations of 72.8–83.7 wt%, CaO of up to 5.5 wt% and Na2O + K2O varying between 10.3–15 wt%.

The major element distribution between immiscible silicate and carbonate melts is illustrated in Fig. 4 as \( D_{Ls/Lc} \). Overall, the carbonate melts are enriched in Ca, Mg, Mn, Fe2O3, Ti, F, and Cl (\( D_{Ls/Lc} > 1 \)) while Na, K, Al, Si, and S are concentrated in the silicate liquid (\( D_{Ls/Lc} < 1 \)).

Using these data, we calculated the parental melt composition from which Ls and Lc were formed (Table 1), using the compositions and modal abundances of Ls, Lc, and Ls* (see Supplementary Data 1). It should be noted that the phonolite liquids (Ls) as well as the calculated parental melt (Lp) are relatively rich in CaO, which indicates that a more primitive phonolite melt, which resembles melt compositions from lower parts of the magma chamber (ULST), has been entrapped.

**Discussion**

The composition of primary carbonatite melts is controversially discussed as the vast majority of >500 carbonatite occurrences worldwide are calcitic or dolomitic while the only active carbonatite volcano Oldoinyo Lengai erupts natrocarbonatitic lavas. Several authors (e.g.,) proposed that Ca-Carbonatites derive from Na-carbonatitic melts and have lost their alkalis by fenitization or other fluid-driven processes. Chen et al. deduced from melt inclusions in the calciccarbonatitic Oka complex which contain i.a. nyrereite that its parental liquid was natrocarbonatitic and that such alkali-rich carbonate melts were more common than preserved in the carbonatite rock record.

Contrastingly, a recent experimental study of Weidendorfer et al. shows that Na-carbonatites can evolve from moderately alkali-rich Ca-carbonatite liquids at crustal pressures (100 MPa, 1200–590 °C) through crystal fractionation. They proposed that a parental melt (i.e., their "multiphase" composition: 8–9 wt% Na2O + K2O, Fig. 5) represent such a moderately alkali-rich Ca-
carbonatite melt that could have exsolved from nephelinites, but natural examples of such melts have not been reported, yet. However, experimental findings of Kjarsgaard\textsuperscript{37} on CaO-rich nephelinites at 200 – 500 MPa and 900 – 1040 °C show that low to

Table 1: Selected electron microprobe analyses of conjugate immiscible silicate (Ls) – carbonate (Lc) melts.

|       | Lc7 | Ls7\textsuperscript{‡} | Lc10 | Ls10-1\textsuperscript{‡} | Lc100 | Ls100\textsuperscript{§} | Lc101 | Ls101\textsuperscript{‡} | Lp   |
|-------|-----|------------------------|------|-------------------------|-------|------------------------|-------|------------------------|------|
| SiO\textsubscript{2} | 14.88 | 54.61 | 15.3 | 57.19 | 15.58 | 60.48 | 16.30 | 61.65 | 54.30 |
| TiO\textsubscript{2} | 0.46 | 0.58 | 0.67 | 0.44 | 0.68 | 0.21 | 0.48 | 0.13 | 0.26 |
| Al\textsubscript{2}O\textsubscript{3} | 1.34 | 20.15 | 1.234 | 20.44 | 0.82 | 21.02 | 0.89 | 22.04 | 19.78 |
| Cr\textsubscript{2}O\textsubscript{3} | 0.079 | bdl | bdl | bdl | 0.13 | bdl | bdl | 0.24 | 0.04 |
| FeO | 2.31 | 2.11 | 2.34 | 1.73 | 3.04 | 1.40 | 3.16 | 2.10 | 1.68 |
| MnO | 0.553 | 0.37 | 0.731 | 0.30 | 1.40 | 0.508 | 1.05 | 0.058 | 0.2 |
| MgO | 0.741 | 0.117 | 0.565 | 0.03 | 0.49 | 0.07 | 0.32 | 0.11 | 0.33 |
| CaO | 51.61 | 0.69 | 46.78 | 0.36 | 52.39 | 0.69 | 51.58 | bdl | 3.83 |
| P\textsubscript{2}O\textsubscript{5} | n.a. | n.a. | n.a. | n.a. | 0.12 | 0.07 | 0.18 | bdl |
| Na\textsubscript{2}O | 4.00 | 6.44 | 3.83 | 6.03 | 3.35 | 5.20 | 3.96 | 4.77 | 5.1 |
| K2O | 0.707 | 8.51 | 0.496 | 8.46 | 0.56 | 7.23 | 0.43 | 6.14 | 6.49 |
| SO\textsubscript{2} | 0.445 | 0.91 | 0.512 | 2.02 | 0.30 | 0.239 | 0.33 | 0.359 | 0.76 |
| Cl | 0.4005 | 0.199 | 0.4157 | 0.173 | 0.41 | 0.188 | 0.49 | 0.175 | 0.22 |
| F | 4.036 | 0.461 | 3.966 | 0.157 | 3.97 | 0.25 | 4.20 | 0.16 | 0.42 |
| Sub total | 81.56 | 95.15 | 76.84 | 97.34 | 100.48 | 97.56 | 102.42 | 98.35 | 94.01 |
| Less O = F,Cl | 1.79 | 0.24 | 1.76 | 0.11 | 1.76 | 0.15 | 1.88 | 0.11 | 0.23 |
| Total | 79.77 | 94.91 | 75.08 | 97.23 | 98.72 | 97.41 | 100.54 | 98.25 | 93.84 |
| CO\textsubscript{2} | 20.23 | 24.92 |

\textsuperscript{Lp} represents the calculated parental phonolite melt. All Ls-Lc EPMA analyses are shown in Supplementary Data 1. bdl below detection limit, n.a. not analysed.
\textsuperscript{†} CO\textsubscript{2} in carbonate liquid estimated by difference to 100 wt% total.
\textsuperscript{§} CO\textsubscript{2} with C measured quantitatively.
\textsuperscript{‡} Ls composition corrected for coalescing nm-sized Lc melt droplet component. Modal % Lc in Ls in parantheses.

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**Fig. 3** Compositions of conjugate immiscible carbonate and silicate melt. Conjugate immiscible carbonate and silicate melt compositions plotted as a function of the partition coefficient of SiO\textsubscript{2} between carbonate and silicate melt (\(D_{\text{SiO}_2}\)) showing the compositional gap between the two melts. Calculated parental phonolitic melt (Lp) is given in Table 1. LST layer 1034 bulk rock composition is taken from\textsuperscript{40}.

**Fig. 4** Major element distribution between immiscible silicate and carbonate liquids. Partition coefficients (\(D_{Ls/Lc}\)) for major element oxides between immiscible silicate and carbonate liquids in hauyne-entrapped melt inclusions. Mg, Ca, Mn, Fe, F, Ti, and Cl partition into the carbonate melt while Na, K, Al, Si, S are concentrated in the silicate liquid. In general our data agrees well with experimental data from Kjarsgaard\textsuperscript{37} on carbonated nephelinite at 200 MPa and 900–960 °C and natural data from Guzmics et al.\textsuperscript{22} on heated perovskite-hosted coexisting immiscible melt inclusions from nephelinitic rocks (Kerimasi volcano) indicating that equilibrium between the immiscible melts has been attained. All Fe is shown as FeO\textsubscript{tot}.
moderately alkali (4.23–17.76 wt% Na₂O + K₂O) and Ca-rich carbonatite melts at SiO₂-contents between 1.11–11.72 wt% can be generated, namely by liquid immiscibility (Fig. 5).

The immiscible carbonatite melts in our melt inclusions trend towards such moderately alkali- (D_Ls/Lc = 1.8; D_Rhod/Lc = 10.7) and highly Ca-rich (D_Ca/Lc = 0.07) compositions at elevated SiO₂ and Al₂O₃ contents (Figs. 4, 5). This is especially indicated by the most primitive carbonatitic liquid Lc10 in our study with SiO₂ + Al₂O₃ of 16.5 wt%, CaO of 46.8 wt%, and Na₂O + K₂O of 4.3 wt% (Table 1). Furthermore, the preferred partitioning of F (D_Ls/Lc = 0.07) and Cl (D_Ls/Lc = 0.6) into carbonate liquid (Lc) results in high to moderate F (average 4.9 wt%) and Cl (average 0.39 wt%) contents while Mg, Mn, Fe, and Ti also have Ls-Lc D’s < 1 (Fig. 4). It should be noted that primary carbonatite melts must contain some Si, Al, Fe, Mg, F, Cl, and P as fluorspar, apatite and other accessory silicates and oxide minerals are commonly observed to crystallize in carbonatite melts53. Presumably, the carbonatitic liquids found in this study are parental to the Ca-carbonatites occurring in the LST by segregation and fractionation45 after separation from the phonolitic melt. More importantly, the overall composition of these primary carbonatites (low to moderate alkalis, high CaO, significant SiO₂ and Al₂O₃, high F and Cl) would be ideal parental magmas to the common intrusive calcicarbonatites57 as they further separate, fractionate, and accumulate.

Concerning the genesis of Na-carbonatites, the “multiphase” compositions of Weidendorfer et al.60 are compositionally close to Lc10 (Fig. 5) at somewhat lower SiO₂ and Al₂O₃ concentrations. However, the separation of Ls-Lc was quenched by the volcanic eruption and further separation at lower temperatures would produce less SiO₂ and Al₂O₃ and more alkali-rich carbonatite compositions (Fig. 5) approaching the multiphase compositions of Weidendorfer et al.60. Thus, their conclusion that Na-carbonatite and Ca-carbonatitic rocks may have similar, moderately alkaline Ca-carbonatitic parental melts is corroborated by this study.

In conclusion, our data confirms that carbonatitic melts can be formed by liquid immiscibility from an alkaline, silica-under-saturated, highly-differentiated phonolite magma under crustal pressures and temperatures. These primary carbonate liquids are of moderately alkaline Ca-carbonatitic compositions with significant amounts of silica, and they are ideal parental melts to the common intrusive Ca-Carbonatites (e.g.33,81) but may also fractionate towards Na-rich carbonatites such as those found at the Oldoinyo Lengai volcano60.

**Methods**

**Electron microprobe.** Quantitative analyses of carbonate and silicate melt inclusions were done with a JEOL JXA 8530F field-emission electron microprobe. Prior to analyses all elements were standardized on matrix-matched natural and synthetic reference materials (Table 2). Acceleration voltage was set to 15 kV.

| Table 2 Electron microprobe analytical conditions at 15 and 10 kV and 1–10 μm spot size. |
|---|---|---|---|---|---|---|
| Element | Channel | Diff. crystal | X-ray line | Beam current | Peak/Bkg. counting time (s) | Reference material |
| F | 1 | LDE1 | Kx | 15 | 30/15 | Ast_Topas |
| C | 1 | LDE2 | Kx | 15 | 10/5 | P_Fe3C |
| Na | 2 | TAP | Kx | 10 | 5/2.5 | H_Jadeite |
| Mg | 2 | TAP | Kx | 10 | 10/5 | U_OlivineSanCarlos |
| Al | 2 | TAP | Kx | 10 | 10/5 | H_Disthener8 |
| Si | 2 | PETI | Kx | 10 | 10/5 | U_Hypersthene |
| K | 3 | PETI | Kx | 10 | 5/2.5 | H_SandineP14 |
| Ca | 3 | PETI | Kx | 10 | 10/5 | H_DiopsideST48 |
| Cl | 4 | PETI | Kx | 15 | 30/15 | Ast_Tugtupite |
| S | 4 | PETI | Kx | 10 | 5/2.5 | Ast_Celestite |
| P | 4 | LIFH | Kx | 10 | 10/5 | U_Apatite_P |
| Ti | 5 | LIFH | Kx | 10 | 10/5 | Ast_Rutile |
| Fe | 5 | LIFH | Kx | 10 | 10/5 | U_Fayalite |
| Cr | 5 | LIFH | Kx | 10 | 10/5 | Ast_Cr2O3 |
| Mn | 5 | LIFH | Kx | 10 | 10/5 | Ast_Rhodonite |
Given the small size of carbonate and silicate melts, in a second analytical session the accelerating voltage was set to 10 kV in order to decrease the beam interaction volume. The electron beam size was adjusted depending on size of the melt inclusions between 1 and 10 µm. Firstly, all elements except Fe and Cl were analyzed with a beam current of 10 nA and counting times of 10 s on the peak and 5 s on the background except for Na and K, which have been measured with 5 s on the peak and 2.5 s on the background within the first round of elements to avoid migration of alkalis. Secondly, the same spots were measured for Fe and Cl. Due to the interference of FeKα with high intensity LDE1 multilayer diffraction crystal we followed the procedure of Fletetakia et al. by estimating the FeL2 Fe3C standards and samples and varied by 0.00204 sinθ within the paper.

Data availability
The data supporting the findings of this study are provided as Supplementary Data 1 within the paper.

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