

Silica is unlikely to be soluble in upper crustal carbonatite melts

Received: 19 July 2022

Michael Anenburg ¹✉ & Tibor Guzmics ²

Accepted: 9 November 2022

Published online: 21 February 2023

Check for updates

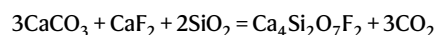
ARISING FROM Berndt, J. & Klemme, S. *Nature Communications* <https://doi.org/10.1038/s41467-022-30500-7> (2022)

A consensus among all experimental studies is that the solubility of silica (SiO₂) is low in upper crustal carbonatite melts of below 5 kbar and 1000 °C (mostly much less than 5 wt% SiO₂)^{1,2}, in agreement with most natural melt inclusion studies^{3–6}. Recently, Berndt and Klemme (B&K hereafter) documented haüyne-hosted melt inclusions from the Laacher See volcano exhibiting carbonatite–silicate liquid immiscibility formed at 720–880 °C and 1–2 kbar, with measured carbonatite melt containing high SiO₂ (~15 wt%), and moderately low Na₂O and K₂O (combined contents below 8 wt%)⁷. Their reported silica contents are exceptionally high, never before observed in natural melt inclusions, and never synthesised in experimental studies at upper crustal conditions. If correct, their results significantly increase the permissible silica range contained in natural carbonatite melts, but our results show that their reported composition cannot be liquid, rejecting the existence silica-rich carbonatite melts at these conditions.

To test whether a silica-rich carbonatite melt can exist, we attempted to synthesise a melt with the average composition of B&K's carbonatite melts (all in wt%, SiO₂: 15.5%, TiO₂: 0.57%, Al₂O₃: 1.07%, Cr₂O₃: 0.10%, FeO: 2.72%, MnO: 0.94%, MgO: 0.53%, CaO: 50.8%, P₂O₅: 0.16%, Na₂O: 3.76%, K₂O: 0.55%, SO₃: 0.41%, Cl: 0.44%, F: 4.04%, H₂O: 5.06%, CO₂: 35.3%). The percentage sums to -122% due to excess CO₂ in our experiment, compared to CO₂ contents measured by B&K. This is to ensure stability of carbonatite melt, because low CO₂ partial pressures will require unrealistically high alkali contents for immiscibility¹. Temperature and pressure were set to 880 °C and 2 kbar, B&K's upper limit. The Laacher See rocks formed at an oxygen fugacity of ΔNNO + 1 to +2⁸, so we attempted to use a Re–ReO₂ oxygen buffer (≅ΔNNO + 2 at run conditions) by placing several layers of powdered Re metal with a tiny sprinkling of ReO₂⁹. The starting materials were packed into a Ag₅₀Pd₅₀ capsule and run over 66 hours inside a piston cylinder using a 5/8" pressure vessel and an NaCl–Pyrex–MgO assembly. The experiment was quenched to room temperature, the capsule contents were exposed using sandpaper, and the contents were dried and then impregnated and reimpregnated with epoxy resin. All polishing and sample preparation was conducted dry to preserve potential water-soluble materials.

The experiment resulted in a mineral assemblage dominated by calcite and cuspidine (Fig. 1a, b). Accessory phases are perovskite, haüyne, and spinel. ReO₂ reacted to form perrhenate (ReO₄⁻) which was sequestered in the haüyne anion site. No ReO₂ was found among the products, so oxygen fugacity was not strictly buffered to Re–ReO₂, but the coexistence of Re⁰ metal and Re⁷⁺ perrhenate indicates it was not far from it. The resulting microstructure strongly resembles solid-state sintering, full of porosity and fine grain sizes of several micrometres. Liquid-like menisci and other wetting textures are not present. Carbonatite melts overwhelmingly quench to dendritic intergrowths of carbonate minerals^{10–12}, which are likewise not present in this experiment. These observations indicate that no wide spread melting has occurred during the experiment. Rare features resembling melt pools (Fig. 1c) contain nanoscale grains of KReO₄ (Fig. 1d), together with other elements (Fig. 1e). Although it is challenging to determine whether the detected elements originate from the melt pools or the surrounding minerals, the relatively high Ca and C counts indicate that a substantial CaCO₃ component is present in this melt. The 1 atm melting point of KReO₄ is roughly 550 °C, so we expect that its melting point at 2 kbar is below 880 °C. Thus, we inadvertently introduced a low melting point flux into the experiment by employing the Re–ReO₂ buffer, and even then, no widespread melting of the capsule contents occurred. This demonstrates that the carbonatite melt composition reported by B&K cannot be liquid in upper crustal conditions.

One may argue that the H₂O/CO₂ ratio in our experiment was not sufficiently high to trigger melting. This can be examined using thermodynamic relationships. The two dominant coexisting minerals are calcite and cuspidine, which can be linked by the reaction:



Where CaF₂ and SiO₂ are thermodynamic components, and CO₂ is the carbonic component of a mixed H₂O–CO₂ gas phase. Any increase in H₂O would dilute the chemical potential of CO₂, and given fixed F and Si contents (as constrained by B&K's analytical results), would necessarily cause decomposition of calcite.

¹Research School of Earth Sciences, Australian National University, Canberra, ACT 2600, Australia. ²Lithosphere Fluid Research Lab, Eötvös University, Budapest 1117, Hungary. ✉e-mail: michael.anenburg@anu.edu.au

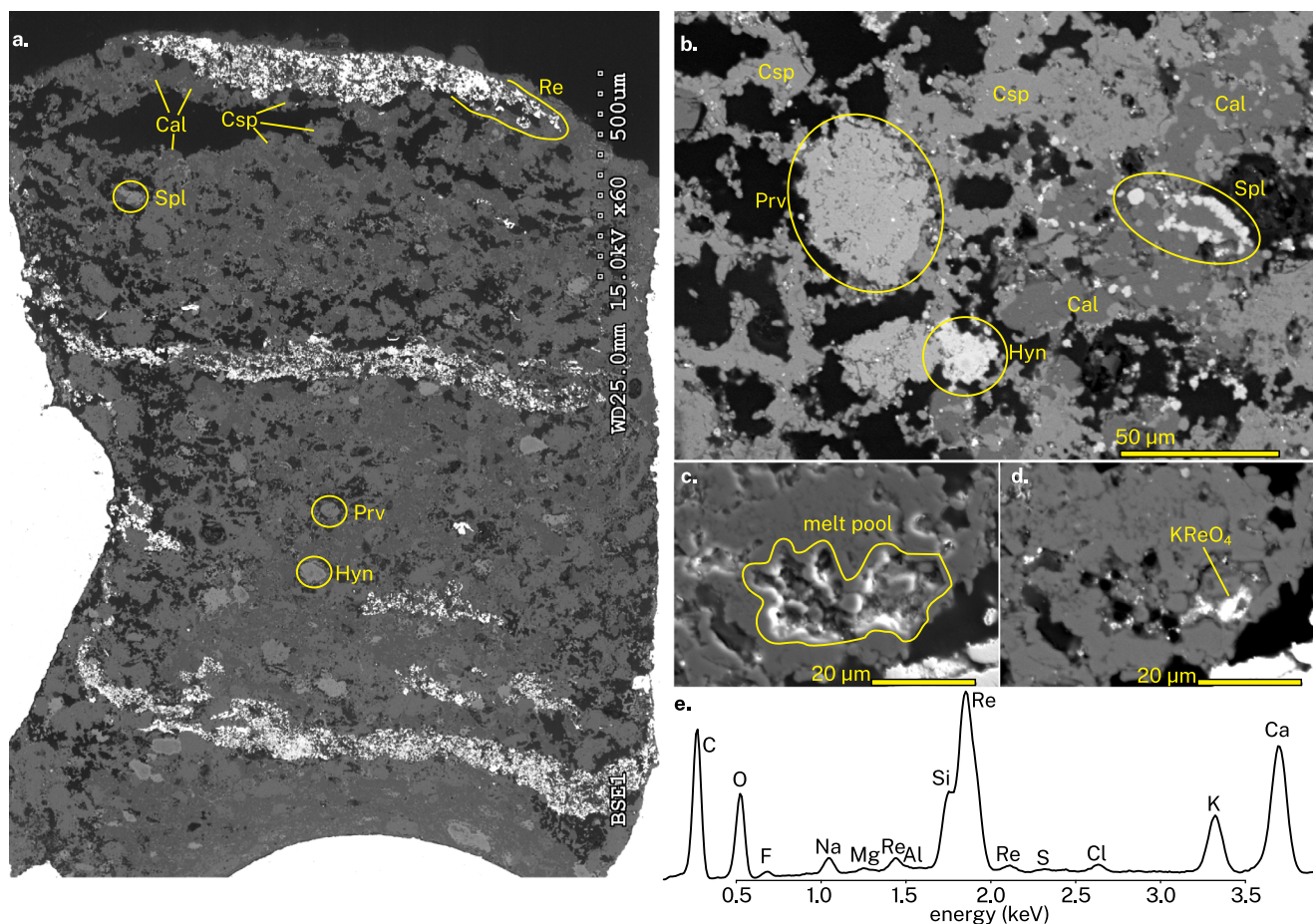


Fig. 1 | Experimental results. **a** backscattered electron image of the entire experimental capsule. Black regions are former CO₂–H₂O gas filled cavities, now impregnated with epoxy resin. Irregular white outline is the AgPd capsule. **b** closeup image of a representative region. **c** secondary electron image showing an

area suspected as a former melt pool, enclosed by straight crystal faces. **d** backscattered electron image of the same region, showing bright potassium perhenate. **e** an energy-dispersive X-ray spectroscopy (EDS) spectrum of the KReO₄-rich area.

Therefore, any H₂O-induced melting of the composition would lead to a fluorinated hydrous calcsilicate melt, not a carbonatite. As for the effect of other experimental parameters, we cannot foresee a scenario in which moderate changes in either temperature, pressure, or composition can cause an essentially solid experiment to completely melt.

Fig. 2 shows compositions of immiscible silicate-carbonatite melts and silicate-saturated carbonatite melts at crustal pressures and temperatures between 650 and 1050 °C. It shows that natural and experimental carbonatite melts are on the right side of the solvus with low SiO₂ (<4–5 wt%), regardless of their fluorine contents (up to 14 wt%). In contrast, B&K's carbonatite melts are on the left side of the solvus, together with their presumed conjugate silicate melts⁷, and contain a silica/alkalis ratio too high for them to be immiscible between 650 and 1050 °C. These high-silica carbonatite melts may exist at mantle temperatures (>1200 °C) and pressures (>1.5 GPa), where the coexisting silicate melt cannot be an evolved phonolite with SiO₂ contents higher than 57 wt% and MgO between 0.1 and 2.2 wt%^{1,10,13,14}.

We ascribe the spurious compositions of B&K's reported carbonatite melts to three factors. First, alkali carbonates are extremely unstable under an electron beam. In a previous study we observed that Na counts drop substantially within just a few seconds, when measured using a 10 nA beam defocused to 15 μm¹⁵. B&K used a maximum spot size of 10 μm, in which the current density is 2.25 times higher. More commonly, they used smaller

spot sizes (1–5 μm) in which current densities are at least an order of magnitude higher. We observed Na-loss on coarse grained crystalline materials¹⁵, whereas B&K's are quenched liquids, consisting of nanoscale and potentially poorly crystalline phases. In such conditions, Na-loss is essentially instantaneous and even a short analysis time of 5 seconds strongly underestimates the Na contents of analysed materials (Fig. 2). Second, while B&K correctly state that their silicate melt compositions are contaminated by nanoscale droplets of carbonatite melt and correct for it, similar nanoscale droplets of silicate melt are observed in their carbonatite melts⁷. No correction was applied for these mixtures by B&K. Therefore, their reported carbonatite melt compositions are not pure and contain some degree of silicate melt contamination (Fig. 2). Finally, as our experiments resulted in häyneyne, the same mineral host of B&K melt inclusions, this raises the possibility that some häyneyne signal was measured together with the carbonatite melts.

To summarise, we could not replicate B&K's findings in an experiment. Their results strongly deviate from possible carbonatite compositions based on previous phase equilibria and melt inclusion studies. Their analyses are likely to have suffered alkali loss during EPMA measurement. We therefore conclude that B&K do not provide evidence for silica-rich carbonatite melts in upper crustal conditions. Additionally, B&K's findings cannot be a "missing link" between CaO-rich and extrusive Na-carbonatitic magmas⁷, as the link has already been described before^{3,11,15–17}.

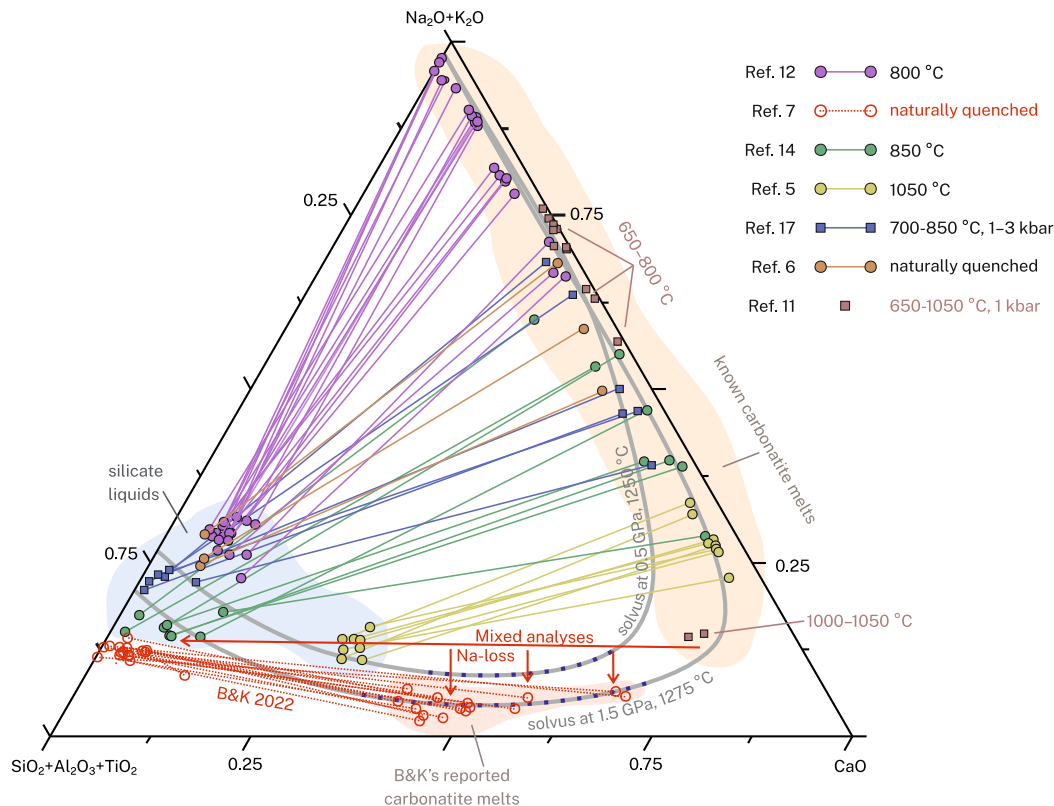


Fig. 2 | Composition of silicate-saturated carbonatite melts plotted on the pseudo-ternary diagram in the system $\text{Na}_2\text{O}+\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2+\text{Al}_2\text{O}_3+\text{TiO}_2-\text{CO}_2$ (all in wt%, projected from CO_2). Squares and circles are experimental and melt inclusion data, respectively. Grey curves show experimental silicate-carbonatite solvi in the system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2+\text{Al}_2\text{O}_3-\text{CO}_2$. Purple dots on solvi show “single liquid” areas. Solid and dotted tie lines connect the coexisting and immiscible

silicate (left) and carbonatite (right) melt pairs. Temperatures next to brown squares indicate experimental temperature¹¹. Carbonatite melt compositions with $F > 3$ wt% were corrected by assuming that all F is paired with Ca, with remaining Ca considered as CaO. Red arrows suggest possible analytical issues on the B&K carbonatite melt data.

Data availability

All data and calculations require to produce Fig. 2 are available in the supplementary file. Source data are provided with this paper.

References

- Brooker, R. A. & Kjarsgaard, B. A. Silicate-carbonate liquid immiscibility and phase relations in the system $\text{SiO}_2-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}-\text{CO}_2$ at 0.1–2.5 GPa with applications to carbonatite genesis. *J. Petrol.* **52**, 1281–1305 (2011).
- Vasyukova, O. V. & Williams-Jones, A. E. Carbonatite metasomatism, the key to unlocking the carbonatite-phoscorite-ultramafic rock paradox. *Chem. Geol.* **602**, 120888 (2022).
- Veksler, I. V. & Lentz, D. in *Melt Inclusions in Plutonic Rocks* (ed Webster, J. D.) **36**, 123–149 (Mineralogical Association of Canada, 2006).
- Yaxley, G. M., Anenburg, M., Tappe, S., Decree, S. & Guzmics, T. Carbonatites: classification, sources, evolution, and emplacement. *Annu. Rev. Earth Planet. Sci.* **50**, 261–293 (2022).
- Guzmics, T. et al. Liquid immiscibility between silicate, carbonate and sulfide melts in melt inclusions hosted in co-precipitated minerals from Kerimasi volcano (Tanzania): evolution of carbonated nephelinitic magma. *Contributions Mineral. Petrol.* **164**, 101–122 (2012).
- Mitchell, R. H. Peralkaline nephelinite-natrocyanatite immiscibility and carbonatite assimilation at Oldoinyo Lengai, Tanzania. *Contributions Mineral. Petrol.* **158**, 589–598 (2009).
- Berndt, J. & Klemme, S. Origin of carbonatites-liquid immiscibility caught in the act. *Nat. Commun.* **13**, 2892 (2022).
- Berndt, J., Holtz, F. & Koepke, J. Experimental constraints on storage conditions in the chemically zoned phonolitic magma chamber of the Laacher See volcano. *Contributions Mineral. Petrol.* **140**, 469–486 (2001).
- Pownceby, M. I. & O'Neill, H. S. C. Thermodynamic data from redox reactions at high temperatures. IV. Calibration of the Re-ReO₂ oxygen buffer from EMF and NiO + Ni-Pd redox sensor measurements. *Contributions Mineral. Petrol.* **118**, 130–137 (1994).
- Martin, L. H. J., Schmidt, M. W., Mattsson, H. B. & Guenther, D. Element partitioning between immiscible carbonatite and silicate melts for dry and H₂O-bearing systems at 1–3 GPa. *J. Petrol.* **54**, 2301–2338 (2013).
- Weidendorfer, D., Schmidt, M. W. & Mattsson, H. B. A common origin of carbonatite magmas. *Geology* **45**, 507–510 (2017).
- Berkesi, M., Bali, E., Bodnar, R. J., Szabó, Á. & Guzmics, T. Carbonatite and highly peralkaline nephelinite melts from Oldoinyo Lengai Volcano, Tanzania: The role of natrite-normative fluid degassing. *Gondwana Res.* **85**, 76–83 (2020).
- Poli, S. Carbon mobilized at shallow depths in subduction zones by carbonatitic liquids. *Nat. Geosci.* **8**, 633–636 (2015).
- Guzmics, T. et al. Natrocarbonatites: a hidden product of three-phase immiscibility. *Geology* **47**, 527–530 (2019).
- Anenburg, M., Mavrogenes, J. A., Frigo, C. & Wall, F. Rare earth element mobility in and around carbonatites controlled by sodium, potassium, and silica. *Sci. Adv.* **6**, eabb6570 (2020).
- Guzmics, T. et al. Carbonatite melt inclusions in coexisting magnetite, apatite and monticellite in Kerimasi calciocarbonatite, Tanzania: Melt evolution and petrogenesis. *Contributions Mineral. Petrol.* **161**, 177–196 (2011).

17. Kjarsgaard, B. A., Hamilton, D. L. & Peterson, T. D. in *Carbonatite Volcanism* (eds Bell, K. & Keller, J.) Vol 4, 163–190 (Springer-Verlag, 1995).

Acknowledgements

M.A. is supported by Australian Research Council (ARC) Linkage grant LP190100635. T.G. is supported by Betta Üzletlanc Ltd. We thank Jasper Berndt and Stephan Klemme for fruitful discussions that preceded the submission of this manuscript.

Author contributions

M.A. performed the piston cylinder experiment. T.G. compiled and analysed conjugate silicate-carbonatite pairs. Both authors wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-023-35840-6>.

Correspondence and requests for materials should be addressed to Michael Anenburg.

Peer review information *Nature Communications* thanks Gerhard Wörner for their contribution to the peer review of this work.

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2023