Geochemical Perspectives Letters

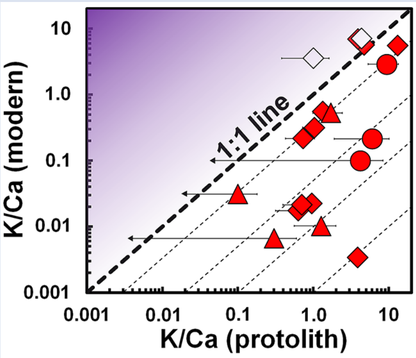
Published by the European Association of Geochemistry

Radiogenic Ca isotopes confirm post-formation K depletion of lower crust

M.A. Antonelli[1*], D.J. DePaolo[1,2], T. Chacko[3], E.S. Grew[4], D. Rubatto[5]

doi: 10.7185/geochemlet.1904

Abstract



Heat flow studies suggest that the lower crust has low concentrations of heat-producing elements. This could be due to either (i) greater fractions of basaltic rock at depth or (ii) metamorphic depletion of radioactive elements from rocks with more evolved (andesitic to granodioritic) compositions. However, seismic data suggest that lower crust is not predominantly basaltic, and previous studies (using Pb and Sr isotopes) have shown that lower crustal rocks have experienced significant losses of U and Rb. This loss, however, is poorly constrained for K, which is inferred to be the most important source of radioactive heat in the earliest crust. Our high precision Ca isotope measurements on a suite of granulite facies rocks and minerals from several localities show that significant losses of K (~60 % to >95 %) are associated with high temperature metamorphism. These results support models whereby reduction of heat production from the lower crust, and consequent stabilisation of continental cratons in the Precambrian, are largely due to high temperature metamorphic processes. Relative changes in whole rock K/Ca suggest that 20-30 % minimum (granitic) melt removal can explain the K depletions.

Received 18 October 2018 | Accepted 4 January 2019 | Published 6 February 2019

Introduction

Samples from lower continental crust (LCC) can be brought to the surface in two major ways, either (i) as coherent high grade terranes, through tectonic processes, or (ii) as individual xenoliths, through deep-seated volcanism. Based on analysis of these samples, it has been established that much of the LCC was heated to granulite facies conditions (>~800 °C) and lost significant amounts of its original heat producing element budget (Rudnick and Gao, 2014), yet it is uncertain whether this is a sufficient explanation for modern heat flow data without invoking greater fractions of mafic crust at depth (Hacker *et al.*, 2015).

Metamorphic heating results in the breakdown of primary hydrous mineral phases to anhydrous mineral assemblages. Typical reactions involve the transformation of amphibole and mica into feldspar, pyroxene, sillimanite/kyanite, and (at higher pressures) garnet. These transformations are typically accompanied by the generation of granitic liquids (rich in incompatible elements and containing dissolved H_2O) that are generally lost from the system, but found preserved as microscopic melt inclusions (*e.g.*, Bartoli *et al.*, 2016; Stepanov *et al.*, 2016; Ferrero *et al.*, 2018). There is also evidence that fluid loss in the absence of melt generation could contribute to the geochemical changes, as suggested by the common observation of high Th/U in granulite facies rocks (Rudnick and Gao, 2014). Generation and loss of melt, however, is viewed in the more recent literature as being the primary mechanism affecting granulite and ultrahigh temperature (UHT) rocks (*e.g.*, White and Powell, 2002; Guernina and Sawyer, 2003; Kelsey and Hand, 2015). The lower U, Th, (and K) concentrations and higher density of LCC (Rudnick and Gao, 2014; Hacker *et al.*, 2015) could therefore be attributed to the effects of melt loss during high temperature (HT) metamorphism accompanied by anatexis.

Previous work suggesting that U is lost from LCC is based on Pb isotopes and by comparison with Th (Rudnick and Gao, 2014), which can also be lost during partial melting at extreme conditions (Ewing *et al.*, 2014; Stepanov *et al.*, 2014). However, ancient K-loss during melting of LCC is hard to constrain because there are few means to establish K content of the protoliths (Rudnick *et al.*, 1985). Previous studies show that Rb is preferentially lost during granulite facies metamorphism relative to Sr and K (DePaolo *et al.*, 1982; Rudnick *et al.*, 1985), and that there can also be K loss relative to Ca (Ewing *et al.*, 2014; Stepanov *et al.*, 2014). However, this argument has considerable uncertainty for K when the protoliths are unavailable for analysis, and the magnitude of K loss from

1. Department of Earth and Planetary Science, University of California - Berkeley, Berkeley, CA 94720, USA
2. Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
3. Department of Earth and Atmospheric Sciences, University of Alberta, Canada
4. School of Earth and Climate Sciences, University of Maine, USA
5. Institute of Geological Sciences, University of Bern, Switzerland
* Corresponding author (e-mail: Mantonelli@berkeley.edu)

LCC remains poorly constrained. To address this problem, we use measurements of radiogenic ^{40}Ca in lower crustal granulite facies rocks and minerals. The K-Ca system is well-suited for this purpose because ^{40}K decays to ^{40}Ca (and ^{40}Ar, $t_{1/2}$ ~1.25 Gyr), the two elements are separated from each other during partial melting, and the daughter product is generally more compatible than the parent (Marshall and DePaolo, 1989).

Samples and Analytical Procedures

We report radiogenic ^{40}Ca variations (ε_{Ca}) in granoblastic to porphyroblastic mafic, granitic, and pelitic whole rocks and mineral separates from four localities: the Napier Complex, Antarctica (NC); the Slave Province, Canada (SP); the Ivrea-Verbano Zone, Italy (IVZ); and the Lhasa Block, Tibet (Sumdo eclogite, SE). The rocks span a wide range of chemical compositions and metamorphic pressure and temperature conditions, including granulite/UHT (n = 17), amphibolite (n = 3), and eclogite facies (n = 1), and range in age from Archean to Mesozoic (Supplementary Information, SI, and Tables S-1 through S-4). The SE is not likely to have lost significant amounts of K and is included only for reference (Fig. 1). Ca isotopic compositions were measured by TIMS at the University of California, Berkeley, and are reported in epsilon notation relative to Bulk Silicate Earth (BSE, SI, Table S-5), according to Equation 1.

$$\varepsilon_{Ca} = \left(\frac{\left[{}^{40}Ca/{}^{44}Ca \right]_{measured}}{\left[{}^{40}Ca/{}^{44}Ca \right]_{BSE}} - 1 \right) \times 10^4 \qquad \text{Eq. 1}$$

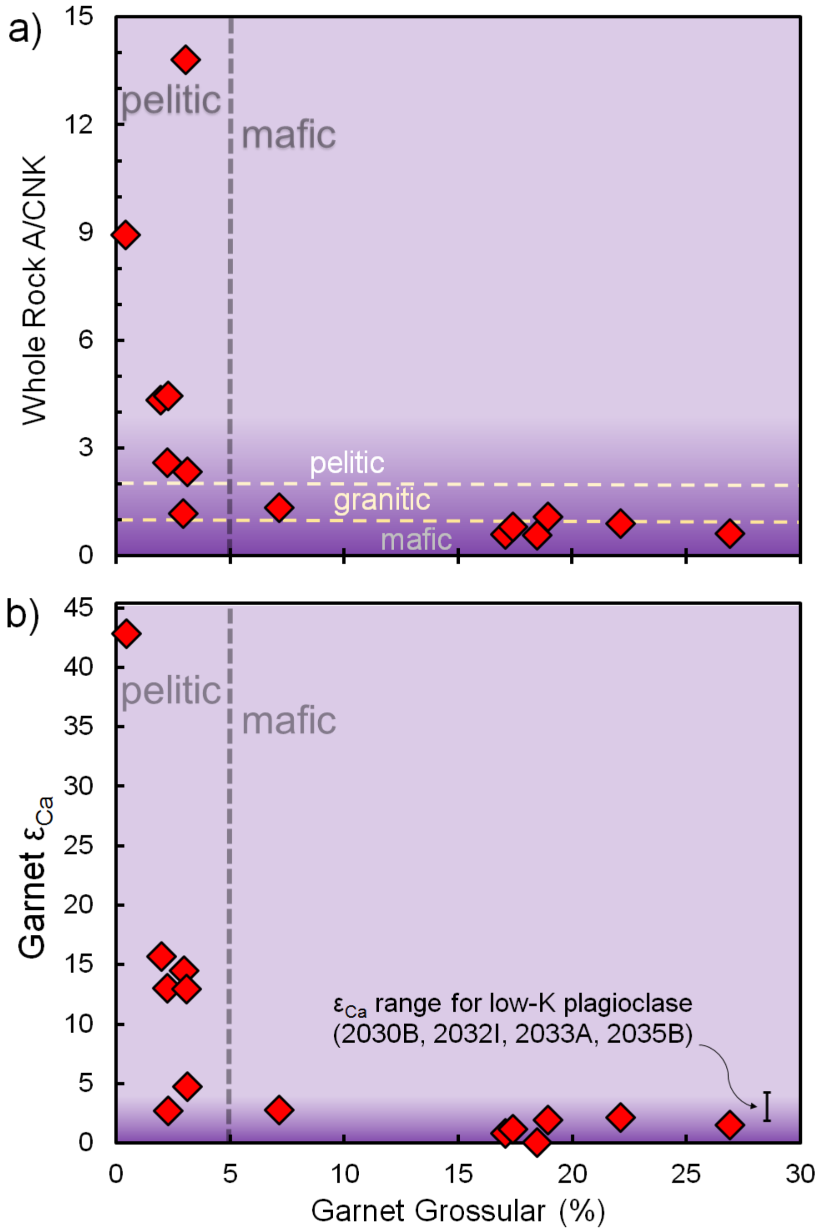


Figure 1 Garnet grossular content *versus* **(a)** whole rock peraluminosity index (A/CNK) and **(b)** garnet ε_{Ca} values (for samples containing garnet, n = 14). 2σ uncertainties (±1 for ε_{Ca}) are smaller than the symbols. Approximate mafic, granitic, and pelitic compositional zones are separated by dashed lines (SI). Darker purple band in **(b)** represents Bulk Silicate Earth (ε_{Ca} = 0) composition, corresponding to $^{40}Ca/^{44}Ca$ = 47.156 (SI).

ε_{Ca} in Low-K Metamorphic Rocks and Minerals

Garnet is an ideal mineral for ε_{Ca} analyses because it effectively excludes K, is easy to separate, and commonly contains substantial amounts of Ca. Given a clean mineral separation, any excess radiogenic Ca in garnet must be inherited from ^{40}K that decayed to ^{40}Ca in the protolith, prior to garnet formation. We find that clean garnet separates have ε_{Ca} ranging from 0 to +42 (Table S-5). Higher ε_{Ca} values are found in garnets with lower grossular content [molar Ca/(Ca+Fe+Mg+Mn) < ~5 %], from rocks with generally higher whole rock peraluminosity [defined as molar $Al_2O_3/(CaO+Na_2O+K_2O)$ and denoted A/CNK in Fig. 1a]. In mafic granulites, both garnet and low-K plagioclase separates (which were sampled in the absence of garnet), have a narrow ε_{Ca} range from 0 to +3 (Fig. 1b). Whole rock and high-K feldspar separates were also measured (Fig. S-1) in order to obtain rough K-Ca isochrons (Fig. S-2), which are in general agreement with more precise dating methods for the various regions (SI).

Protolith K/Ca Estimates

Large depletions in K associated with metamorphism can be detected with our data on garnet mineral separates. Garnet and whole rock measurements for 2040C (NC), for example, have indistinguishable (yet highly elevated) ε_{Ca} values (+12.5, see Table S-5) due to a nearly complete loss of K from the rock during metamorphism, resulting in a near zero K/Ca similar to that of garnet. For rocks where K-loss is less extreme, protolith K/Ca values are evaluated from ε_{Ca} (garnet or low-K plagioclase/whole rocks, SI) and the time interval between protolith formation and granulite facies metamorphism.

Using the metamorphic and protolith ages for each locality ('two-stage-model', SI), we are able to estimate the protolith K/Ca values using Equation 2, adapted from Marshall and DePaolo (1989).

$$[K/Ca]_{protolith} = \frac{\varepsilon_{Ca}(t_2) - \varepsilon_{Ca}(t_1)}{Q_{Ca}\left(e^{\lambda_K t_1} - e^{\lambda_K t_2}\right)} \qquad \text{Eq. 2}$$

Where $\varepsilon_{Ca}(t_2)$ and $\varepsilon_{Ca}(t_1)$ are ε_{Ca} values at metamorphic age (t_2) and protolith age (t_1), respectively; λ_K is the total decay constant of ^{40}K (assumed 0.554 Gyr^{-1}), and Q_{Ca} (~1.0804) is a factor incorporating the branching ratio of ^{40}K decay and the abundances of ^{40}K, ^{44}Ca, and ^{40}Ca relative to BSE.

In Figure 2, we show the effect of protolith age uncertainty on $[K/Ca]_{protolith}$ for our NC samples, based on Equation 2. This equation provides a *minimum* constraint on $[K/Ca]_{protolith}$ values because of three assumptions implicit in our use of the equation: (i) the oldest protolith age estimates for the various localities, (ii) single stage evolution from BSE [$\varepsilon_{Ca}(t_1) = 0$] to garnet ε_{Ca} values [$\varepsilon_{Ca}(t_2)$], and (iii) that garnets form out of the bulk protolith Ca pool at the time of metamorphism. Younger protolith ages, multiple stages for $[K/Ca]_{protolith}$ (*e.g.*, increases driven by weathering/metasomatic processes), and/or partial loss of radiogenic Ca from K-bearing minerals prior to garnet formation (through earlier melting events), would all require higher $[K/Ca]_{protolith}$ to reach the same initial ε_{Ca} values at the time of metamorphism.

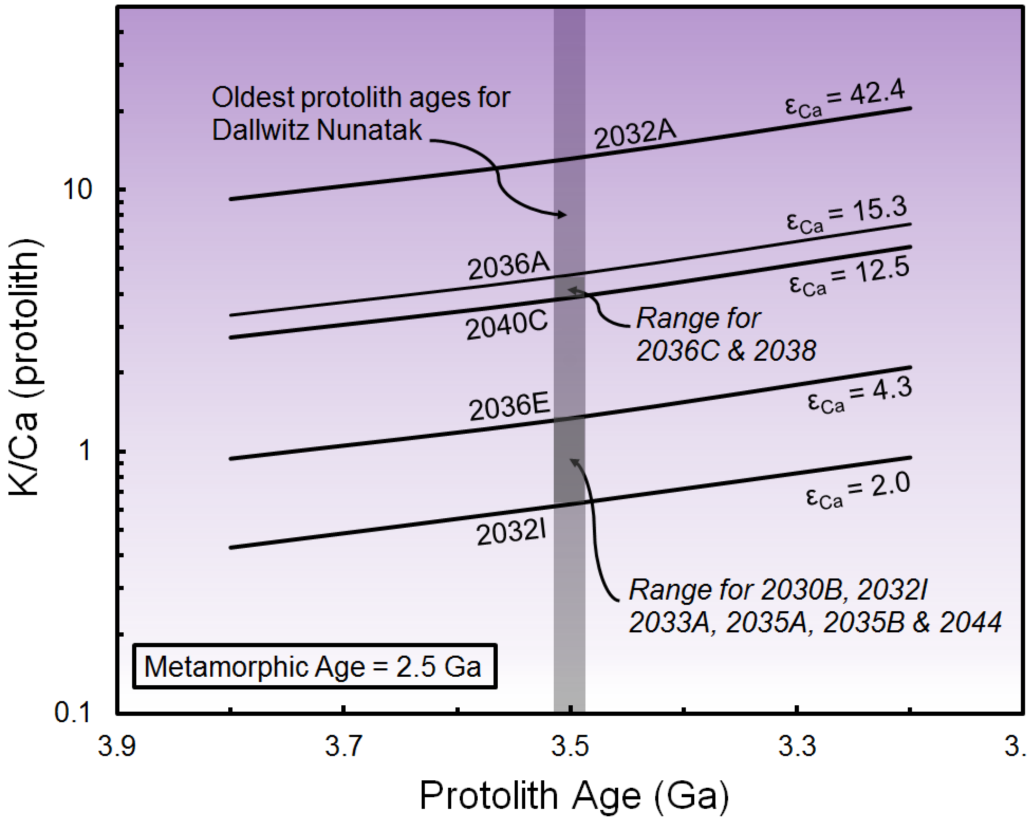


Figure 2 Dependence of $[K/Ca]_{protolith}$ on protolith age for samples from Dallwitz Nunatak (NC, n = 12) based on Equation 2. Curves are labelled by sample and delineate constant values for initial ε_{Ca} at 2.5 Ga with varying protolith ages. Grey band demarcates oldest protolith age found at Dallwitz Nunatak, in the northern Napier Complex (SI).

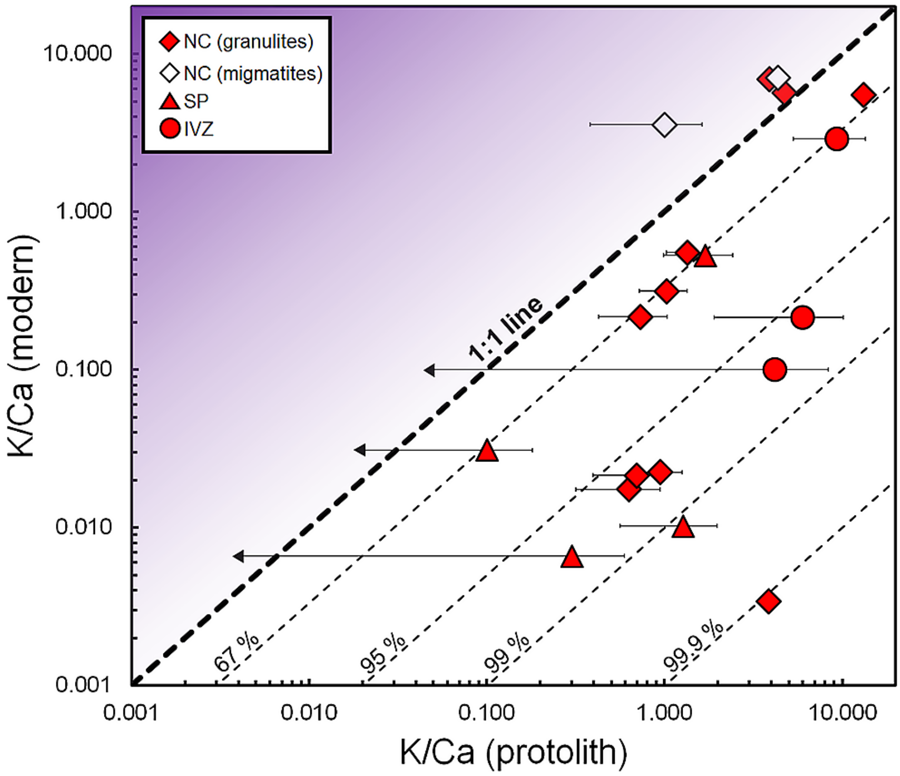


Figure 3 Whole rock K/Ca (modern) *versus* K/Ca (protolith) based on ε_{Ca} [Equation 2]. NC granulites (n = 10), NC migmatites (n = 2), SP (n = 4), IVZ (n = 3). Contours indicate relative K-loss (in %) assuming constant Ca. Uncertainties in protolith K/Ca are calculated using Equation 2, using our 2 sd on ε_{Ca} (±1); arrow terminations represent samples within error of BSE. Protolith-metamorphic ages: 3.5-2.5 Ga (NC); 3.0-2.5 Ga (SP); and 0.6-0.3 Ga (IVZ) (SI). Uncertainties for modern K/Ca are <~5 %.

Potassium Loss during High-T Metamorphism

Including data from the other localities, we find as expected that mafic samples have lower $[K/Ca]_{protolith}$ (<1), and pelitic samples have higher $[K/Ca]_{protolith}$ ranging from 1 to ~13. Comparing these estimates with $[K/Ca]_{modern}$ in the whole rocks (Fig. 3), we are able to assess K-mobility during granulite metamorphism (see Fig. S-3 for data labels).

Our results indicate that most granulites have measured K/Ca that is substantially lower than that calculated for the protolith, indicating significant K-loss during metamorphism. The samples fall into 3 rough groups: one group has no K-loss, or a slight K enrichment, and the other groups cluster at 67 % and 97 %; one NC sample suggests greater than 99.9 % K-loss (Fig. 3). Samples with younger ages and lower ε_{Ca} have larger uncertainties. Two pelitic granulites and migmatites from the NC have an apparent increase in K/Ca relative to their protolith compositions, which can potentially be explained by the presence of (externally derived) captured melt. Our data suggest that granulite facies samples with less than ~2 wt. % modern whole rock K_2O have generally lost K, and samples with >2 wt. % have generally gained K (relative to Ca, Figure S-4). Although we are unaware of K-loss estimates for the NC and SP, our data agree with previous estimates for the IVZ, where granulite facies samples have about 2/3 less K than their lower temperature (amphibolite facies) counterparts (Ewing *et al.*, 2014). Our results are also in agreement with previous work on the Napier complex that found Pb and Sr isotope evidence for significant losses of Rb relative to Sr and U relative to Th (*e.g.*, DePaolo *et al.*, 1982; Kelsey and Hand, 2015).

Melt-loss Modelling

Although there is still some debate as to whether or not granulites need externally derived fluids in order to initiate melting (Aranovich *et al.*, 2016; Clemens *et al.*, 2016), the conclusion from melting experiments (Gao *et al.*, 2016) and from trapped melt inclusions in peritectic minerals (Bartoli *et al.*, 2016; Stepanov *et al.*, 2016; Ferrero *et al.*, 2018) is that granulites are often associated with loss of granitic melt. Given that we can quantify relative K/Ca decreases, we are also able to place constraints on the amount of melt loss required to form our samples by modelling the partitioning of K and Ca between melt and residual minerals.

To estimate K/Ca fractionation during partial melting, we use a modified non-modal batch melting model, where the bulk distribution coefficient for K (D_K) is a function of the mass fraction of remaining residual K-feldspar (the most significant K-bearing mineral at granulite facies conditions), and the bulk distribution coefficient for Ca (D_{Ca}) is a function of the mass fraction of residual plagioclase + clinopyroxene (SI, Fig. S-5).

Model Results

Comparing our model estimates for $[K/Ca]_{solid}/[K/Ca]_o$ *versus* $[K_2O]_{solid}$ (at various values of F) to our ε_{Ca}-based $[K/Ca]_{mdrn}/[K/Ca]_{protolith}$ estimates and $[K_2O]_{mdrn}$ analyses for granulite facies samples, and assuming that melt is completely lost from the system, we find that most of the samples are consistent with 20-30 % melting, with the most extreme sample suggesting melt fractions of ~50 % (Fig. 4). Although the distribution coefficients used in our model are currently rough estimates, varying K and Ca distribution coefficients over a range of likely values (Fig. S-6) does not significantly change the results, which depend most significantly on $[K/Ca]_{protolith}$.

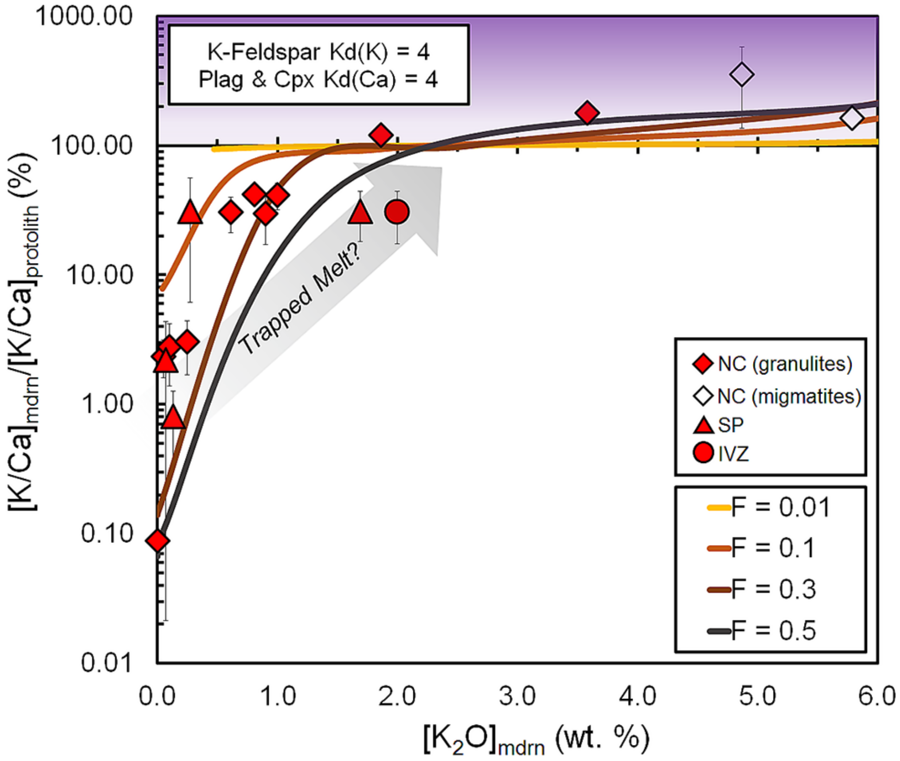


Figure 4 ε_{Ca}–based $[K/Ca]_{mdrn}/[K/Ca]_{protolith}$ [Equation 2] *versus* measured $[K_2O]_{mdrn}$ (excluding amphibolites and eclogites). Predictions from our melting model [Equations S-2 through S-4], for various starting compositions (same as in Fig. S-5) varying degree of partial melting (F) (coloured lines). NC granulites (n = 10), NC migmatites (n = 2), SP (n = 4), IVZ (IV-16-24, n = 1). Vertical error bars calculated using Equation 2, combining with those from XRF (<~5 % for K_2O/CaO); horizontal error bars are smaller than the symbols. Arrow shows effect of trapped melt on residual solids. Samples plotting above 100 % are consistent with model predictions for high K/Ca protoliths, but petrographic evidence (see SM) suggests that these potential enrichments result from (externally derived) trapped melt.

The model results generally agree with other approaches for estimating melt production during granulite facies metamorphism, including pseudosection analyses (White and Powell, 2002; Redler *et al.*, 2012; Yakymchuk and Brown, 2014; Green *et al.*, 2016; Palin *et al.*, 2016) and other methods (Guernina and Sawyer, 2003; Bartoli, 2017). These estimates typically range from ~20-50 % total melt depending on protolith compositions and P-T-time conditions.

Discussion and Conclusions

Although our assumption of complete melt segregation may be an overestimate, significant melt loss is a common feature associated with granulite facies terranes (*e.g.,* Brown, 2002; Guernina and Sawyer, 2003), and a minimum of 50-70 % of generated melt (assuming 40 % total melt) must be lost in order to retain a HT mineral assemblage (White and Powell, 2002). If melt is not fully lost from the system, our model requires greater total melt fractions in order to match $[K/Ca]_{mdrn}$ measured in the samples today. This suggests that our melting model (which uses minimum $[K/Ca]_{protolith}$ estimates and assumes total loss of melt), provides minimum estimates for total melt fractions.

Based on ε_{Ca} data, and assuming conservative protolith ages for each locality, we find that many LCC samples from the Napier Complex, Ivrea-Verbano Zone, and the Slave Province have undergone significant amounts of K depletion, with relative K/Ca decreases ranging from ~60 % to greater than 95 %. These results confirm that K, which is inferred to be the most important heat producing element in the Archean, is efficiently mobilised and removed from the lower crust during HT metamorphism. This observation implies that greater fractions of mafic rock in the lower crust are not necessary to explain modern heat flow data, and supports crustal evolution models where continental stabilisation is promoted through HT metamorphism and depletion of radioactive elements from the lower crust.

Acknowledgements

We thank N. Botto, S. Matveev, A. Locock, W. Yang, T. Teague, and S.T. Brown for their technical expertise, C. Yakymchuk and S. Ferrero for helpful discussions, and N.J. Pester for modern hydrothermal fluid samples. This research was primarily supported by a U.S. National Science Foundation (EAR100500) grant to DJD. TC acknowledges funding from a Natural Sciences and Engineering Research Council of Canada (NSERC) discovery grant, and MAA acknowledges NSERC postgraduate funding that aided in supporting this work. ESG thanks the Australian Antarctic Division for the opportunity to participate in the 1977-1978 Australian National Antarctic Research Expedition and for logistic support, and acknowledges NSF grant DPP 76-80957 to UCLA.

Editor: Helen Williams

Author Contributions

MAA and DJD designed research; MAA performed analyses; MAA, DJD, and TC analysed data; ESG, TC, DR and DJD provided samples collected in the field; MAA and DJD wrote the paper with input from TC, DR and ESG.

Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article1904.

Cite this letter as: Antonelli, M.A., DePaolo, D.J., Chacko, T., Grew, E.S., Rubatto, D. (2019) Radiogenic Ca isotopes confirm post-formation K depletion of lower crust. *Geochem. Persp. Let.* 9, 43–48.

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