Phase relations of Ca-Mg-carbonates and trace element partition coefficients between carbonates and dolomitic melt at 6 (and 9) GPa

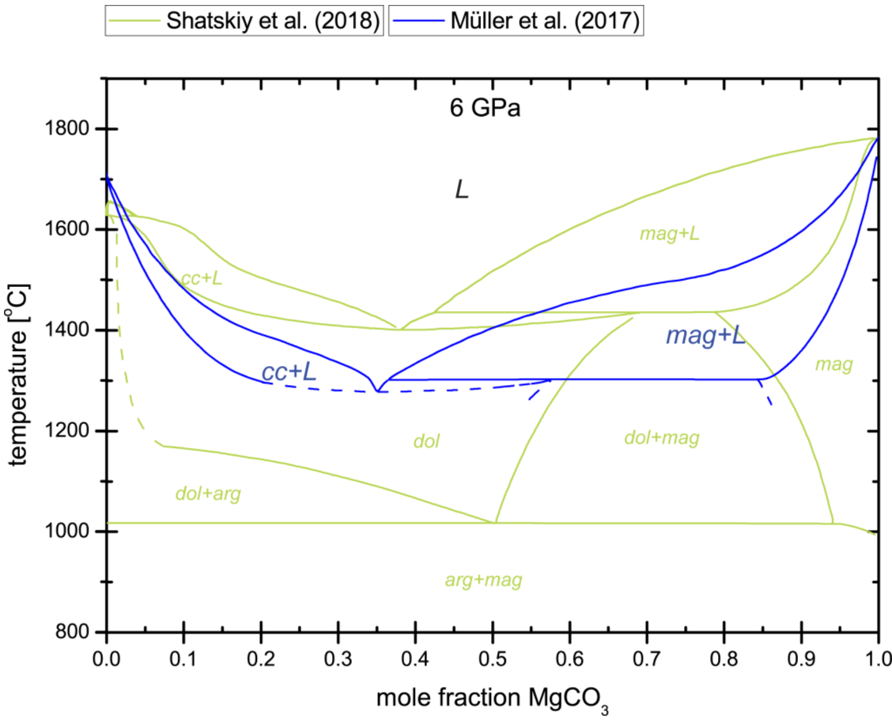
– Sieber M. J., Wilke F. D., Reichmann H-J., Koch-Müller M.

Introduction / Motivation

- The **onset and composition** of incipient melting of carbonated peridotites and carbonated eclogites are **influenced by the** pure **$CaCO_3$-$MgCO_3$ system** [1, 2, 3]

  → making the understanding of the phase relations of Ca-Mg carbonates fundamental in assessing carbon fluxes in the mantle

  → raising question to which extent the trace element signature of the incipient melt will also be affected by the melting of carbonates
- Despite this relevance, the melting relations of Ca-Mg-carbonates were poorly constrained (compare blue [4] and green [5] solidus and liquidus in figure on the right)



[1] Brey,G.P., Bulatov,V.K., Girnis,A.V., Lahaye,Y. (2008) *Experimental melting of carbonated peridotite at 6-10 GPa*. Journal of Petrology, 49, 797-821. **[2]** Dasgupta,R., Hirschmann, M.M., Withers,A.C. (2004) *Deep global cycling of carbon constrained by the solidus of anhydrous, carbonated eclogite under upper mantle conditions*. EPSL, 227, 73-85. **[3]** Yaxley, G.M., Green,D.H. (1994) *Experimental demonstration of refractory carbonate-bearing eclogite and siliceous melt in the subduction regime*. EPSL, 128, 313-325. **[4]** Müller,J., Koch-Müller,M., Rhede,D., Wilke,F.D., Wirth,R. (2017) *Melting relations in the system CaCO3-MgCO3 at 6 GPa*. Amer Miner, 102, 2440-2449. **[5]** Shatskiy,A., Podborodnikov,I.V., Arefiev,A.V., Minin,D.A., Chanyshev,A.D., Litasov,K.D. (2018) *Revision of the CaCO3–MgCO3 phase diagram at 3 and 6 GPa*. Amer Miner, 103, 441-452. **Figure:** © Sieber,M.J., Wilke, F., Koch-Müller,M. (2020) *Partition Coefficients of trace elements between carbonates and melt and suprasolidus phase relations of Ca-Mg-carbonates at 6 GPa*. American Mineralogist. All rights reserved

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Methods and Results I : phase diagram at 6 GPa

- multi-anvil experiments were performed to (re-) investigate the supra-solidus phase relations of Ca-Mg-carbonates and to investigate the trace element partitioning between carbonates (magnesite, calcite) and dolomitic melt
  - Enhancing equilibrium between solids and liquid, the multi-anvil press was roted 360° throughout the entire run duration and rotation was stop within <30 sec before quenching
- The obtained supra-solidus phase relations (grey circles and white diamonds in figure on the right) are confirmed by thermodynamic modelling of the system (not shown)

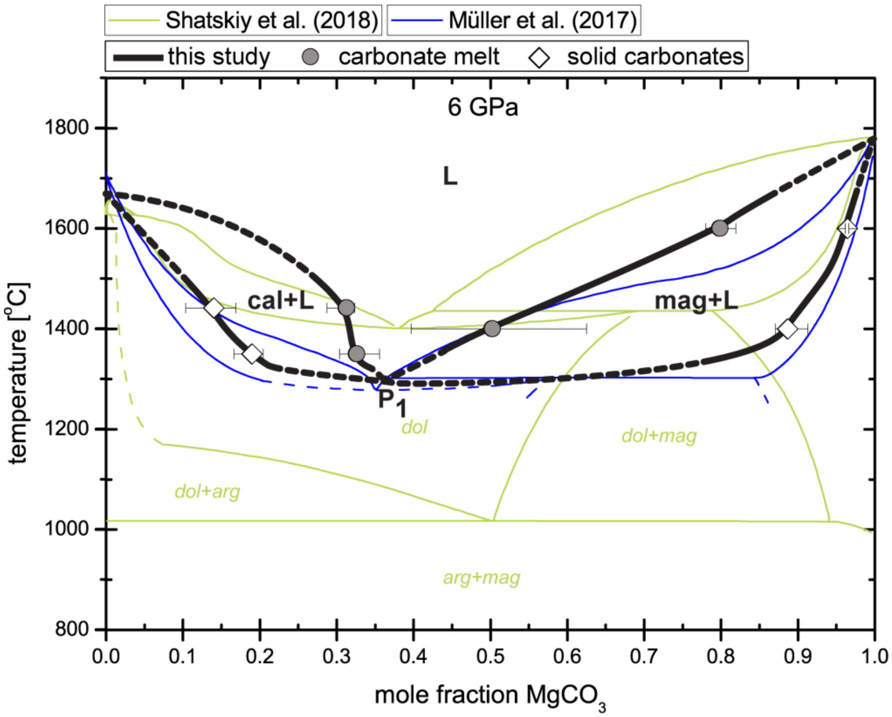

Figure: © Sieber,M.J., Wilke, F., Koch-Müller,M. (2020) *Partition Coefficients of trace elements between carbonates and melt and suprasolidus phase relations of Ca-Mg-carbonates at 6 GPa*. American Mineralogist. All rights reserved

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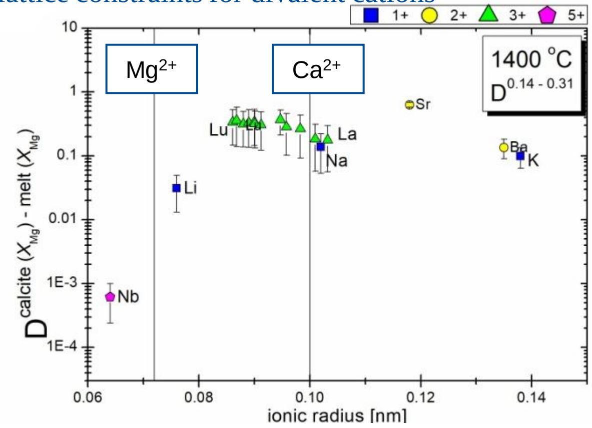
Results II : partition coefficients at 6 GPa

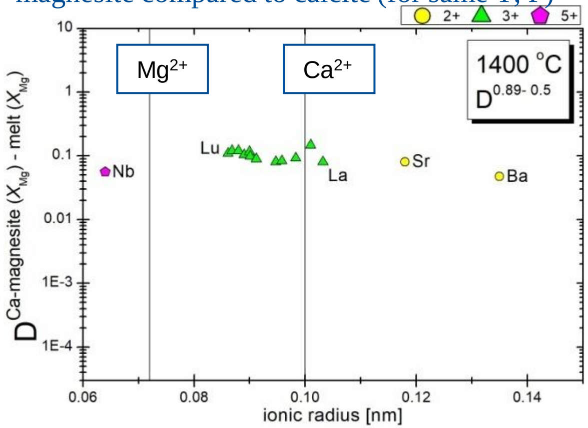
Calcite ($Ca_{0.86-0.81}Mg_{0.14-0.19}(CO_3)_2$) to **dolomitic melt** ($Ca_{0.31-0.??}Mg_{0.??-0.??}(CO_3)_2$)

- Na, K, Sr, Ba, Y, and REEs are slightly incompatible with D~0.1–0.8.
- trace element distribution seems to follow lattice constraints for divalent cations



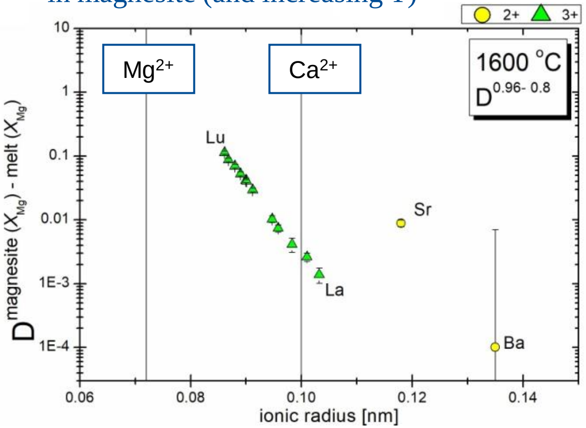
Ca-magnesite ($Ca_{0.11}Mg_{0.89}(CO_3)_2$) to **dolomitic melt** ($Ca_{0.31-0.??}Mg_{0.??-0.??}(CO_3)_2$

- single valent Li, Na, K are incompatible (bdl)
- D for Y+REEs are ~ 0.1
- Sr^{2+}, Ba^{2+} are ~10 times less compatible in Ca-magnesite compared to calcite (for same T, P)



Magnesite ($Ca_{0.04}Mg_{0.96}(CO_3)_2$) to Mg-rich **dolomitic melt** ($Ca_{0.31-0.??}Mg_{0.??-0.??}(CO_3)_2$

- strong fractionation of Y+REEs
- the compatibility of cations with ionic radii ≳ Ca^{2+} decreases with decreasing Ca content in magnesite (and increasing T)



Abbreviations: bdl: below detection limit of Laser Ablation Inductively Coupled Plasma Mass Spectrometry measurements; D: partition coefficient between solid carbonate and carbonate melt; REE: rare earth elements; T: temperature; X_{Mg} molar fraction of Mg in Ca-Mg-CO_3

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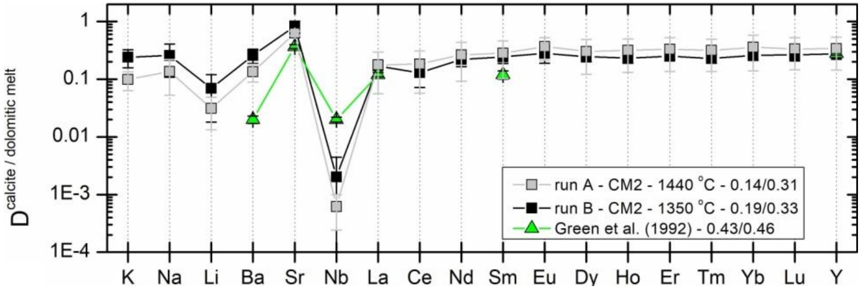
Implications

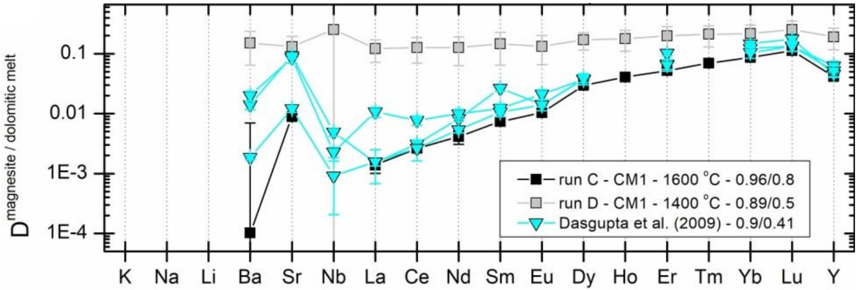
(I) Ca-Mg-carbonates will (partially) melt at ~200 km depth for temperatures above ~1300 °C

(II) The Sr and REE signature of a (Ca-rich) carbonatitic melt in equilibrium with calcite-pargasite-peridotite[6] can be approximated by the pure carbonate system



Green et al. (1992) reported D's between a sodic, dolomitic magma and pargasite-augite-garnet-carbonate at 2.5 GPa and 1000 °C

(III) The Sr and REE signature of a (Mg-rich) carbonatitic melt in equilibrium with a magnesite-garnet-lherzolithe[7] can not be approximated by melting in the pure carbonate system (note the difference in temperature)



Dasgupta et al. (2009) reported D's between a carbonatitic melt and magnesite-garnet-lherzolithe (6.6 GPa, ~1250–1300 °C)

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[6] Green,T.H., Adam,J., Siel,S.H. (1992) *Trace element partitioning between silicate minerals and carbonatite at 25 kbar and application to mantle metasomatism*. Mineralogy and Petrology, 46, 179-184. **[7]** Dasgupta,R., Hirschmann,M.M., McDonough,W.F., Spiegelman,M., Withers,A.C. (2009) *Trace element partitioning between garnet lherzolite and carbonatite at 6.6 and 8.6 GPa with applications to the geochemistry of the mantle and of mantle-derived melts*. Chemical Geology, 262, 57-77. **Figures:** © Sieber,M.J., Wilke, F., Koch-Müller,M. (2020) *Partition Coefficients of trace elements between carbonates and melt and suprasolidus phase relations of Ca-Mg-carbonates at 6 GPa*. American Mineralogist. All rights reserved

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