EXPERIMENTAL QUANTIFICATION OF THE PARTITIONING OF ZN BETWEEN DOLOMITE AND BRINE

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Motivation

- Sediment hosted Zn-Pb deposits – Most abundant sources of Zn and Pb worldwide
  - Sphalerite and Galena
- Common gangue minerals: dolomite, quartz, calcite
- Characterization of ore forming fluids key to understanding formation of these deposits
  - Fluid inclusion studies - salinity, major element compositions, and temperature
- What are the concentrations of the metals Zn and Pb in the ore forming fluids fluids?

Sphalerite ore
Central Tennessee Zn district
Photo credit: Martin Appold

Motivation

- Measuring Zn and Pb concentrations in fluid inclusions has been problematic
  - Matrix effects
  - Mineral inclusions
  - "Accidentals"
- Element partitioning theory (Smith-Schmitz and Appold, 2018)
  - Measured Zn/Ca in calcite, published Ca concentrations in fluids, published distribution coefficients
  - 10's of ppm Zn for Central Tennessee mineralizing fluid
- Dolomite
  - Commonly ore stage gangue mineral in ore deposits, diagenetic mineralization, low grade metamorphism
  - Incorporates Zn into crystal lattice
  - No experimental distribution coefficients

Theoretical Background

Elements partition between a mineral and the precipitating fluid in a defined manner. The exchange reaction for the substitution of Zn into dolomite is as follows:

$$\mathrm{CaMg(CO_3)_{2(dol)}} + \mathrm{Zn^{2+}_{(aq)}} \rightleftharpoons \mathrm{CaZn(CO_3)_{2(dol)}} + \mathrm{Mg^{2+}_{(aq)}}$$

- From which the following mass action expression can be derived

$$D = \frac{m^{Mg^{2+}} * X_{dol}^{CaZn(CO_3)_2}}{m^{Zn^{2+}} * X_{dol}^{CaMg(CO_3)_2}}$$

- D = experimental distribution coefficient
- m^{i} = molar concentration of the metal ion *i* in aqueous solution
- X_{dol}^{i} = mole fraction of the metal *i* in solid solution in dolomite

Methods: precipitating fluids

- Mix of 2 solutions
  - Cation bearing solution
  - Carbonate bearing solution
- Supersaturated with respect to dolomite

$$\mathrm{SI} = \log \frac{\alpha^{Ca^{2+}} * \alpha^{Mg^{2+}} * (\alpha^{CO_3^{2-}})^2}{K_{sp}}$$

- Compositions typical of MVT fluids (Na, Cl, Ca, K, pH)
- 4:6 atomic Mg:Ca
- 10, 100, 1000 ppm Zn

Remote lab during COVID-19 shutdown

Methods: experimental setup

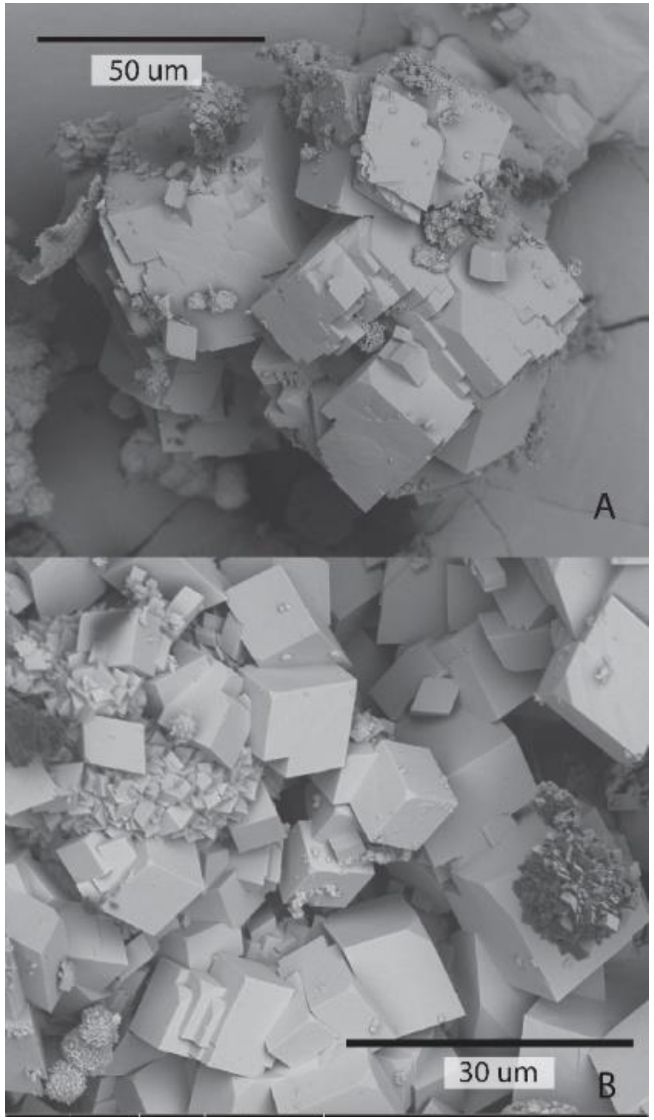
- 100 ml Hastelloy® C reaction vessel
- Temperatures
  - 125, 150, and 200° C
- Pressure of 100 bar
  - 90:10 Ar:CO_2
- Experimental duration
  - 10, 20, 40, 80 days
- 27 total experiments

Reaction vessel, heating mantle, and controller


90:10 Ar:CO2 gas mixture

Experimental products

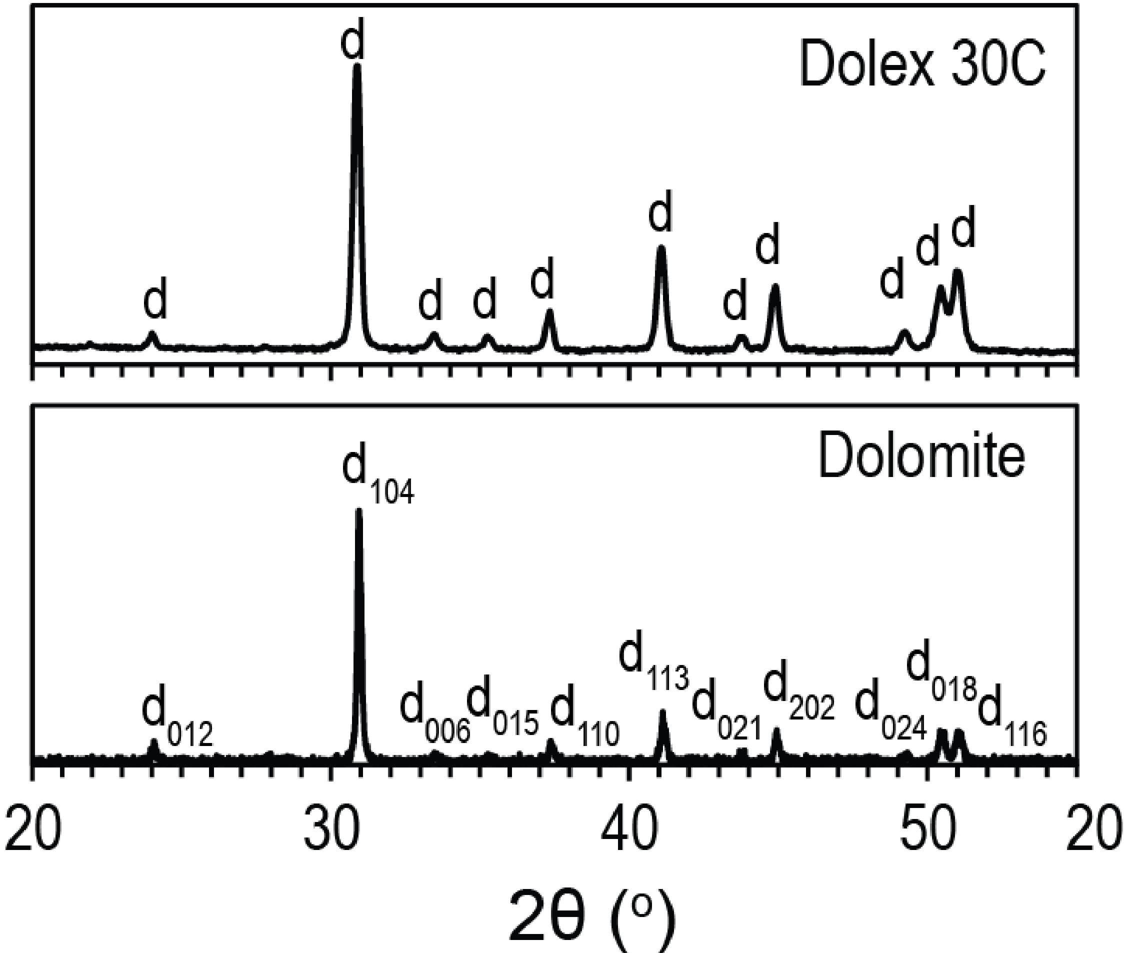
- Filtered and collected final fluids
  - Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis
- Collected, washed, and dried experimental precipitates for analysis
  - Powder X-ray diffraction (PXRD)
    - Crystallographic structure
  - Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)
    - Precipitates in polished epoxy mounts
    - Elemental composition



BSE images of dolomite precipitates

Analyses: PXRD

- Primary precipitate for 200 and 150° C experiments - ordered dolomite
- Minor magnesite in 200° C experiments (< 6%)
- 125° C precipitates less ordered
  - Ordering increased with greater experimental time



Representative PXRD spectrum of experimental precipitate (top) compared with dolomite XRD spectrum from RRUFF online database (bottom)

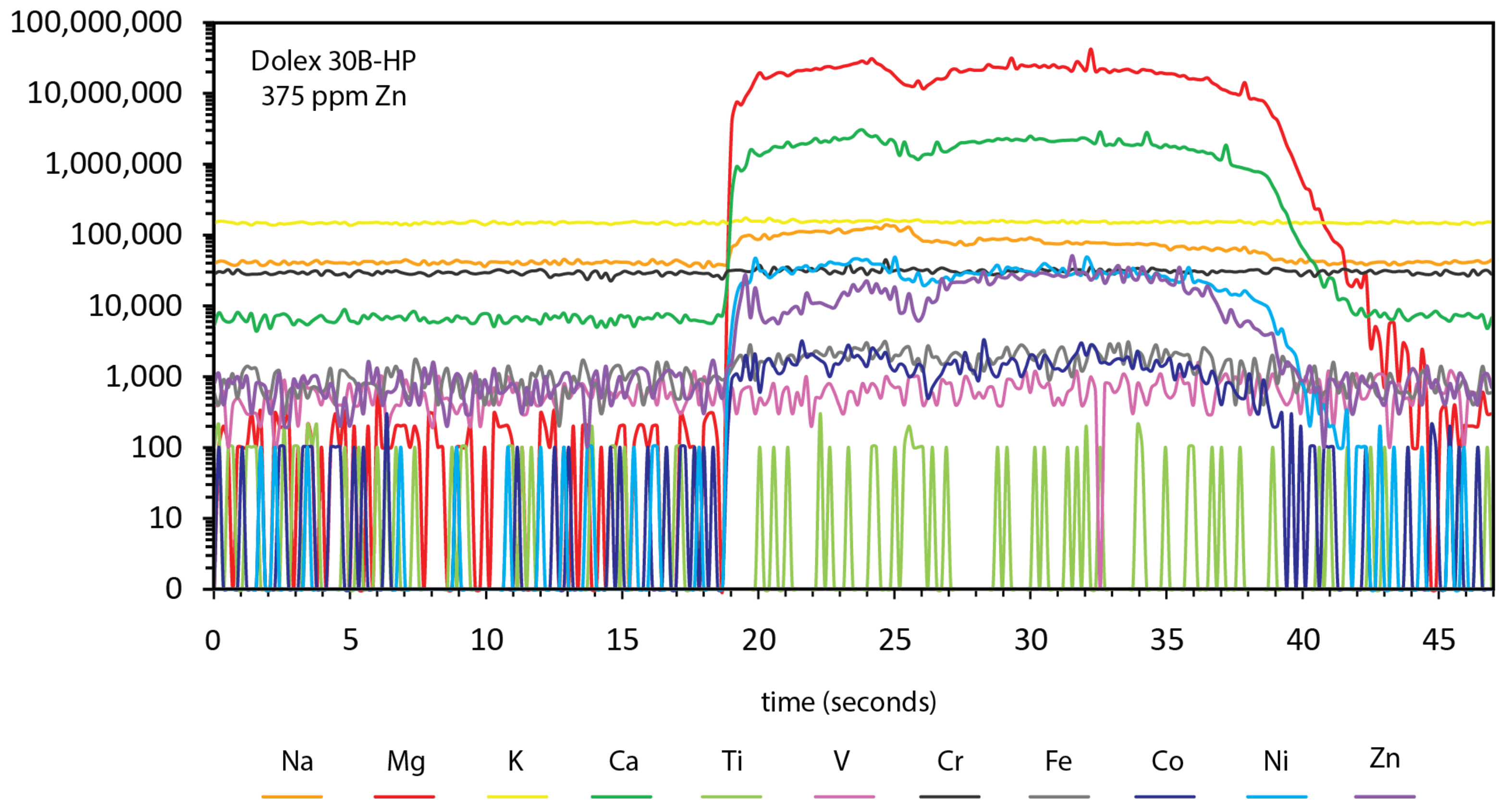
Analyses: Compositions

- LA-ICP-MS

$$\frac{X_{dol}^{CaZn(CO_3)_2}}{X_{dol}^{CaMg(CO_3)_2}}$$

- ICP-AES
  - Speciation calculations
    Geochemist Workbench®

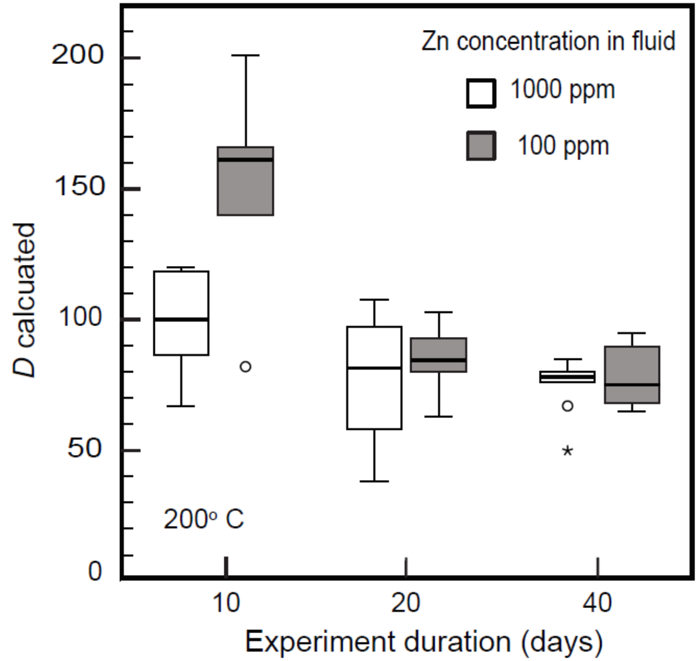
$$\frac{m^{Mg^{2+}}}{m^{Zn^{2+}}}$$



LA-ICP-MS spectra of experimental precipitates

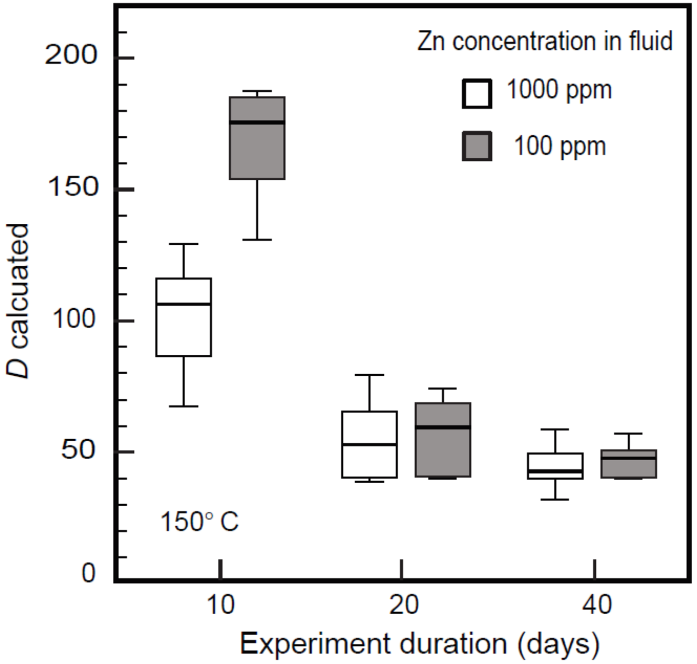
Results: *D* values

$$D = \frac{m^{Mg^{2+}} * X_{dol}^{CaZn(CO_3)_2}}{m^{Zn^{2+}} * X_{dol}^{CaMg(CO_3)_2}}$$



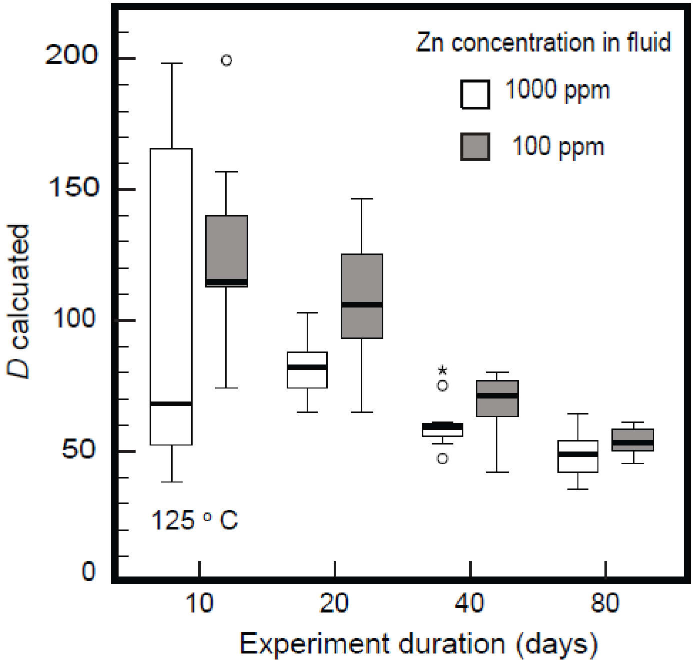
200° C

- Likely reached equilibrium
- 200° C *D* = 75±10



150° C

- Near equilibrium
- 150° C *D* ≤ 43



125° C

- Approaching equilibrium
- 125° C *D* < 48

Conclusions

- Demonstrated a reliable method for precipitating dolomite under the hydrothermal conditions of sediment hosted ore formation
- Confident in 200° C *D* value of 75
- 150° C experiments close to equilibrium
  - Additional longer experiments to verify
- *D* values have utility in any system in which it is necessary to determine Zn concentration in a fluid that precipitated dolomite under hydrothermal conditions
  - Sediment hosted ore deposits
  - Sedimentary diagenetic environments
  - Low grade metamorphic environments

Acknowledgements

Department of Geological Sciences at the University of Missouri

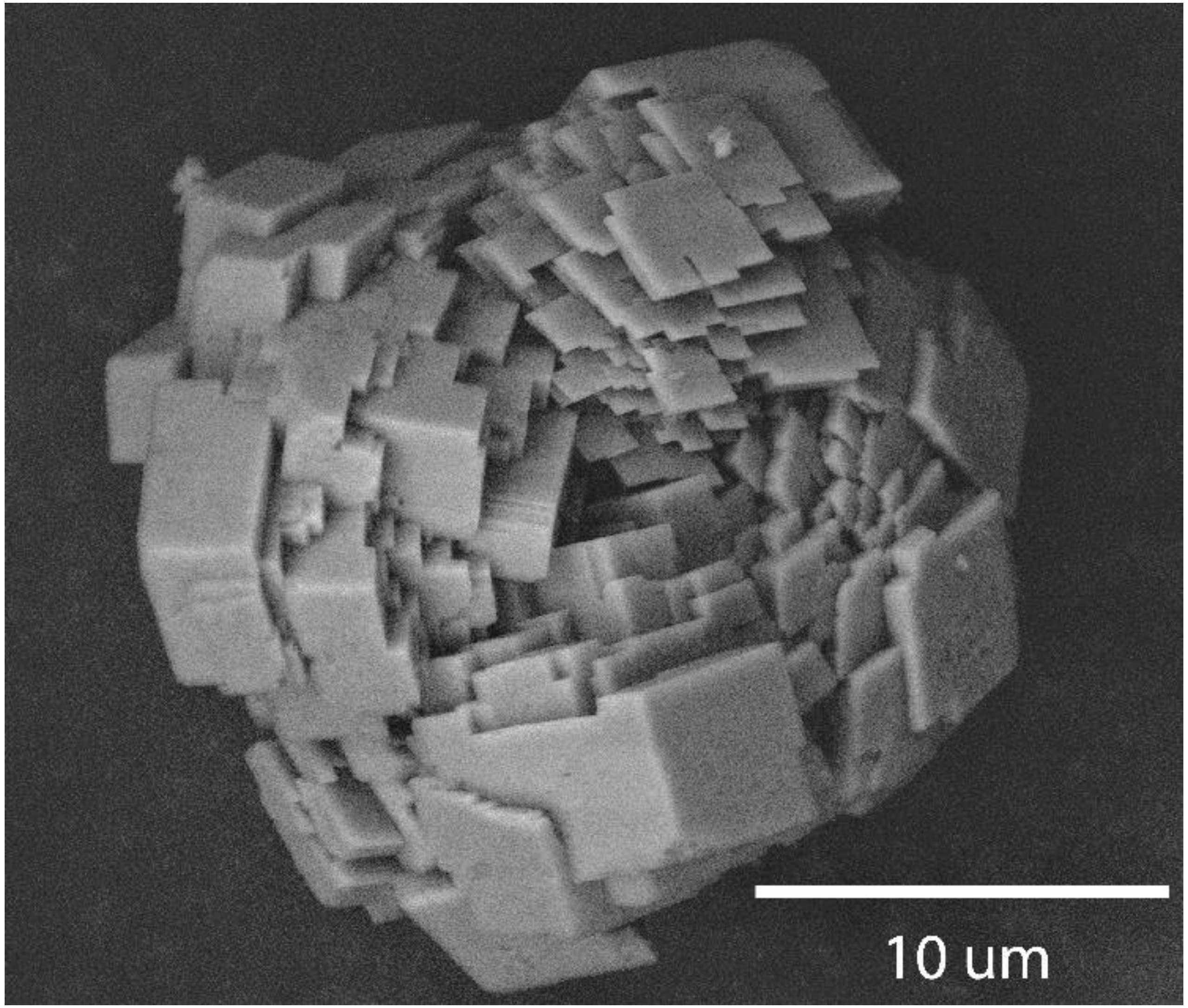
Analytical assistance and training provided by:

Dr. Barry Shaulis, Eric Pollock, Dr. James Murrowchick

Funding for this study provided by:

University of Missouri Research Council grant

University of Missouri Graduate Student Research award



BSE image of dolomite precipitate

QUESTIONS?