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:

\[
\text{CaMg(CO}_3\text{)}_2(\text{dol}) + \text{Zn}^{2+}_{\text{aq}} \rightleftharpoons \text{CaZn(CO}_3\text{)}_2(\text{dol}) + \text{Mg}^{2+}_{\text{aq}}
\]

• From which the following mass action expression can be derived

\[
D = \frac{m^{\text{Mg}^{2+}} \cdot X_{\text{dol}}^{\text{CaZn(CO}_3\text{)}_2}}{m^{\text{Zn}^{2+}} \cdot X_{\text{dol}}^{\text{CaMg(CO}_3\text{)}_2}}
\]

• \( D \) = experimental distribution coefficient
• \( m^i \) = molar concentration of the metal ion \( i \) in aqueous solution
• \( X_{\text{dol}}^i \) = 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
  \[
  \text{SI} = \log \frac{\alpha^{Ca^{2+}} \times \alpha^{Mg^{2+}} \times (\alpha^{CO_{3}^{2-}})^2}{K_{sp}}
  \]

- 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:CO₂
- Experimental duration
  - 10, 20, 40, 80 days
- 27 total experiments
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
  \[ \frac{X_{\text{dol}}^{\text{CaZn(CO}_3\text{)}_2}}{X_{\text{dol}}^{\text{CaMg(CO}_3\text{)}_2}} \]

- ICP-AES
  - Speciation calculations
    Geochemist Workbench®
  \[ \frac{m_{\text{Mg}^{2+}}}{m_{\text{Zn}^{2+}}} \]

LA-ICP-MS spectra of experimental precipitates
Results: $D$ values

\[ D = \frac{m_{Mg^{2+}}^{CaZn(CO_3)2} \cdot X_{dol}^{CaMg(CO_3)2}}{m_{Zn^{2+}} \cdot X_{dol}^{CaZn(CO_3)2}} \]

- **200° C**
  - Likely reached equilibrium
  - $200° C \ D = 75 \pm 10$

- **150° C**
  - Near equilibrium
  - $150° C \ D \leq 43$

- **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
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BSE image of dolomite precipitate