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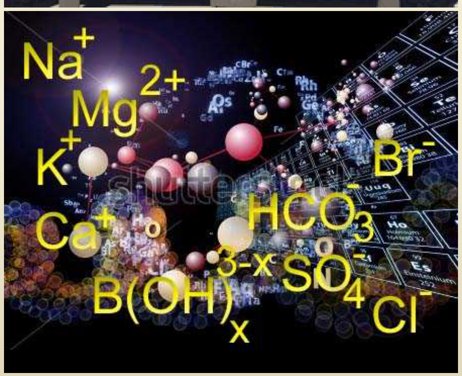

Partitioning of Fission Products (Cs, Sr and I) into Salt Phases

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Outline

- Motivations for the Investigation
- Materials
- Experimental Procedure & Methods
- Results
- Conclusions

Motivations for this Investigation

- A number of countries are considering reposing nuclear waste in bedded salt formations.
- Current geochemical models cannot completely account for element behavior in the event of a repository intrusion by brine solutions.
- Lack of data for sequestration of common radionuclide elements in salt phases.
- Wastes commonly contain fission products (e.g., ^{137}Cs, ^{90}Sr and ^{129}I).
- Should brine solution intrude the repository and mobilize the fission products (FP's), will the FP's partition into salt phases?

Partitioning of Cs, Sr and I

- Salt phases include:
  - Sylvite [KCl]
  - Carnallite [$KMgCl_3 \cdot 6H_2O$]
  - Langbeinite [$K_2Mg_2(SO_4)_3$]; Leonite [$K_2Mg(SO_4)_2 \cdot 4H_2O$]
  - Polyhalite [$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$]
  - Gypsum [$CaSO_4 \cdot 2H_2O$]
- Partitioning of Cs^+ for K^+ (radii: 196 vs 168 pm, resp.)
- Partitioning of Sr^{2+} for Ca^{2+} (radii: 133 vs. 120 pm, resp.)

  (We do not expect partitioning of Sr^{2+} for Mg^{2+} because of the size difference).
- Partitioning of I^- for Cl^- (radii: 210 vs. 181 pm, resp.)
- Partitioning of I^- for SO_4^{2-} (radii: 210 vs. 218 pm, resp.)

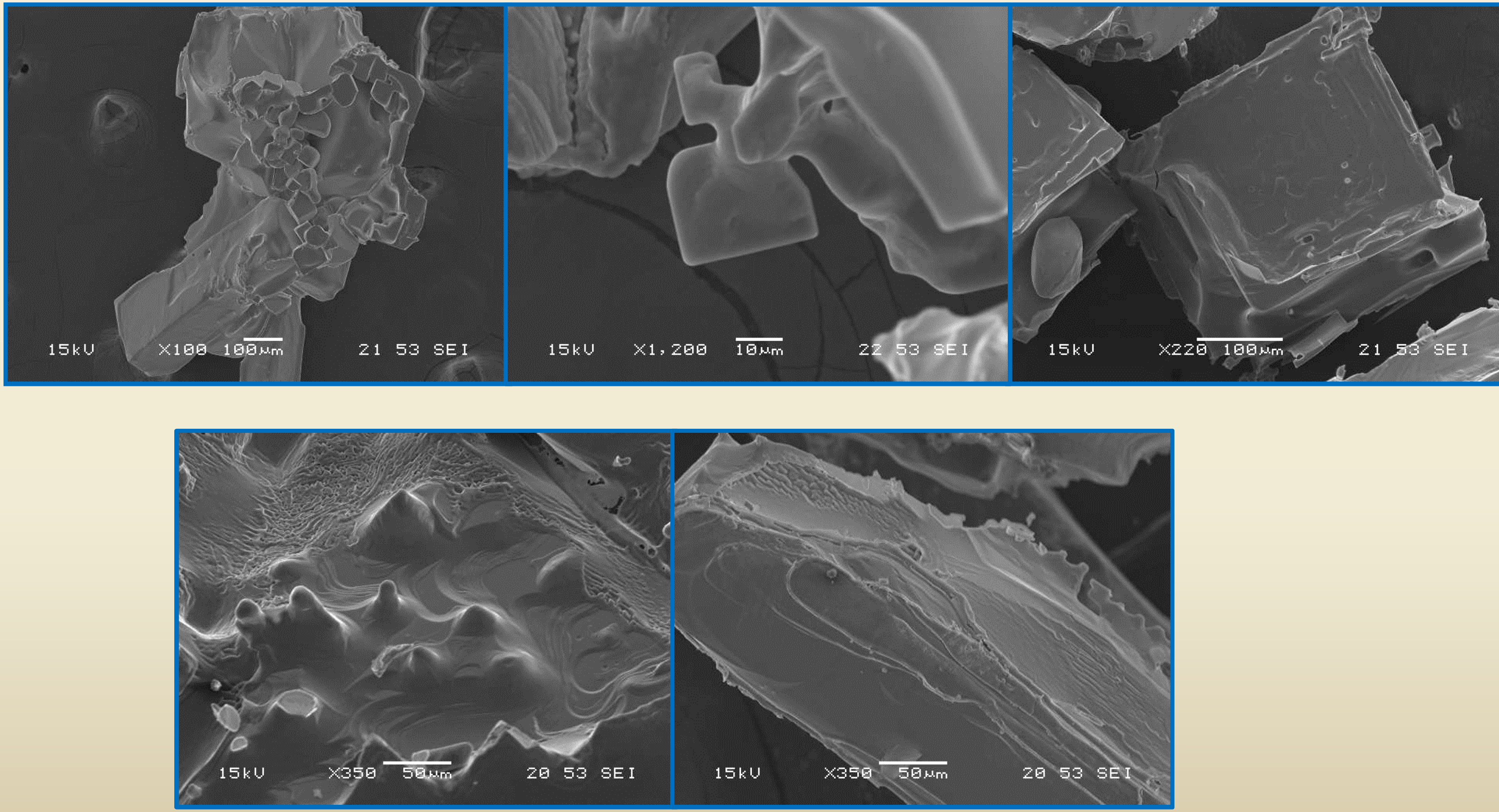
Materials & Experimental Methods

- Stoichiometric solutions of each phase (sylvite, carnallite, langbeinite, leonite, polyhalite and gypsum).
- Addition of 100 to 500 ppm Cs and Sr (as chlorides).
- Addition of 100 to 1,000 ppm I (as KI).
- Four temperatures (28, 50, 70 and 90ºC) in at least duplicate.
- Solutions made to be near-saturated at temperature of experiment.
- Lids removed from bottles to spur evaporation and eventual saturation.

Characterization & Analytical Methods

- Characterization of precipitated solids by SEM, BSEI.
- Solids identification by XRD.
- Solutions analyzed for concentrations of major and minor elements by ICP-AES (K, Mg, Na, Si, Al, Fe & Mn), and IC (S & Cl). Concentrations of trace elements by ICP-MS (Cs & Sr) and IC (I).
- Quantitative EMPA for major (K, Mg, S, & Cl), minor (Na, Al, Si, & Ca), and trace elements (Cs, Sr, Ba, & I) elements in salt phases.
- Major, minor and trace elements distributions in salt phases by ToF-SIMS.

SEM Images of Precipitated Phases



XRD-Mixture of phases

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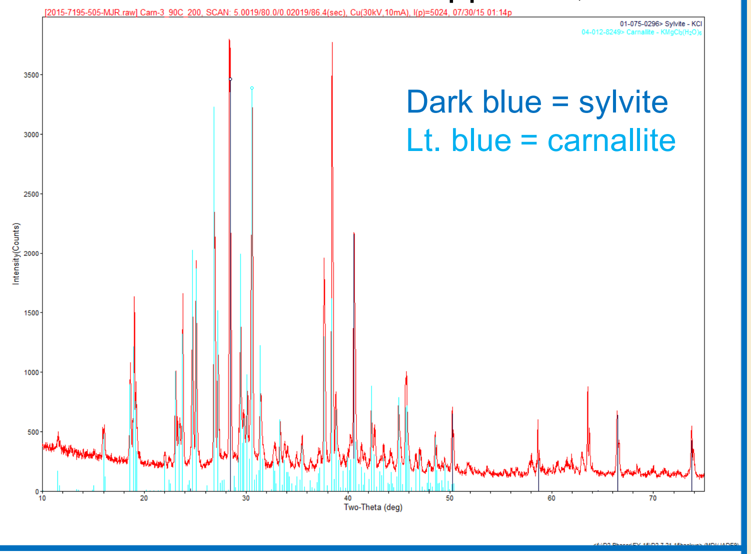
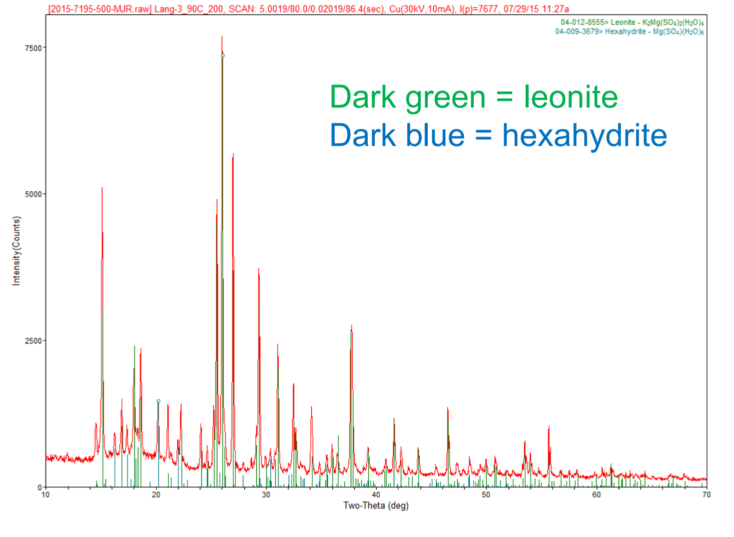
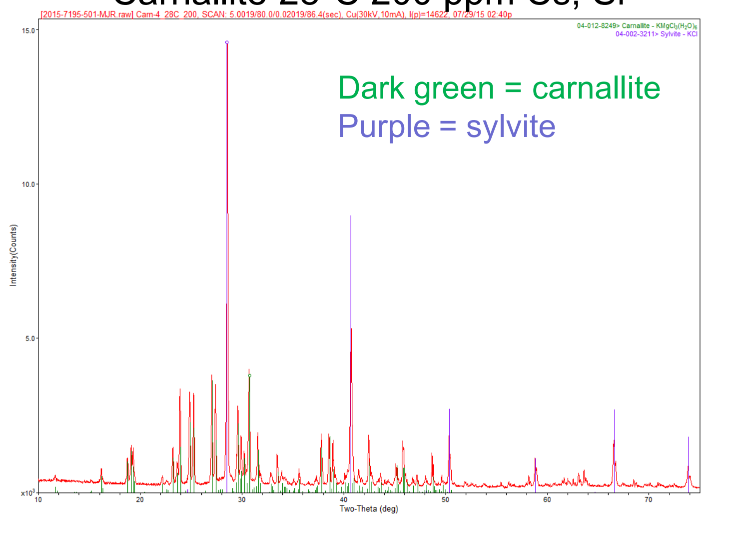
Carnallite 90ºC 200 ppm Cs, Sr



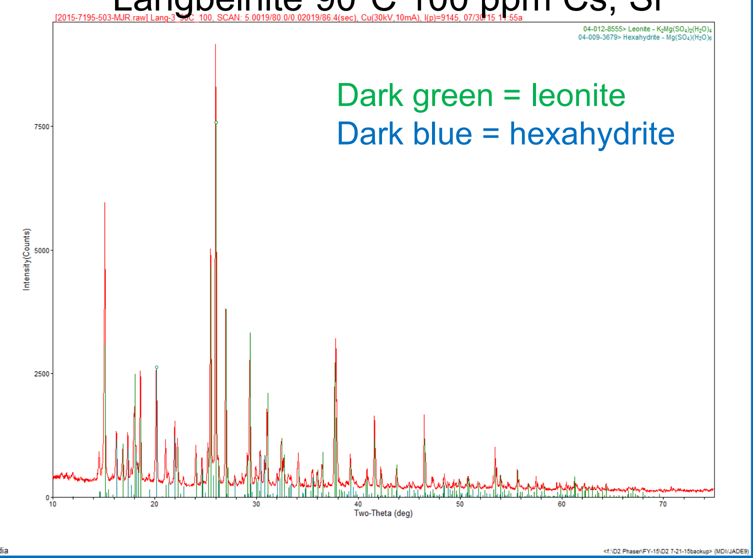
Langbeinite 90ºC 200 ppm Cs, Sr



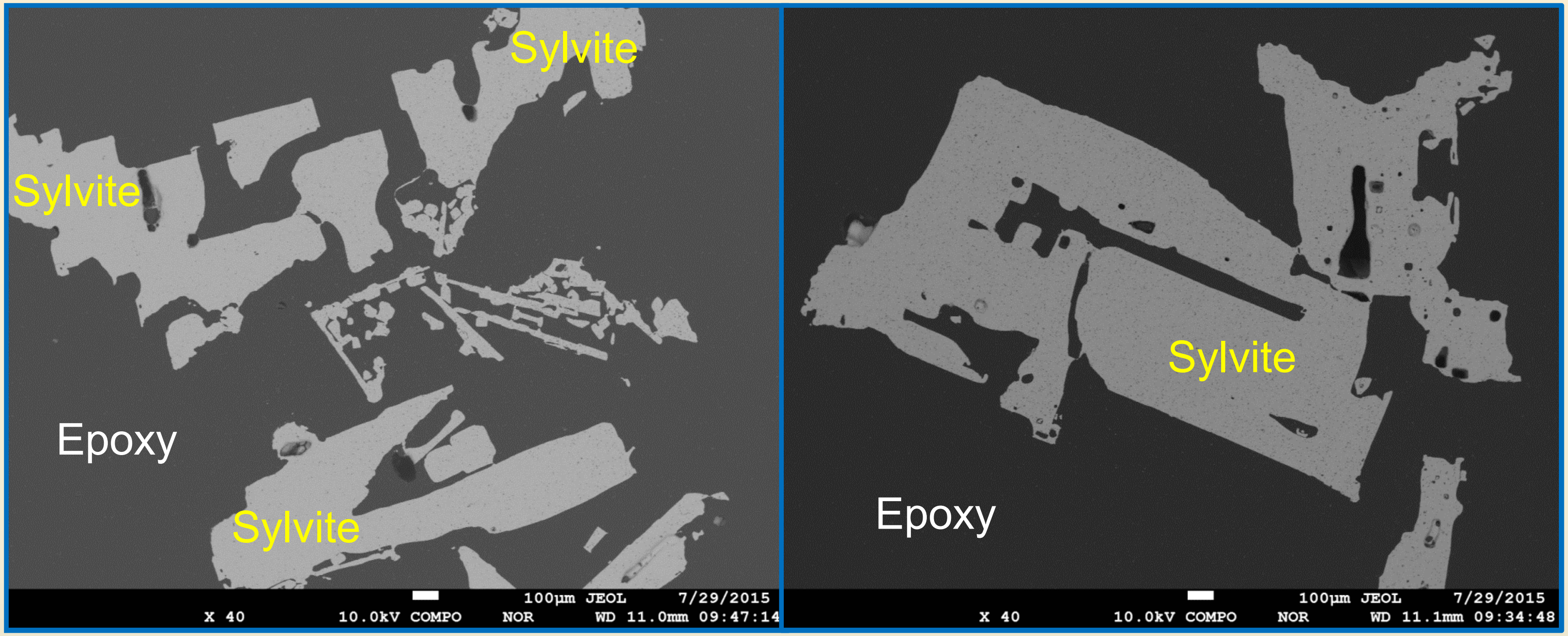
Carnallite 28ºC 200 ppm Cs, Sr



Langbeinite 90ºC 100 ppm Cs, Sr



BSEI--Sylvite Precipitates

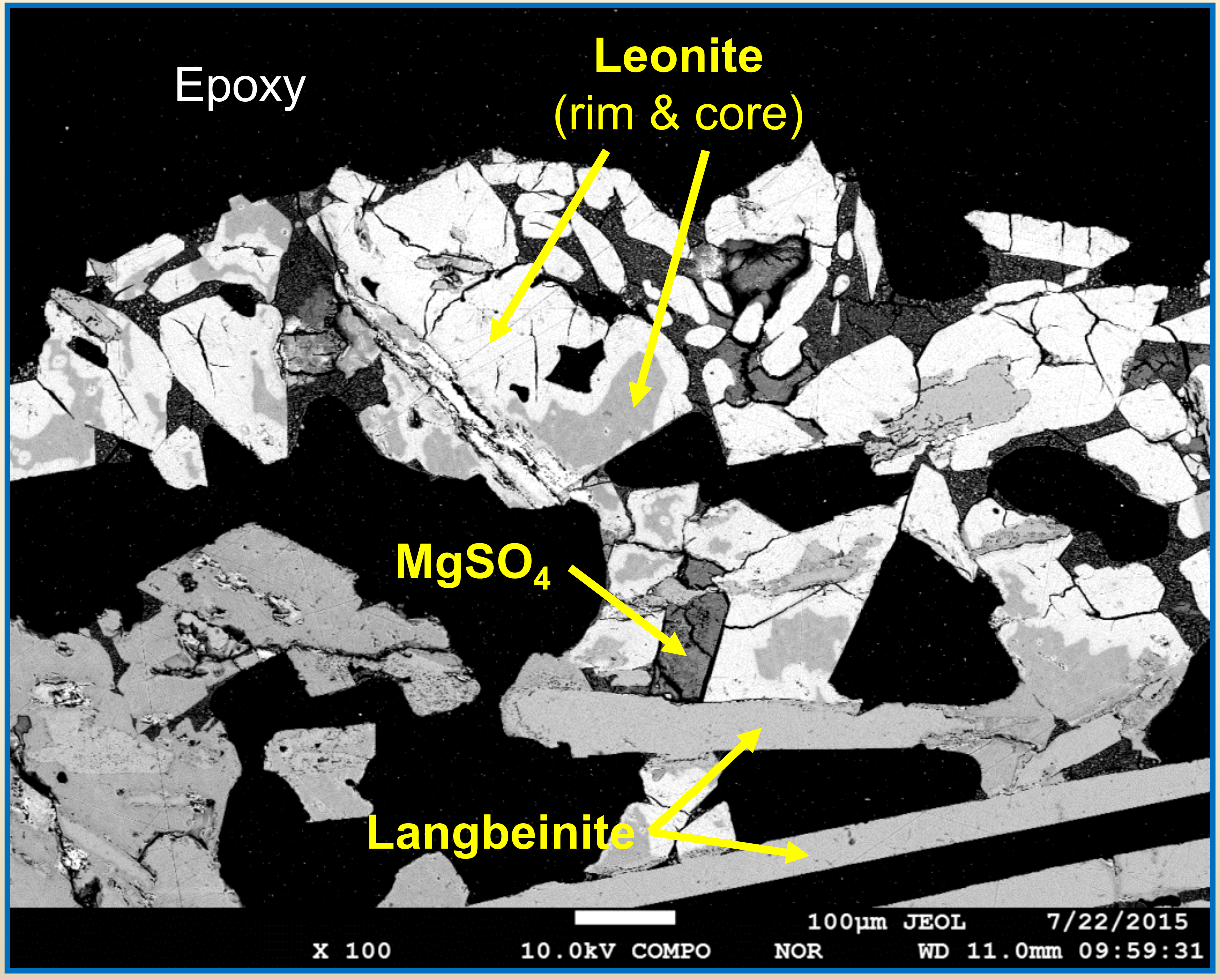


Well-bounded to “skeletal” crystals (hopper crystals in 3-dimensions)

BSEI--Carnallite Precipitates

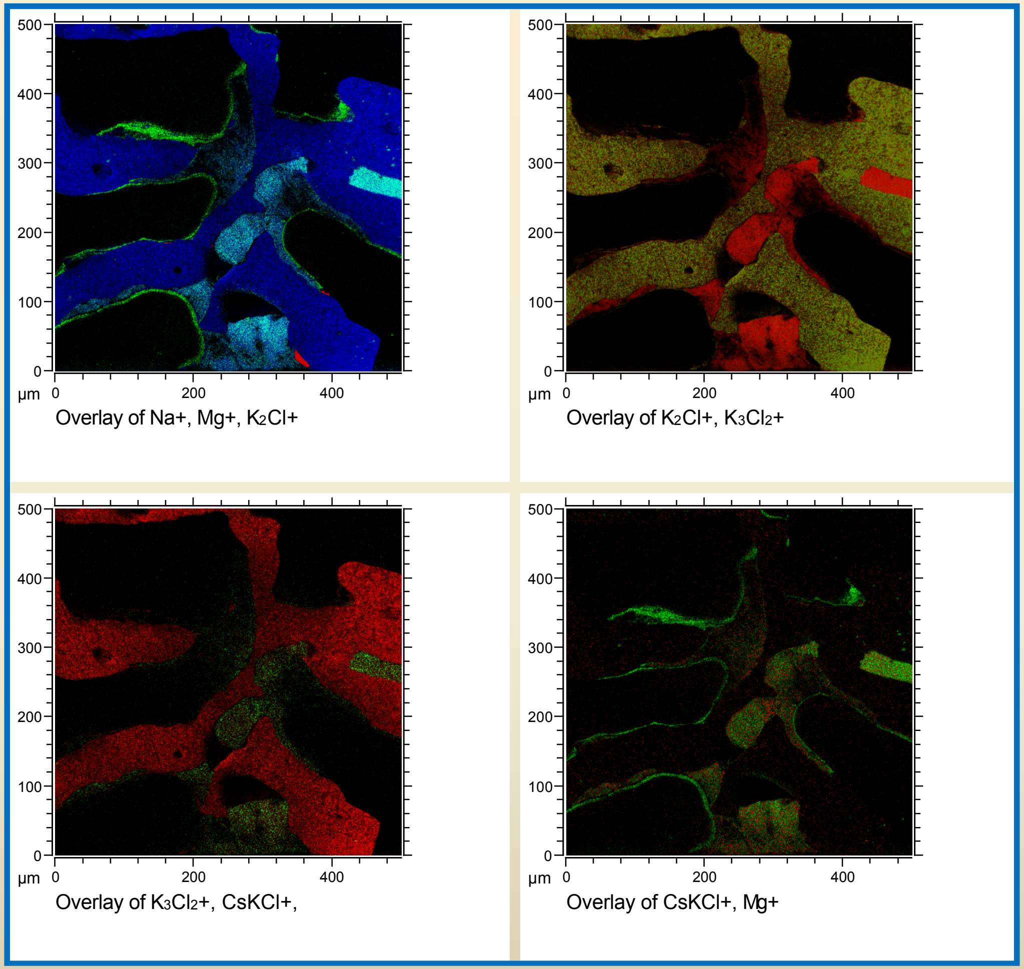
Sylvite precipitates first with "skeletal" morphology and then interstitial carnallite (two separate phases; medium and dark).

BSEI--Langbeinite-Leonite Precipitates



ToF-SIMS distribution of cesium

Carnallite 90ºC 200 ppm Cs, Sr



$$D^{Cs}{}_{Carn} = \left[\frac{C^{Cs}{}_{xl} / C^{K}{}_{xl}}{C^{Cs}{}_{soln} / C^{K}{}_{soln}} \right]$$

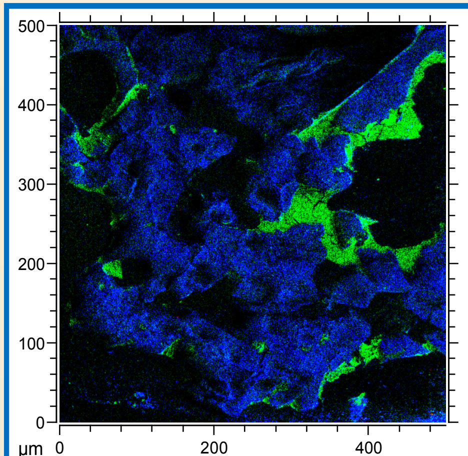
Concentrations of Cs, K in crystals and solution in ppm

$1.6 > D^{Cs}{}_{carn} > 0.55$

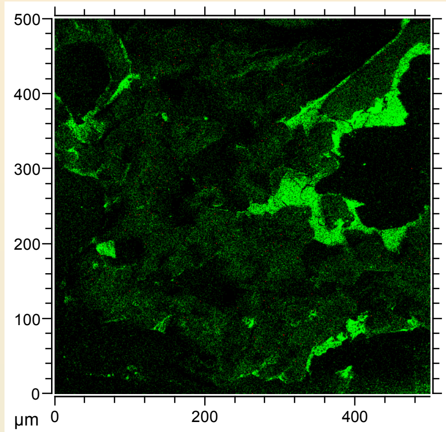
$1.7 > D^{Cs}{}_{leon} > 1.0$

ToF-SIMS distribution of Cs, I

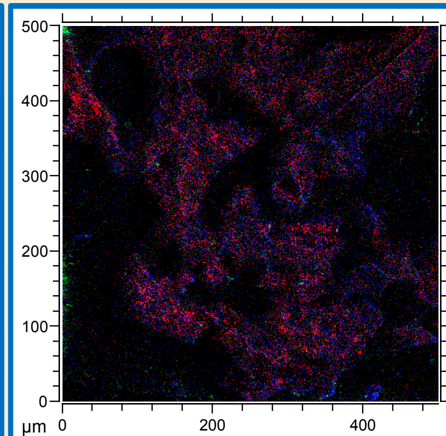
Langbeinite 90ºC 200 ppm Cs, Sr



Overlay of Na^+, Mg^+, K_2Cl^+



Overlay of $CsKCl^+$, Mg^+



Overlay of I^-, $MgCl_3^-$, KCl_2^-

Concentrations of I and Cl in crystals and solution in ppm.

$$0.12 > D^{I}{}_{carn} > 0.061$$

$$0.21 > D^{I}{}_{sylv} > 0.023$$

Conclusions

- Partitioning of cesium into carnallite, leonite and langbeinite quantified.
  - Strong uptake of Cs into carnallite, leonite and langbeinite.
- Partitioning of iodine into carnallite and sylvite quantified.
  - Partitioning of iodine favors solution.
  - Potential inverse correlation between temperature and partitioning of iodine, especially in carnallite.
  - Possible exchange between I^- and SO_4^{2-}?

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