Isotopic Evidence from Late-Stage Calcite and Brecciated Host Rocks from Abandoned Uranium Vanadium Deposits in Montana and Wyoming Suggests a Possible Hydrothermal Source

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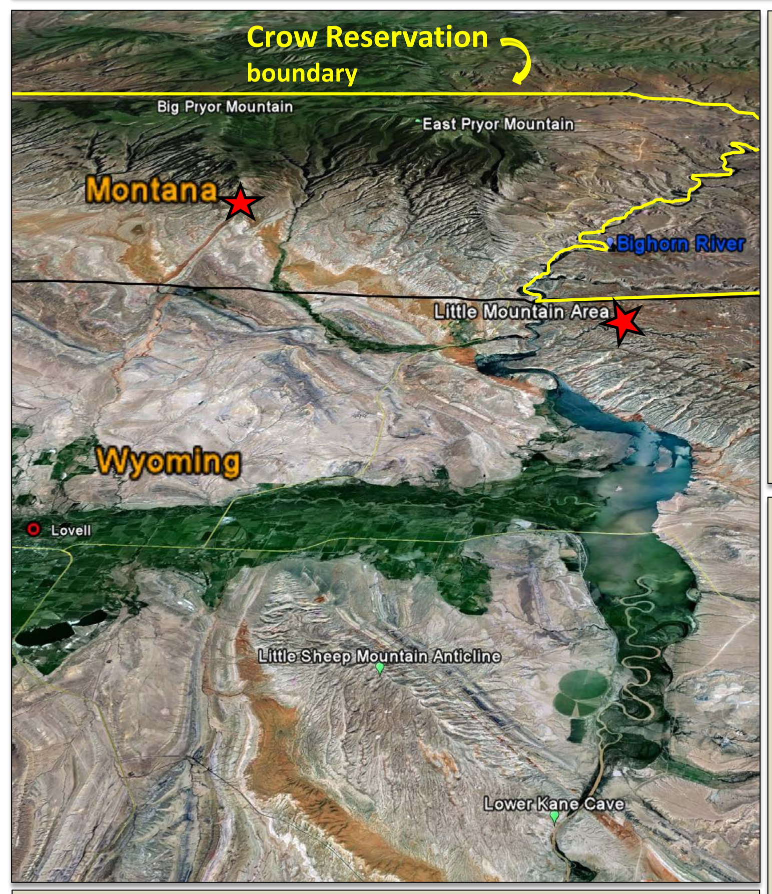
ABSTRACT:

Hand samples within the upper paleokarst unit of the Mission Canyon Member of the Madison Group were collected from mineralized areas on Big Pryor Mountain and East Pryor Mountain, Montana and the Little Mountain area, Wyoming. Vein fill material and brecciated host rock were prepared and sent to the stable isotope lab at the University of Michigan for carbon and oxygen stable isotope analyses. Some samples examined using a Field Emission Scanning Electron Microscope with an EDS Energy-Dispersive x-ray Spectrometer, Cathodoluminescence microscope and a standard petrographic microscope reveal several episodes of fluid migration. Comparing these isotopic values with the value of carbonates that precipitated from Mississippian aged ocean waters gives an indication of the diagenetic processes that have affected $\delta^{18}O$ and $\delta^{13}C$ values of the carbonates in the mining districts. Results from the $\delta^{18}O$ values of the late-stage calcite vein material sampled have the most negative $\delta^{18}O$ values (-11.99 to -23.48 ‰) and a wide range of $\delta^{13}C$ values (-0.40 to -6.20‰). The $\delta^{18}O$ values for the late-stage calcite veins are depleted relative to the brecciated host rock, indicating that fluids were not in equilibrium with the host rocks and that the system was open to outside fluid flow. This isotopic depletion and the presence of disseminated sulfides as well as ytterbium (a rare earth element) detected by EDS, suggests that the fluids were hydrothermal in nature.



FIELD STUDY AREA: The Montana study area is focused on Big Pryor Mountain mining district (red star) in the Pryor Mountains, Carbon County, Montana. The Wyoming study areas are in Big Horn County in the Little Mountain mining district (red star) area northeast of Lovell and the Lower Kane Cave area in the Little Sheep Mountain anticline, about 30 miles south of the Montana study area.

STATEMENT OF PROBLEM:

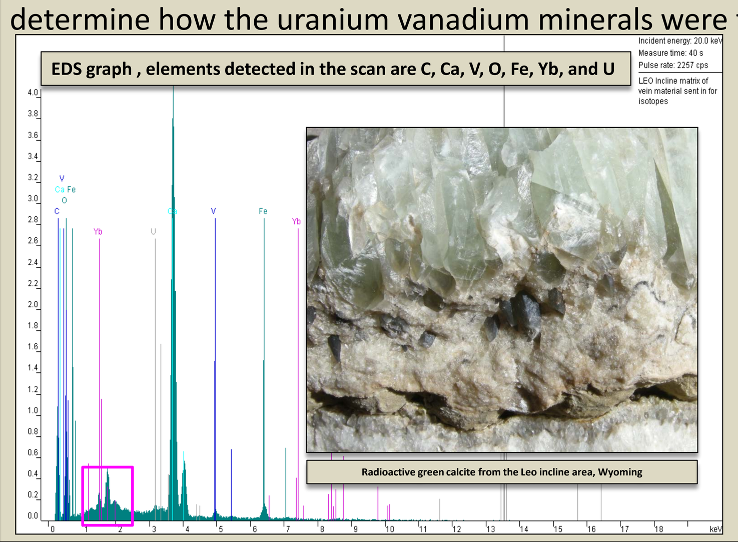
The uranium vanadium mines in the Pryor Mountain and the Little Mountain mining districts are hosted in the Madison Formation. Are these deposits a product of:

- Top-down leaching
- Bottom-up hydrothermal metasomatism or a
- Mixed mode involving both hydrothermal and meteoric components.
- Which model addresses the physical and chemical characteristics of these deposits?

RESEARCH QUESTIONS:

- What is the exact nature of structural control on these deposits, if any?
- Can breccia pipes be traced deeper than the upper 200 feet of the Madison Limestone?
- Was mineralization coeval with brecciation? What was the relative timing of these events?
- What paleo-geographic setting does this area of the Madison Limestone represent, would it fit the description for favorable MVT formation?
- Which model best addresses the overall characteristics of these deposits?

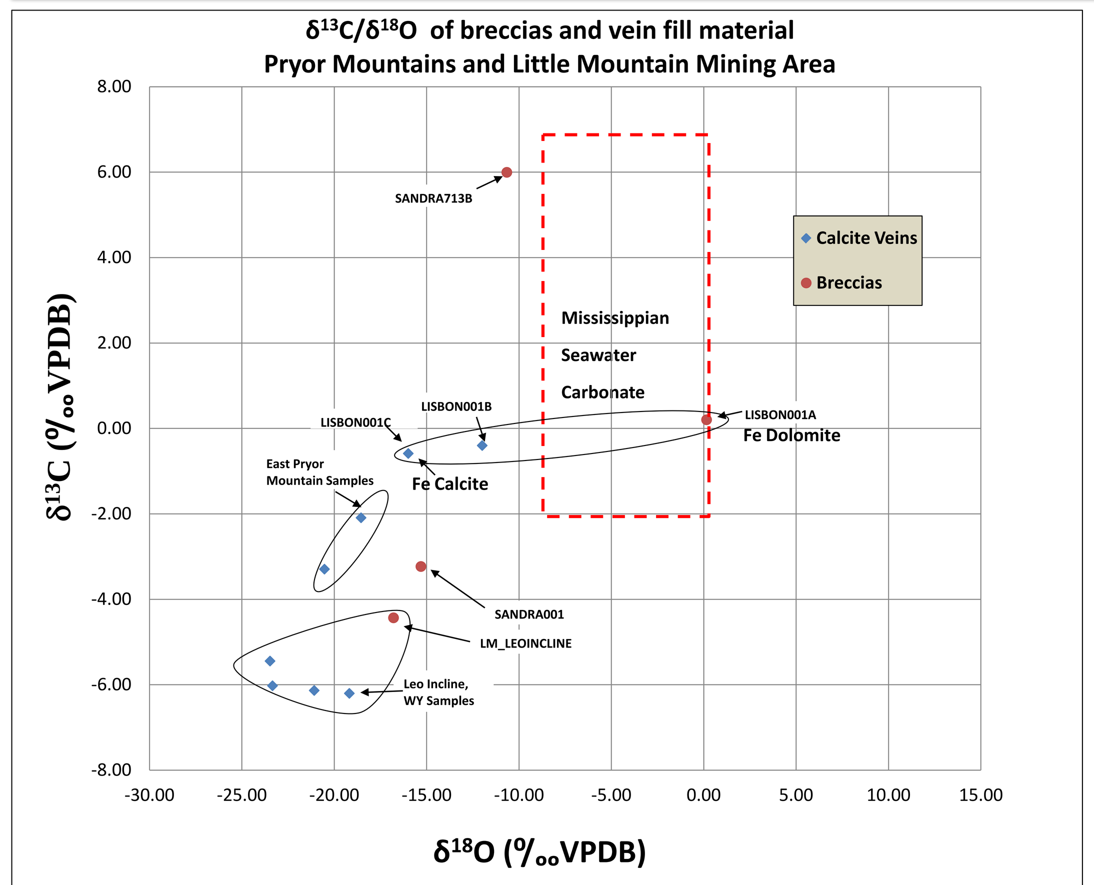
HOW ISOTOPES HELP ANSWER THESE QUESTIONS: Using stable isotopes of carbon (C) and oxygen (O) can help characterize water sources which produced the veins of calcite and dolomite present in the mining districts. In some of the mine sites uranium vanadium minerals are present within the fracture fill material and some calcite veins have U, V and REE in the mineral. Knowing the temperature of the fluids may help to determine how the uranium vanadium minerals were formed.



Mode I dilational fracture with calcite and yellow uranium minerals lining the fracture in dolomitic limestone boulder from the Little Mountain area, Wyoming.

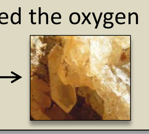
ISOTOPE STANDARDS:
Various isotope standards are used for reporting isotopic compositions; the compositions of each of the standards have been defined as 0 ‰ (zero per mil). Per mil (‰) notation is used to describe a unit expressing the ratio of stable-isotopic abundances of an element in a sample to those of a standard material. Per mil values are equivalent to parts per thousand. Stable-isotopic ratios are computed as follows: $\delta X = {}^{R(sample)}/_{R(standard)} \times 1,000$ where X is the heavier isotope and R is the ratio of the heavier, less abundant stable isotope to the lighter, stable isotope in a sample or standard (Kendall and Caldwell, 1998), so: $\{\delta^{18}O = {}^{18}O/{}^{16}O^{sample}/{}^{18}O/{}^{16}O_{Standard} \times 1000\}$ and $\{\delta^{13}C = {}^{13}C/{}^{12}C^{sample}/{}^{13}C/{}^{12}C_{standard} \times 1000\}$. The δ (delta) values for oxygen and carbon stable isotopic ratios discussed in this report are referenced to the following standard materials: Vienna Pee Dee Belemnite (VPDB) and in figures A and B, Pee Dee Belemnite (PDB) based on Veizer et al., (1999). Most current literature report values based on VPDB because its use implies that the measurements have been calibrated according to IAEA (International Atomic Energy Agency) guidelines for expression of delta (δ)values relative to available reference materials on normalized per mil scales (Coplen, 1994). Older literature may refer to PDB which is the original standard from which the equivalent VPDB has been derived since there is no longer a supply of PDB material.

View looking south from Lisbon Mine, near top of Red Pryor Mountain, on crest of anticline. The Triassic Chugwater Formation stands out as the prominent red formation in the view of the south plunging nose of the anticline. The reddish soil in the foreground is part of the lower Pennsylvanian Amsden Formation that unconformably overlies the karst surface developed on the Mississippian Madison Limestone. The Amsden has been tectonically thinned locally along the margins of Pryor Mountains uplift (Lopez, 2000). It is incorporated into the collapse breccia pipe features of the study areas.

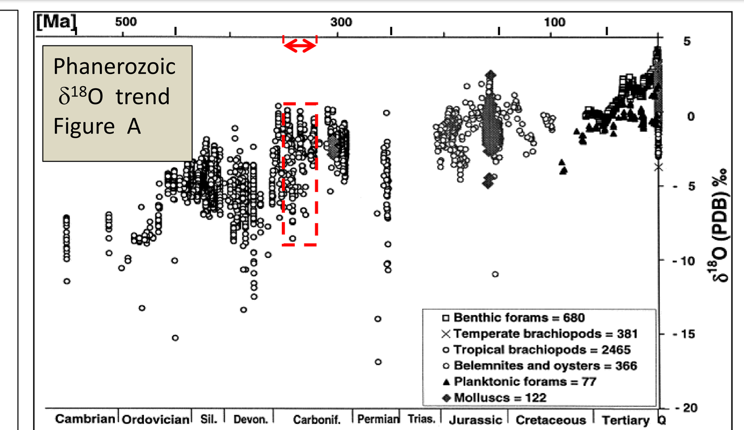


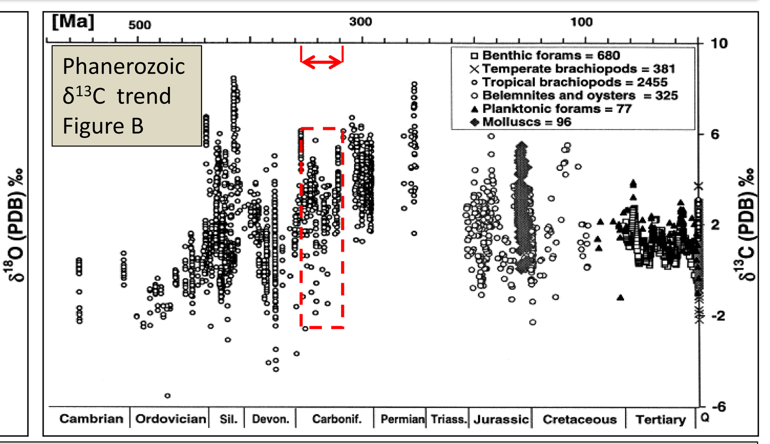
STABLE ISOTOPE DATA: from brecciated host rock and vein fill material in the Pryor Mountains, Montana and Little Mountain Area, Wyoming. Red filled circles are the breccia host rocks and blue squares are vein fill material. Red dashed box derived from Veizer et al, 1999, represents approximate value for Mississippian seawater carbonate derived from graphs to right. Sample groups are circled.

DISCUSSION GRAPH:
The $\delta^{13}C$ and $\delta^{18}O$ values for samples of breccia and vein fill material from the Pryor Mountain Area and Little Mountain area can be seen the graph above. The stable isotopic compositions of late-stage calcite from each location show a slightly different signature. Overall the $\delta^{18}O$ values of the late-stage calcite vein material sampled in this study have the most negative $\delta^{18}O$ values (-11.99 to -23.48 ‰) and a wide range of $\delta^{13}C$ values (-0.40 to -6.20‰). The $\delta^{18}O$ values for the breccias sampled range from (0.15 to -16.79‰). Only one breccia sample falls within the expected range in $\delta^{18}O$ values for Mississippian carbonates. Overall $\delta^{18}O$ values for the late-stage calcite veins are depleted relative to the brecciated host rock, indicating that fluids were not in equilibrium with the host rocks and that the system was open to outside fluid flow. This isotopic depletion may reflect higher temperatures during vein filling, isotopically depleted fluids, or some combination of both factors (Budai and Wiltschko, 1987). At elevated temperatures the oxygen fractionation between water and calcite is decreased, resulting in calcite precipitates with more negative oxygen isotopic compositions. The more enriched the oxygen composition of a fluid, the higher the temperature must have been to precipitate such depleted calcites. The presence of disseminated sulfides, REE, herkimer style quartz and saddle dolomite crystals may indicate that the fluids were hydrothermal in nature.

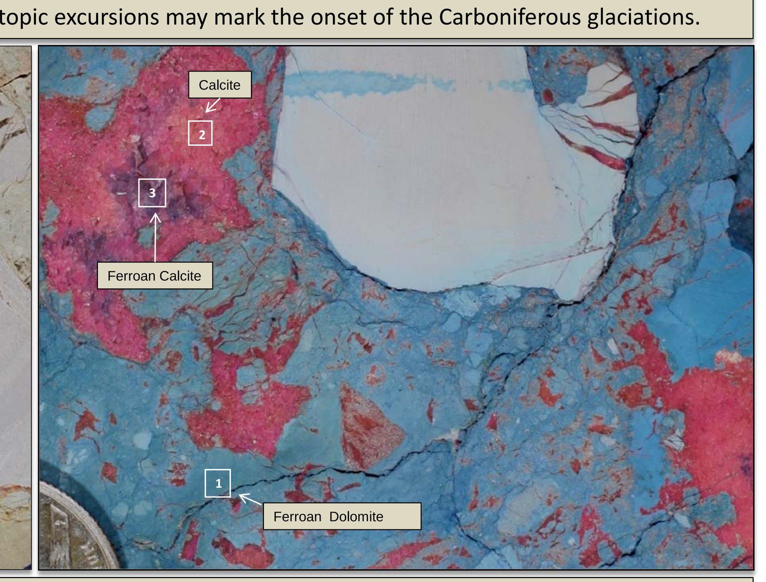


DISCUSSION FIGURE:
Some of the possible sources of fluids related to late-stage veining include Cretaceous marine or meteoric water, connate fluids, and basinal brines (Budai and Wiltchko, 1987). Meteoric water would have the most depleted oxygen composition. Estimates of the Late Cretaceous paleo-latitude indicate that this area was less than 10° north of its current position based on paleo-magnetic reconstructions (Harrison and Lindh, 1982). Paleo-climate studies indicate that the Late Cretaceous was a time of global warming, so higher latitudes received less depleted meteoric water than in the present. Meteoric water at the latitude of the Pryor and Big Horn Mountains today has oxygen isotopic compositions ranging from -10 to -12 per mil (SMOW) (Anderson and Arthur, 1983). Using these values, calcite precipitated from meteoric water would have oxygen isotopic compositions of -10 to -8 per mil (PDB), so highly depleted meteoric water still cannot account for the highly depleted compositions found in the veins sampled. This suggests that elevated temperatures may have played a role in vein filling to produce such depleted oxygen isotopic compositions. If the vein-filling water were marine or connate (with initially more enriched oxygen values relative to meteoric water), then temperature would have needed to be even higher to precipitate such depleted calcite veins. Previous studies in nearby locations, suggest that the sources of waters for vein-filling fluids were likely modified marine waters or basinal brines (based on fluid inclusion and isotopic analysis; Budai and Wiltchko, 1987; Wiltchko et al., 2009). This indicates that an elevated geothermal gradient was necessary to heat the initially more isotopically enriched fluids to a temperature great enough for precipitation of such depleted late carbonate veins. The most depleted oxygen isotopes come from the latest stage veins sampled, which suggests the possibility that the elevated fluid temperatures are a relatively recent phenomenon.





Phanerozoic $\delta^{18}O$ (Figure A) trend based on 1654 brachiopod and belemnite measurements at Bochum and Ottawa. Phanerozoic $\delta^{13}C$ trend (Figure B) compiled from 3918 measurements (brachiopods, belemnites, oysters, foraminifera) and 96 measurements for (mollusk) shells (Figures from Veizer et al, 1999, who compiled data from many authors to produce the two graphs). Red dashed boxes yield approximate values used for Mississippian Seawater Carbonate (350 – 318 Ma) this study. Most of the rocks in this study are late Mississippian in age. Samples of both brecciated Mississippian host rock and late-stage calcite from fractures associated with mineralized areas were analyzed for stable carbon and oxygen isotope values. The positive spike in both $\delta^{13}C$ and $\delta^{18}O$ in the Carboniferous periods reflects possible climatic changes during that time, resulting in differences in $\delta^{13}C$ and $\delta^{18}O$ in the rock record. A positive $\delta^{13}C$ shift that reaches a maximum value of > +7‰, which is among the highest peaks known in the Phanerozoic in North America and Europe is paralleled by a positive shift in $\delta^{18}O$ values in brachiopod calcite (Veizer et al., 1999). These isotopic excursions may mark the onset of the Carboniferous glaciations.



Hand sample from Lisbon Mine area, Pryor Mountains, Montana; sample was cut in half and polished and stained. On left, sample is unstained and right side the sample is stained with alizarin red and potassium ferricyanide. The turquoise stained portion of the rock is 1 the ferroan dolomite breccia host rock (LISBON001A) in graph, the red vug filling 2 is the calcite (LISBON001B) in graph and the last episode of vein fill is 3 the purple ferroan calcite (LISBON001C) in graph.

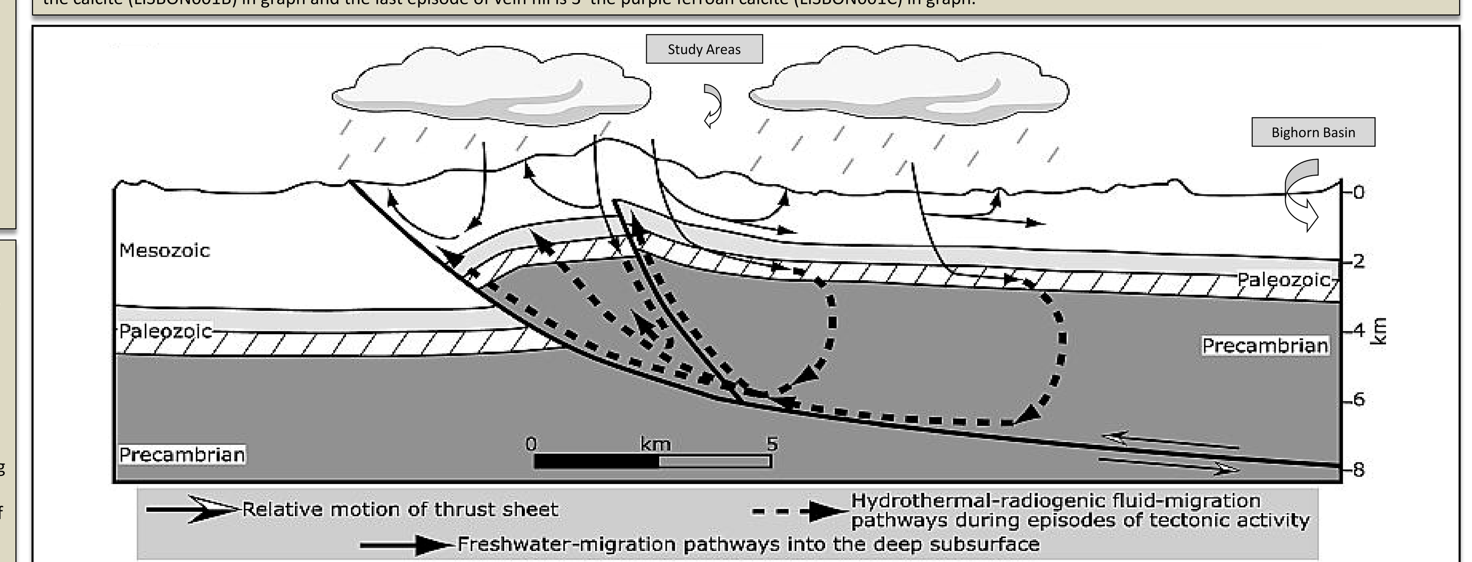
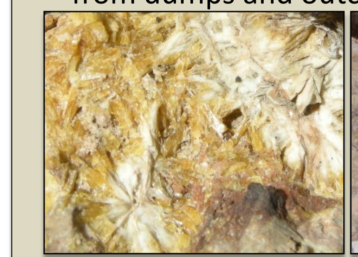


Figure adapted from Katz et al, 2006; Huntoon, 1993, showing freshwater-migration pathways and hydrothermal fluid-migration possible pathways which could account for depleted $\delta^{18}O$ late-stage calcite and dolomite precipitated along brecciated mineralized zones.

METHODS:

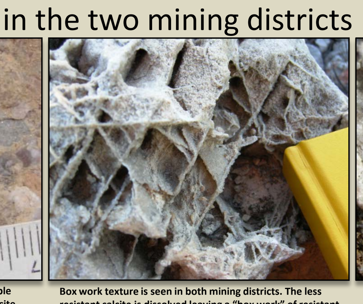
Field Work:

- The field sites were visited to see the aspect and exposure of the abandoned mines in the Pryor Mountain area, Montana and Little Mountain area, Wyoming; samples were collected from dumps and outcrops of select mines in the two mining districts

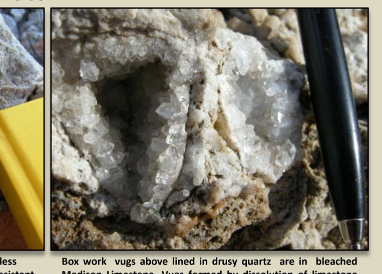


Barite - much of the barite is golden colored. This sample has both golden and white barite. Initial EDS measurement has detected REE elements including Ce and Nd.

Many of the samples contain minor sulfides; this hand sample from the Lisbon Mine area, MT has late stage pyrite and calcite filling fractures in a floating clast breccia., inch scale



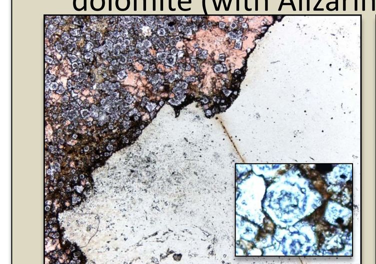
Box work texture is seen in both mining districts. The less resistant calcite is dissolved leaving a “box work” of resistant conjugate shear fractures which have been filled by quartz.



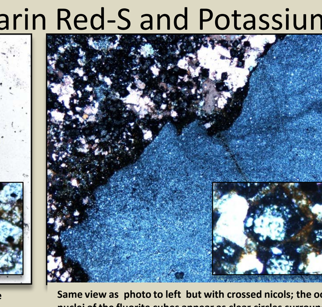
Box work vugs above lined in drusy quartz are in bleached Madison Limestone. Vugs formed by dissolution of limestone between the fracture networks within a brecciated portion of the mineralized rocks.

Initial and Ongoing Analytical work:

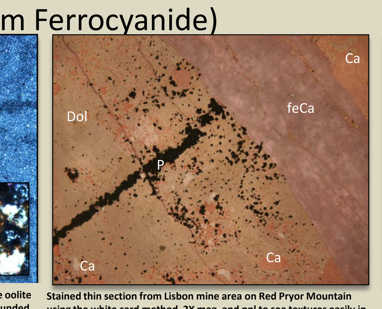
- Petrographic microscope - incorporating stained thin-sections to distinguish calcite from dolomite (with Alizarin Red-S and Potassium Ferrocyanide)



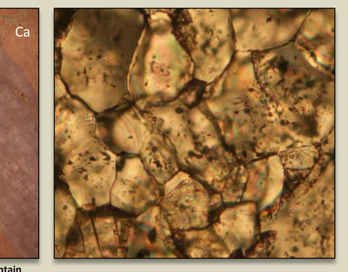
Photomicrograph of stained thin section from the Dandy Mine area in the Pryor Mountains; 2X magnification, ppl; fluorite crystals replacing oolites in original biosparite host rock; red area is sparry calcite; dark areas are hydrocarbon residue coating large silicified clast of calcite. Inset photo is 10X magnification, ppl, same slide to show oolite detail



Same view as photo to left but with crossed nicols; the oolite nuclei of the fluorite cubes appear as clear circles surrounded by dark isotropic fluorite; microcrystalline quartz on left. Inset photo is 10X magnification, xpl, same slide to show oolite detail



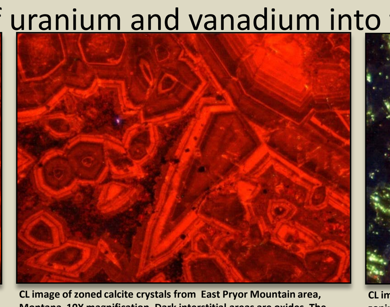
Stained thin section from Lisbon mine area on Red Pryor Mountain using the white card method, 2X mag. and ppl to see textures easily in the stained thin section. The red portions are microspar calcite filling in voids in the dolomite host rock; the central light violet vein is sparry ferroan calcite. The dark areas are pyrite. Dol, Ca, feCa and P are labels for dolomite, calcite, ferroan calcite and pyrite.



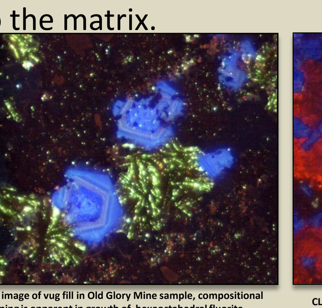
Lisbon Mine thin section, hydrothermal saddle dolomite crystals with characteristic baroque curved grain boundaries and undulose or strained extinction. Crossed nichols and 10X magnification.

- Staining of carbonate rocks - to distinguish dolomite and calcite (see rocks center poster)
- Cathodoluminescence microscopy (CL) – to gain information on the spatial distribution of trace elements i.e. (Fe^{2+} and Mn^{2+}) in calcite/dolomite grains and cements; mapping of cement zones can be used to determine the timing and origin of some cements and possibly of the introduction of uranium and vanadium into the matrix.

CL image of syntaxial fracture fill material from Lisbon Mine area, Little Mountain area, Wyoming; compositional zoning is apparent in growth of crystals reflecting multiple episodes of fluid migration, 10X magnification. The calcite is green in color and contains ytterbium Yb.



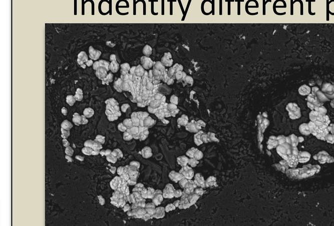
CL image of zoned calcite crystals from East Pryor Mountain area, Montana, 10X magnification. Dark interstitial areas are oxides. The calcite has Yb Ytterbium detected with EDS (Energy Dispersive-x-ray Spectroscopy) .



CL image of vug fill in Old Glory Mine sample, compositional zoning is apparent in growth of hexaoctahedral fluorite crystals which are blue and violet in the CL the uranium vanadium minerals are green fluorescent and the red areas are vanadium enriched dolomite filling in the small voids in the quartz matrix, 10X magnification.

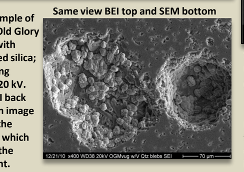
CL image of sample from Old Glory Mine sample fluorite and zoned dolomite, 4X magnification.

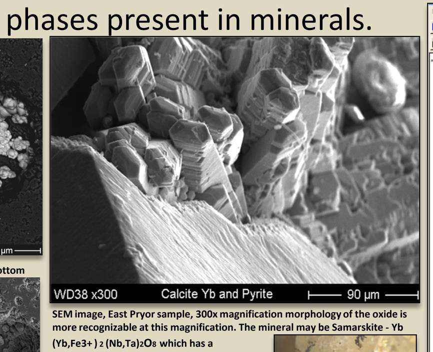
- Scanning Electron Microscope (SEM) imaging and spot elemental analysis (with EDS – Energy Dispersive x-ray Spectroscopy) – x-ray mapping and backscattered electron imaging (BEI) to indentify different phases present in minerals.



SEM images of sample of silicified breccia Old Glory Mine vugs filled with vanadium enriched silica; 400x mag., working distance 38 mm, 20 kV. Top image is a BEI back scattered electron image which highlights the heavier elements which appear lighter in the image than at right.

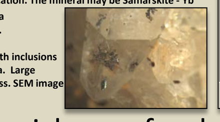
Same view BEI top and SEM bottom

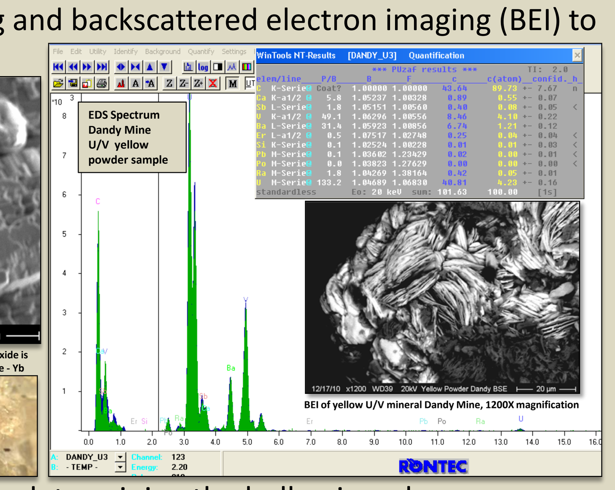




SEM image, East Pryor sample, 300x magnification morphology of the oxide is more recognizable at this magnification. The mineral may be Samarskite - Yb $(Yb,Fe^{3+})_2(Nb,Ta)_2O_8$ which has a monoclinic prismatic crystal form.

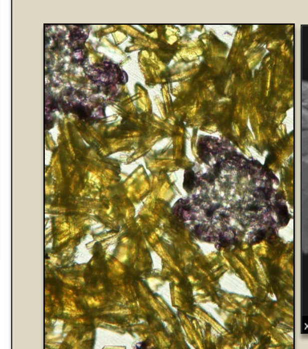
Photo to right is calcite crystal with inclusions from the East Pryor Mountain area. Large crystal is approximately 1 cm across. SEM image is from same sample.



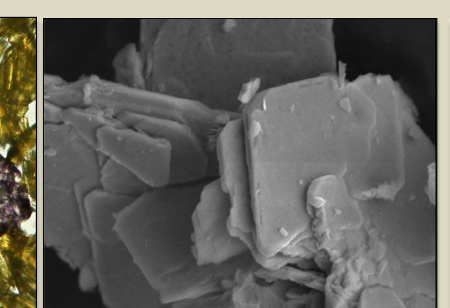


BEI of yellow U/V mineral Dandy Mine, 1200X magnification

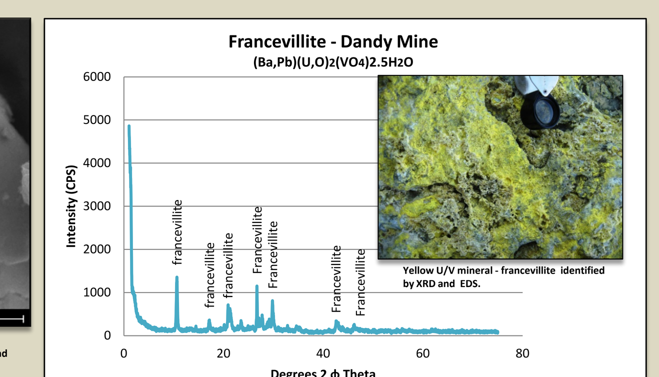
- X-Ray Diffraction analysis (XRD) – quick easy for determining the bulk mineralogy



Photomicrograph of thin section; vug in Old Glory Mine silicified breccia sample; 40 X Magnification, ppl, light purple mineral is fluorite U/V mineral is francevillite



Francevillite Scanning Electron Microscope image, 1500x magnification working distance 39mm. Morphology of mineral is displayed in this image and recognizable in the photomicrograph to the left.



Yellow U/V mineral - francevillite identified by XRD and EDS.

- Stable isotope analysis ($^{18}O/^{16}O$ and $^{13}C/^{12}C$) – used to help characterize water sources

Future Analytical Work:

- Strontium Isotope geochemistry ($^{87}Sr/^{86}Sr$) – useful in documenting deep brines that are highly radiogenic (percolating from the crust) from near-surface waters

Future/On Going Field Work:

- Fracture and joint analysis in the field to determine fracture density of the units

1. Obtaining a 3-D representation of a breccia pipe system by selecting several areas to view all four members of the Madison Limestone at several locations in the field area to determine the vertical (and lateral) distribution of breccia zones to obtain a detailed morphological and stratigraphic “cross-section” of a breccia pipe system.

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