PS Unique Microstrutures and Complex Micro-Mineral Associations in a Single Keokuk Geode*

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Abstract

From a suite of Keokuk geodes collected in Hamilton, Illinois, we selected a single geode for a detailed micro- mineralogical study. Keokuk geodes are specific to the dolomitic beds of the lower Warsaw unit in the Keokuk Formation. This sedimentary marine deposit is a consequence of a regressing epicontinental sea during the Mississippian period. Optical microscopy and scanning electron microscopy revealed a surprisingly complex network of elaborate intergrowths linking multiple generations of minerals which exhibit a wide array of crystal habits. This geode has a chalcedony shell as well as quartz and calcite euhedra, typical of geodes from this locality. Platy hexagonal kaolinite crystals are littered throughout the geode on and in quartz, calcite, and siderite. Kaolinite included calcite exhibits several habits including flow structures with ripple marks, a stair-stepped box texture, and euhedral crystals. Manganese carbonate micro-spheres grew from micro-drusy quartz and exhibit a variable Fe and Mn composition corresponding to the rhodocrosite- siderite series. Siderite appears as hallow spheres, about 5-10 microns in diameter, with growth rims indicating multiple phases with varying iron concentrations. Siderite also coats calcite euhedra with a multi-layered crust a few microns thick. Micro-crystals of acicular siderite grow from edges of kaolinite grains that settled atop the siderite-coated calcite. Most unusually, siderite appears as a box-like rectangular-to-rhombic lattice with a sub-botryoidal texture and incorporates the larger siderite spheres. This unique microstructure creates a ‘framework’ resulting from the systematic replacement of calcite along cleavage planes. The subsequent dissolution of calcite leaves the framework exposed to oxidation, resulting in the iron oxide goethite. Organics are also present in the form of 50-100 micron bitumen particles which host microcrystals of K and Na salts. Several additional minerals have been tentatively identified including: ponite, pyrite, sylvite, hollandite, feldspar, barite, and an unidentified REE carbonate. The mineralogy of this geode offers a microcosm illustrating the complex geologic process of secondary mineralization that occurs during the lithification and diagenesis of sedimentary beds.

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UNIQUE MICROSTRUCTURES AND COMPLEX MICRO-MINERAL ASSOCIATIONS IN A SINGLE KEOKUK GEODE

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Abstract

From a suite of Keokuk geodes collected in Hamilton, Illinois, we have selected a single geode for a detailed micro-mineralogical analysis. Optical microscopy has revealed a surprisingly complex network of elaborately inter-grown minerals exhibiting a wide array of crystal habits, linking multiple generations of mineral growth. Through scanning electron microscopy, we have tentatively identified 14 minerals, 7 of which are unique to this study. Typical of geodes from this locality, we observe a chalcedony shell, lined with quartz and calcite euhdra, growing radially inward. We identified kaolinite, dolomite, pyrite, barite, goethite, and also noted the presence of bitumen, all of which are reported in literature. Unique to this study, we observe spherical carbonates exhibiting varying Mn and Fe concentrations corresponding to the rhodochrosite-siderite series, including ponite. Siderite also appears in a never before reported three dimensional microstructure we describe as a 'framework'. We also identified feldspar, hollandite, halite, and sylvite, as well as observed an unidentified Fe-carbonate containing Cr, Ni, and Mo and a REE-carbonate. The mineralogy of this geode offers a microcosm illustrating the complex geologic process of secondary mineralization and offers great insight into the diagenetic history of the midwest region.

Introduction

Locality and Geologic Setting

Keokuk geodes refer specifically to geodes collected from the locality around Keokuk, Iowa and are unique to the dolomitic beds of the Lower Warsaw and Keokuk Formations. These sedimentary beds were deposited during the regression of an epicontinental sea during the Mississippian Period.

Figure 1: Map of Keokuk geode locality; x's indicate locations geodes have heave been found (http://rockhoundbill.blogspot.com/2015/04/-march2015geodes.html).

Figure 2: Geologic map of Illinois indicates that the Keokuk Formation is exposed in Hamilton (Illinois State Geologic Survey, http://isgs.illinois.edu/content/bedrock-geology-map-illinois).

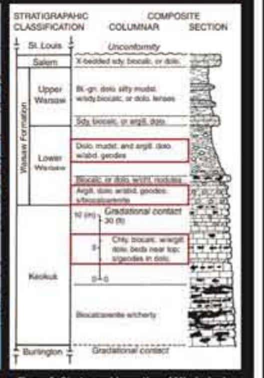
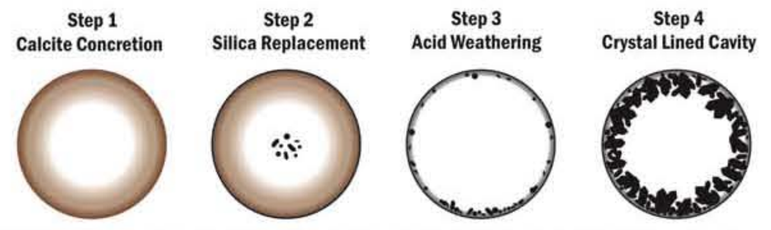


Figure 3: Stratagraphic section of Mississippian rock around the Keokuk-Hamilton area. Red boxes indicate the dolomitic beds in which geodes are present (Sinotte 1969).

Geode Formation

A geode is is defined by a discrete shell lined with inwardly radiating crystals. While geodes are common in volcanic rocks, sedimentary geodes such as those in this study have a very different paragenetic story. According to a report by Hayes (1964), the paragenetic process of a Keokuk geode is as follows:



Concentric layers of calcite grow around a nucleus and incorporate non-carbonate material which increases in concentration away from the center, essentially blending into the host rock.

During early diagenesis, silica replacement begins at the outer edge of the calcite concretion, replacing calcite with chalcedony and creating a distinct chalcedony shell. Simultaneously, double terminated quartz and chalcedony sphericals nucleate from silica detritus within the calcite concretion.

In what is described as 'acid weathering', hydrothermal fluids traveling through the geode dissolve the inner calcite core leaving the more resistant silica material intact including the chalcedony shell and quartz euhedra.

Meteoric waters fill the cavity and provide the solution for which crystals grow from the chalcedony shell, thus forming the crystal lined cavity which defines a geode. During this phase of diagenesis, changes in temperature and depth as well as chemical changes in the solution influence the precipitation of minerals inside the geode.

* It is proposed by Hayes that during lithification, the increase in pressure can fracture the calcite concretions. During the early stages of diagenesis, when the shell forms, growth of chalcedony travels along the fracture and appears to divide the geode into two distinct cavities creating the appearance of a 'double geode'.

Figure 4: Paragenetic process of a Keokuk geode

Figure 5: Geode types: Silica, Silica and Calcite, and Calcite (modified from Sinotte 1969)

Methods

To perform such a detailed mineralogical analysis, a single geode was chosen to be the sole focus of this study. The geode was picked at random and cut open, revealing the characteristics of a 'double geode'. Loose gains were disaggregated and washed, then using a Leica binocular microscope, the most interesting grains were extracted. Those grains were then mounted, carbon coated, and sent into the SEM for further optical and chemical analysis.

Observations

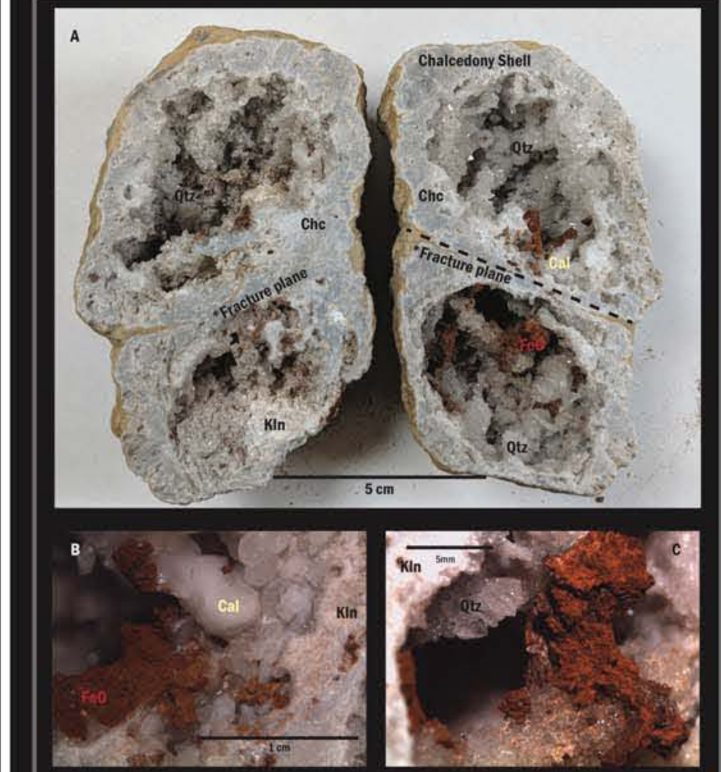


Figure 6: Leica binocular microscope images of geode show the
A) Selected geode, cut in half, reveals a 'double geode' , chalcedony shell, quartz, calcite, kaolinite and an iron oxide debris.
B) Chalcedony shell with chalcedony sphericals and kaolinite inclusions, calcite euhedra, and iron oxide microcubes and debris.
C) A closer look at the iron oxide debris reveals a cross-hatch like texture and a 2mm cluster of rhombic crystals with the same oxidative coloring; chalcedony, quartz euhedra, and kaolinite are also observed here.

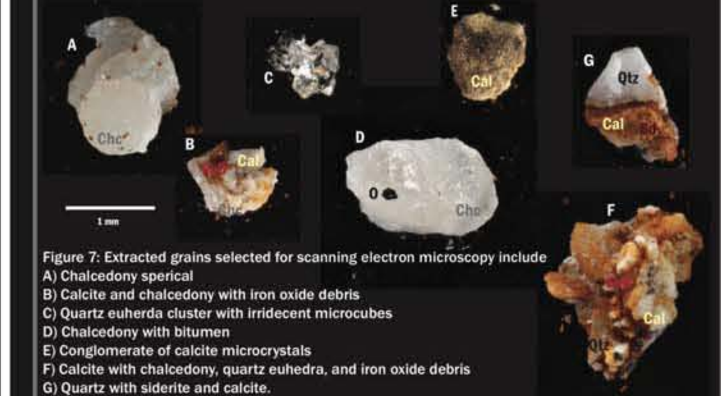


Figure 7: Extracted grains selected for scanning electron microscopy include
A) Chalcedony sperical
B) Calcite and chalcedony with iron oxide debris
C) Quartz euherda cluster with irridecent microcubes
D) Chalcedony with bitumen
E) Conglomerate of calcite microcrystals
F) Calcite with chalcedony, quartz euhedra, and iron oxide debris
G) Quartz with siderite and calcite.

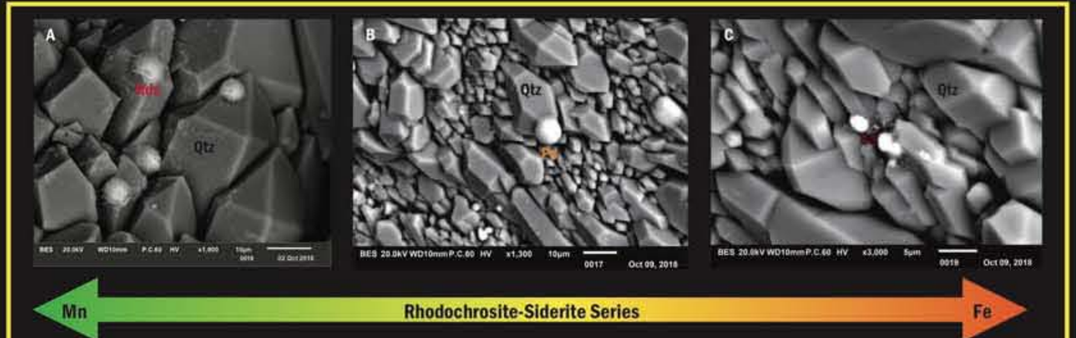


Figure 10: Micron-sized carbonate spheres grew from micro-druzy quartz and exhibit a variable Mn and Fe concentration corresponding to the rhodochrosite-siderite series.
A) Rhodochrosite micro-spheres on micro-druzy quartz; spheres which appear darker in BES images corrospond to a higer Mn to Fe ratio.
B) Ponite, the iron bering variety cf rhodochrosite, marks the midpoint between rhodochrosite and siderite; ponite micro-spheres are identified here growing from micro druzy quartz.
C) Siderite micro-spheres on micro-druzy quartz; spheres which appear brighter is BES images corrospond to a higher Fe to Mn ratio.

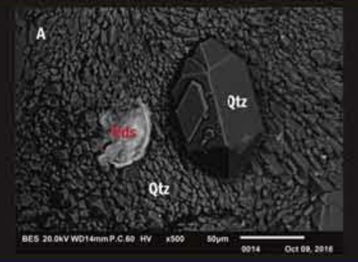
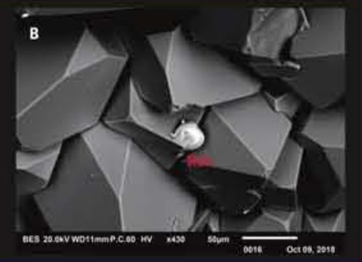


Figure 11: Rhodochrosite associated with quartz exhibit a similar disk-like habit to the rhodochrosite in Figure 15J.
A) Rhodochrosite appears as a beveled-disk growing from micro-druzy quartz.
B) Rhodochrosite with the same habit as A, is seen here growing on a larger quartz euhedra.



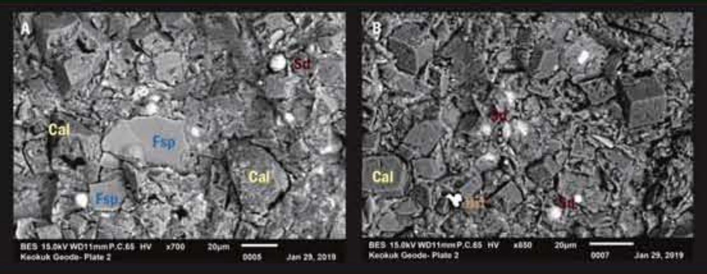
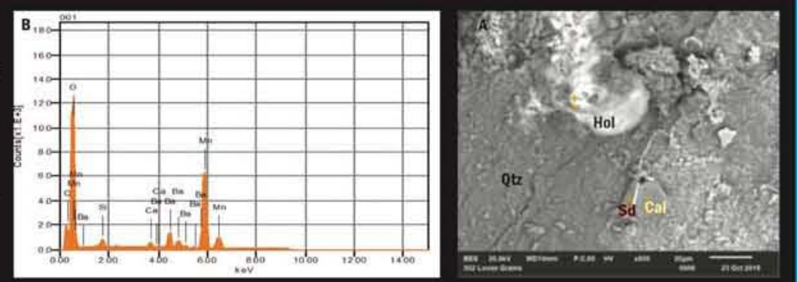


Figure 12: BES images of grain E from Figure 7 reveal a conglomerate of rhombic calcite crystals around 20 microns each.
A) Feldspar and sperical siderite growths similar to thoes seen in Figure 10C amungst the calcite euhedra
B) Prismatic barite crystals sit amongst the calcite euhedra, also with sperical siderite growths.

Figure 13: A) An amorphous growth of hollandite grows from quartz; remnants of thesiderite 'framework' including calcite are also seen here. B) Elemental spectra shows a high concentration on Mn, Ba, and O, corrosponding to hollandite.



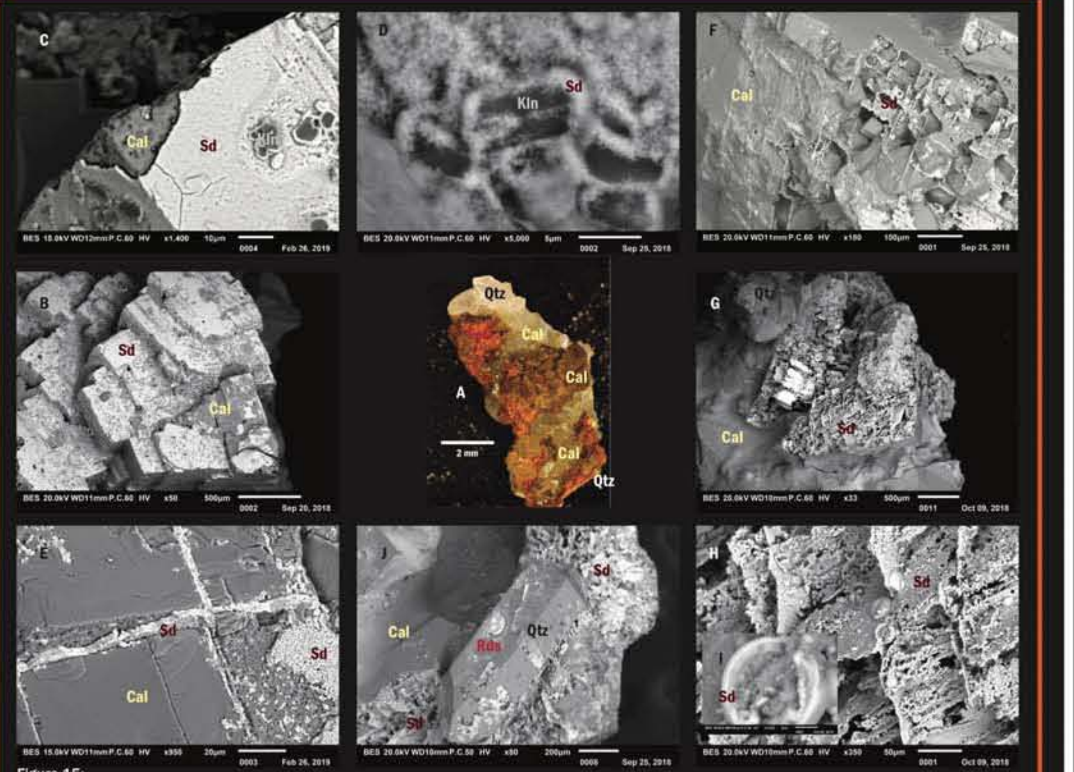


Figure 15:
A) Chalcedony and calcite matrix with quartz euhedra, a brown cluster of saddled rhombic microcrystals, and an abundance of an iron oxide debris like Figure 6C.
B) Brown cluster of crystals from A is revealed to be calcite with a thin coating of siderite.
C) Exposed calcite corner; siderite coating is only a few microns thick and incorperates kaolinite.
D) Further magnification reveals siderite growing from the coating between and around the kaolinite crystals, forming acicular crystal clusters along the edges of the prismatic faces of the individual kaolinite crystals.
E) In places where the siderite coating is missing, siderite fills in fractures along the cleavage planes of the calcite.
F) Dissolution of calcite exposes an inner-network of siderite.
G) Complete dissolution of calcite leaves the siderite framework exposed
H) A closer look at the framework reveals walls of siderite with a micro-botryoidal habit, incorporating larger (20 micron) siderite spheres.
I) Siderite spheres withing the framework are hollow and exhibit growth rims of varying Fe concentrations.
J) Located at the bottom left of the grain seen in A is a quartz euhedra

Figure 16: From Figure 7grain E
A) BES image of unidentified Fe-carbonate as a splay of crystals on top of calcite.
B) SED image reveals Fe-carbonate is growing from calcite, indicating the mineral is real
C) Elemental spectra of the Fe-carbonate indicates a high concentration of Cr and Ni with the presence of Mo.

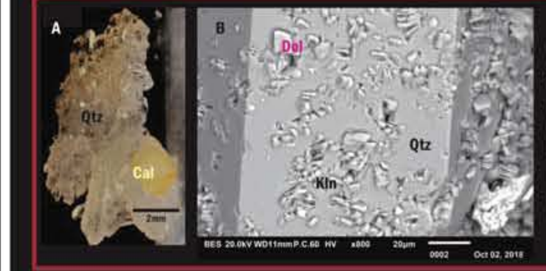


Figure 8:
A) Quartz euhedra cluster with kaolinite and a calcite euhedra
B) Quartz with kaolinite inclusions
C) Calcite euhedra exhibits a pitted like texture from the kaolinite inclusions.

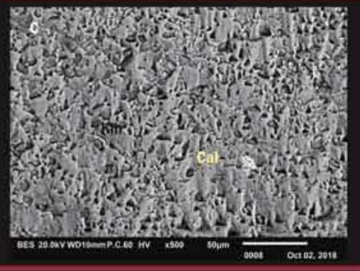
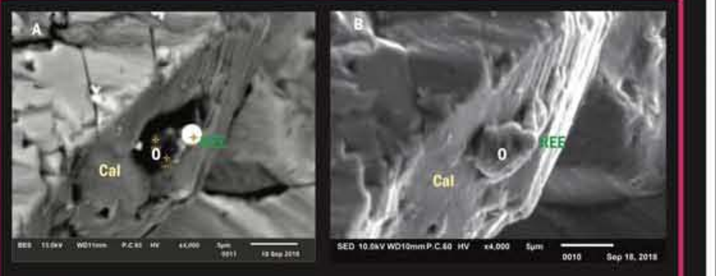


Figure 9: Kaolinite included Calcite microtextures where
A) Calcite exhibits microstructures which mimic ripple marks; platy hexagonal kaolinite crystals lay flush with the calcite
B) Calcite exhibits a stair-stepped-box like structure; this is a similar texture to that seen in Figure 8B with exhagerated calcite growth around kaolinite which is obsereved in the pits.

Figure 14: BES images of the quartz cluster seen in Figure 7C.
A) Goethite after pyrite microcubes nestled amongst quartz euhedra
B) Pyrite included in quartz.

Figure 17: Examples of bitumen particles
A) Bitumen with siderite on quartz, can be seen as the dark spot on grain D from Figure 7.
B) Bitumen with sylvite, halite, and siderite on kaolinite included calcite like that seen in Figure 9A, all on top of a quartz euhedra.
C) Cubic microcubes of halite precipitating from the bitumen particle in B.



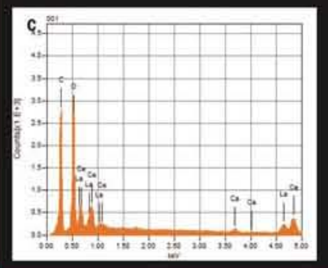
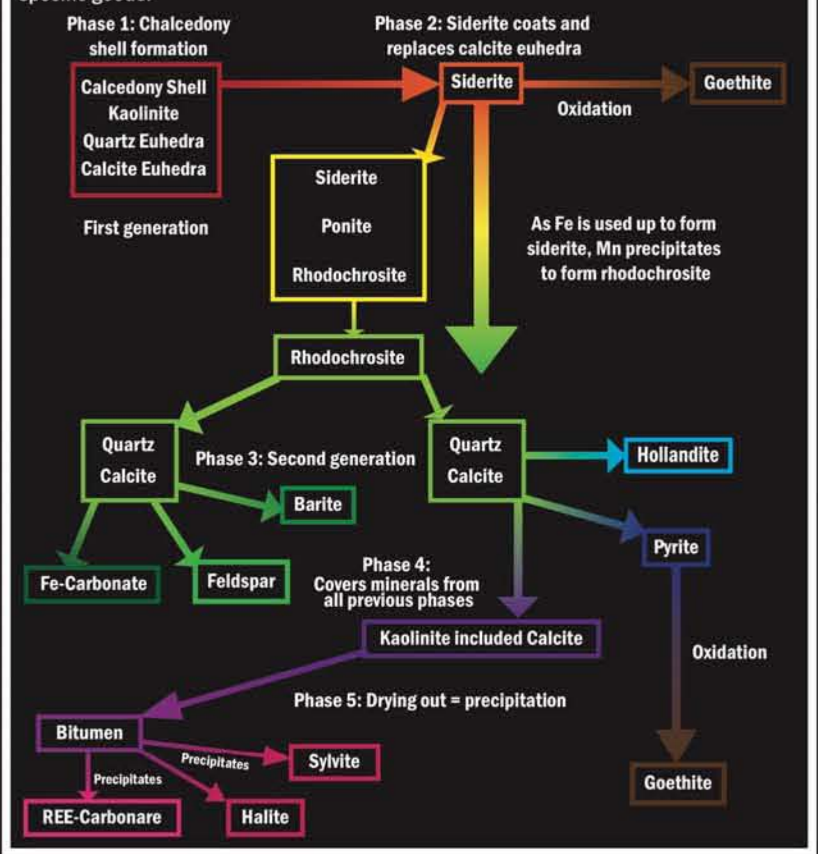


Figure 18: Micro-sphere of an unidentified REE-carbonate growing from bitumen on top of calcite.
A) BES image of the REE-carbonate on bitumen
B) SED image of REE-carbonate reveals spherical habit and apears to have precipitated from the bitumen particle
C) Elemental spectra shows the presence of REEs La and Ce.

Results

From the micro-minerals we have observed, the paragenetic process of this geode is far more complex than imagined. Below is a possible paragenetic sequence for this specific geode:



Conclusion

From the optical and chemical analysis performed during this study, we have observed an elaborate network of intergrowths which link several generations of mineral growth, suggesting a much more complex paragenetic process than has been described in literature. These unique microstructures and mineral associations present evidence for a dynamic system within the diagenetic environment in which the geode formed. In addition to the chalcedony shell, quartz, calcite, and bitumen, which are ubiquitous to Keokuk geodes, we have observed dolomite, kaolinite, pyrite, goethite, and barite. We have made the first documented observations of an REE-carbonate and Fe-carbonate containing Cr, Ni, and Mo. We have also tentatively identified feldspar, siderite, ponite, rhodochrosite, hollandite, sylvite, and halite. The microcosm of minerals of a single geode has exposed the complexity of the secondary mineralization process. Further research could provide great insight into the diagenetic history of the Keokuk region.

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