Final Report

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Magmatic Fluid Evolution from Porphyry Cu-Au to High-Sulfidation Au-Ag Deposits: Fluid Inclusion Evidence from the Pierina (Peru) and Summitville (USA) Deposits

By

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A. Introduction

The MRERP-funded project "Magmatic Fluid Evolution from Porphyry Cu-Au to High-Sulfidation Au-Ag Deposits: Fluid Inclusion Evidence from the Pierina (Peru) and Summitville (USA) Deposits" terminated December 31, 2005, following a three month no-cost extension. This final report presents the major scientific findings of the research project, supporting data, future plans for presentations and publications, and addresses three reporting requirements as stated in program announcement No. 04HQPA0007. These requirements are to provide (1) a comparison of actual accomplishments with the goals and objectives established for the period, the findings of the investigator, or both, (2) reasons why established goals were not met, if appropriate, and (3) other pertinent information including, when appropriate, analysis and explanation of cost overruns or high unit costs.

B. Research Goals, Objectives and Products

The overall goal of the research project was to improve our understanding of the evolution of magmatic fluids from the porphyry Cu ± Au environment to the high-sulfidation (HS) epithermal Au ± Cu ± Ag environment through a quantitative fluid inclusion study of the Pierina (Peru) and Summitville (USA) deposits. Research objectives related to this goal were designed to address gaps in our understanding of the evolution of magmatic fluids during the porphyry-epithermal transition and were framed as research questions. Paraphrasing the proposal narrative, the key questions concerned the involvement of single or multiple evolving magmatic fluids, mechanism of fluid and metal emplacement at the deposit level, role of the vapor transport of metal-ligand complexes, and origin of late stage barite and steam-heated fluids. Planned products for the project were (1) chemical and isotopic data on fluid inclusions, (2) digital images of fluid inclusions, (3) a performance report, (4) presentations at scientific conferences, and (5) publications in peer-reviewed journals. The data are presented in four tables and as copies of digital images attached to this report; all information is also contained on a CD with the images in a PowerPoint format.

The project was a collaboration between Southern Illinois University and the USGS and was closely associated with the USGS project of Robert O. Rye entitled "Geochemical and Stable Isotope Studies of the Life Cycle of Ore Deposits and Technology Transfer". The research plan was designed to take advantage of the state-of-the-art and emerging techniques for the analysis of single fluid inclusions being developed in Rye's laboratory and other USGS – Denver laboratories. It was anticipated that the PI would interact with other task members of the aforementioned project and thereby facilitate discussion and integration of several different but allied USGS endeavors. Moreover, it was suggested that results of the study could lead to improved ore deposit and environmental models that in turn would enhance our ability to perform effective mineral resource assessments of porphyry - epithermal systems and to understand the geochemical cycles involved with the devolatilization of magmas.

C. Accomplishments

The research accomplished the overall goal of improving our understanding of the evolution of magmatic fluids from the porphyry to the HS epithermal environment. The fluid inclusion study of a deep drill hole extending 1442 m below the Summitville deposit to a porphyry Cu-like environment produced exciting results that addressed most of the research objectives. Petrographic, microthermometric, and chemical data on fluid inclusions in this deposit collectively support a model of a continuously evolving system where deep-seated, pervasive magmatic fluids underwent extensive phase separation below the brittle-ductile transition, and acid-sulfate condensate from the ascending vapors both altered the host rocks and subsequently introduced metals to rocks depleted in their buffering capacity. In this vapor transport model of metals the mechanisms of cooling and condensate-meteoric groundwater mixing were important triggering mechanisms of metal deposition. Moreover, the study demonstrated that the quartz-latite porphyry host unit crosscuts a quartz monzonite intrusion at depth, which is opposite of the age relationship previously cited. The principal alteration and vein assemblages in the deep drill hole record the late-stage collapse of high-level acid-sulfate fluids along structures that resulted in argillic and advanced argillic alteration and minor Cu mineralization overprinting earlier formed phyllic alteration and pyrite-quartz veins. To my knowledge, this study provides the first single-inclusion LA-ICP-MS analyses for a HS epithermal deposit; all other published studies using this technique have focused on porphyry Cu or other deep seated deposits. Finally, throughout the course of the study the PI interacted with numerous other MRP scientists and engaged in stimulating discussions regarding the developing results and their implications for ore-forming processes, theories and models. Such interactions routinely occurred with Robert Rye, Barney Berger, Albert Hofstra, Gary Landis, Paul Emsbo, Dana Bove and Brian Rusk (Mendenhall Fellow) of the Central Region, and on separate occasions with Peter Vikre and David John of the Western Region, and Phil Bethke and Skip Cunningham of the Eastern Region. These interactions were enormously helpful and thought-provoking for the PI.

The PI pursued a direction of research that was beyond the proposed scope of the project. Preliminary Raman Spectroscopy (USGS – Reston) and XANES/XAFS (Argonne National Laboratories) data were acquired in an attempt to establish the composition of some unusual yellow inclusion fluids, the identity of multiple daughter phases, and the Cu and As speciation in the inclusion fluids. Initial interpretations imply that the yellow fluid is a S-C compound and that Cu is present in the fluids as a chloride complex, whereas As is bound to oxygen. Both lines of research are promising and will be pursued further.

More detailed discussions of the work accomplished and the major findings of the Summitville study are presented in the following sections. The data products delivered with this report include a summary of findings (contained herein), data on the alteration and vein mineralogy (Table 1), data on fluid inclusion petrography and microthermometry (Table 2), reduced data on the measured inclusions (Table 3), LA-

ICP-MS analyses of single inclusions (Table 4) and selected digital images of drill core, samples and fluid inclusions (attached images, CD). A multi-authored presentation of the Summitville results and interpretations is planned for the next national meeting of the Geological Society of America and preparations are underway for their publication in a major peer-reviewed journal. Two additional papers may ultimately be published as an outgrowth of this work; one emphasizing the unusual yellow fluids and another involving metal speciation in the Summitville HS system.

Two research objectives of the proposed project were not accomplished due to the quality of the fluid inclusion records. Vein and phenocryst quartz and their contained fluid inclusion records at Pierina both were found to be considerably less abundant and smaller than those at Summitville. Moreover, samples from below the Pierina ore body were unavailable for study. Therefore, it was decided early in the project to focus on the more promising fluid inclusion record at Summitville. Similarly, fluid inclusions in barite at Summitville were studied petrographically but sparse sample material precluded an adequate evaluation of the role of late-stage fluids in the formation and enrichment of the deposit.

D. Research Approach and Methods

To establish an overall lithologic and mineralogic framework for interpreting the fluid inclusion record at Summitville several preliminary studies were conducted on the entire drill core (995 m) available from the deep drill hole (DDH-14). These studies included logging the core to determine intrusive relationships among igneous units and breccias and to establish alteration assemblages, zonation and timing. Digital images were made of the entire core and of selected samples illustrating diagnostic features. Hyperspectral data, petrographic examination under transmitted and reflected light, and SEM analysis in back-scatter, secondary-electron, and cathodoluminescence modes were utilized to identify clay and other fine-grained minerals, sulfide mineralogy, and reveal cryptic textures of vein quartz such as growth zoning, dissolution surfaces and cross cutting stages.

The fluid inclusion study emphasized secondary fluid inclusions in igneous quartz. Quartz phenocrysts in the quartz latite porphyry and quartz aggregates in the quartz monzonite were particularly well suited for such an investigation. Quartz is an excellent host for fluid inclusions because it readily fractures and seals through dissolution-reprecipitation and can withstand high internal pressures without significant deformation of inclusion volumes. Ideally, igneous quartz will contain a record of all fluids that have pervaded the host rocks since the time of crystallization, although deciphering the relative ages of distinct fluid generations is typically quite difficult. Hydrothermal quartz related to mineralization is scarce in the Summitville system where it is present as a subsidiary component in pyrite-quartz veins of the deep phyllic alteration and more rarely in mineralized structures (e.g., Missionary Vein) or mineralized cavities as quartz phenocryst overgrowths.

The fluid inclusion record of igneous and hydrothermal quartz was studied in approximately 55 chips or sections from Pierina and Summitville. The petrographic features noted and digitally documented included size, form, vapor/liquid ratio, daughter mineral assemblage, and occurrence (planar, clusters, isolated). Such features served to distinguish inclusion types, fluid inclusion assemblages (FIAs), and vertical trends in such inclusion parameters. Cooling and heating runs were performed on over 300 inclusions using a Linkham 600 stage at the USGS in Denver. Phase behavior that was recorded included the temperatures of formation, first melting (T eutectic) and final melting of solids formed during freezing runs, and the temperatures of halite, sylvite or other daughter mineral dissolution, and vapor→liquid or liquid→vapor homogenization during heating runs. These microthermometry data were reduced using MacFlinCor software, published phase diagrams and equations, and sample paleodepths to estimate relevant compositional systems (e.g., H_2O-NaCl-KCl), trapping temperatures and pressures, total salinity, density and other parameters of the inclusion fluids.

Approximately 200 inclusions were analyzed for selected cation concentrations using the LA-ICP-MS instrumentation at Leeds University, UK. Previously mapped inclusions were targeted and ablation behavior was noted for each analysis, particularly the tendency for quartz spalling. Signal data were reduced with a MATLAB-based program provided by the laboratory. Large, hypersaline inclusions within 20 microns of the surface generally provided broad, single peaks that were well above background, whereas small or vapor-rich (low density) inclusions yielded very weak or spiky signals. Rapid spalling of the quartz commonly produced Cu and As peaks that preceded associated Na, K, Fe, and Mn peaks. Perhaps, this phenomenon was related to the early tapping of more volatile components enriched in vapor bubbles or near-by inclusions. Analysis of daughter-bearing minerals occasionally produced similarly separated signal peaks. These analytical uncertainties and a high variability in the calculated elemental values make interpretations of these data less than straight forward.

E. Summary of Results and Interpretations

Hand specimen study of the deep drill core revealed several igneous rock types and minor hydrothermal breccias. Of particular interest, were the contact relationships between quartz latite porphyry (the main phase of a volcanic dome that hosts the Summitville deposit) and a quartz monzonite intrusion at depth. Previous studies suggested the intrusion was the source of the magmatic ore fluids and younger than the quartz latite porphyry. However, the porphyry phase exhibits both chilled margins and small xenoliths of quartz monzonite at their mutual contacts. Therefore, the latite porphyry is the youngest major igneous unit to have been affected by intense alteration and its magma source at depth most likely also generated the magmatic ore fluids during the later stages of crystallization. Radiometric ages for alteration alunite and igneous sanidine are coincident within analytical uncertainty, lending further support to this genetic linkage. Consequently, future geochemical analysis of the unaltered melt inclusions found in some quartz phenocrysts of the porphyry may provide insights into the redox state, metal contents, and melt-fluid element partitioning of the mineralizing magma intrusion.

The alteration study of the deep drill core revealed a deep, early chlorite-kaolinite-pyrite assemblage confined to aphyric lavas of intermediate (?) composition. It is overprinted by pervasive quartz-sericite-pyrite (QSP) alteration that extends throughout the drilled section. The QSP alteration, in turn, is overprinted by zones of pervasive and fracture-filling kaolinite±pyrophyllite±dickite±alunite-pyrite in the upper part of the available drill core and by pyrophyllite±kaolinite+pyrite deep in the hole. Clay-pyrite fractures appear to be most closely associated with copper sulfide (enargite, chalcocite, bornite, chalcopyrite) veins and veinlets. Zunnyite was the principal silicate intergrown with enargite in the deepest Cu vein. Minor occurrences of molybdenite have been reported from this drill hole.

Secondary fluid inclusions are abundant in igneous quartz from the deposit level to the bottom of the deep drill hole ~1442 m below the deposit. Vapor-rich inclusions (>60 % vapor) predominate over liquid-rich (<40 % vapor) inclusions throughout the entire interval. However, minor hypersaline (halite±sylvite±unknown phases±opaques) are present at depths greater than ~540 below the deposit and exceedingly rare above this depth. The upper limit of hypersaline inclusions is regarded as a fluid density interface where pervasive dense magmatic fluids undergoing phase separation existed below the interface and vapor condensate and meteoric groundwater constituted the bulk of the fluids above the boundary. Furthermore, magmatic brines trapped within ~500 m of the interface produced relatively large, irregular inclusions containing up to 7 or more daughter phases. By contrast, deeper hypersaline inclusions are relatively small, subhedral to euhedral in form, and commonly contain only halite and sylvite phases. Additionally, a small proportion of the liquid-rich inclusions within ~200 m above and below the fluid density boundary contain an unusual yellow liquid concentrated in sulfur and carbon that is immiscible with aqueous fluids at room temperature.

The halite-bearing inclusions below the fluid interface have consistent microthermometric properties with average homogenization (vapor→liquid) temperatures ($Th_{v\text{-}l}$) of 370 °C and halite dissolution temperatures yielding average salinities of 40 wt. % $NaCl_{eq}$. However, liquid-rich inclusions near the bottom of the drill hole have an average $Th_{v\text{-}l}$ of 340 °C and salinity of ~15 wt. % $NaCl_{eq}$, whereas those within 400 m below the interface have a higher $Th_{v\text{-}l}$ of 400 °C but lower salinity of ~6 wt. % $NaCl_{eq}$. Liquid-rich inclusions immediately above the interface yield a considerably lower average $Th_{v\text{-}l}$ of 285 °C and a similar average salinity of 7 wt. % $NaCl_{eq}$. At the deposit level, liquid-rich inclusions have an average $Th_{v\text{-}l}$ of 240 °C and salinity of 5 wt. % $NaCl_{eq}$, although the salinities calculated range up to ~20 wt. % $NaCl_{eq.}$

The LA-ICP-MS analyses of the Summitville inclusions do not reveal any major chemical trends over the sampled vertical interval but do indicate the maximum extent of metal enrichment in the hypersaline fluids: Fe ~37 wt. %, Mn ~23 wt. %, Cu ~4 wt. %, Zn ~5 wt. %, Pb ~3 wt. % and As ~3000 ppm. Au was detected in the ppm range in a few inclusions. Liquid- and vapor-rich inclusions respectively have lower maxima of these elements, as expected, but can also achieve metal concentrations in the thousands ppm range.

Collectively, these data are consistent with a pervasive magmatic fluid undergoing extensive phase separation below the brittle-ductile transition zone near the 400 °C isotherm. If the fluids expelled from the magma were of moderate salinity, perhaps around 6 wt. % $NaCl_{eq}$, then sufficient boiling occurred to produce a residual brine of around 40 wt. % $NaCl_{eq}$. However, if the source intrusion was within 3 km of the paleosurface, as seems probable for the Summitville system, then both brines and vapors were likely expelled from the magma simultaneously, although the expelled fluids must have continued to undergo phase separation. Heat and volatiles in the vapor state were slowly transported upward to the fluid density interface but the transfer of mass and energy across the interface and brittle-ductile transition probably was impeded. Phase separation intensified as the rising fluids toward the interface due to decreasing pressure. Such a model accounts for the extreme enrichment of the residual fluids and apparently higher temperatures immediately below the fluid interface.

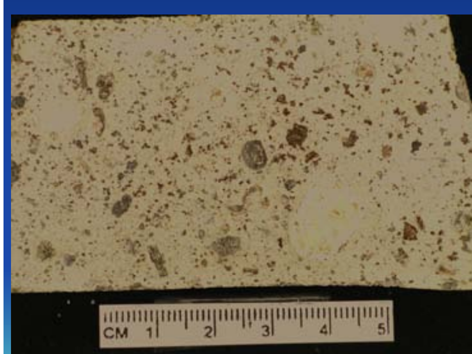
The transfer of volatiles across the brittle-ductile transition would be most effective during periods of receding isotherms and along major through-going faults. The documented lower temperatures and moderate fluid salinities of the trapped fluids above the fluid interface imply that significant vapor condensation occurred in the more freely circulating, cooler meteoric groundwater above the brittle-ductile transition. However, the intense alteration by acid-sulfate condensate at the high level of the deposit must have resulted from a vapor plume rapidly rising along a network of connected faults, fractures and breccia bodies. The deposit is substantially enriched in S, Cl, Cu, As, and Au; essentially the same elemental suite that fluid inclusion and high-temperature volcanic gas analyses indicate are partitioned preferentially into vapors during phase separation from magmatic fluids. Thus, it is plausible that mineralization of the intensely altered rocks was also accomplished through vapor activity. Such a dominant role for vapors in alteration-mineralization is consistent with the presence of moderate salinity inclusions with elevated metal contents and the near absence of hypersaline inclusions in the deposit. Although the involvement of dilute magmatic fluids at the deposit level can not be precluded, the Summitville data combined with other relevant information supports the transport of metals to the deposit site by vapors the deposition of metals triggered by cooling and the mixing of vapor condensate and meteoric groundwater. Finally, during the collapse of the waning hydrothermal system, downward percolating acid-sulfate fluids produced the argillic overprint of QSP-altered rock and weak Cu-mineralization along fractures at depth.

Photodocumentation of Summitville Drill Core

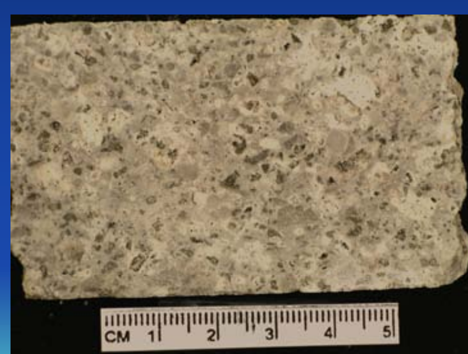
Intrusive Relations

Principal Rock Types

Qz Latite Porphyry

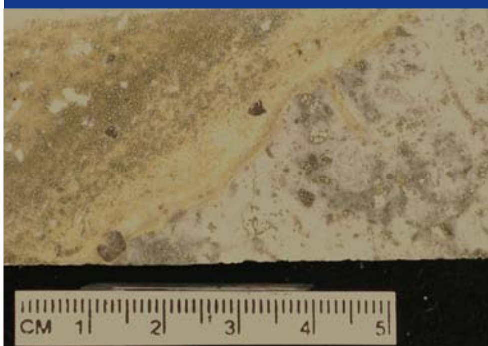


Qz Monzonite



Intrusive Relations

Qz Latite Porphyry cross cuts Qz Monzonite



- Overprinting by high level acid-sulfate fluids w/collapse of system

Alteration Assemblages

Stages at Depth (DDH-14)

2. Qz-Sericite-Py- pervasive with Pyrite-quartz veins

Alteration Assemblages

Stages at High Level (DDH-14)

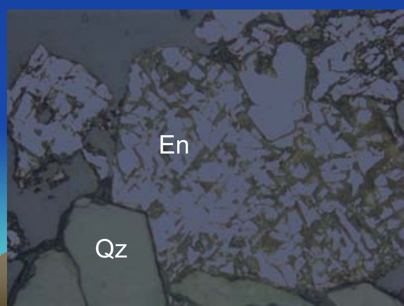
Qz-kaolinite, pervasive

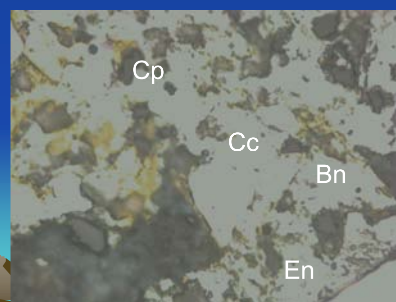
Qz-Alunite , pervasive

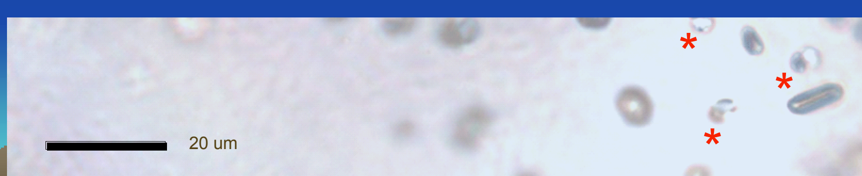
Mineralization

3. Hematite-Geothite
2. Barite+/-Base Metals
1. Enargite-Covellite-Pyrite

Gold inclusions in enargite (not covellite) and in FeOx (remobilized during weathering)

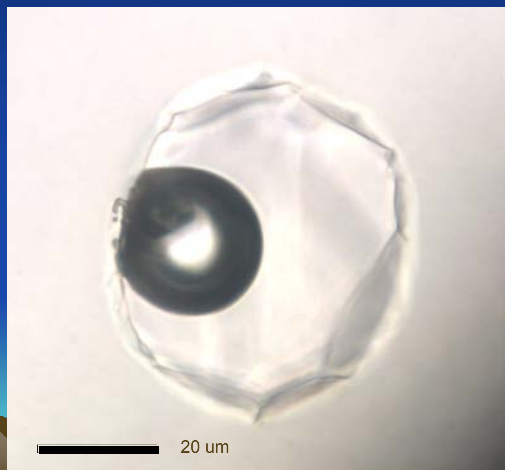






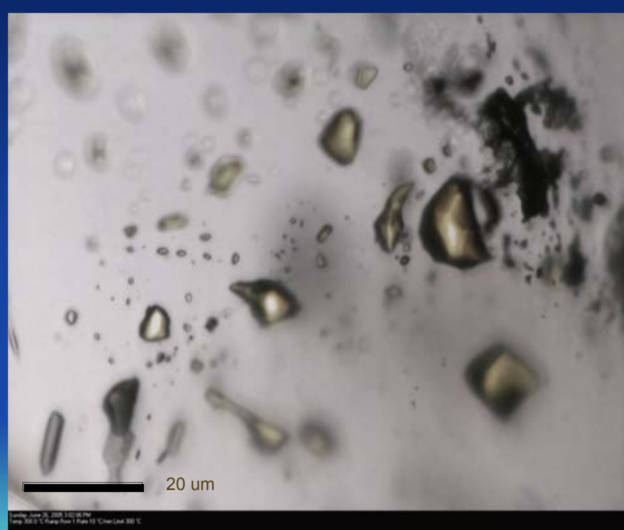
Fluid Inclusion Study

- Large melt inclusion in qz phenocryst of qz-latite ppy
- AZ-W40



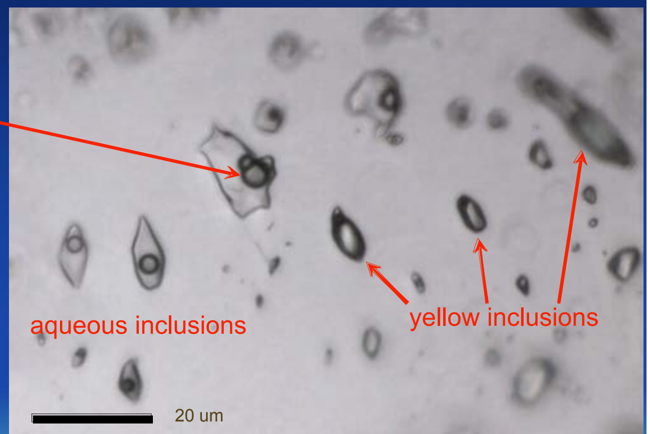
Fluid Inclusion Study

- DDH14-1501
- Yellow, immiscible liquid inclusions near fluid interface ~540 m below deposit level



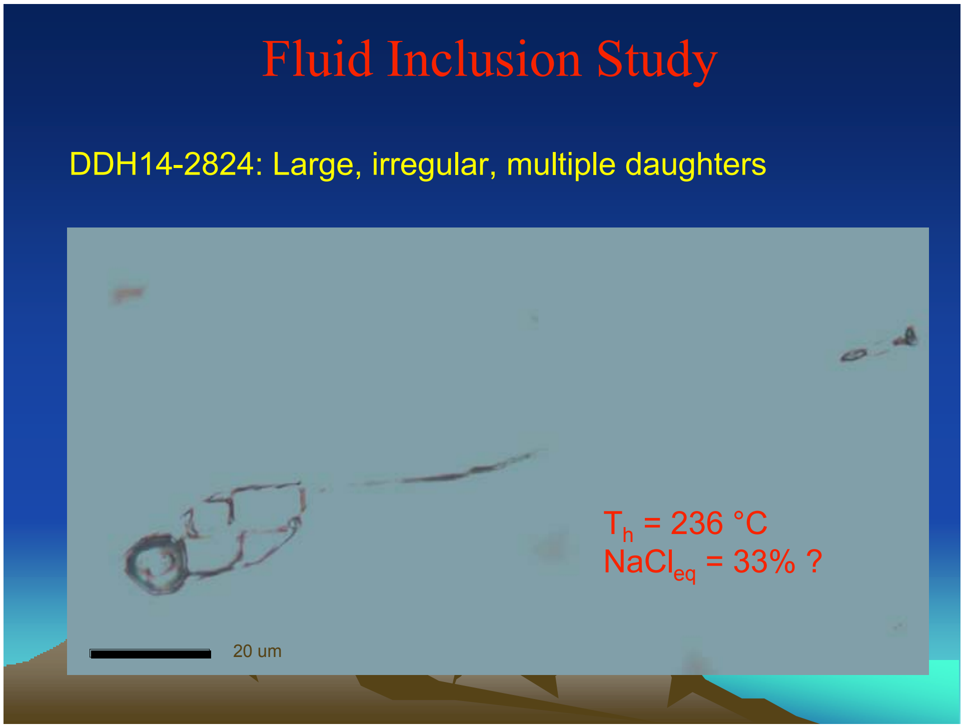
Fluid Inclusion Study

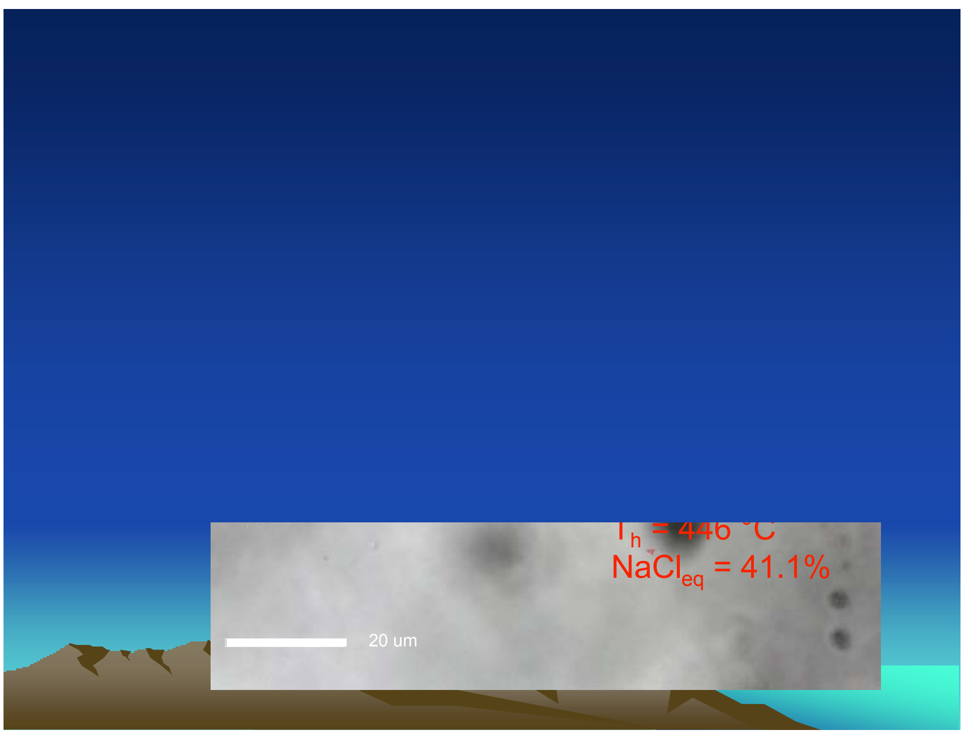
- DDH14-1501
- Yellow, immiscible liquid in aqueous inclusion near fluid interface



Fluid Inclusion Study

DDH14-1851: Large, irregular, multiple daughters; and vapor-rich inclusion


Fluid Inclusion Study
DDH14-2824: Large, irregular, multiple daughters
T_h = 236 °C
$NaCl_{eq}$ = 33% ?
20 um


$NaCl_{eq}$ = 41.1%
20 um

Fluid Inclusion Study

DDH14-4124

Deep, hypersaline inclusions