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Fluid inclusion studies of samples from the Exploratory Study Facility, Yucca Mountain, Nevada

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1. Introduction

This report summarizes results of research on fluid inclusions from the calcite samples gathered in the Exploratory Study Facility (ESF), Yucca Mountain, Nevada. The study of the 12 samples collected from the first 200 m of the ESF in 1995 was carried out in the Institute of Mineralogy and Petrography in Novosibirsk, Russia. The results were published as a report (Dublyansky and Reutsky, 1995), and as abstracts of several conferences (Dublyansky at al., 1996 a and b; Dublyansky, 1998a). The results will be briefly summarized in section 5.

A short repeat study on the same sample set was performed in June 1998 at Virginia Tech, Blacksburg, VA, U.S.A. in the laboratory of Prof. R. Bodnar. One of the purposes of this study was to verify the quality of the data and the validity of the results. Some new data were obtained during this study (the report is attached as Appendix 1).

Samples for present study were collected from the ESF on June 1998. They were studied in October, 1998 at Fluid Research Laboratory, Virginia Tech, Blacksburg, VA, U.S.A.

2. Technical details on sampling, sample preparation and equipment used

2.1. Sampling

Samples for this study were collected in the ESF on June 8 and 9, 1998 from the Experimental Study Facility (ESF), which is a horseshoe-shaped 7.8 km-long tunnel excavated in the tuffs. In compliance with the Integrated Sampling program, locations of each sample were marked on the tunnel walls by plastic plates, and each sample was assigned an individual number and bar code. In this report we will also discus the data from our first set of samples that was collected in March 1995 when only the first 200 m of the tunnel had been excavated. This first set of samples characterizes stratigraphically higher welded tuff Tiva Canyon, located above the design repository level and separated from the potential repository horizon - welded tuff Topopah Spring - by a layer of a highlyporous non-welded bedded unit (see Appendix 2). One sample from the second set (2206) is also from Tiva Canyon tuff. The remainder of the set-1998 was gathered from the Topopah Spring tuff.

2.2. Sample preparation

Calcite is cleavable mineral; therefore the potential for damaging inclusions when preparing samples is always of concern. All possible precautions have been taken to avoid any mechanical or thermal damage to the inclusions during the preparation of samples for fluid inclusion studies. Working with the first set of samples we used cleavage chips instead of polished plates. The samples from the second set have been cut using a low-speed *Buehler Isomet* saw set at ~120 rpm with cold water as a coolant. Freshly cut surfaces have been manually ground and polished using grinding powder (600 grit and 5 micron) and *Buehler Metadi* water-based diamond fluid (1 micron). Polished surfaces have been mounted on glass slides using cyanoacrylic glue and the operations were repeated to produce doubly polished sections. The fact that fluid inclusions with homogenization temperatures as low as $35 \,^{\circ}$ C were preserved in the prepared section: indicates that during the preparation, the samples cannot have been exposed to temperatures higher than 34 $^{\circ}$ C.

2.3. Analytical procedures and equipment used

Prepared thick sections have been examined under an Olympus BX-60 microscope at different magnifications. Inclusion petrography was documented with Polaroid digital camera; sometimes, for the purpose of rapid mapping a Sony video printer was used.

Thermometric studies were performed on a Linkam THMSG stage. Part of the homogenization temperature measurements on the first set of samples was made on a stage manufactured at the Institute of Mineralogy and Petrography in Novosibirsk, Russia.

Homogenization. A cycling technique was applied to measure homogenization temperatures. Temperature in the stage was increased in increments of 1 °C. The sample was held at each temperature for 1 or 2 minutes for thermal equilibration. Each inclusion was examined for the presence of a bubble, after which the next heating step was performed. If the presence or absence of a bubble in an inclusion at a certain temperature was not apparent (typically, for small inclusions less than 5 micron in size) the sample was cooled down to 20 °C (homogenized inclusions would net heterogenize after such cooling). This procedure made it possible to obtain precise

measurements on assemblages of up to 20-25 inclusions. Significant scatter of individual measurements indicates a "disturbed" character of the inclusion association (i.e., due to possible stretching or leakage). Conversely, group of inclusions that homogenize within a few-degree range may be considered as representative of the true ancient temperatures.

Freezing. The inclusions in the Yucca Mountain calcites proved to be difficult subjects for cryometric studies due to their small sizes and the low salinity of entrapped fluids. The results of freezing experiments can only be interpreted if all three phases, solid, liquid and vapor, are present in an inclusion during the final melting. In comparatively lowtemperature minerals such as the Yucca Mountain calcite, inclusions that were homogenized by heating almost never heterogenized upon cooling to room temperature. Therefore, to carry out freezing experiments we had to artificially stretch inclusions. This was being done by heating them to 250 °C and/or cooling to the temperature of liquid nitrogen.

Other methods. In discussion below we will use the data obtained earlier (Appendix 1). Gas chromatographic analyses were carried out on the chromatograph LHM-8 with two different types of gas detectors (flame-ionisation detector and catharometer). Gas was extracted from samples by heating them to 250-500 °C. Raman spectrometric analyses were performed at Virginia Tech, Blacksburg, VA using a Dilor XY Raman microprobe with Princeton Instruments CCD detector and Lexial Argon ion 5 watt laser. Analyses of carbon and oxygen isotopes were carried out at McMaster University, Hamilton, Ontario, Canada, using a VG SIR4 mass spectrometer with an Autocarb analyser.

3. Occurrences of calcite in the ESF

Calcite in the ESF occurs as various epigenetic formations. In places it forms "common" veniets (i.e., veinlets in which the opening of a fissure is entirely filled with calcite). An example of such veinlet is given in Fig. 1.



Fig. 1. Station 67+81.0. Dune Wash fault zone. Sample 2210. Calcite veinlets in Topopah Spring welded tuff.

Such veinlets, however, are rare.

Another rare, but fascinating occurrence is calcite coating floors of small tectonic cavities. like one shown in Fig. 2. Thin and apparently stress-related fissures propagate in various directions from such cavities: some of such fissures are filled with milky-white calcite.



Fig. 2. Heater along the first statisty in Topopah Spring turf with mystalling statistics of the foot is floor.



Fig. 3. Station 37 ± 37.0 . Northern Ghost Dance Fault Alcove (#6) station 0 ± 55.1 . Sample 2222. Low-angle veinlet and micro-breccia.

Calcite also occurs along low- to steep-angle fractures forming complex bodies, which consist of "common" veinlets build up of massive milky-white calcite, calcite-cemented breccias, and crusts featuring free-growth crystals in fissure's opening. The shape of such bodies is often irregular, as it is shown in Fig. 3.

Calcite forms crusts, 1 to 3 cm thick on the floors of lithophisal cavities (Fig. 4). It is noteworthy that thin fractures, intersecting these cavities, if present, do not contain calcite.



Fig. 4. Station 35077. Sample 222 clustes phisa in Teponah Spring tutt featuring cluster long on the floor

Calcite also coats fracture walls or, in fractured zones, surfaces of brocken fragments of bedrock tuffs (Fig. 5- A). On some occasions, it forms small individual euhedral crystals (Fig. 5-B).



Fig. 5. Station 52.13. Sample 2215. A – Translucent blocky calcite, coating brocken fragments of tuff (scale bar is 2 cm); B – Close up: individual euhedral calcite crystal on tuff surface (arrow on A; scale bar is 5 mm).

4. Fluid inclusion results

Samples collected in the ESF in 1998 were assigned numbers from SPC00532201 through SPC00532232. Below we use the last four digits to identify the samples. Numbers of stations reflect distance from north portal, except for alcoves, where distance is indicated from the main tunnel.

Quantitative fluid inclusion results were obtained on seven samples. In three more samples, two-phase gas-liquid inclusions suitable for thermometry have not been found.

Samples from the first 200 m of the ESF (results of previous studies)

The samples, collected on March 1, 1995 and studied in Novosibirsk in 1995 and partly in Blacksburg, VA, in June 1998 (see Appendix 1) are labeled according to the numbers of the steel sets between which they were taken. All samples are from Tiva Canyon tuff (Tpc unit).

Thermometric data are given below:





Figure 1



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Station: To-Date

Field description. Calcite crust on the foot wall of the opening, up to 2 cm thick. Bedrock tuff appears to be altered (calcitized). In one location, the crust has pink color (possible presence of disseminated fluorite).

Bedrock: Tiva Canyon Tuff (Tpc unit).

Depth from land surface: ~70 m.

Minerals and textures. On the visual basis, there occur several generations of calcite. (1) 1 mm-thick layer of slightly brownish calcite on the contact with the bedrock tuff. White empty globules 0.1-0.2 mm in size often occur on its surface (opal?). (2) 1 cm-thick layer of translucent large-crystalline calcite with freegrowth crystals at its top. Under the microscope, up to four generation of calcite, separated by hiatuses (dissolution) or layers of opal can be distinguished. The final, fifth layer contains crystals of free growth with welldeveloped pinacoidal face, intergrowth.

Colorless and violet globules of *fluorite* are associated with the latest stages of calcite growth. They are often overgrown by calcite and make the latter look violet. Part of the globular aggregates reside on the calcite surface. Sometimes fluorite forms individual crystals on the calcite surface up to ~ 0.2 mm in size. Crystals are irregularly colored from



Fig. 6. Sample 2206. Quartz and culcute. Scale bar is 1 num.



Fig. 7. Sample. 2206. Black – group of inclusions along growth zone: gray – inclusions along low-angle plane: white – inclusions forming a 3-D group.

light- to dark-violet. Crystals are isometric (100, 111, 110) but often distorted.

Opal has botrioidal appearance. *Quartz* occur as globules 1-2 mm in diameter. The tips of crystals in globules are 0.1 and less mm in size. Some individual crystals have size of up to 2 mm (Fig. 6). They have perfect shape, translucent and have diamond luster. Some of them are overgrown by a thin layer of opal. Crystals of fluorite were observed on the surface of quartz.

Fragments of tuff 2 to 15 mm in size occur in the middle of the crust. They are cemented by opal and calcite. Translucent euhedral crystals (zeolite?) occur on the surface of these fragments.

Fluid inclusions. Calcite contain numerous all-gas inclusions. All-liquid aqueous inclusions are abundant. Two-phase gas-liquid inclusions are rare. They occur as 3-D groups. groups along low-angle planes and along growth zones.

The results of thermometric studies are shown in Fig. 7. Homogenization temperatures for each group of inclusions plot within narrow, 4-5 °C-vide interval. The result, therefore is quite consistent and measured temperatures may be considered true minimum temperatures of paleo fluids.

Station: 52-13

Bedrock: Middle Nonlythophisal crystal poor Topopah Spring Tuff (Tptpmn unit)

Depth from land surface: ~ 260 m.

Field description. Steep-angle fracture lined with thin, ~0.5 mm, crust of dark powdery to violet micro crystalline fluorite (subsample 2215A). In places this layer of fluorite is covered by a crust of translucent blocky calcite crystals (subsample 2215B).

Minerals and textures, subsample 2215B. *Calcite* is water-clear, blocky. It forms 0.5 to 3 mm thick crust on the fracture wall, as well as coats broken fragments of tuffs (Fig. 8-A).





Fig. 8. A - calcite coating fragments of tuff (scale bar is 2 cm); B - close up: individual calcite crystal on the surface of tuff fragment (arrow in A). Scale bar is 0.5 mm.

Sometimes it is must individual crystals (Fig. 8-B). Tuff on the contact with calcite and fluorite appears to be unaltered. Calcite contains globules of slightly brownish *fluorite* up to 1 mm in diameter, as well as numerous angular solid inclusions (they have not been identified).

Fluid inclusions. Calcite contain all-liquid inclusions. Two-phase gas-liquid inclusions suitable for thermometry have not been found.

Station: 35-64.6

Bedrock: Middle Nonlithophysal crystal-poor Topopah Spring Tuff (Tptprnn unit).

Depth from land surface: ~260 m.

Field description. Local opening in a vertical fracture (otherwise closed) 5-10 cm wide. Calcite encrusts one wall of the opening but do not occur in the fracture.

Textures. Water-clear calcite forms crystals 1-



Fig. 9. All-gas inclusions. A – scale bar 100 μ : B – scale bar 25 μ .

4 mm m such the shape of crystals is distorted: their action prependicularly to the bedrock is significantly less than in other directions. Calcite is crystallated on the agglomerations of the sand-stated particles and entrap these agglomerations. Outer layers of calcite are typically translucent and this mustard-colored material is readily visible through them. In some instances sandy material forms elongated layers 0.1-0.3 mm thick. Calcite sometimes grows in both directions from these layers.

Fluid inclusions. Calcite contains all-gas (Fig. 9), all-liquid, and gas-liquid inclusions.

All-gas inclusions occur randomly and typically are restricted to the portions of calcite, closes to the substratum. On one occasion, however, I observed gas inclusions clearly restricted to calcite growth zones (Fig. 10). This indicates the primary character of these inclusions.



Fig. 10. All-gas inclusions aligned along the growth zones (two of them are not in focus). Such alignment indicate the primary character of inclusions. Scale bar is 100 u.



Fig. 11. Group of fluid inclusions. Scale bar is 20 μ .

The two-phase gas-liquid inclusions are rare. They restricted to zones of calcite closest to the tuffaceous substratum. Blocky sparry calcite of outer parts of the crust is devoid of the twophase inclusions and contains only all-liquid inclusions. Two-phase inclusions form groups along the low-angle planes (Fig. 11) or along steep-angle curvilinear surfaces (probably, healed fractures). The result of thermometric studies is given in Fig. 12. As it is apparent from the figure, homogenization temperatures



Fig. 12. Sample 2217. Black and gray – inclusions along low-angle plane (see Fig. 11); white – inclusions along steep-angle bent zone (healed fracture). Measurements show significant scatter, indicating possible "disturbed" character of fluid inclusions in this sample. The highest temperatures (>50 °C) should probably be neglected.

exhibit significant scatter, which indicates possible "disturbed" character of inclusions in this sample (stretching or leakage). The highest temperatures (>50 °C) should probably be neglected.

Freezing experiments.

Freezing experiments were carried out on four inclusions from two groups. Two inclusions from the group shown in Fig. 11 yielded final melting temperature, T_{fm} of -0.9 and -0.95 °C, which corresponds to the salinity of 1.57 and 1.65 wt. %, NaCl-equiv.). Two inclusions from another group yielded T_{fm} of -0.3 and -0.4 °C (0.53 and 0.71 wt. %, NaCl-equiv.).

I attempted to perform freezing experiment on one all-gas inclusion (shown in Fig. 13). Some tiny light-colored phases appeared upon rapid cooling to a temperature of \sim -100 °C. On heating, these phases re-grouped to form one rounded phase. This phase disappeared in the same inclusion at temperatures from -30 to -10 °C. The behavior of this phase did not show any dependence on the temperature regime: it disappeared when the temperature in the stage was increasing and when it was decreasing.

Similar results were obtained from one all-gas inclusion from sample 2220.



Fig. 13. Sample 2217. All-gas inclusion (see Fig. 9-A) containing unidentified phase (arrow) at -35 °C.

Station: 45-26

Bedrock: Middle Nonlythophisal crystal poor Topopah Spring Tuff (Tptpmn unit)

Depth from land surface: ~ 230 m.

Field description. Lithophisa ~60 cm wide and 40 cm high. No other cavities around. The bottom of the cavity is lined with calcite. The walls of the cavity are covered by a ~1 mm thick layer of white α -quartz and tridimite crystals (identified by XRD).

Minerals and textures. Tuff on the contact appears to be altered to a depth of 3-8 mm. Three individual crystals of garnet (~3 mm in size; identified by XRD) were found in this altered zone and in calcite. Calcite often appears to be crystallized as porous mass, composed of isometric crystals ~ 1mm in size. In other places calcite is massive. Fragments of tuff (3 to 10 mm in size) incorporated in the calcite look altered, almost decomposed.

Fluid inclusions. Calcite contains all-liquid inclusions, as well as all-gas inclusions (Fig. 14). Two-phase gas liquid inclusions suitable for thermometric studies have not been found.



Fig. 14. All-gas inclusion in the middle of an individual grain of calcite. Scale bar is 50μ .

Station: 38+37.0

Bedrock: Middle Nonlithophysal crystal-poor Topopah Spring Tuff (Tptpmn unit).

Depth from land surface: ~260 m.

Field description. Cavity in the bedrock tuff, 60 cm wide and 35 cm high. Thick, up to 2 cm crust of calcite coats cavity floor, as well as the lower part of hanging walls. There are individual euhedral crystals of calcite up to 1.0-1.5 cm large. No apparent feeder-fissure.

Minerals and textures. A 1 mm-thick layer of white quartz (alteration?) occurs on the contact with the bedrock tuff. After that a 1.5 cm layer of milky-white calcite is deposited. It reveals traces of competitive growth, induction surfaces. In places, this zone is strongly corroded; a new-formed water-clear and well shaped crystals of calcite < 1mm in size are present in the corrosion cavities. This calcite also occur as thin, ~ 1 mm, veinlets in bedrock tuff. The described "Calcite-1" is cut by nearly horizontal and rough surface of dissolution, on which "Calcite-2" is deposited. It is also milky-white, but somewhat more translucent than the "Calcite-1". Both calcites form flattened crystals of free growth; crystals of the "Calcite-1" are "blade-shaped", whereas



Fig. 15. Primary inclusions of opal in calcite near the crystal surface (top of the picture). Scale bar is 100 μ .

crystals of the "Calcite-2" are blocky. The orientation of crystals is also different.

Opal is often present as primary solid inclusions. Inclusions have half-spherical shape with flat side aligned along the growth zones. Such inclusions often occur at the latest stages of calcite growth, close to the surface of blocky sparry crystals (Fig. 15).

Fluid inclusions. All-gas inclusions are abundant in this sample. In contrast with most other samples studied from the ESF, where allgas inclusions mostly restricted to the earliest generations of calcite, in this sample such inclusions occur throughout the calcite crust.



Fig. 16. Two-phase inclusions from a group along growth zone. Homogenization temperatures are 37 (A) and 38 °C (B). Scale bars correspond to 10 μ in both images.



Homogenization temperature, °C

Fig. 17. Sample 2220. Black – group of inclusions along growth zone; dark gray – inclusions along low-angle plane; light-gray – inclusions forming a 3-D group; white –individual inclusions.

All-liquid inclusions are also abundant. Gasliquid inclusions suitable for thermometry are rare. They occur along growth zones (Fig. 16), low-angle planes and form 3-D groups.

The results of thermometric studies are shown in Fig. 17. Inclusions in individual groups homogenize within narrow temperature intervals (3 to 8 °C). This indicate that obtained temperatures reflect true minimal temperatures of paleo fluids.

Freezing experiments performed on several inclusions with $T_h = 36-40$ °C yielded no numeric results. Two inclusions from a growth zone showed $T_{fm} = +0.3$ and +0.4 °C, which indicates metastability. Ice in two more inclusions from another group melted at exactly 0 °C (ice crystals grew and diminished very fast as the temperature in the stage oscillated between -0.1 to +0.1 °C). The data suggest that aqueous fluid in inclusions is very diluted (essentially, it is fresh water).

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Topopah Middle Nonlithophysal anystal-poor Topopah Middle Nonlithophysal anystal-poor

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Field description. Vertical opening associated with calcite-cemented breccia-vein. Calcite





and the provident of the provident of a crust. Supple 15, "Stressed" and the the process of a crust. Super parts of the summer of the process of the crust supersuper contemporation of the provident of the super-



Fig. 19. SEM microphotograph of a mineral (possibly containing Fe. Min. and T¹ from miff alteration zone, overgrown by caloue. Soale bar is S¹ u.

encrusts both walls of the opening. Sometimes it forms near horizontal plates with crystals on both sides. These may be fragments of wall linings fallen on the cavity floor.

Textures. Calcite occurring as breecia cement is milky-white semi-translucent. It cements small angular fragments of tuff. The latter appears to be altered. Calcite forming crusts is water-clear translucent. It forms nearly isometric blocky crystals growing on tuff or isometric blocky crystals growing on tuff or clay substratum.

A white powdery layer occur on the contact between one crust and the bedrock turff. This layer consists of tridimite (supposedly, early vapor-phase alteration of turff). The layer also contain tabular crystals with metallic lustor (Fig. 19). Similar orystals with metallic lustor another sample (2226) appeared to be a amother sample (2226) appeared to be a mixture of oxides of Fe. Mn and Ti.

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Calcite contains solid inclusions of an unidentified translucent cubic mineral (possibly fluorite).

Fluid inclusions. All-gas inclusions have not been found in this sample. All-liquid inclusions are abundant. Gas-liquid inclusions are rare. They occur as groups along healed fractures. Inclusions in such groups are typically small (1-5 μ in size).

Results of thermometric studies are shown in Fig. 20. The scatter in the data is significant. It should be noted, that inclusions associated with healed fractures yield larger scatter (up to 13 °C within a group), than do isometric, possibly primary inclusions forming a 3 D group (8 °C). At this stage, the hightemperature part of the data (>40 °C) should probably be disregarded.

Freezing experiments were carried out on several large inclusions possessing large bubbles (stretched). They yielded T_{fm} of +0.2 to -0.3 °C. This indicates metastable ice melting and low-salinity fluids.

Station: 37-37.0 Alcove 6 - Northern Ghost Dance Fault Alcove.

Station within alcove: 0+55.1

Bedrock: Middle Nonlithophysal crystal-poor Topopah Spring Tuff (Tptpmn unit).

Depth from land surface: ~ 230 m.

Field description. Low-angle veinlet partly made up of crystalline calcite, partly cementing breccia fragments of tuff (Fig. 21). At both ends, when it enters shattered tuffs, it splits onto several incontinuous fragments.



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Textures. Calcite is milky-white, massive. It completely fills the fracture opening. In places this massive calcite contains cavities (dissolution?) with their inner surfaces composed of the euhedral heads of tabular calcite crystals. Near the contact (2-4 mm), calcite is small-crystalline, granular.

Fluid inclusions. In the vicinity of the tuff fragments, calcite contains numerous and large (visible under binocular microscope) all-gas inclusions. All-liquid inclusions are also abundant.



Fig. 22. Gas-liquid inclusions: A - group of fluid inclusions along a low-angle surface ($T_h = 36-37$ °C); B - individual inclusion ($T_h = 35$ °C). Scale bars correspond to 10 μ in both images.

Gas-liquid inclusions are rare. They occur in groups (also containing all-liquid inclusions; Fig. 22) aligned along low- to steep-angle planes.

Thermometic study. The results of thermometric study are shown in Fig. 23. All studied inclusions (35) homogenized within a very narrow interval of 5 °C. The result is quite consistent. Obtained temperatures may be considered true minimal temperatures of ancient fluids.



Homogenization température. "C



Freezing experiments. One large artificially stretched inclusion was subjected to freezing (Fig. 24). The ice in inclusion melted at +0.35





Fig. 24. Freezing experiment in untificially stretched inclusion: A = T = -20 C. inc. frozen: B = $T_{\rm c} = -0.35$ C.



Fig. 25. Freezing experiment on the all-gas inclusion: A – three phases at T < -30 to -50 °C: B – one condensed phase: C – homogeneous inclusion (at T >-30 to -5 °C). Scale bar is 20 to

⁶C indicating metastability and low salinity of trapped fluids.

in one all-gas inclusion, several segregations of a condense i phase appeared upon fast (50-"C min) cooling at T (<00-C (Fig. 25-A). They re-grouped in one b cation to form one light-colored condensed trase with rounded shape (Fig. 25-B). The shape of this phase did not change on cooling or heating. Upon heating, the phase disappeared at apparently random temperatures varying from -30 to -5°C. The phase does not luminesce under UV excitation. The behavior is similar to one observed in the sample 2217.

Station: 37-37 - Alecone rook Sorthern Ghost Dance Fault Alecone

Station within alcove: 0-405

Bedrock: Middle Nonlithophisal crystal-poor Topopal: Spring Tuff (Tpipmn unit).

Depth from land surface: ~220 m.

Field description. Calcite crust lining the wall of a steep-angle open fracture.

Minerals and textures. Calcite forms crystals on both sides of the crust. From one side. closest to the tuff contact, crystals have an appearance of a confined growth: their shape is clistorted. Textural relationships reveal presence of the two generations of calcite,



Fig. 26. Granular character of Calcite-1 (A) and sharp "phantom" crystals in Calcite-2 (B). Scale bars correspond to 0.5 mm in both immuges

which grow the up site directions from central "seam".

Calcite-1 probably gree within some porous medium. Crystals are <1 mm in size, semitranslucent. Calcite-1 often has a granular appearance (Fig. 26-A) and associates with delicate "nets" composed of filamentous silical as well as with micro druses of quartz and micro inclusions of fluorite. Calcite-2 does not contain silicate phases, but traps abundant allgas inclusions. Its crystals 2-5 mm in size are euhedral, blocky, translucent. They often reveal zoning indicating shape of crystals during the formation of the crust (Fig. 26-B).

Quartz forms micro-druses composed of perfectly shaped water-clear crystals up to 2 mm in size.

Fluorite occurs as cubic violet micro crystals (0.1-0.2 mm in size), aggregates of several crystals (Fig. 28), as well as slightly brownish spherules inside calcite and quartz. The relationships with host minerals indicate its syngenetic character.

Fluid inclusions. Calcite-2 contain abundant all-gas inclusions (Fig.__). All-liquid inclusions are present in both generations of calcite. Two-phase gas-liquid inclusions occur along curvilinear low-angle planes (healed



Fig. 27. Fluorite in calcite. Scale bar is 30 µ



Fig. 28. All-gas inclusion in calcite and quartz crystals. Scale bar is 20 μ

fractures; inclusions are small, 4-10 μ); large inclusions with slightly flattened shape were found in low-angle planes.

Thermometric study. Results of the thermometric study are shown in Fig. 29. The data display substantial scatter. Larger scatter is characteristic for inclusions associated with healed fractures. Thermometric data on large inclusions associated with low-angle planes (possible growth zones) are somewhat more consistent.





Station: 29+76

Bedrock: Middle Nonlythophisal crystal poor Topopah Spring Tuff (Tptpmn unit)

Depth from land surface: ~ 290 m.

Field description. Lithophisa 60 cm wide and 30 cm high. Calcite coats the floor of the cavity forming crust up to 1.5 cm thick. Bedrock of the inner surface of the lithophisa is covered by a ~1 mm thick layer of quartz crystals (vapor-phase alteration?).

Minerals and textures. Calcite is milky-white, semi-translucent. Tabular crystals, in places cut by corrosion and covered by layers of opal. This sequence again is cut by corrosion, after which another "portion" of calcite and opal was deposited.

Opal also occurs as primary inclusions, group of which follow the growth zones. The surface of calcite crystals is often covered by small, several micron in size "droplets" of ideally translucent opal.

Fluid inclusions. Calcite contain abundant allliquid inclusions. Two-phase gas-liquid inclusions suitable for thermometry have not been found.

Station: 0-25.5 - Alcove 5.

Field description. Low-angle veinlet. There is a gradual transition from a hair-wide fissure with alteration zone of ~ 1 cm on both sides (bleached tuff), to calcite-cemented micro breccia (cement is not abundant), to large calcite crystals on the floor of the fissure's widening, to massive crystalline calcite filling (partly or entirely) a 1.0-1.5 mm wide fissure.

Minerals and textures. There is a ~ 1 mm-thick iayer of α -quartz (identified by XRD) on the contact between tuff and calcite. Similar rims are typical of samples from lithophisae, where



Fig. 30. Fe-Mn-Ti mineral. A – embedded in calcite: B – overgrown by layers of opal and calcite. Scale bars correspond to 1 mm in both images





Fig. 31. Solid inclusions of opal in calcite + one twophase aqueous inclusion ($T_h = 37$ °C). Scale bar corresponds to 25µ in both images.

they are often composed of tridimite. Also, stringers and tabular crystals of a mineral containing Fe, Mn, and Ti[•]. It occurs in altered tuff, as well as in calcite-opal crust where it sometimes serve as a "seed" for crystallization of opal and calcite (Fig. 30).

Thin, ~ 0.5 mm fractures in tuff are often filled with calcite.

Botrioidal opal forms a layer within calcite crust. It also occurs as water-clear blobs and thin films on the surface and at the tips of calcite crystals. Besides, opal is present as solid inclusions in calcite (Fig. 31). The shape

Analysis on microprobe Contective (ded concentrations) TiO₂ (2.16), MgO (0.38 - Mr(2.6622), FeO (31.12)



Fig. 32. All-gas inclusion in calcite crust (A, scale bar is 25μ) and in calcite veinlet in tuff (B, scale bar is 100μ).

of these inclusions and their association with growth zones indicates that deposition of these two minerals occurred simultaneously.

Fluid inclusions. All-gas inclusions often occur near the contact between calcite and tuff, culoite and opal, as well as in thin, ~0.5 mm wide, veinlets the penetrating bedrock tuff (Fig. 32).

Gas-liquid inclusions are rare. They occur as groups along growth zones (Fig. 33) and low-angle planes.



near the contact with opal (upper right corner). T_a = 39-40 °C. Scale bar is 20 μ

Thermometric study. The results of thermometric study are given in Fig. 34. All inclusions (42 from 3 groups) homogenized within a narrow interval of 7 °C.

The result is quite consistent; measured temperatures may be considered true minimal temperatures of paleo fluids.



Homogenization temperature. °C

Fig. 34. Sample 2226. Black – inclusions along growth zone: Gray – inclusions in low-angle zones.

Summary

Brief summary on the fluid inclusion distribution in studied samples is given in table below. Table also shows the presence or absence of fluorite.

Sample	Inclusions		Fluorite
	All-gas	Gas- liquid(*)	
2206	+	+	+
2215	-	-	+
2217	÷	+	-
2218	+	-	-
2220	+	+	-
2221	-	+	-
2222	+	+	. –
2224	+	+	+
2225	-	-	-
2226	+	+	-

Notes: (*) - only inclusions suitable for thermometry; all samples contain all-liquid inclusions

In terms of the measured homogenization temperatures the following observation may be important. Two samples that yielded temperatures higher than other samples (SS#85-86 and 2206) are both from Tiva Canyon tuff. Also, both these samples are from the eastern part of the exploratory block, closest to the Paintbrush Fault zone which might have served as major avenue for upwelling fluids. Although it is premature to make strong conclusions on the basis of only two samples, this possible trend needs to be studied in the future.





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5. Age of calcite from the ESF

The age of the hydrothermal activity at Yucca Mountain is of critical importance from the standpoint of the suitability of the site as a potential host of a high-level nuclear waste disposal facility. With this in mind we made an attempt to measure absolute ages of calcites, for which hydrothermal origin was proven through fluid inclusion studies.

Four samples from the first sample set (1995) were subjected to TIMS U-series dating at McMaster University, Hamilton, Ontario, Canada (laboratory of Prof. D.Ford). Three analyses (SS#30-31, SS#39-40, and SS#58-59) have failed because of high content of detrital thorium in the samples. One sample, SS#45-46, yielded the following results:

- Concentration of U = 0.1396 ppm;
- Activity ratio ²³⁴U/²³⁸U = 1.4734;
- Calculated initial value ${}^{234}U/{}^{238}U = 1.7648;$
- 230 Th 234 U = 0.8416;
- ²³⁰Th/²³²Th = 14 (sample is contaminated with detrital thorium);
- Age (uncorrected for detrital thorium) = 169,185 (+13,094/-11,820) years; and
- Age (corrected for detrital thorium) = 160,244 (+13,231/-11,944) years (two standard deviation errors).

This age, 160 ka, represents first direct datum on the age of hydrothermal activity at Yucca Mountain.

There is, also, indirect information suggestive of a youthful age for this activity. Szabo and Kyser (1985, 1990), Whelan and Stuckless (1992) and Whelan et al. (1994) reported Useries ages of 310, 280, 227, 190, 185, 170, 142, 30, and 26 thousand years and ¹⁴C ages of 45, 44, 43, 42, 40, 39, and 21 thousand years for calcite samples recovered from drill cores from the upper 400 m of the Yucca Mountain vadose zone. Paces et al. (1998) determined ages of 28 thousand years and older for calcite samples removed from the ESF.

Although the hydrothermal origin for these calcites is not presently proven, taking into account the high "percentage" of calcites in the ESF containing fluid inclusions yielding elevated homogenization temperatures (6 out of 12 studied samples in set-1995 and 7 out of 10 studied samples in set-1998), the probability that at least some of these dated calcites are hydrothermal is quite high.

Naturally, more data need to be obtained on hydrothermal calcites from the Yucca Mountain subsurface in order to constrain the timing of fossil hydrothermal activity. Geologically youthful character of this system, however, is fairly certain.

6. Discussion

6.1. Methodology: the study of epigenetic calcite for paleo hydrologic reconstruction

Long-term stability of the regional hvdrogeologic system is of significant concern for all sites intended for geological isolation of nuclear or other hazardous wastes. Fracturefilling calcites in crystalline and other rocks may represent "footprints" of paleo hydrologic systems. Integrated studies of stable and radiogenic isotopes and fluid inclusions in calcite veinlets, accompanied by U-series and/or U/Pb dating are used in a number of national programs to constrain the past thermal and fluid history of the prospective waste disposal sites. Pertinent examples are: Chalk River Site in Canada (Bukata et al., 1998), Olkiluoto Site in Finland (Blith et al., 1998), and Äspö Hard Rock Laboratory in Sweden (Wallin and Peterman, 1995).

At Yucca Mountain, the "descending meteoric water" interpretation was based on extensive isotopic studies; one crucial method, fluid inclusion studies, was either not applied, or its results were inadequate (e.g., Roedder et al., 1994).

6.2. Hydrothermal origin of mineral crusts in the Yucca Mountain subsurface

The origin of the epigenetic calcites found at Yucca Mountain is a subject of debate. The officially accepted hypothesis is that they formed as a result of pedogenic processes with rain waters percolating along interconnected fractures in the vadose zone and carrying dissolved carbonate from overlying soils (e.g., NAS/NRC, 1992; Roedder et al., 1994; Stuckless et al., 1998). A competing hypothesis suggested a hydrothermal origin for these calcites (Szymanki, 1989; Hill et al., 1995; Dublyansky at al., 1998).

The results of our studies show that hydrothermal origin of 13 calcite samples removed from the ESF is beyond reasonable doubt. Below, we summarize results that imply a non-pedogenic hydrothermal origin for the calcite crusts that we studied from the ESF.

Mineralogy and textures

The presence of crystalline quartz and, particularly, fluorite within calcite crusts is not compatible with the postulated rain water origin of these mineral-forming fluids. Quartz and fluorite were reported by the USGS researchers (Paces et al., 1996):

Nearly all low-temperature secondary mineral occurrences consist of calcite and various silica phases including quartz, chalcedony and opal. (p. 8)

and

Other phases are present (fluorite, clay minerals, zeolites, Mn-oxides, organic phases) but are volumetrically inconsequential. (p. 9)

No explanation have been offered for their presence.

The large-crystalline character of the calcite, predominance of euhedral sparry crystals is not compatible with a meteoric water film mode of deposition. The "per-descensum" (meteoric) concept essentially ascribes the calcites at Yucca Mountain to a speleothemic, or flowstone, origin. Flowstones (i.e., layered formations deposited from gravitational water films), are well studied (e.g., Hill and Forti, 1997). Due to their deposition from thin films of water, they are always built up of tiny palisade calcite crystals and do not form large euhedral crystals (Kendali and Broughton, 1978):

... distinctive fabrics of of pulisude calcite are formed because precipitation usually occurs from thin water films that flow over the growing speleothem surfaces. Large crystal terminations do not form on the speleothem surface because they form projections that disturb the water flow away from the projections which, as a consequence, are gradually eliminated. (p. 519)

The size of the free-growth crystal tips forming on the outside layer of flowstone is controlled by the thickness of water film from which the flowstone grows (typically, << 1 mm). By contrast, at Yucca Mountain calcite often forms perfectly shaped free-growth crystals up to 6-8 mm in size. Such textures are not compatible with the postulated film-water origin for the Yucca calcite crusts; instead, they clearly indicate a phreatic (saturated) environment during their formation.

Another generic feature of the flowstones is fine rhythmic lamination. This lamination appears due to the fact that the waters depositing calcite seep through and acquire CO_2 from the soil. Biological activity of the latter varies with the seasons of the year, as well as in concert with the longer-period climatic changes. Percolating soil waters carry varying amounts of humic substances (humic and fulvic acids) and lavers of calcite deposited from these waters acquire different coloration as a consequence. Even in apparently colorless specimens typical of speleothems from cold climatic settings this banding is readily revealed through luminescence under the UV or other excitation. This feature makes flowstone an excellent source of information on past environments (Shopov, 1997). In contrast, the calcites from

the ESF do not reveal rhythmic lamination, either on a visual basis or under UV luminescence. One calcite sample studied by means of Raman spectrometry did not show luminescence under Ar-laser excitation, either. When excited with photographic flash, the Yucca Mountain samples typically yield the uniform 1-8 s-long bluish-white luminescence that is characteristic of the low-temperature hydrothermal calcite from elsewhere (Dublyansky, 1997).

Elevated formation temperatures

The geological history of Yucca Mountain precludes any thermal event such as burial cr intrusions of magmatic bodies that could have led to thermal re-equilibration of the inclusions studied in the calcites. Therefore, the measured temperatures, 35-75 °C, may be considered to reflect the minimum possible formation temperatures for these calcite samples. Such elevated temperatures are not compatible with the postulated vadose zone setting.

Presence of gases at less-than-atmospheric pressure

Presence of inclusions filled with gases with pressures less than atmospheric is not compatible with a vadose zone setting. If these inclusions were trapped "air-water wapor- CO_2 " phase, representative of the unsaturated zone atmosphere, as was suggested earlier (Roedder et al., 1994), these gases in inclusions should have retained pressures of about 1 atmosphere.

Presence of gaseous aromatic hydrocarbons

Aromatic hydrocarbons cannot be attributed to soil- and other unsaturated-zone environment. The presence of aromatic and probably other heavy hydrocarbons in all-gas inclusions further reinforces this conclusion and suggests the relation of studied calcite with the petroleum (essentially, gas) potential of the Paleozoic sedimentary rocks underlying Yucca Mountain. Existence of such potential was suggested by Mattson et al. (1992) on the basis of the Conodont Alteration Index analysis.

Stable isotopic properties

Stable isotopic studies of speleothems represent an established method of paleo climatic reconstruction. Changes in delta ¹⁸O values from one growth layer to another provide a proxy of the paleo temperature record, whereas the changes of the delta ¹³C may be used to constrain the evolution of vegetation on the land surface (Ford, 1997). Stable isotopic data provide another insight into the origin of the Yucca Mountain calcites.

Typically, vadose-zone speleothems formed from water films (e.g., stalactites) display stronger response to the climate change as compared to preatic, subaqueous speleothems. Variations of delta ¹⁸O are greater in a meteoric water flowstone (e.g., 8 ‰ for Jewel



Fig. 35. Stable isotopic properties of hydrothermal calcite from the ESF across crusts. On each graph upper line represents $\delta^{13}C$ and lower line $-\delta^{13}O$.

Cave. South Dakota) and smaller in a subaqueous speleothem (2.5 ‰ for Devil's Hole, Nevada; Ford. 1997). At Yucca Mountain, calcites display variations of delta ¹⁸O much smaller than would be expected for vadose speleothems deposited over long intervals during the late Tertiary and Quaternary. In some samples they are less than 0.5 ‰ (Fig. 35). Such "dead-flat" behavior of oxygen is not compatible with the vadose-zone speleothemic (or film water) origin. At the same time, such behavior is quite typical of the low-temperature hydrothermal calcite from elsewhere (Dublyansky and Ford, 1997).

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Isotopic parameters of parent fluids

Calcite studied from the ESF has isotopic values: δ^{18} O from -10.6 to -12.14 and δ^{13} C from -2.6 to -6.0 ‰ PDB. It was deposited from waters with the temperature of up to 50 °C. By applying well-established temperaturedependent fractionation coefficients (Friedman and O'Neil, 1997; Faure, 1986) it may be calculated that the parent waters that deposited calcite crusts had δ^{18} O of -4.9 to -5.7 ‰ SMOW and δ^{13} C varying from +0.2 to -3.2 ‰ PDB (calculated for 50 °C). These values deviate significantly from the modern values of waters in the Yucca Mountain Tertiary aquifer (δ^{18} O -14.0 to -12.8 ‰ SMOW and δ^{13} C -12.7 to -4.9 ‰ PDB; NAS/NRC, 1992, p. 157).

Paces et al. (1998) established variations in the ⁸⁷Sr/⁸⁶Sr values across calcite crusts from ESF from about 0.7125 to 0.710. These values match those of the semi-confined Paleozoic carbonate aquifer (0.71175; Peterman et al., 1994) that underlies the modern aquifer beneath Yucca Mountain. Salinity of waters in the Paleozoic aquifer (150 mg/l of NaCl; Peterman et al., 1994) is also consistent with relatively low salinities measured in fluid inclusions.

6.3. Relation of epigenetic minerals to the oil and gas potential of Paleozoic rocks

Gas inclusion composition with aromatic hydrocarbons is not compatible with the aerated vadose (unsaturated zone) setting. Perhaps the only reasonable source of such hydrocarbons is organic material in the Paleozoic carbonates, which underlay the Tertiary volcanic rocks of Yucca Mountain. These Paleozoic carbonates are known to have some natural gas potential (Mattson et al., 1992). Also, the SE-NW trending block of rocks within Calico Hills and Shoshone Mountains located approximately 5 km east of the repository block is designated as having "thermal potential for oil and gas" on the map entitled "Yucca Mountain area showing tectonic features and conodont alteration index distribution" (YMP-97-137.2) (Appendix 3).

6.4. Implications of the data obtained from fluid inclusions for the Yucca Mountain Total System Performance Assessment

The possibility that saturated thermal environment may occur at certain stage of the planed repository life needs to be fully appreciated. This should lead to a reconsideration of many key-elements of the Total System Performance Assessment for the Planed Yucca Mountain repository. As far as I am concerned, the scenario of repository flooding by hot waters is not considered in any of the recent versions of the TSPA.

One example emphasizing the importance of such re-assessment is the issue of the waste package degradation. It was explicitly stated in the Third Interim Report of the Peer Review Panel on the TSPA (posted on the homepage of the Yucca Mountain Site Characterization Project at

http://www.ymp.gov/nonjava index.htm) that:

No rational materials selection can be made without knowledge of the characteristics of the waters in contact with the waste packages. These characteristics include: temperature, pH, Eh and ionic concentrations (Cl, SO₄, NO₃, CO₃, Fe^{++-} , Ca, etc.).

Clearly, decisions made on the typical meteoric water compositions measured from the Yucca Mountain subsurface will be inadequate in case of the intrusion of the deepseated thermal fluids into the repository zone.

Also emphasized in the Report is the fact that the most corrosion-resistant and recently chosen as a base-case option, alloy C-22

...is susceptible to localized corrosion only when wet in a critical temperature range. If C-22 remains passive in this range, its anticipated life, prior to penetration, is thousands of years. If it is not passive, then its life, prior to penetration, is as little as a few tens of years.

Therefore:

There is a need to determine the critical temperature range, and the times in this range when different scenarios can occur.

Such vital determination cannot be made without scientifically sound and sufficiently detailed understanding of the hydrothermal history of Yucca Mountain.

Fluid inclusion studies may provide necessary information with regard to the expected compositions and temperatures of waters in contact with the waste packages. Coupled fluid inclusion, isotopic and absolute-age studies are required for determining the pattern and timing of the past excursions of thermal waters into the repository zone. Although the presence of hydrothermal fluids within the modern unsaturated zone at Yucca Mountain in the geologically recent past is beyond reasonable doubt, this fact only indicates the possibility of the hazard for the potential high-level nuclear waste site. Much more data need to be acquired and analyzed in order to assess the degree of this hazard. Specifically, three questions need to be addressed:

1. What is the age and what was the recurrence period of the hydrothermal activity?

2. What was the volume of fluids involved at different stages of this activity? and

3. What was the spatial structure of ancient hydrothermal system?

This may be accomplished through concerted effort of researchers, involving:

a). Detailed fluid inclusion studies in calcite and other mineral phases from the ESF as well as from drill cores. Such study may provide important information on the spatial structure of the ancient hydrothremal system;

b). Careful dating of calcite samples hosting fluid inclusions with elevated homogenization temperatures. Such study would constrain the temporal structure of ancient hydrothermal system; and

c). Detailed isotopic study of mineral phases (C, O, Sr, He) may provide important information on the pattern of fluid migration, origin of fluids, etc.

Appendix 1: Fluid Inclusions in calcite Samples from the ESF, Nevada Test Site, Nevada

Report assembled for the Office of the Attorney General of the State of Nevada

Fluid Inclusions in Calcite Samples from the ESF, Nevada Test Site, Nevada

Study performed by Yuri Dublyansky on June 15-19, 1998 at Virginia Tech, Blacksburg, Virginia

Report assembled by Yuri Dublyansky for the Office of the Attorney General of the State of Nevada

> July 1998 Washington, DC

9-803020070

Report to the Attorney General, State of Nevada ...

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