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This is a SPECIAL PROCEDURE GCP-14. R1

NWM-USGS-GCP-14. R1
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Extraction and Recovery of H₂O From Calcite-Hosted Inclusion Fluids

1.0 PURPOSE.

- 1.1 To assure the accuracy, validity, and applicability of the methods used to extract inclusion fluids from calcite and determine the oxygen isotopic composition of these fluids, this procedure provides a guide for USGS personnel and contractors to perform the described activity. From this procedure, the Department of Energy (DOE) and the Nuclear Regulatory Commission (NRC) can evaluate these activities for meeting requirements of the NNWSI Project, and competent, trained personnel can reproduce the work.
- 1.2 This procedure describes the components of the work, the principles of the methods used, and their limits. It also describes the detailed methods to be used for calibration, operation and performance verification of any equipment. In addition, it defines the requirements for data acceptance, documentation, and control; and it provides a means of data traceability.

2.0 SCOPE OF COMPLIANCE.

- 2.1 This procedure applies to all USGS personnel and their contractors who may perform work referred to in Para. 1.1, or use data obtained from this procedure if it is deemed to potentially affect public health and safety as related to a nuclear waste repository.
- 2.2 All data derived from this procedure that are presented to support licensing of the NNWSI Project repository, and any equipment calibrations or recalibrations that may be required shall be in accordance with this technical procedure. Variations are allowed only if and when this procedure is formally revised, or otherwise modified, as described in Section 8.

- 3.0 PERSONNEL RESPONSIBILITIES. The Principal Investigator (PI) is responsible for assuring full compliance with this procedure. Per QMP-2.02 and QMP-2.03, the PI shall require that all personnel assigned to work under this procedure shall have the necessary technical training, experience, and personal skills, to adequately perform this procedure; and they shall have a working knowledge of the USGS QA Manual. Responsibilities of others including the reviewer(s), contributing investigators, Branch/NHP Chief, QA Office and the Chief, Branch of NNWSI are as described in Para. 4.3, QMP-5.01.

- 4.0 DETAILED PROCEDURE. Minerals deposited from water-based fluids frequently will trap small quantities of the depositing fluid. These fluid inclusions can be studied in situ or removed and subjected to various analytical techniques. The utility of studies of inclusion fluids for determining the temperature of mineral formation, the chemical properties

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of the depositing fluid, and the source of the depositing fluid are exhaustively discussed by Roedder (1984). The procedures for extracting inclusion fluids from minerals by crushing in a vacuum were developed by Hall and Friedman (1963) and Rye and O'Neil (1984). Crushing releases much of the fluid trapped in inclusions allowing the water to be collected and converted to H₂ for determination of the H/D ratio.

4.1 Objective: Recent calcite vein material found in rocks of the southern Great Basin contains fluid inclusions which are suitable for extraction and isotopic analysis (Winograd et al., 1985). The calcite vein material exposed in Trench 14 at the NTS will be sampled in detail and inclusion fluids extracted for the determination of their δD values. Sampling will follow procedures outlined in NWM-USGS-TP-GP-27, RO "Trench Wall and Natural Outcrop Sampling for Coordinated Studies". The δD value of a groundwater or hydrothermal fluid is closely tied to the source of the water, and in conjunction with the oxygen isotope data collected from the calcite itself, should provide evidence of the fluid's origin.

4.2 Methods Used:

4.2.1 Sample Preparation - Vein paragenesis must be determined prior to sampling of the vein material for inclusion fluid studies. Discrete stages of the vein filling will be separated, either manually or by cutting with a diamond saw. Enough sample will be loaded to provide 2 to 5 microliters of extractable water. The quantity of mineral required is determined experimentally, but generally between 5 and 30 grams of material is sufficient. Foreign matter is physically removed from the mineral fragments and the fragments rinsed in distilled water.

4.2.2 Inclusion Fluid Extraction - Extraction of inclusion fluids from coarsely crystalline minerals will be done by crushing the material in a vacuum in a stainless steel crush tube. As described in Rye and O'Neil (1968), the crush tube consists of 7/8 inch OD stainless steel tubing that has been crimped and welded shut on one end. A valve is attached to the open end with a compression fitting utilizing a teflon ferrule.

4.2.2.1 The sample material is loaded into the crush tube and the valve attached.

4.2.2.2 The crush tube is attached to a vacuum manifold and the sample material outgassed at 80 to 120°C overnight to remove adsorbed water.

4.2.2.3 During outgassing, the crush tube valve is periodically checked for leaks.

4.2.2.4 The crush tube valve is closed and the outgassed sample is removed from the manifold. The end of the crush tube is placed in a five-ton hydraulic press and the mineral matter crushed. This crushing reduces the average grain size of the mineral fragments to less than -1 millimeter.

4.2.2.5. The crush tube is reattached to the vacuum manifold and the released volatiles are removed from the vessel. Volatiles condensible in liquid N₂ are frozen out (generally only water and sometimes CO₂ occur in significant quantities); non-condensable volatiles are pumped away. During extraction of the condensibles the crush tube and the mineral fragments are warmed to temperatures on 120 ± 15°C to hasten the desorption of water from the mineral fragments and the walls of the crush tube. Condensibles are collected for a minimum of 30 minutes.

4.2.2.6. After the non-condensibles are pumped off, the liquid N₂ trap is warmed to the temperature of solid CO₂. At this temperature any CO₂ trapped with the water sublimates and is pumped off.

4.2.2.7 The water is then transferred to a sample tube for storage until it can be converted to H₂ or transferred directly to the water reduction manifold and converted to H₂ immediately (see technical procedure NWM-USGS-GCP-17, R0 "Determination of the Isotopic Ratio H/D in H₂O). The yield of H₂O is determined by calculation after conversion to H₂ for mass spectrometric analysis to within ± 0.1 microliter.

4.3 Alternative Method(s) Considered: Fluids may also be extracted from minerals by heating fragments of the mineral until the internal pressure causes the inclusions to burst; i.e. decrepitation. It is particularly useful when samples are small or contain limited quantities of fluid extractable by the crushing procedure, either because of small numbers of inclusions or because of the generally small size of the inclusions. If water yields are low, this technique will be used in lieu of or in conjunction with the crushing technique. Outgassing and collection of condensible procedures are the same for either technique.

4.4 Materials/Equipment Required: The following materials are required for this procedure:

- o 300 to 1000 milliliter liquid nitrogen dewars
- o Glassblown manifold with Kontes greaseless or Eck & Krebs cocks
- o 5 and 10 amp variable voltage transformers
- o 0 to 100 micron Hastings vacuum gauges and meters
- o High-vacuum sample tubes with Kontes greaseless or Eck & Krebs cocks
- o Mercury diffusion pumps
- o DuoSeal mechanical pumps
- o Apiezon vacuum greases
- o Silicon vacuum grease
- o Nupro hi-vacuum stainless steel valves
- o 7/8" OD 304 stainless steel tubing with .040" walls
- o Heating tapes
- o Watlow sleeve heaters
- o Dry ice
- o Butyl cellulolve

- 4.5 Assumptions Affecting the Procedure: Extraction of fluids from minerals assumes that the fluids exist in sufficient quantities to overcome isotopic fractionation effects that result when very small quantities of water are released into a vacuum manifold. For our purposes, precise data require 2 or more microliters of H₂O. Some water will always adsorb onto the walls of the apparatus and be extremely difficult to recover. If this adsorbed water is a significant proportion of the total, isotopic fractionation of the sample may occur.
- 4.6 Data Information: The completed data sheets will report, for each sample, the following pertinent information: sample identity, date of extraction, weight of sample material loaded, time of outgassing, temperature of outgassing, time of condensible collection, micromoles of CO₂ recovered if measurable, final pressure of non-condensibles produced by the sample (measured on log scale, so precision of determination varies with pressure), and any other noteworthy observations.
- 4.6.1 Quantitative/Qualitative Criteria - Total quantity of water recovered is determined during the conversion of the water to H₂ for mass spectrometer analysis (see technical procedure NWM-USGS-GCP-17, RO "Determination of the Isotopic Ratio H/D in H₂O").
- 4.7 Limitations: See Para. 4.5.
- 4.8 Other: Water extracted by this procedure is converted to H₂ for the determination of its H/D ratio by technical procedure NWM-USGS-GCP-17, RO "Determination of the Isotopic Ratio H/D in H₂O".
- 5.0 CALIBRATION REQUIREMENTS. Calibration is not required as a part of this technical procedure. When calibrations are required, all instruments and methods when applicable, will be calibrated in compliance with the Instrument Calibration Procedure (NNWSI-USGS-QMP-12.01) prior to obtaining data that will be cited to support licensing the NNWSI Project.
- 6.0 IDENTIFICATION AND CONTROL OF SAMPLES. Samples will be collected as part of this procedure.
- 6.1 Sample Identification: As part of the data records and documentation, and in compliance with QMP-8.01, all samples will be identified as follows: Unique numbers will be assigned to samples in the field and recorded in a notebook at the time of collection. Depending on the nature of the sample, numbers may be marked directly on the specimen or on a cloth or plastic sample bag or other suitable container holding the specimen. Orientation of the sample prior to sampling, if from outcrop, will be indicated with arrows. The number and arrows will be marked with a permanent ink surface marker.
- 6.2 Control and Storage: In compliance with QMP-8.01, the collected and identified samples shall reside in the custody of Joe Whelan who shall store them in either Room B1115 or 1117 in Building 21 or in a secured cabinet in Building 21, Denver Federal Center, Denver, Colorado.

6.3 Special Treatment: None.

7.0 QUALITY ASSURANCE RECORDS. All information collected and recorded under this procedure that is to be used in support of the NNWSI Project licensing process is required to be a part of the official USGS record. Input needed to process the information as a record includes: title or description, subject, originator, date of the document, and whether it is an original, a revision or an addendum.

Specific items from this procedure that will constitute a record are photographs or drawings indicating the portion of the sample of the vein that was sampled; weight of material crushed; and micromoles of H₂O (and CO₂, if measurable) recovered.

7.1 Notebooks or other organized documentation will be prepared as appropriate by the PI or a contributing investigator to record data from this procedure and shall include any information considered by the originator to be pertinent. When data are kept in loose-leaf form, each page will be numbered consecutively and chronologically. All documents will be signed or initialed and dated by the investigator on a daily basis when entries are made. Any revisions will be lined out, initialed, and dated.

7.2 All data collected and the applicability of methods used in this procedure will be reviewed and cosigned by a peer or supervisor of the investigator knowledgeable with the objectives of this procedure in accordance with NNWSI-USGS-QMP-6.01, Para. 4.2.2; and as such are acknowledged by both the investigator and the reviewer to be acceptable and meaningful data that meet appropriate quantitative and qualitative acceptance criteria. Unacceptable data shall be identified appropriate to the form of the data.

8.0 MODIFICATIONS. When field modifications become necessary, per Para. 4.8, QMP-5.01, the PI shall fully document the changes, submit the documentation for the same review signature and distribution process as for the original procedure, and indicate whether the change should result in a subsequent revision to the technical procedure. The documentation will be reviewed within 30 days.

9.0 REFERENCES CITED.

Hall, W.E., and Friedman, I.F., 1963, Composition of fluid inclusions, Cave-In-Rock fluorite district, Illinois, and Upper Mississippi Valley zinc-lead district: Economic Geologist, v. 58, p.886-911.

Roedder, E., 1984, Fluid inclusions: Reviews in Mineralogy, v. 12, Mineralogical Society of America, 643 p.

Rye, R.O. and O'Neil, J.R., 1968, The O¹⁸ content of water in primary fluid inclusions from Providencia, north-central Mexico: Economic Geologist, v. 63, p. 232-238.

Winograd, I.J., Szabo, B.J., Coplen, T.B., Riggs, A.C., and Kolesar, P.T., 1985, Two-million-year record of deuterium depletion in Great Basin ground waters: Science, v. 227, p. 519-522.

- 10.0 **ATTACHMENTS.** There are no attachments included with this technical procedure.
- 11.0 **APPROVAL.** This technical procedure shall become effective upon its approval as noted by completion of all the following signatures and dates.

<u>Joseph F. Whelan</u> Prepared by: Joseph F. Whelan	<u>7-10-88</u> Date
<u>G. P. Landis</u> Technical Reviewer: G. P. Landis	<u>July 11, 1988</u> Date
<u>C. E. Hedge</u> Branch Chief: C. E. Hedge	<u>7/13/88</u> Date
<u>L. R. Hayes</u> Chief, Branch of NNWSI: L. R. Hayes	<u>7/15/88</u> Date
<u>J. R. Willmon</u> Quality Assurance: J. R. Willmon	<u>7/19/88</u> Date