

PROJECT ADMINISTRATION DATA SHEET

☒ ORIGINAL ☐ REVISION NO. _____

Project No. G-35-650 (R-6007-0A0) GTRC/GIT ^{XXX} DATE 8 / 20 / 85

Project Director: C. Weaver & J. Wampler School/Lab ^{XXX} Geo. Sci. _____

Sponsor: Bendix Aerospace

Grand Junction, CO 81502-1569

Type Agreement: Subcontract No. 85-680-E Under DOE Prime DE-AC07-76GJ01664

Award Period: From 7/8/85 To 11/30/85 (Performance) 11/30/85 (Reports)

Sponsor Amount: This Change 6/30/86 12-31-86 Total to Date

Estimated: \$ _____ \$ _____

Funded: \$ 40,000 \$ 40,000

Cost Sharing Amount: \$ N/A Cost Sharing No: N/A

Title: Sample analysis for K-AR Studies of Polo Duro Basin Bedded Salts

ADMINISTRATIVE DATA

OCA Contact

Ralph Grede x4820

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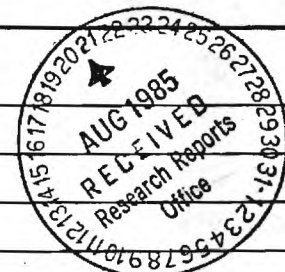
2) Sponsor Admin/Contractual Matters:

* Dr. Anthony (Tony) ZaikowskiMs. Ann MitchellAllied Bendix AerospaceAllied Bendix AerospaceBox 1569Box 1569Grand Junction, CO 81502-1569Grand Junction, CO 81502-1566303/242-8621303/242-8621Defense Priority Rating: N/AMilitary Security Classification: N/A

(or) Company/Industrial Proprietary: _____

RESTRICTIONSSee Attached Sub Contractor Supplemental Information Sheet for Additional Requirements.

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GTRC / XXX

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Title Sample Analysis for K-AR Studies of Paleoproterozoic Redded Salts

Effective Completion Date: 6/30/86

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☐ None

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404/894-3893

1 April 1986

Dr. Charles A. Jones, Director
CRWM Project Division
Bendix Field Engineering Corporation
P. O. Box 1569
Grand Junction, CO 81502-1569

Dear Dr. Jones:

I have today sent to you by a courier service two copies of the camera-ready final report of our work under Subcontract #85-680-E for Project Number 7N0130505, entitled "Sample Analysis for K-Ar Studies of Palo Duro Basin Bedded Salts." Thank you for your great patience during the many delays in getting this report done.

I think you will find the analytical data we obtained to be very important in assessing the geological history of the Palo Duro salt, and it is partly for this reason that I have taken extra time to re-check the critical data and to prepare the report carefully.

Although the body of the report was carefully prepared, I am not sure that the cover sheet has all of the necessary information. May I ask you to see that the copies of the report that I have sent you reach the proper hands in your organization and that any necessary addition of information to the cover sheet be made.

Sincerely,

J. M. Wampler
Associate Director

cc: Dr. Charles E. Weaver
Mr. Ralph Grede
Dr. Anthony Zaikowski
Ms. Ann Mitchell

S A M P L E A N A L Y S I S F O R K - A R S T U D I E S
O F P A L O D U R O B A S I N B E D D E D S A L T S

Technical Report

March 1986

J. M. Wampler and Charles E. Weaver

of

Georgia Institute of Technology

Prepared for

Bendix Field Engineering Corporation

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The content of this report was effective as of March 1986. This report was by Georgia Institute of Technology under Subcontract #85-680-E with Bendix Field Engineering Corporation under Contract E511-13730 with Battelle Project Management Division, Office of Nuclear Waste Isolation.

ACKNOWLEDGEMENTS

Anne Hall and Ady Padan prepared the clay samples used in this work and did the mineralogical analyses of these samples. Dr. Padan also did many of the potassium-argon analyses of clay samples and did much of the work in the experiments in which salt specimens were crushed in vacuum. Dr. A. A. Hassanni-Pak assisted in the early work on stepwise dissolution of salt specimens and completed this work almost single-handedly during the illness of one of the principal investigators. We are indebted to Dr. Norman Hubbard for suggesting that it might be possible to obtain potassium-argon dates for fluid inclusions in salt from the Grabbe #1 well and that potassium-argon data from dissolved salt might be used to define isochrons.

ABSTRACT

Clay samples from the San Andres formation contain potassium in at least three minerals, mostly in illite but also in K-feldspar and chloritic material. The sharpness of the illite peaks suggests that the illite is detrital, but the character of authigenic illite formed in an evaporitic environment is unknown. Potassium-argon ages for $<2\text{-}\mu\text{m}$ clay samples are nearly all intermediate between the age of the formation (about 255 Ma) and the apparent ages of coarser, detrital material in the rock (about 345 Ma), evidence that diagenetic change has been minimal. Measurements of potassium and argon isotopes released by stepwise dissolution of salt specimens show generally good correlation of $^{40}\text{Ar}/^{36}\text{Ar}$ with $^{40}\text{K}/^{36}\text{Ar}$. If data for certain steps are combined, because some potassium was probably carried over from one step to the next whenever a millimeter-size fluid inclusion opened, the correlation becomes good for each of five specimens analysed. For each specimen, the line that best fits the data may be interpreted as an isochron for rock that formed in equilibrium with air in the Permian Period. The data rule out the possibility of recent recrystallization of the rocks sampled and indicate that the millimeter-size fluid inclusions have not interacted significantly with the surrounding salt since soon after they were formed.

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1 INTRODUCTION

Mineralogical and isotopic analyses of salt core samples from the Palo Duro Basin, Texas, were undertaken to aid in the characterization of Permian, San Andres Formation salt rock horizons that may be suitable for the long-term storage of high-level nuclear waste. Samples were provided by the Texas Bureau of Economic Geology, Well Sample and Core Library. Samples studied are from the Grabbe #1 well in Swisher County and the J. Friemel #1 well in Deaf Smith County.

The investigation was divided into two parts. One part was to determine the significance of potassium-argon apparent ages obtained from the illitic clay minerals. The second part was to evaluate the feasibility of obtaining meaningful potassium-argon data from the water-soluble salt and from fluid inclusions. The questions to be addressed were as follows:

- (1) Do potassium and ^{40}Ar exhibit correlated release behavior in their siting within the salt, fluid inclusions in salt, and clay?
- (2) Have metamorphic and/or water-rock interactions led to the redistribution of potassium and ^{40}Ar ?
- (3) Do isochrons exist for the samples ($^{40}\text{Ar}/^{36}\text{Ar}$ versus $^{40}\text{K}/^{36}\text{Ar}$) and, if so, how well can they be determined?
- (4) What are the geochronological implications of the analytical results? Is there evidence for dissolution and recrystallization of the salt? If so, when did it occur?

A new procedure in which potassium and argon are released by stepwise dissolution of rock salt specimens was used to examine the potassium-argon relations in the salt and in fluid inclusions within the salt. By dissolving specimens in a stepwise manner, the potassium and argon from the larger fluid inclusions can be partially separated for analysis from the potassium and argon within the solid salt. Stepwise dissolution also allows a determination of whether the argon isotopes and potassium are distributed within a specimen in a way that defines an isochron. An important aspect of the procedure is that each specimen remains in vacuum between the several steps of dissolution, so there is no opportunity for the specimen to be contaminated with atmospheric argon between steps. Although the argon released from the dissolving salt may be measured at the end of each step, the potassium is in a brine formed by the dissolved salt and cannot be removed right away. But by isolat-

ing the brine formed in each step from that formed in the other steps, the potassium content of each portion of the dissolved salt can be determined later.

Some salt specimens were crushed in vacuum, in a preliminary search for fluid inclusions having argon enriched in ^{40}Ar relative to atmospheric argon. By identifying salt intervals having such inclusions in advance, it was possible to focus the more time-consuming stepwise dissolution work on specimens that were likely to show useful potassium-argon relations.

2 MINERALOGICAL AND POTASSIUM-ARGON ANALYSES OF CLAY MINERALS

2.1 PROCEDURES

For samples from the Grabbe #1 well, composed primarily of anhydrite or dolomite, it was necessary to dissolve the sulfates and carbonates in order to identify and describe the less abundant silicates. It was not necessary to remove anhydrite or dolomite from the mud-rich samples of the J. Friemel #1 well. A method of sulfate and carbonate removal which is non-destructive to clays, described by Bodine and Fernald (1973) and modified by Mullin (1982), was used in this study. A 0.2 M solution was prepared using 83.64 g of sodium (tetra) ethylenediamine tetraacetate (EDTA) per liter of distilled water. Powdered samples weighing 2.5 g were treated with 250 ml of the EDTA solution, boiling in a round-bottomed flask for 1.5 to 2.5 hours. A reflux condenser prevented loss of water during the boiling period. After cooling, the residue was separated from the EDTA solution in an automatic superspeed centrifuge. The supernatant EDTA solution containing dissolved carbonates and sulfates was decanted, and the silicate residue was washed twice with distilled water. In order to saturate any expandable clays present with a known cation (Na), the insoluble residue was then washed three times with a 1 N NaCl solution. The residue was then washed with distilled water another three times to remove any excess salt. After each washing, the sample was centrifuged and the supernatant liquid was decanted.

After washing, the residue was dispersed in distilled water using an ultrasonic system and then centrifuged, using an International Centrifuge Universal Model UV centrifuge, at 750 rpm for 3 minutes, 20 seconds to separate the $<2\text{-}\mu\text{m}$ and $>2\text{-}\mu\text{m}$ fractions. The $>2\text{-}\mu\text{m}$ residue was recycled several times to obtain all of the $<2\text{-}\mu\text{m}$ fraction. A slurry of each size fraction was sedimented onto preweighed slides and allowed to dry in air. The remainder of each sample was dried in preweighed glass bottles. The percentage of EDTA-insoluble residue relative to the original amount of rock was determined by weight. From the total EDTA-insoluble residue, the percentages of residue $<2\text{ }\mu\text{m}$ and $>2\text{ }\mu\text{m}$ were determined by weight.

After modified randomly packed bulk samples were prepared, water-soluble minerals were removed from the predominantly halite samples before EDTA treatment. Whole specimens of chaotic mudstone salt and massive salt were immersed in beakers of distilled water. After the salt dissolved, any anhydrite bands

were left intact with the remaining water-insoluble residue. The dissolved material was decanted and the remaining residue was collected, dried, weighed, and finely ground. After modified randomly packed bulk samples were prepared of the water-insoluble residues, 2.5 g of each was weighed out and treated with EDTA. For some specimens, the anhydrite band in the salt was accessible and sampled directly, so there was no need to dissolve salt from around the band.

Portions of the $<2\text{-}\mu\text{m}$ fractions used for x-ray analysis were set aside for subsequent potassium-argon analyses. Thin slabs for preparation of thin sections and specimens for scanning electron microscopy were cut from sections adjacent to the locations of the x-ray samples.

A Phillips-Norelco x-ray diffraction unit, operated at 20 mA and 45 kV, was used for the x-ray analysis. The incident beam is defined by a 1° divergence slit. The diffracted beam is defined by a 0.015-cm receiving slit and a 1° scatter slit. The scanning rate is $1^\circ (2\theta)$ per minute, with a linear ratemeter operating at a two-second time constant. X-ray intensities are recorded on a stripchart with a chart speed of 0.6 cm/min. Oriented samples of the $<2\text{-}\mu\text{m}$ and $>2\text{-}\mu\text{m}$ fractions were scanned from 2° to $40^\circ (2\theta)$. Bulk samples were scanned from 2° to $50^\circ (2\theta)$.

For all of the clay samples finer than $2\text{ }\mu\text{m}$, potassium-argon analyses were done by the microanalytical method presented by Wampler *et al.* (1985) and described step by step in the Quality Assurance Specification that is part of the contract under which this work was done. Briefly, the procedure involves loading one to ten milligrams of clay in a fused-quartz capsule that will retain all of the potassium while argon is released from the clay by heating. The released argon is mixed with a known amount of an isotopic reference material (virtually pure ^{38}Ar), purified, and isotopically analysed by procedures that are described in more detail in a following section of this report (Section 3.2.6). After the isotopic analysis of argon has been completed, the capsule and its contents are dissolved for potassium analysis by atomic absorption spectrophotometry.

Three samples of material coarser than $2\text{ }\mu\text{m}$ were analysed by the conventional potassium-argon method using procedures slightly modified from those described by Dooley and Wampler (1983). In this work, argon is released by fusion of a sample in a resistance-heated furnace, then purified and measured in the usual way. Potassium is measured in a solution prepared by dissolving a separate sample of the material.

2.2 RESULTS AND DISCUSSION

Eighteen samples, including three size fractions of one sample, were analysed. The mineralogical data are summarized in Table 2-1 and the potassium-argon data in Table 2-2. Samples from the Grabbe #1 well represent a variety of lithologies: chaotic mudstone-salt, anhydrite, muddy anhydrite, and anhydritic dolomite. All of the J. Friemel #1 samples are "muddy" anhydrite bands which occur within massive salt and chaotic mudstone-salt.

Illite and quartz are present in all samples. The remaining clays are primarily chloritic material present in varying proportions: discrete chlorite (Ch), swelling chlorite (Sch), chlorite/vermiculite (Ch/V), and chlorite/smectite (Ch/S). The clay suites from the Grabbe samples are more variable than those from the Friemel samples, indicating the chloritic clays have responded to the depositional environments. The abundance of Ch/S in the muddy anhydrite bands in both the Friemel and Grabbe wells suggest chloritization is less advanced in these clay-rich samples. Some kaolinite may be present in the Friemel samples.

Minor K-feldspar is present in half of the samples. Its abundance is usually less than five percent.

The amount of illite present was estimated using the potassium values obtained in the potassium-argon analyses (Table 2-2). It was assumed that the illite contains 10% K_2O . The assumed value may be one or two percent high, but since some of the potassium is in feldspar and a minor amount is in the chloritic material (based on energy-dispersive x-ray analysis during scanning electron microscopy), the estimates of illite content are probably fairly good. Estimated illite contents range from 12% to 60%.

The crystallinity index (C.I.) is a measure, in millimeters, of the 10\AA peak-width at half-height. The peak-width is a function of the temperature of formation of the illite (Weaver and Associates, 1984). Values smaller than 3.0 indicate the illite has been exposed to a burial temperature greater than 270°C . On the basis of the C.I. values, all of these illites have been exposed to temperatures in excess of 200°C , suggesting that they did not form in the sediments where they now occur. However, we know little about the nature of illite that might form under evaporitic conditions.

The potassium-argon data and apparent ages are shown in Table 2-2. The samples analysed are from the San Andres Formation of Early Guadalupe age.

Table 2-1. Mineralogical Data for Clay Samples From the Palo Duro Basin

Well	Depth	Size		K-	"Illite"		
Cycle	(feet)	(μ m)	Clay Suite	spar	(%)	C.I.	Lithology
<u>Grabbe #1</u>							
Cycle 5	2369.6	<2	SCh,Ch,I	A	37	2.7	Mudstone-salt
	2411.0	<2	SCh,Ch,Ch/V,I	P	41	2.0	Anhydrite band
	2461.8	<2	SCh,Ch,I	P	43	3.8	Mudstone-salt
Cycle 4	2599.8	<2	Ch/S,Ch,I	P	31	2.2	Mudstone-salt
	2692	<2	SCh/Ch,Ch,I	P	23	2.2	Anhydrite band
	2694	>2	Ch/S,Ch,I	P	35	2.0	Muddy anhydrite
	2700	<2	S,Ch,I	P	28	---	Muddy anhydrite
	2709.9	<2	I,Ch,Ch/V	P	60	2.7	Anhydrite-dolomite
<u>J. Friemel #1</u>							
Cycle 4	2583.0	<2	Ch/S,Ch,I	A	26	2.7	Muddy anhydrite
	2614.0	<2	Ch/S,Ch,I	A	12	2.8	Muddy anhydrite
	2621.6	<2	Ch/S,Ch,I	A	26	2.8	Muddy anhydrite
	2622.6	>2	Ch/S,Ch,I	A	24	1.5	Muddy anhydrite
	2623	<2	Ch/S,Ch,I	A	15	1.8	Muddy anhydrite
	2636.6	<1	Ch/S,Ch,I	A	31	2.8	Muddy anhydrite
	2636.6	>1,<2	Ch/S,Ch,I	P	43	1.5	
	2636.6	>2	Ch/S,Ch,I	P	23	1.5	
	2701.1	<2	Ch/S,Ch,I	A	36	3.3	Muddy anhydrite
	2710.0	<2	Ch/S,Ch,I	A	37	3.5	Muddy anhydrite

SCh = swelling chlorite, Ch = chlorite, Ch/V = chlorite/vermiculite, Ch/S = chlorite/smectite, I = illite, K-spar = K-feldspar; A = absent, P = present; C.I. = Crystallinity Index (peak width at half height of 10Å illite peak, in mm); % illite = based on % K, assuming illite has 10% K₂O and no K-feldspar is present.

Table 2-2. Potassium-Argon Data for Clay Samples From the Palo Duro Basin

Well	Depth	Size	Potassium	$^{40}\text{Ar}^*/^{40}\text{Ar}^{(a)}$	Apparent Age
Cycle	(feet)	(μm)	(%)	(%)	(Ma)
<u>Grabbe #1</u>					
Cycle 5	2369.6	<2	3.1	81.2	296
	2411.0	<2	3.4	74.3	293
	2461.8	<2	3.6	79.9	254
Cycle 4	2599.8	<2	2.6	69.7	322
	2692	<2	1.92	63.3	314
	2694	<2	1.95	71.4	311
	2694	>2	2.92	87.2	347
	2700.0	<2	2.3	70.8	284
	2709.9	<2	5.0	86.3	295
<u>J. Friemel #1</u>					
Cycle 4	2583.0	<2	2.2	73.2	312
	2614.0	<2	0.99	64.9	294
	2621.6	<2	2.2	48.3	300
	2622.6	>2	2.03	69.4	341
	2623	<2	1.24	1.3 (b)	3
	2636.6	<1	2.6	36.6	280
	2636.6	>1, <2	3.6	76.5	334
	2636.6	>2	1.88	63.7	348
	2701.1	<2	3.0	31.6	279
	2710.0	<2	3.1	67.3	276

(a) $^{40}\text{Ar}^*$ denotes radiogenic argon.

(b) Sample evolved an oily substance of very low vapor pressure during heating, probably ethylene glycol induced for x-ray analysis.

According to the geological time scale of Harland et al. (1982), the age of the Permian System ranges from 286 to 245 million years (Ma). The age of the San Andres Formation should be approximately 255 Ma. Excluding the sample from 2623 feet, the potassium-argon apparent ages range from 254 to 348 Ma. The excluded sample evolved an oily substance of very low vapor pressure, presumably ethylene glycol, when it was heated for argon isotopic analysis, which indicates that the sample used for this analysis was, by mistake, a sample that had been heat-treated during the x-ray studies.

In a detrital clay suite, the detrital character of the material is usually most evident in the coarsest illites. The $>2\text{-}\mu\text{m}$ fraction of three samples was analysed. These have greater apparent ages, 341 to 348 Ma, than the fine materials and have narrow 10\AA peaks, 1.5 to 2.0 nm. These coarse illites are probably mixtures of some older material with illite that either crystallized or, more likely, recrystallized during late Paleozoic metamorphism. This recrystallization may be related to the tectonic activity that occurred in the Ouachita-Marathon orogenic belt in Early Pennsylvanian time.

Aside from the sample from 2461.8 feet, with an apparent age of 254 Ma, the $<2\text{-}\mu\text{m}$ fractions have apparent ages ranging from 276 to 322 Ma (Permian to Mississippian). These ages are greater than the depositional age of the San Andres sediments (about 255 Ma) indicating the presence of detrital material. However, most of these apparent ages are closer to 255 Ma than to the apparent age of the coarser material (about 345 Ma), suggesting that much of the illite could be authigenic but that older feldspar, K-bearing chlorites, and detrital illite are increasing the apparent ages of the $<2\text{-}\mu\text{m}$ fractions. The apparent age of a finer fraction, the $<1\text{-}\mu\text{m}$ fraction from 2636.6 feet, is only 280 Ma, while the 1- to $2\text{-}\mu\text{m}$ fraction from the same depth has an apparent age of 334 Ma, close to the presumed average apparent age of the source material. This shows that detrital material is a significant part of the $<2\text{-}\mu\text{m}$ fraction in one case.

It is of interest to note that the potassium-argon apparent age of the $<2\text{-}\mu\text{m}$ fraction of most shales is less than the depositional age, yet in the San Andres formation the apparent ages of this size fraction are greater than the age of the rock. Apparent ages less than the depositional age usually indicate that some diagenesis, formation of illite layers, occurred after deposition and during burial. That the apparent ages of the San Andres illites ($<2\text{ }\mu\text{m}$) are slightly greater than the age of the formation may merely

reflect the effect of shallow burial on detrital illite, or it may indicate that they are mixtures of authigenic and detrital illite (and other potassium-bearing phases) having average ages less than that of detrital material and greater than that of authigenic material.

The sample from 2461.8 feet has an apparent age of 254 Ma, which is the approximate age of the San Andres Formation. As a San Andres age was found for only one sample, it cannot be concluded that the illite is authigenic; however, with the present data we cannot prove it is not authigenic.

It should be noted that there is a good linear relation between the apparent ages and the crystallinity index. As the crystallinity increases, the potassium-argon ages increase. Thus, if authigenic illite is present it could be identified by x-ray analysis.

3 POTASSIUM-ARGON ANALYSES OF SALT SPECIMENS WITH FLUID INCLUSIONS

3.1 PREPARATION AND DESCRIPTION OF THE SPECIMENS

The salt specimens used in the stepwise dissolution experiments were taken from two different levels of The Grabbe #1 well, selected from core sections that consist of relatively pure halite. The specimens designated as SDS-5, SDS-6, and SDS-7 were taken from the same level about 8 cm above a band of gray anhydritic siltstone that is identified as the 2510.4-foot level. Thus these specimens are from a depth of 2510.1 feet. The specimens designated as SDS-8 and SDS-9 were both taken from just above a gray band at a depth of 2600.3 feet. In all cases care was taken to avoid using strong force in separating these fragments from the core sections. Fragments were removed by gently separating portions of the salt bounded by already existing fractures. In some cases, some of the salt surrounding the intended specimen was carefully dissolved away in order to allow the specimen to be freed from the core section with minimal force.

After each specimen had been removed from the core, it was examined carefully under a binocular microscope. All of the specimens consisted largely of halite, but each contained a variety of mineral inclusions and fluid inclusions. Each specimen was immersed in ethanol (100%), in which halite is only very slightly soluble, in order to remove superficial contamination before it was placed in the apparatus for stepwise dissolution. In fact, the ethanol served as an excellent medium in which to examine the specimens under the binocular microscope. When each specimen was removed from the ethanol it was immediately dried with cellulose tissue. The amount of salt dissolved by the ethanol is negligible in comparison to the masses of the specimens, but was sufficient that fresh cleavage surfaces were slightly dulled by etching.

Specimen SDS-5 was the first of three specimens taken from a depth of 2510.1 feet. The specimen was a cleavage fragment of a single crystal, and its mass was 2.76 g. The specimen was broken from the outside of the core by taking advantage of fractures that had formed earlier when the core section had been broken apart. The specimen had a variety of small fluid inclusions and mineral inclusions. The fluid inclusions were generally rectangular in outline; the largest such inclusion was about 1-mm long and contained a small

gas bubble. The inclusions were not uniformly distributed in the crystal but rather occurred in clusters. A group of very small fluid inclusions of irregular form were distributed along a plane parallel to one of the cleavage surfaces; a number of these were elongated and their long axes were parallel. One part of the surface of the specimen appeared to be a saw-cut surface, and there were incipient cleavages extending up to 2 mm into the crystal from this surface. A few such shallow fractures occurred elsewhere. There were a number of small mineral inclusions of irregular form, consisting mostly of soluble salt (virtually all of the specimen dissolved), but each was associated with some of the fine red material (presumably iron oxide) that is a common impurity in rock salt.

Specimens SDS-6 and SDS-7 were also taken from the 2510.1-foot level, but they were from the central portion of the core section rather than the outside. The core section was cut with a saw at about the 2510.2-foot level to obtain a cross-sectional slab of core from which the specimens could be removed with minimal use of force. The 2.49-g specimen SDS-6 was composed of fragments of two halite crystals joined along an irregular interface. One of these crystals was unusually pure, having only very small fluid inclusions and little of the ubiquitous red impurity. The other crystal had a lot of inclusions and red material, concentrated near the interface between the two crystals. The largest fluid inclusion, one of two inclusions of appreciable size that were close to one another, had dimensions of about 0.7 mm by 0.5 mm by 0.3 mm and contained a gas bubble. One notable fracture extended into this part of the specimen, but otherwise this specimen showed only very slight fracturing near edges.

SDS-7 was a cleavage fragment of a single crystal of halite, and its mass was 1.38 g. This specimen contained a fluid inclusion larger than any in the other specimens. This inclusion had a somewhat irregular shape with dimensions about 1 mm by 1 mm by 3 mm. A gas bubble in the fluid moved easily from one end of the inclusion to the other as the orientation of the crystal was changed during examination. A small salt crystal was included near one corner of the larger crystal, where it was associated with small reddish impurities. Some fractures were evident at the surface of the specimen, but none of them penetrated more than a fraction of a millimeter into the crystal.

Specimen SDS-8, the first of two specimens from a depth of 2600.3 feet, weighed 1.61 g. It consisted of three separate crystals of halite having

somewhat irregular interfaces with one another. Fluid inclusions in this specimen were mostly quite small, and they were mostly near a portion of the surface of the specimen where other small impurities were concentrated. These included many specks of the common red impurity and some small black impurities. One larger fluid inclusion, which had a gas bubble, was present in a part of the crystal where other impurities were not concentrated. Some superficial fractures were observed in the specimen, and there was one deeper fracture associated with an interface between crystals.

SDS-9 was a fragment of a single crystal of halite and had a mass of 1.82 g. This specimen was selected because it had an unusual concentration of impurities in a more or less cylindrical zone near its center. This zone contained a lot of red material as well as some dark impurities, and there appeared to be a fluid inclusion of moderate size at one end of the zone, but it could not be seen clearly. Small inclusions were present throughout the specimen, and an included salt crystal was present near one corner. A fracture near this included crystal extended a few millimeters into the specimen; a few other minor fractures were noted.

Because of the preliminary nature of the experiments in which salt specimens were crushed to release argon, the specimens used in that work were not as fully described as those used for the dissolution experiments. Three specimens from the 2599.8-foot level were the first to be crushed. The first of these had some fluid inclusions up to about 1 mm in size, but the other two had only smaller inclusions. Three other specimens, all from the 2509.4-foot level, were crushed. The first of these contained an inclusion with a moving gas bubble. The second (B2) and third (A2) specimens from 2509.4 feet contained fluid inclusions of moderate size and some small mineral inclusions. Some sylvite may have been among the minerals included, but its presence has not been confirmed.

3.2 ANALYTICAL PROCEDURES

3.2.1 Introduction

As originally envisioned, the apparatus for stepwise dissolution would have been designed so that the salt specimen would have remained in one place, and the brine formed by dissolution of the salt would have drained into a moveable container. After each step in the dissolution, an empty container would have been moved into place to collect the brine formed during the next step. Later it was realized that a simpler apparatus could be used, if the specimen were moveable rather than containers for brine. In the simpler apparatus, the brine drains into one of five fixed chambers, called sumps, during each step of the dissolution, and the specimen is moved from sump to sump between steps.

Although earlier work in this laboratory provided a good bit of information about the behavior of argon released by dissolution of salt under vacuum, the new procedures used in this study were under development as the work progressed. Not all aspects of the procedures were well defined at the outset of the work, so changes in procedure were introduced as the need for them became evident. Consequently, the description of procedures that follows necessarily includes some discussion of phenomena observed during the analyses that led to changes in procedure. Also included are some interpretations made after the laboratory work had been completed, which provide a basis for significant changes in procedure in any future work.

3.2.2 The Apparatus Used for Stepwise Dissolution Experiments

The stepwise dissolution experiments were done in a borosilicate glass apparatus comprising five vertical cylindrical chambers of 20-mm diameter, called sumps. The sumps are attached to and interconnected by a horizontal cylinder of 30-mm diameter (Figure 3-1). Above each sump is a tube section of 10-mm diameter, which may easily be opened to remove liquid from the sump and then resealed. In each sump is a pedestal of borosilicate glass, which is used to hold a salt specimen several centimeters above the bottom of the sump when the sump is in use. Each pedestal has within it a cylindrical piece of iron so that it may be manipulated from outside the apparatus with

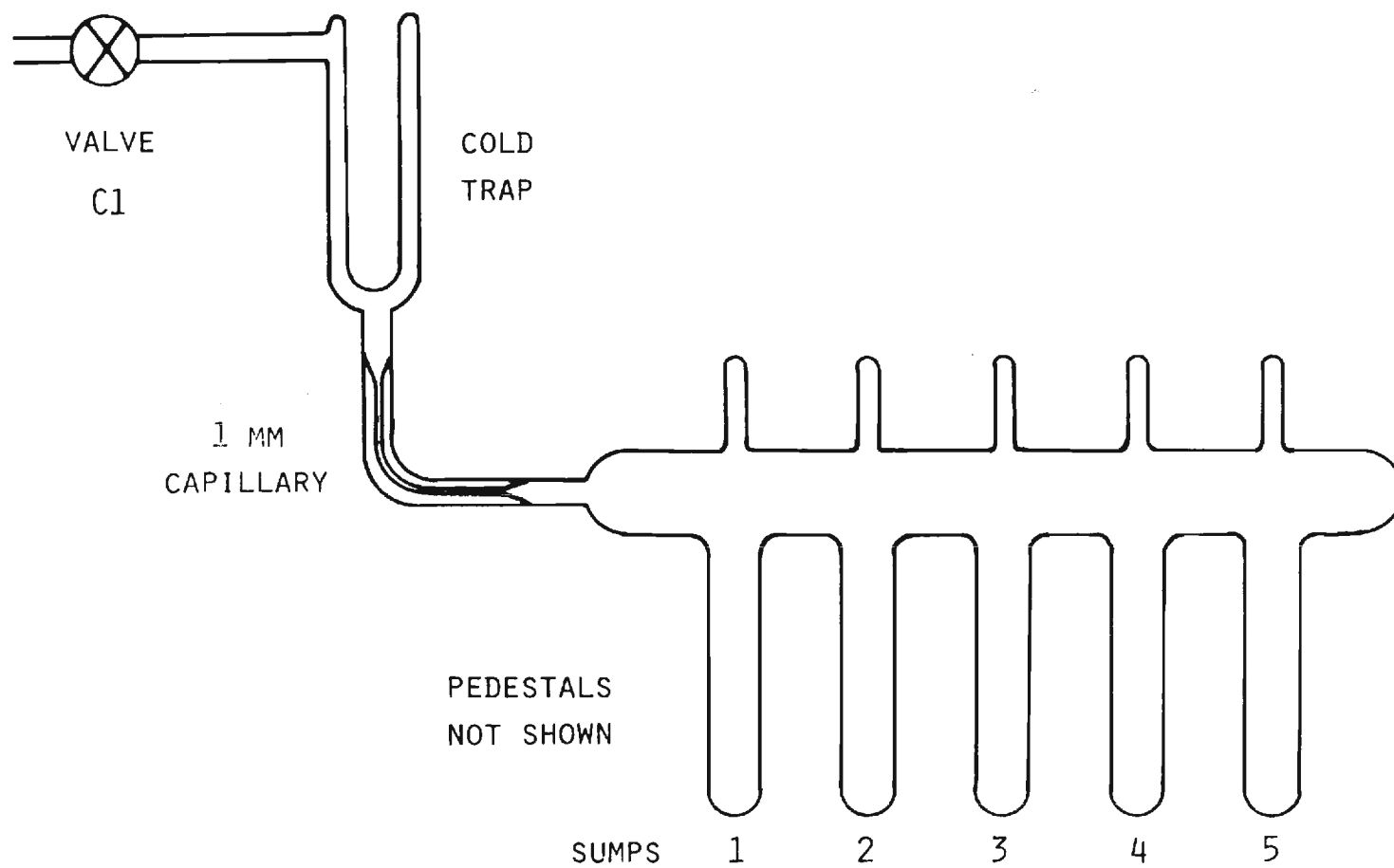


Figure 3-1. Diagram of the Apparatus Used for Stepwise Dissolution of Salt Specimens

magnets. Movement of the pedestals in this way is necessary from time to time to stir liquid and to move a specimen from one sump to another.

The apparatus comprising the sumps is connected by a section of capillary tubing to a cold trap and thence to a valve (designated "Cl") leading to the vacuum manifold used for purification and isotopic analysis of argon. The capillary tubing serves to prevent excessively rapid flow of gas during pump-down and of water vapor to the cold trap when the apparatus is evacuated. The cold trap keeps water from leaving the apparatus (other than in insignificant amounts) when the valve Cl is open.

3.2.3 Loading and Evacuation of the Apparatus

To prepare for a stepwise dissolution experiment, 1 ml of distilled water is put into each of Sumps 1, 2, and 3. (In the first experiment, 10 ml of water was used, all in Sump 1, but it soon became evident that degassing of the water is easier if a minimal amount of water is used and is distributed among several sumps). A salt specimen is then placed in Sump 5 and the apparatus is sealed.

Before evacuation, the finger of the cold trap is filled with dry ice, preferably with some ethanol to maintain good heat exchange between the glass and the evaporating dry ice. After other valves are set to direct flow to a mechanical vacuum pump, the valve Cl is opened. Soon, as pressure in the apparatus drops, the gases dissolved in the water cause effervescence. The rate of effervescence decreases quickly, and, without mechanical stirring, degassing of the water would become relatively slow. Stirring the water in each sump (1, 2, and 3) by moving the pedestal up and down rapidly for a brief period (about 30 seconds) allows most of the gas remaining in the water to escape; then valves are used to bring the diffusion pump in series with the mechanical pump. Further stirring of the water in each sump for brief periods over a total of several minutes reduces the amount of gases remaining in the water sufficiently that further release of argon may be monitored with the mass spectrometer.

At all times after evacuation of the apparatus has begun, except when it is intended for the salt to be dissolving, it is important to keep the salt specimen warmer than the water in the apparatus. Otherwise, water would condense on the salt and slowly dissolve it. During evacuation, the water in

the apparatus is cooled by evaporation as water vapor moves to the cold trap. But after valve C1 has been closed, the coolant is removed from the cold trap to allow the accumulated ice to melt. A convenient way to keep all the water cold after the cold trap has warmed up is to cool one of the sumps with ice water. This keeps the water-vapor pressure in the apparatus at a value well below that where water would condense on the salt (which remains at room temperature). Under the reduced vapor pressure, evaporation keeps any water that is not in the sump surrounded by ice water well below room temperature. In time, all such water will evaporate and recondense in the cold sump.

3.2.4 Elimination of Contaminating Argon

A major goal of this work has been to determine whether the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of argon released by stepwise dissolution of each salt specimen are correlated with the corresponding $^{40}\text{K}/^{36}\text{Ar}$ ratios in a way that would define a potassium-argon isochron for the specimen. In such work it is essential that argon from sources other than the specimen should not affect the data for the specimen significantly (Hayatsu and Carmichael, 1977). It is also important that argon from the atmosphere that may superficially contaminate the specimen as a consequence of its handling and preparation be eliminated before dissolution begins.

In the absence of prior information about the amount of argon in the salt, a satisfactory criterion for the amount of contaminating argon that may be permitted (from sources other than the specimen) can be based on the detection limit for ^{36}Ar . In this work, the minimum uncertainty in measurement of ^{36}Ar was equivalent to about 0.1 fmol, so contaminating argon (in which ^{40}Ar is about 300 times more abundant than ^{36}Ar) is negligible if it amounts to less than 30 fmol.

Contaminating argon may come from several potential sources (other than the specimen itself) within the dissolution apparatus: 1) leaks, 2) degassing of the apparatus, and 3) degassing of the water. Leaks sometimes develop in an apparatus of this sort, usually where dissimilar materials are joined, but such leaks are normally quite evident in tests carried out before an analysis begins. No evidence of leaks in the dissolution apparatus has been observed during the course of this work.

Tests of the apparatus carried out with neither water nor salt present have shown that degassing of the material of the apparatus (which would include any virtual leaks) should not normally be a significant source of argon, a result that is supported by a lot of prior experience with similarly constructed apparatus. But there are two important caveats associated with this conclusion. First, heating the apparatus will cause degassing of argon, and the amount of argon so released may be significant unless the apparatus was earlier heated under vacuum to a higher temperature. Second, mechanical strain may release argon from within materials. The dissolution apparatus was heated (with an air gun) under vacuum after it was constructed, and blank runs have demonstrated that further heating has not been necessary, even though some exposure of the inner walls to air occurs whenever a new specimen is loaded. Very rarely, in other parts of the apparatus for argon isotopic analysis, the stress occasioned by closing or opening a valve has produced a pulse of gas, including argon, which presumably escaped from an interstitial location between metal crystals. Such occurrences are unpredictable, but they are so infrequent that a spurious result from this cause is unlikely. Finally, it is possible that abrasion of glass might release some argon when a pedestal is manipulated with magnets, but there has been no evidence in this work of appreciable abrasion.

As noted in the section above, degassing of water is a relatively slow process after there is no longer enough dissolved gas to cause effervescence. Diffusion of argon through water is so slow that some active mechanism must be used to get dissolved argon out the water in a reasonable period of time. Vigorous stirring is effective, but it is not an elegant way to release such argon, and it may cause some abrasion of the glass. Distillation of the water provides a simple way to release dissolved argon, and it was expected that only a very small fraction of the released argon would re-dissolve in the distillate. Distillation is easily effected by cooling an initially dry sump with ice-water. Over a period of several hours, water will evaporate from other parts of the apparatus and condense in the sump cooled by ice-water. If water at or a little above room temperature is used to supply heat to the sump(s) from which water is evaporating, the distillation can be completed in a shorter time. Calculations based on the Henry's Law coefficient for argon show that, volume for volume, argon in equilibrium between water and gas should be much more abundant in the gas phase (by a factor of 17 at 0°C).

Since the volume of the dissolution apparatus is many (50-100) times the volume of water used in this work, it was expected that each distillation should reduce the amount of residual argon by a factor of the order of 1000. In fact, the distillation procedure was not nearly so effective, for reasons that were not understood until the work had been completed. Nevertheless, repeated distillation could be used to reduce the amount of residual argon to a negligible level. In practice, distillation was typically stopped when the amount of argon released by distillation was less than 300 fmol. It was assumed that the amount of argon remaining in the water would then be less than 30 fmol.

No experiments have been done with a salt specimen in the apparatus without water, which could show how argon degasses from the salt under vacuum. But experience has shown that by the time the argon in the water has been reduced to a negligible amount, degassing of the salt is no longer important as a source of argon. This is in contrast to the behavior of ordinary rock specimens, which generally will evolve argon for days after being placed under vacuum unless they are heated to speed the process. The difference is presumably a consequence of the impermeability of rock salt, in contrast to the character of most rocks in which low solubility and a high degree of brittleness can contribute to an intricate network of very fine pores within the rock. It is standard practice in conventional potassium-argon work to "bake" rock samples under vacuum before analysis, but such heating was avoided in this work for several reasons. Most important of these reasons is the likelihood that heating might have altered the distribution of argon within the salt specimens. Since blank runs have shown that the rate of degassing of argon from the salt is negligible by the time the water is thoroughly degassed, the only reason one might consider for baking the specimens would be speculation that atmospheric argon might have become trapped in the salt during handling and preparation in such a way that gentle heating would release it without appreciably disturbing the distribution of other argon in the salt. It seems reasonable to expect that any contaminating argon that may have been trapped in this way should be near enough to the surface that it would be released during the first dissolution step. So instead of heating the specimens on the chance that contamination could be so eliminated, the approach used in this work has been to consider the data from the first dissolution step as suspect in regard to the possible occurrence of contaminating argon.

3.2.5 Stepwise Dissolution and Transfer of Argon for Analysis

After the contaminating argon in the apparatus has been reduced to a negligible level, as shown by "blank" analyses, the first step in dissolution of the sample can begin. As noted above, a salt specimen will gradually dissolve by deliquescence if the liquid water in the apparatus is at the same temperature as the salt, but such dissolution proceeds very slowly. In order to hasten the dissolution, the sump containing the specimen may be cooled so that water condenses on the glass around the specimen. If the specimen is touching the glass, some of the condensing water will flow onto the salt. An effective way to control the condensation of water is to hold a small piece of dry ice against the outside of the glass so that water accumulates inside the glass near the point of contact. As in the distillation of water to remove contaminating argon, described above, the condensation of water proceeds more rapidly if the sump containing the evaporating water is surrounded by water, at or a little above room temperature, to act as a heat source.

The dissolution procedure begins with the salt specimen atop the pedestal in Sump 5. Since the area where water condenses may be controlled with the dry ice, and since the specimen may be moved to a limited extent, it is possible to control to a certain degree which part of the specimen dissolves most rapidly. As more water condenses, the brine formed by dissolution of salt drains downward into the sump. To terminate the dissolution, it is necessary only to stop cooling the glass near the specimen and to cool one of the other sumps (not the one to which the specimen will next be moved) with ice water. Using magnets to control the pedestal, the specimen is then lifted out of the sump and either transferred to the next sump or left poised between the two sumps. After the argon released in the first step has been analysed, and any following blank runs have been completed, the following dissolution steps are carried out in the same manner as the first. The only exception is that in the last step the specimen may be placed in the bottom of the sump rather than on a pedestal. In such a case, some stirring is usually required to effect complete dissolution.

It should be noted that the brine cannot drain completely from a specimen as a dissolution step is brought to a close. The film of water that does not drain from the specimen will evaporate, leaving a small amount of once-dissolved salt to be carried over with the specimen to the next sump. Thus,

the potassium released in one step is not cleanly separated from that released in the subsequent step. If potassium is uniformly distributed in a specimen and if the amount of salt dissolved per step is kept reasonably constant, this problem should have only a minor effect on the results. But in this study, the amount of salt dissolved per step was often quite variable, and the data show that potassium was in some cases distributed non-uniformly, so the carry-over of potassium from one step to the next may have had an important effect on the results.

It was expected that there would be little trouble effecting a clean separation of the argon released in one step from that to be released in the subsequent step (but this expectation turned out to be incorrect). The apparatus was designed so that argon in the gas phase should be swept almost completely out of the apparatus when the valve C1 is opened to transfer the argon to the manifold where it is mixed with the reference isotope ^{38}Ar and purified prior to isotopic analysis. Whenever C1 is to be opened for transfer of argon, the cold trap within the apparatus is first cooled with dry ice. Argon is then swept toward the cold trap as a consequence of the flow of water vapor to the cold trap, the water vapor acting in the same way as the vapor in a diffusion pump. Earlier work in this laboratory had shown that flow of water vapor through a capillary is fully effective to sweep argon out of the portion of the apparatus that is upstream from the capillary. There is no indication in the data obtained in this study that the sweeping action did not act as expected for argon that was in the gas phase, but there is plenty of evidence that a significant portion of the argon released by a dissolving sample may remain dissolved in the liquid and not be affected by the sweeping action.

In the first dissolution step for the first specimen, a special circumstance (the specimen got stuck beside the pedestal during the attempt to move it to the next sump) made it impossible to stir the brine that had drained to the bottom of the sump during dissolution. The argon in the gas phase was transferred from the apparatus for analysis, and then the valve C1 was closed. The water from the brine that had formed was distilled to another sump overnight, and a "blank" argon analysis was performed the next day to see if a significant amount of argon had been dissolved in the brine. It was a surprise to find almost as much argon in the blank run as in the original analysis. In both analyses, the argon was enriched in ^{40}Ar relative to atmospheric

argon, and the amount of radiogenic argon in the blank run was nearly as great as in the original analysis, so it is clear that most of the argon in the blank run was argon released from the specimen during the first dissolution step but not released from the brine. In retrospect, this phenomenon is not hard to understand, because observation of pressure changes during gas transfer have indicated that the amount of gases other than argon released by dissolution of these salt specimens is generally quite small. Usually there was no bubbling action in the brine as it formed, and it is evident that molecular diffusion is not very effective in getting argon out of the brine in a short time. A second blank run, after the water in the apparatus was again distilled from one sump to another, showed that a small fraction of the argon from the sample had been retained in the apparatus during the second transfer of argon (for the first blank run).

In the later dissolution steps for the first specimen, the brine formed was stirred by moving the pedestal up and down vigorously before transfer of the argon for analysis. Blank runs following the analyses showed that stirring is effective in getting most of the argon out of the brine. For all the other specimens, the distillation procedure described in the section above was routinely used as a means of releasing argon from the brine formed in each step. A blank run was usually carried out after each step in the dissolution of a specimen; although these blank runs indicated that the distillation procedure was not as effective as it was expected to be, the reason for this was not understood until after the analytical work had been completed.

As indicated above, a complete distillation of water containing dissolved argon, in this apparatus, should leave only about one-tenth percent of the argon dissolved in the recondensed water. But the blank runs carried out in this work show that the amount of water retained in the recondensed water was typically from one to ten percent of the argon that had been in the apparatus during the distillation. The key to understanding this phenomenon came from a review of all the data, which showed a correlation between the rate of distillation and the relative amount of argon dissolved in the recondensed water. In those cases where the distillation was allowed to proceed slowly during the night, with no heat source other than air for the sump from which the water was evaporating, the amount of argon retained in the water (as seen in the blank run following the original transfer of argon out of the apparatus) was three percent or less of the original amount of argon. When the distillation

was done more rapidly, by providing a source of heat to the sump from which the water was evaporating, the amount of argon in the succeeding blank run was from three to ten percent of the original amount of argon. Since the percentage of argon dissolved in the recondensed water was in all cases greater than the expected equilibrium amount, and since that percentage is directly related to the rate of distillation, a reasonable explanation of the phenomenon is that the flow of water vapor during distillation concentrates argon in the space immediately above the condensing water, so that more argon is dissolved in the water than would be dissolved under equilibrium conditions. The mechanism for concentrating the argon is presumably the same as that which causes argon to be swept out of the dissolution chamber when water vapor flows to the cold trap -- the same as the action of flowing vapor in a diffusion pump. Although the vapor does not flow through a capillary during the distillation, the rate of flow must be sufficient to create a dynamic steady state in which argon is considerably enriched in the sump where water is condensing. If this interpretation is correct, a simple solution to the problem is to use a cold finger above each sump for the condensation of water so that the water vapor does not flow into a "dead end" where argon may be appreciably concentrated.

There is another possible explanation of the relatively large amounts of argon found in the blank runs. This possibility is that argon was trapped in the ice that formed in the cold trap as gases were transferred out of the dissolution apparatus, rather than having been concentrated in the recondensed water. Trapping of argon by ice that forms in a cold trap at liquid-nitrogen temperature (-196°C) is a well-known phenomenon, but Wampler and Yanase (1974) reported that argon is not so trapped by ice forming in a cold trap cooled by a melting-ethanol slush (-112°C). Ice forming in a trap cooled by dry ice (-79°C) should be even less prone to trap argon than when an ethanol slush is used. But since the amount of ice and the rate at which it formed were greater in this work than in the earlier experiments that showed trapping of argon by ice to be negligible, the possibility that the ice trapped some of the argon in this work must be considered. Such trapping would be most likely during the brief period between the time when the trap is first cooled with dry ice and when the valve C1 is opened for transfer of the gases. During this period, argon will become concentrated in the portion of the apparatus comprising the cold trap and the tube leading to the valve, because of the

action of the flowing vapor. But that volume is much greater than the volume of ice formed, so, while undoubtedly some small fraction of the argon becomes trapped in the ice, it does not seem likely that a significant amount of argon would end up within the ice. Unfortunately, no experiments were done during the course of the analytical work to show conclusively whether or not an appreciable fraction of the argon in the apparatus can be trapped in the ice, because the early results were interpreted as showing that the phenomenon would not be important. Such experiments may be done easily and will be used in future work to ensure that argon can be quantitatively transferred out of the apparatus for measurement.

3.2.6 Isotopic Analysis of Argon

Immediately before each sample of argon is released from the dissolution apparatus, a valve is closed to isolate the vacuum manifold where the argon is to be mixed with the reference isotope ^{38}Ar and purified prior to the isotopic analysis. Then a known amount of the isotopic reference material is released from a reservoir into the manifold, and the valve C1 is opened so that the gases released during dissolution may flow into the manifold. A cold trap at -112°C collects the small amount of water vapor that the trap within the dissolution apparatus does not hold. A second cold trap at -183°C collects carbon dioxide and any other gases condensible at this temperature, and the remaining non-inert gases are removed by reaction with hot titanium. (Because the amounts of gas released by the salt specimens used in this study were generally quite small, only a minute or two was required for purification.)

The argon mixture is then admitted to the mass spectrometer for isotopic analysis, according to procedures that are standard in this laboratory. These procedures ensure that there is no isotopic fractionation during the transfer, that the amount of argon transferred to the mass spectrometer does not exceed the maximum amount measurable by the instrument, and that the amount of argon can be determined with reasonable accuracy even when the isotopic reference material has not been used (which was the case for all of the blank runs).

After the transfer of argon to the mass spectrometer is complete, a valve leading to the diffusion pump is opened so that the manifold where the argon had been purified may be evacuated in preparation for the next analysis. The valve C1, which connects the dissolution apparatus to the manifold, is left

open at the beginning of this evacuation to ensure that any argon in the dissolution apparatus (in the gas phase) is pumped away. After three minutes C1 is closed and the next step in the dissolution procedure may begin. (In the analyses of the first specimen studied in this work, C1 was closed before transfer of argon to the mass spectrometer, because it was assumed that the flow of water vapor would carry all gaseous argon out of the dissolution apparatus. But a blank run showed that nearly one percent of the ^{38}Ar reference material that had been mixed with a sample of gas was sealed in the dissolution apparatus by closing C1 at this stage. Apparently the flow of water vapor beyond the cold trap in the dissolution apparatus is not sufficient to sweep argon effectively out of the small portion of the apparatus that is between the trap and the valve. The procedure was then changed so that this portion of the apparatus would be evacuated along with the manifold to which it connects.)

The isotopic analysis is carried out by scanning over the argon mass spectrum according to a procedure that is standard in this laboratory. The procedure allows graphical averaging to be used to compensate for a very small instrumental drift and provides two independent sets of data for the argon isotope ratios so that any mistakes in reading the data are likely to be recognized. The sensitivity of the instrument is usually not quite the same for the different isotopes of argon (mass discrimination), so the raw data are corrected on the basis of calibration runs in which atmospheric argon is used as a reference material to determine the relative sensitivity of the instrument for ^{36}Ar and ^{40}Ar . The ratio $^{40}\text{Ar}/^{36}\text{Ar}$ in atmospheric argon is assumed to be 295.5 (Steiger and Jäger, 1977). The sensitivity for argon is assumed to vary linearly with mass, so that the sensitivity for ^{38}Ar equals the average of the sensitivities for the other two isotopes.

The mass spectrometer has a small, but persistent, background spectrum in the argon mass range that is caused by organic molecules. Usually, this background has only a small effect on the measurement of ^{36}Ar and no significant effect on measurement of the other argon isotopes. Since the major peaks in the mass spectrum of the organic material are at odd mass numbers, a correction for the effect of the background spectrum may be made from measurements of the signals at these odd mass numbers. Normally the magnitude of this correction is so small that uncertainty in the accuracy of the correction is of no consequence.

Experience obtained over a long period of time indicates that the probable relative error in measurement of the ratio $^{40}\text{Ar}/^{38}\text{Ar}$ should not be more than about one-half percent under normal conditions. When there is sufficient ^{36}Ar present, the probable error in the measured ratio $^{36}\text{Ar}/^{38}\text{Ar}$ should not be more than one percent. But when the amount of ^{36}Ar is very small, the noise inherent in the weak signal and any uncertainty in the magnitude of the correction for the background spectrum appreciably enhance the relative error of measurement. The error estimates that appear in the following tables of data (Section 3.3) are based on a one-half percent probable error in the ratio $^{40}\text{Ar}/^{38}\text{Ar}$ and a one percent or greater probable error in the ratio $^{36}\text{Ar}/^{38}\text{Ar}$.

After the analyses of the first salt specimen had been completed, but before the analyses of the second specimen had started, the filament of the mass spectrometer failed. It is characteristic of the mass spectrometer to have a somewhat degraded performance for some time before the failure of a filament (when that failure is a consequence of normal evaporation of metal from the hottest part of the filament, rather than a consequence of an accident). The most obvious manifestation of the degraded performance is an increasing "sharpness" of the tops of the peaks in the mass spectrum, which is associated with an apparent decrease in stability and a variability in the relative sensitivities for the different isotopes of argon (that is, changes in the magnitude of mass discrimination). The mass spectrometer record for the first specimen shows clear evidence of such degradation in performance, and data obtained in calibration with atmospheric argon show that the degree of mass discrimination changed by an unusually large amount prior to the failure of the filament. For this reason the estimated errors in the argon analyses for this specimen are greater than for the other specimens.

At the time a new filament was installed, a small modification in the configuration of the mass spectrometer's ion source was made in an attempt to reduce the degree to which the ion source traps argon, causing a slight carry-over of argon from one analysis to the next -- a so-called memory effect. This modification (which was actually a return to the originally designed configuration of the hole that limits the size of the electron beam passing through the ion source) was successful in reducing the magnitude of the memory effect, but it caused a reduction in sensitivity as well. The sensitivity could be restored to a satisfactory level by changing the potential of the ion repeller (relative to the chamber where ions are formed, called the cage) from

the 1-V setting that had been used to a value near -1 V. An examination of the data provided by the manufacturer of the MS-10 mass spectrometer indicates that problems caused by mass discrimination are more likely when the ion repeller is negative with respect to the cage, but a consideration of the physical relationships involved suggested that these problems are a consequence of a variation in the ratio of ion-repeller voltage to cage voltage that occurs as the mass spectrometer scans across the mass spectrum. By changing the voltage divider network so that this ratio of voltages remains constant, problems with mass discrimination should be minimized. Such a change was made, and the calibration data obtained since the change indicate that mass discrimination is now very slight, affecting the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio by less than one percent.

Whenever the mass spectrometer has been opened for a change of filament, enhancement of the background spectrum caused by organic molecules is observed. The background spectrum decreases in magnitude slowly, returning to normal levels after several weeks. For this reason, the corrections applied to remove the effect of the background spectrum were greater than normal for the first few specimens analysed after the filament change. In the case of SDS-6, the first such specimen, the uncertainty of the ^{36}Ar measurements was appreciably increased because of the larger than normal correction for the background.

3.2.7 Potassium Analysis

When the stepwise dissolution of a specimen has been completed, the salt accumulated in each sump is removed and prepared for potassium analysis as follows. A torch is used to open the glass tube above each sump; through this tube distilled water is added as needed to dissolve the salt in the sump and the resulting brine is removed by pipette. More distilled water is used to rinse the sump, at least twice, and the brine and wash water (totalling 25-30 ml) are combined and centrifuged to separate any insoluble residue from the liquid. The liquid is then poured off into a pre-weighed fluorocarbon beaker, from which the water is evaporated, to leave dry salt. (Only traces of insoluble residue were left by these specimens, so it was not necessary to rinse and re-centrifuge the residue to get a satisfactory "yield" of salt.)

Each sample of dry salt is weighed in the fluorocarbon beaker from which the water was evaporated. Then the salt is dissolved in water containing a small amount (2.5 mmol/kg) of CsCl and transferred to a pre-weighed polyethylene bottle. More of the CsCl solution is used to rinse the beaker, and the rinses are added to the solution in the bottle. Finally, more of the CsCl solution is used to bring the mass of solution in the bottle to one hundred times the mass of the original salt. (In a few cases where the mass of salt was less than 0.1 g, a relatively larger amount of solution was used.)

The potassium content of each solution was determined by atomic absorption spectrophotometry, by comparison with reference solutions having nominal potassium contents of 0, 0.5, 1.0, 1.5, and 2.0 mg/kg. These solutions were prepared by dilution of a primary reference solution (prepared from reagent-grade KCl) with water. CsCl and NaCl were added in amounts appropriate to match the sample solutions. For this purpose it was assumed that the salt samples are virtually pure NaCl, and the reference solutions were made to contain 10 g/kg of NaCl. Unfortunately, at this level the potassium content of the salt added to the reference solutions is not negligible. The ACS reagent-grade NaCl available for this work contains about 10 mg/kg potassium, which would have contributed an extra 0.1 mg/kg potassium to each reference solution. To minimize the contribution of potassium from the NaCl, the reagent-grade NaCl was partially recrystallized from distilled water, twice, to reduce its potassium content. The reference solutions were then prepared from the twice-recrystallized salt. Because the amount of potassium contributed to the reference solutions by the recrystallized salt was unknown, the absorbance data from the set of reference solutions were analysed in the manner of the method of standard additions, using readings obtained during aspiration of distilled water to establish the instrumental zero. The results indicate that the salt contributed 0.04 mg/kg potassium to each reference solution (corresponding to 4 mg/kg potassium in the recrystallized salt). The potassium content of each reference solution was accordingly corrected before the working curve was established for determination of the potassium contents of the sample solutions.

The uncertainty in the potassium content of each reference solution is about 0.01 mg/kg, and there is an uncertainty of similar magnitude in the instrumental readings. Blank runs indicate that contamination typically contributes roughly 0.01 mg/kg potassium to a sample solution. The overall

probable error in the potassium measurements is estimated to be 0.02 mg/kg in the sample solutions, which corresponds to a probable relative error in the potassium content of the salt samples that ranges up to 5 percent for those samples having the lowest potassium content, about 40 mg/kg (0.004%).

There is an additional source of error that affects the potassium contents when they are expressed as mass fractions. The dry salt samples were weighed only to the nearest 0.01 g, so the relative error in the amount of salt can be quite large. Typically, in the first step of dissolution of a specimen the amount of salt dissolved was 0.10 g or less. In such cases the relative weighing error is unusually large. This source of error does not affect the potassium-argon ratios, since any weighing error affects the specific argon content equally as it affects the potassium content.

3.2.8 Procedure for Crushing Specimens in Vacuum

The apparatus in which specimens were crushed to release argon from fluid inclusions was an all-metal apparatus connected to the same valve (C1) that was later used for the stepwise dissolution experiments. The specimen to be crushed was placed within a 1.5-inch diameter stainless steel nipple, of the type that is standard in ultra-high vacuum work, on a blank flange that sealed one end of the nipple. The upper end of the nipple was closed by a flange that had provision for a tube leading to the valve and for a stainless-steel bellows through which a rod connected to a rounded piston was sealed. (The rounded piston was in fact the head of a large carriage bolt.) Specimens were crushed by driving the piston down onto the salt with light blows from a hammer on the upper end (outside the flexible bellows) of the rod.

The crushing experiments were done with the valve C1 open so that the effect of crushing could be monitored by the response of an ionization gauge to the gases released. By thus noting the size of the pulse of gas released upon each hammer blow, some feeling for the amount of force necessary to break open the specimens was developed, even though no provision had been made for actually viewing the specimens within the sealed apparatus.

Argon released in the crushing experiments was isotopically analysed in the manner described above for argon released by stepwise dissolution. Several of the crushed specimens were immersed in absolute ethanol, after they had been removed from the apparatus, in an attempt to extract the potassium

that had been present in the fluid inclusions that were opened during the crushing. The ethanol was later evaporated away from the extracted salt, and that salt (of the order of 100 mg) was redissolved in an aqueous medium for potassium analysis by atomic absorption spectrophotometry.

3.3 RESULTS

3.3.1 Observations Made During Dissolution of the Specimens

The potassium-argon data obtained by stepwise dissolution of the five salt specimens described in Section 3.1 are given in Tables 3-1 through 3-5. In these tables, the first column of analytical data gives the amount of dry salt recovered from the solution produced in each step. For most specimens, the total amount of salt recovered from all the steps agrees well with the original mass of the specimen, given the 0.01-g uncertainty in each weighing. The greatest discrepancy is in the case of specimen SDS-7, for which only 1.30 g of salt was recovered from a 1.38-g specimen. Although this specimen contained a fluid inclusion larger than that in any other specimen, the inclusion was not large enough to account for the 0.08-g difference between the masses of the original specimen and the recovered salt.

Although the first step in dissolution was normally one in which only a small amount of salt was dissolved, this practice was not followed in the case of the first specimen, SDS-5, from which 0.31 g was dissolved in the first step. Comparable amounts were dissolved in the next three steps, leaving a disproportionate amount, 1.45 g, to be dissolved in the final step. The largest fluid inclusion in SDS-5 had originally been near one face, which was the upper surface as the specimen was oriented in the apparatus. Observation indicated that the inclusion was still unopened at the end of the second step; it probably opened during the third step, in which a deliberate attempt was made to dissolve salt from the upper surface.

SDS-6 was the only specimen for which more than five steps were used in dissolution, which was a consequence of an attempt to control the dissolution in such a way that the argon to be released from the largest fluid inclusion could be well resolved from other argon within the specimen. Since the apparatus has only five sumps, it was necessary to open the apparatus after the fifth step in order to remove the salt that had been dissolved from the specimen in the first five steps. Because of possible contamination of the specimen with atmospheric argon during this process, the amount of salt dissolved in the sixth step, as in the first step, was very small (less than 0.1 g in each case). In each of the other steps except the last one, less than 0.4 g of salt was dissolved. During steps 2, 3, and 4, the condensation of

Table 3-1. Potassium-Argon Data From Stepwise Dissolution of SDS-5

Step	Amount Dissolved (g)	Potassium (μ g)	Potassium (mg/kg)	$^{40}\text{K}/^{36}\text{Ar}$ $\times 10^{-3}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{Ar}^*/^{40}\text{Ar}$ (%)	$^{40}\text{Ar}^*$ (pmol)	Apparent Age (Ma)
1 (a)	0.31	27.7 ± 0.6	89	4.14 ± 0.23	345 ± 10	14.3	0.98 ± 0.39	193 ± 72
2	0.21	13.5 ± 0.4	64	0.30 ± 0.01	303 ± 6	2.5	1.03 ± 0.90	394 ± 310
3 (b)	0.44	30.2 ± 0.9	69	2.94 ± 0.08	374 ± 8	21.1	2.43 ± 0.22	412 ± 35
4 (c)	0.35	21.6 ± 0.7	62	8.14 ± 0.32	407 ± 9	27.4	0.88 ± 0.06	221 ± 16
5	1.45	87.2 ± 2.9	60	6.97 ± 0.27	414 ± 8	28.6	4.42 ± 0.27	271 ± 18
Combined steps:								
1-5	2.76	180.2	65	2.32	337	12.4	9.73	287
3,4	0.79	51.8	66	4.01	381	22.5	3.30	335

- (a) A five-percent uncertainty in amount of argon has been assumed for the first step, because the isotopic reference material (^{38}Ar) was not used.
- (b) The largest fluid inclusion in the specimen opened during the third step of the dissolution.
- (c) The argon analysis for the fourth step was not followed by a blank run.

Table 3-2. Potassium-Argon Data From Stepwise Dissolution of SDS-6

Step	Amount Dissolved (g)	Potassium (μg) (mg/kg)	$^{40}\text{K}/^{36}\text{Ar}$ $\times 10^{-3}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{Ar}^*/^{40}\text{Ar}$ (%)	$^{40}\text{Ar}^*$ (pmol)	Apparent Age (Ma)	
1	0.06	4.2 ± 0.1	70	1.52 ± 0.05	325 ± 6	9.0	0.24 ± 0.05	303 ± 60
2	0.16	6.5 ± 0.3	41	4.24 ± 0.22	378 ± 10	21.8	0.38 ± 0.04	309 ± 30
3	0.23	11.0 ± 0.5	48	14.0 ± 1.1	547 ± 37	46.0	0.59 ± 0.05	285 ± 25
4 (a)	0.38	16.2 ± 0.8	43	4.88 ± 0.25	380 ± 6	22.2	0.83 ± 0.05	274 ± 20
5 (b)	0.35	35.1 ± 0.7	100	5.13 ± 0.13	420 ± 6	29.7	2.55 ± 0.10	377 ± 15
6 (a)	0.07	7.8 ± 0.2	112	16.4 ± 0.9	448 ± 23	34.1	0.22 ± 0.02	156 ± 15
7 (a)	0.25	18.2 ± 0.5	73	11.8 ± 0.4	420 ± 11	29.6	0.57 ± 0.04	172 ± 11
8	0.89	37.8 ± 1.8	43	6.91 ± 0.34	414 ± 6	27.1	1.94 ± 0.08	274 ± 16
Combined steps:								
1-8	2.39	136.8	57	6.01	403	26.7	7.33	285
5-7	0.67	61.0	91	6.89	422	29.9	3.34	291

(a) The argon analyses for steps 4, 6, and 7 were not followed by blank runs.

(b) The largest fluid inclusion in the specimen opened during the fifth step of the dissolution.

Table 3-3. Potassium-Argon Data From Stepwise Dissolution of SDS-7

	Amount issolved (g)	Potassium (μg) (mg/kg)	$^{40}\text{K}/^{36}\text{Ar}$ $\times 10^{-3}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{Ar}^*/^{40}\text{Ar}$ (%)	$^{40}\text{Ar}^*$ (pmol)	$^{\text{A}}$ Age (Ma)	
1 (a)	0.04	6.6 ± 0.4	164	5.25 ± 0.33	366 ± 6	19.3	0.26 ± 0.02	214 ± 20
2 (b)	0.37	103.3 ± 2.1	279	7.81 ± 0.18	425 ± 5	30.4	5.09 ± 0.16	264 ± 9
3	0.25	43.0 ± 0.9	172	3.33 ± 0.08	326 ± 4	9.4	1.18 ± 0.14	152 ± 18
4	0.27	20.5 ± 0.5	76	12.69 ± 0.36	496 ± 7	40.4	0.96 ± 0.03	252 ± 9
5	0.37	32.9 ± 0.9	89	40.7 ± 1.4	945 ± 20	68.7	1.57 ± 0.03	256 ± 8
Combined steps:								
1-5	1.30	206.2	159	6.92	397	25.7	9.06	237
2,3	0.62	146.2	236	5.60	376	21.4	6.27	232

(a) The argon analysis for the first step was not followed by a blank run.

(b) The large fluid inclusion in this specimen opened during the second step.

Table 3-4. Potassium-Argon Data From Stepwise Dissolution of SDS-8

Step	Amount Dissolved (g)	Potassium (μ g) (mg/kg)	$^{40}\text{K}/^{36}\text{Ar}$ $\times 10^{-3}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{Ar}^*/^{40}\text{Ar}$ (%)	$^{40}\text{Ar}^*$ (pmol)	Apparent Age (Ma)
1	0.10	8.6 ± 0.4 86	0.78 ± 0.04	309.2 ± 3.2	4.5	0.45 ± 0.11	279 ± 63
2	0.37	[32.6] ^(a) [88]	[0.60]	301.8 ± 3.0	2.1	1.02 ± 0.53	[172]
3	0.32	28.3 ± 0.6 89	0.56 ± 0.01	306.7 ± 3.1	3.7	1.70 ± 0.50	317 ± 85
4	0.39	39.6 ± 1.2 102	1.22 ± 0.04	317.5 ± 3.2	6.9	2.14 ± 0.33	287 ± 42
5	0.41	30.3 ± 0.8 74	3.61 ± 0.10	361.9 ± 4.2	18.4	1.67 ± 0.10	293 ± 18
Combined steps:							
1-5	1.59	[139.4] [88]	[0.89]	310.4	4.8	6.98	268
1,3-5	1.22	106.8 88	1.04	314.9	6.2	5.96	296

(a) Numbers shown in brackets are based on an assumed value (88 mg/kg) for the potassium content of the salt dissolved in the second step.

Table 3-5. Potassium-Argon Data From Stepwise Dissolution of SDS-9

Step	Amount Dissolved (g)	Potassium (μ g) (mg/kg)	$^{40}\text{K}/^{36}\text{Ar}$ $\times 10^{-3}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{Ar}^*/^{40}\text{Ar}$ (%)	$^{40}\text{Ar}^*$ (pmol)	Apparent Age (Ma)
1	0.05	7.4 \pm 0.4 149	0.45 \pm 0.03	302.9 \pm 3.1	2.4	0.37 \pm 0.17	267 \pm 114
2	0.43	28.4 \pm 0.9 66	1.30 \pm 0.04	318.4 \pm 3.2	7.2	1.49 \pm 0.22	280 \pm 39
3	0.41	28.0 \pm 0.8 68	0.72 \pm 0.02	311.4 \pm 3.1	5.1	1.84 \pm 0.39	344 \pm 67
4	0.52	33.3 \pm 1.0 64	0.78 \pm 0.03	306.7 \pm 3.1	3.7	1.42 \pm 0.42	231 \pm 64
5	0.40	24.6 \pm 0.8 62	0.045 \pm 0.002	295.4 \pm 3.0	0.0	-	-
Combined steps:							
1-5	1.81	121.7 67	0.19	298.0	0.9	4.92	219

water was controlled so that most of the salt dissolved was from the part of the specimen that had few inclusions. In the fifth step, the condensing water was directed to the other crystal, which resulted in the opening of the largest fluid inclusion. The opening of the inclusion, which had a sizeable gas bubble, was quite evident because of splashing of water as gas expanded. The dissolution was stopped promptly after this event was observed in order to examine the argon that had been released. It could not be determined with certainty whether the other fluid inclusion of appreciable size, nearby, opened during this step or during a subsequent step. The part of the specimen that had contained these inclusions was dissolved away during the seventh step. In the eighth step the remainder of the specimen, an amount disproportionately larger than that dissolved in the earlier steps, was dissolved.

Only a small amount of SDS-7 was dissolved in the first step, but roughly equal amounts were dissolved in the subsequent steps. The large fluid inclusion in this specimen opened during the second step, but the fluid was not observed to splash out in the manner that had been expected. The corner of the specimen having an included salt crystal was gone by the end of the third step.

Only a small fraction of SDS-8 was dissolved in the first step of dissolution, but in the subsequent steps the remainder of the specimen was dissolved in roughly equal increments. The part of the specimen that was relatively rich in impurities was dissolved mostly during the third step. It could not be determined in which step the fluid inclusion with the gas bubble dissolved. (This inclusion was not as large as the largest fluid inclusions in other specimens analysed.) Some splashing of water was noted during the last step (in which the specimen was immersed in water at the bottom of a sump), presumably a consequence of the release of small bubbles of gas (but the amount of argon released during this step was less than in each of the steps 2, 3, and 4).

Except for the first step, in which only a little salt was dissolved, SDS-9 was dissolved in roughly equal increments. The fluid inclusion at one end of the column of impurities probably opened during the second step, but no splashing was noted at the time. This specimen developed an unusually irregular form as it progressively dissolved. During the final step, with the specimen immersed in water, several bubbles were seen to be released and to rise through the water.

3.3.2 Results of the Potassium Measurements

The amount of potassium released in each step is given in micrograms and is also given as a mass fraction expressed as milligrams of potassium per kilogram of dissolved salt, that is, as parts per million (Tables 3-1 through 3-5). The uncertainty indicated for the mass of potassium released in each step is an estimate of probable error, which depends on the concentration of potassium in the solution prepared for atomic absorption spectrophotometry. The corresponding relative errors are in the range 2% to 5%. No attempt has been made to include the effect of carry-over of potassium from one step to the next (described in Section 3.2.5) in these estimates of error.

Because of uncertainty in the mass of the recovered salt, the mass fraction of potassium is quite uncertain in cases where only a small amount of salt was dissolved, but in other cases the relative uncertainty in the mass fraction should not be more than five percent. The values obtained range from just over 40 mg/kg for several steps in the dissolution of SDS-6 to 279 mg/kg for the second step in the dissolution of SDS-7. The potassium content is fairly uniform for all of the steps in the cases of SDS-5, SDS-8, and SDS-9, disregarding the first step for SDS-9 in which a very small amount of salt was dissolved. (It was not possible to obtain a potassium measurement for the second step in dissolution of SDS-8, because the tube containing the solution broke during centrifuging. Although the solution was recovered from the metal centrifuge-tube holder, it was found to be anomalously rich in potassium, obviously a consequence of contamination.)

For SDS-6 and SDS-7, the potassium released in a few of the steps is more than twice as great, per unit mass of salt dissolved, than in other steps. In each of these cases, the first step having a distinctly elevated level of potassium is one in which a large fluid inclusion opened. It is notable that the potassium content of SDS-6 appears to be quite uniform for the salt dissolved before the inclusion opened (41-48 mg/kg for steps 2, 3, and 4). The potassium content of the salt recovered from the fifth step, during which the inclusion opened, is more than twice as great (100 mg/kg), and the two following steps also show elevated potassium contents. The potassium content of the salt dissolved in the final step is 43 mg/kg, essentially the same as in the early steps.

The elevated potassium content of the salt dissolved in the fifth step for SDS-6 may be attributed to the influence of the fluid from the large inclusion. The amount of "extra" potassium in this step is about 20 μg , however, which would correspond to a high concentration of potassium in the fluid if the estimated volume of fluid (about 0.1 mm^3) is correct. The size of the inclusion may have been underestimated as a result of refraction of light within the specimen. It seems quite likely that the elevated levels of potassium seen in steps 6 and 7 may be a consequence of carry-over of potassium from the fifth step. Since the fifth step was terminated promptly after the large fluid inclusion opened, it seems probable that a significant amount of potassium from the inclusion may have remained with the specimen to be carried over to step 6. Since only a small amount of salt was dissolved in step 6, and since the opened inclusion left a re-entrant cavity in the surface of the specimen, it is reasonable to infer that some "extra" potassium may have been carried over to step 7 as well. (These inferences have been influenced by the potassium-argon ratios observed for this specimen. A further discussion follows below after the argon isotopic ratios are introduced.)

The salt dissolved from SDS-7 had an unusually high potassium content in the second step, during which the very large fluid inclusion in this specimen apparently opened, and also in the following step. The mass fraction of potassium in the salt from the second step is more than three times greater than the average for the last two steps, corresponding to about 70 μg of "extra" potassium. The third step also had an elevated level of potassium, and if the "extra" potassium from this step is included, the total of "extra" potassium is about 90 μg , corresponding to a potassium content in the fluid of about 30 g/kg (3%) if the "extra" potassium was all in the fluid and if the volume of the fluid was correctly estimated as about 3 mm^3 . As in the case of SDS-6, it is reasonable to expect that some of the potassium from the inclusion was carried over into the step following the one during which the inclusion opened.

The first specimen analysed, SDS-5, had several fluid inclusions of significant size, but these were probably somewhat smaller than the largest inclusion in SDS-6. The largest inclusion in SDS-5 appeared to have opened during the third dissolution step, but the potassium content of the salt from this step is not appreciably elevated with respect to the other steps. Nor is there any elevation of potassium content in the second step for SDS-9, in which a fluid inclusion of moderate size is thought to have opened.

3.3.3 Results of the Argon Isotopic Measurements

The data in the last five columns of Tables 3-1 through 3-5 are the data needed to construct potassium-argon isochron diagrams and data pertaining to potassium-argon apparent ages calculated in the conventional way. The accuracy of the data in all of these columns depends on the accuracy of measurement of ^{36}Ar . Since ^{36}Ar is much less abundant than ^{40}Ar , it cannot be measured as accurately as ^{40}Ar in most cases. The problem of accuracy in measurement of ^{36}Ar was exacerbated in part of this work by a persistent background spectrum due to organic material in the mass spectrometer after a change in the mass spectrometer's filament. In a few of the dissolution steps in this work, the amount of ^{36}Ar released was so small that the uncertainty in measurement is of the order of 5% of the measured value, but in most cases the uncertainty is not more than 2%. The uncertainties given in Tables 3-1 through 3-5 for the ratio $^{40}\text{Ar}/^{36}\text{Ar}$ range upward from a minimum estimated error of 1%, to 7% for the third step in dissolution of SDS-6, which had a very small amount of ^{36}Ar and a larger than usual uncertainty in the correction for background signal. The values of this ratio are not affected by the problem that some of the argon from each dissolution step was retained in the water within the dissolution apparatus, since we can reasonably assume that the isotopic composition of the argon retained was the same as that of the argon that was successfully transferred out of the apparatus. (In the case of the first specimen, SDS-5, the distillation procedure was not used, so it is possible that there were isotopic differences between the argon retained in the liquid and that which was first transferred out as a gas.) Generally, the isotopic composition of the argon from blank runs could not be measured very precisely because the amount of ^{36}Ar was small, so no attempt was made to correct the originally measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratios on the basis of the data obtained in blank runs.

For most of the analyses, the value given for the ratio $^{40}\text{K}/^{36}\text{Ar}$ includes an amount of ^{36}Ar added on the basis of one or more blank runs that followed the original argon analysis. (In five cases no blank argon analysis was done, as indicated in the tables by footnotes. Generally, these are cases where the amount of argon measured in the original analysis was relatively small.) The added amount of ^{36}Ar is not based directly on the amount of that isotope measured in the blank run(s), because the uncertainty in that measurement is

usually large. Instead the amount of ^{36}Ar added is derived from the amount of ^{40}Ar seen in the blank run(s) and the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio measured in the original argon analysis. The uncertainties given for the $^{40}\text{K}/^{36}\text{Ar}$ ratios are based on the estimated relative errors in the measured amounts of potassium and ^{36}Ar , combined in the usual root-mean-square fashion for random errors. This ratio is also sensitive to systematic errors in calibration and in the isotopic abundance of ^{40}K , but the possibility of such errors is not incorporated in the uncertainties listed, which are to be considered as estimates of probable random error.

The last three columns of Tables 3-1 through 3-5 give the amounts of radiogenic argon (denoted in the tables as $^{40}\text{Ar}^*$) and the apparent ages based on these amounts, calculated on the basis of the assumptions of conventional potassium-argon dating (Dalrymple and Lanphere, 1969, pp. 50-51). The values used for the decay constants and isotopic abundance of ^{40}K , and for the isotopic composition of atmospheric argon, are those adopted by the IUGS Subcommittee on Geochronology in 1976 (Steiger and Jäger, 1977). The uncertainties given for the amounts of radiogenic argon and for the apparent ages are based on estimated probable errors in the argon isotopic measurements and the potassium measurements, combined by formulas that take into account how uncertainty in the amount of radiogenic argon depends non-linearly on the ratio $^{40}\text{Ar}/^{36}\text{Ar}$ (Cox and Dalrymple, 1967). It is important to note that the uncertainty in amount of radiogenic argon rises very rapidly as the percentage of radiogenic argon becomes small and that the calculated apparent age is meaningless if the measured ratio $^{40}\text{Ar}/^{36}\text{Ar}$ is not significantly different than the value for atmospheric argon. It must also be emphasized that the values used for the probable errors of measurement are estimates, based on experience but not precisely known. Hence, the uncertainties given for the apparent ages, calculated from these more fundamental error estimates, should not be considered to be error limits but only to be rather crude indicators of the uncertainty in each age value due to random analytical error. In this work, some of the apparent ages are much less reliable (analytically) than others, and this is indicated clearly by the wide range in error values given in the tables.

At the bottom of each of Tables 3-1 through 3-5 is given a set of data obtained by combining all of the data for the different dissolution steps. Also given in most cases are data obtained by combining the data from certain

selected dissolution steps. The reasons for these selections are given in the discussion of results from the individual specimens, which follows. The order in which the individual specimens are discussed is not the chronological order in which the specimens were analysed, but rather is based on the degree of correlation between the ratios $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{40}\text{K}/^{36}\text{Ar}$ seen in the isochron diagrams. This order of discussion has been chosen because of the increasing complexity of the interpretation required as the degree of correlation decreases.

Figure 3-2 is a plot of $^{40}\text{Ar}/^{36}\text{Ar}$ versus $^{40}\text{K}/^{36}\text{Ar}$ for SDS-8. Only four points are plotted as solid points because the solution to be used for potassium measurement for the second step was contaminated. These data show a high degree of correlation, as indicated by the small deviations of the points from the solid straight line drawn on the figure. This line was determined by the formulas given by York (1969) for least-squares fitting of a straight line with correlated errors. An inverse weighting function, based on the assumption that the relative errors are the same for all coordinates, was used in fitting this line and also in fitting lines to the data from other specimens. In this case, the position of the line is little affected by how the data points are weighted. If the line is considered to be an isochron, the slope corresponds to an age of 291 Ma and the initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratio is 295.5. Note that uncertainty in the intercept must be comparable to the estimated uncertainty in the individual $^{40}\text{Ar}/^{36}\text{Ar}$ data, that is about one percent. That the data actually fit the line better than they probably should, given this level of uncertainty, does not reduce the uncertainty. It is not likely that having the missing potassium content of the salt dissolved in the second step would make much difference in interpretation of the results. If that salt had a potassium content equal to the average value for the rest of the salt from this specimen (as suggested by values given in brackets in Table 3-4), then the best-fit line would have a slope corresponding to an age of 299 Ma and an intercept of 293.8, as indicated by the dashed line on the figure. The scatter of points about this line is more like what one should expect, given the estimated analytical errors. Neither the slopes nor the intercepts differ significantly for these two lines.

On a similar diagram (Figure 3-3), the data for SDS-9 are also seen to be well correlated. Because of the low range of values for the $^{40}\text{K}/^{36}\text{Ar}$ ratio in this specimen, there is a corresponding small range in the $^{40}\text{Ar}/^{36}\text{Ar}$ values

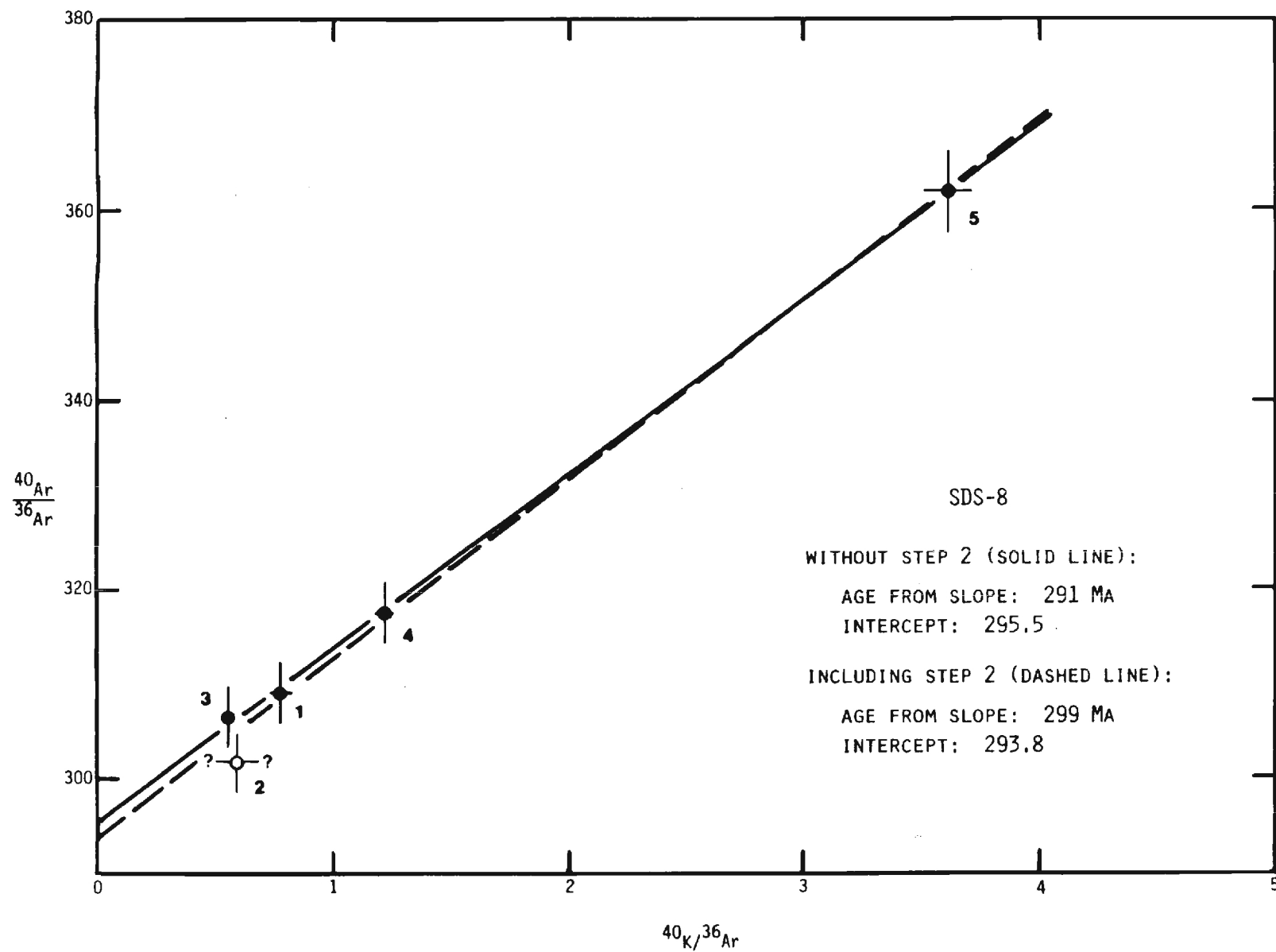


Figure 3-2. Potassium-Argon Isochron Diagram for SDS-8

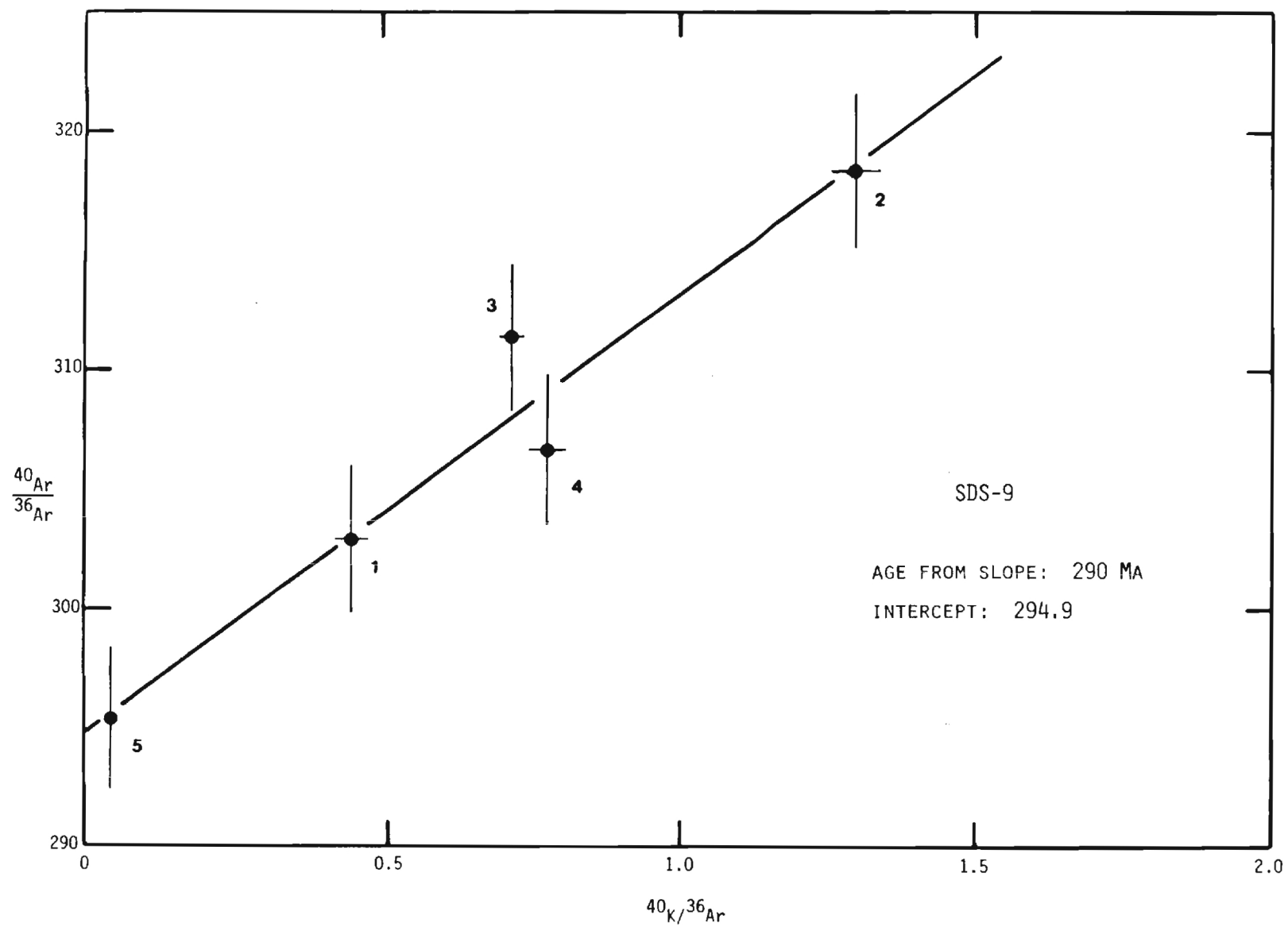


Figure 3-3. Potassium-Argon Isochron Diagram for SDS-9

and the analytical errors for this coordinate are quite large on the scale of this figure. Given the magnitude of these errors, all of the data points may be considered to be on the best-fit line, which has been calculated in the same manner as that for SDS-8. The slope of this line corresponds to an age of 290 Ma and the intercept is 294.9. Clearly, the best-fit lines for the two specimens from the 2600.3-foot depth are indistinguishable. The slopes of these lines are not defined very precisely, however, because both specimens have relatively low $^{40}\text{K}/^{36}\text{Ar}$ ratios.

Figure 3-4 is a diagram of the data for SDS-7, which also show a high degree of correlation. The ratios for this specimen have generally much greater values than for SDS-8 and SDS-9, and the uncertainties in the ratios are comparable to the size of the points plotted, except in one case. The best-fit line has a slope corresponding to an age of 262 Ma and an intercept of 283. Two of the data points fall further away from the line than should be expected from the estimated analytical errors. These are the points for the second and third steps, and their respective deviations from the line are in the senses one would expect if some of the potassium from the large fluid inclusion, which opened during step 2, was carried over into step 3. If these two steps are combined into one, as indicated on the diagram by an open circle, then the four resulting data points for SDS-7 fit very well a line with an intercept of 284 and a slope corresponding to an age of 261 Ma. This line is indistinguishable from the original one on the graph. Compared to the best-fit lines for SDS-8 and SDS-9, the slope is much better determined for SDS-7, but the intercept is less well determined because all the data points are far from the vertical axis in comparison to some of the data points for the other two specimens.

The data for the first two specimens analysed do not have the high degree of correlation shown by the data from SDS-7, -8, and -9. Figure 3-5 presents the data from SDS-6. The best-fit line for these data has a slope corresponding to an age of 146 Ma and an intercept of 342. The scatter of the data about this line far exceeds the uncertainty in the data. This situation would not be much improved if one were to discount the data from steps 1 and 6, in which very little of the specimen was dissolved and which may have included some superficial atmospheric argon contamination. Since the potassium analyses suggest that some potassium from the largest fluid inclusion in this specimen may have been carried over into steps 6 and 7, after the inclusion

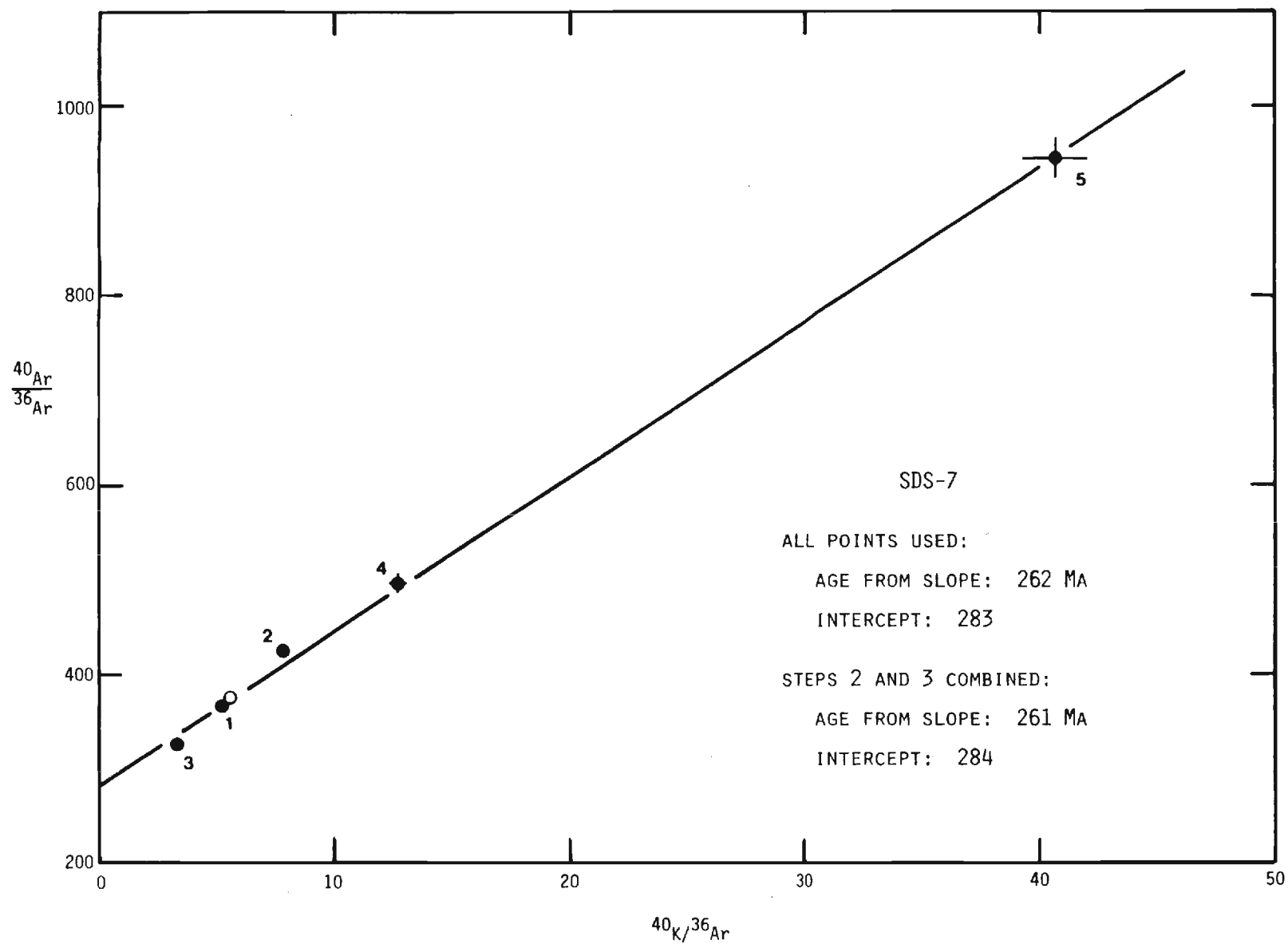


Figure 3-4. Potassium-Argon Isochron Diagram for SDS-7

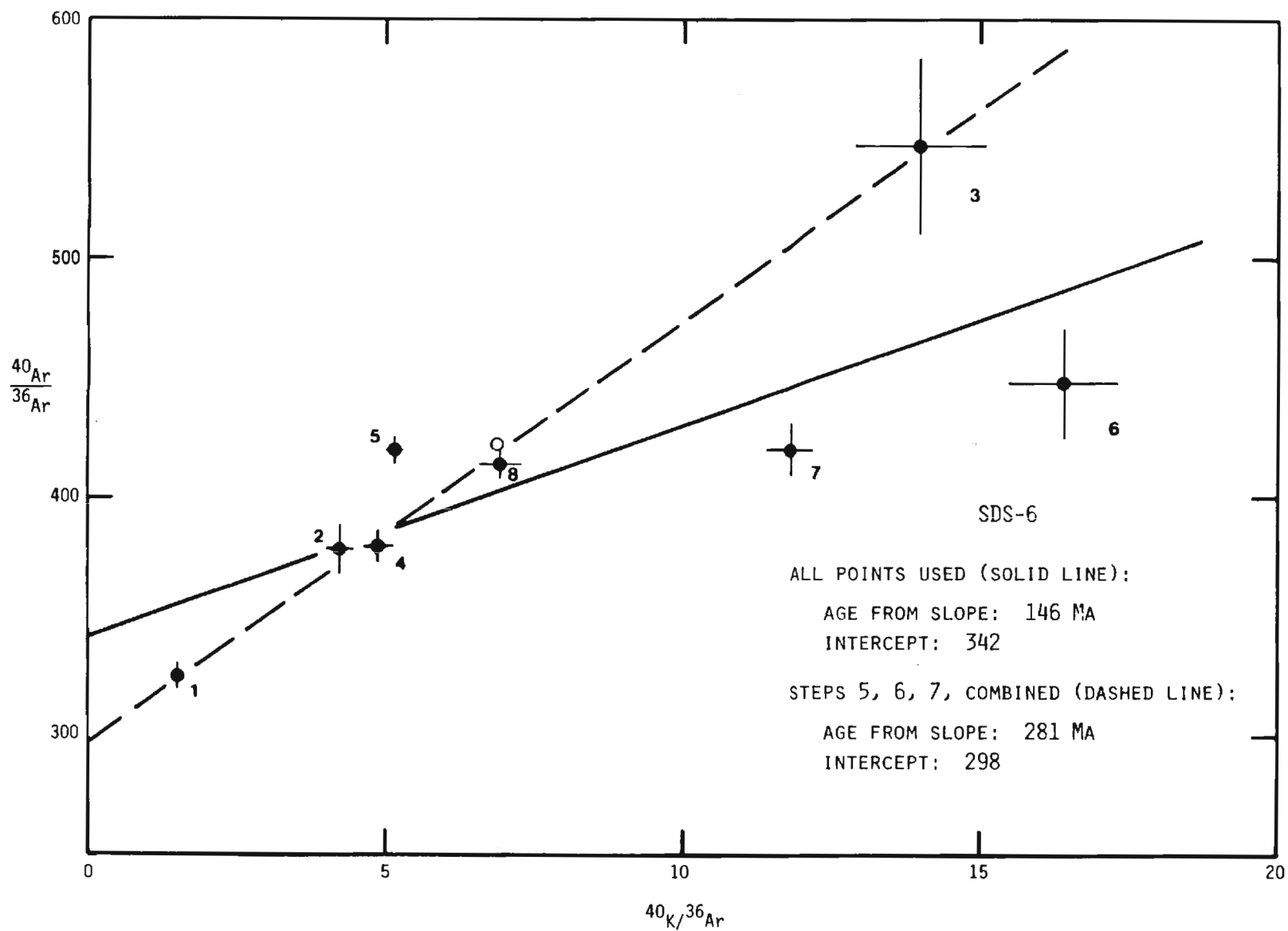


Figure 3-5. Potassium-Argon Isochron Diagram for SDS-6

opened in step 5, it is reasonable to consider the set of data after combining the data from steps 5, 6, and 7. Such a combination, shown as an open circle on the diagram, produces a remarkable improvement in the degree of correlation, and the (dashed) line that best fits the new set of data has parameters that are much more like the best-fit lines seen for the other specimens, a slope corresponding to an age of 281 Ma and an intercept of 298.

The estimated analytical errors for the first specimen analysed, SDS-5, are greater than for the other specimens, partly because of the experimental nature of the work with the first specimen and partly because the mass spectrometer was becoming unstable as failure of its filament was approaching. Figure 3-6 shows the data for this specimen. The line that best fits these data, shown as a solid line on the figure has a slope corresponding to an age of 217 Ma and an intercept of 308. As in the case of SDS-6, the deviations of some of the points from this line are greater than the estimated errors. The deviations of the points for steps 3 and 4 are reminiscent of the pattern originally shown by the points that were combined in the case of SDS-6. Since the largest fluid inclusion in SDS-5 opened during the third step, it is interesting to see the effect of combining the data for steps 3 and 4, even though there is no indication from the potassium data that potassium may have been carried over from step 3 into step 4. When these steps are combined, as shown by an open circle on the diagram, the best-fit line has a slope corresponding to an age of 261 Ma and an intercept of 294. This line is shown as a dashed line on Figure 3-6. Although the parameters of this line are consistent with those of the best-fit lines obtained for the other specimens (after combining data points in some cases), the degree of correlation is not as great as in the other cases.

The procedure of combining data from steps where large fluid inclusions opened with data from one or more subsequent steps, on the assumption that some potassium from the inclusions was carried over into the following step(s), appears to be justifiable not only from evidence obtained from the individual specimens (that is, the elevated potassium levels observed in steps following the opening of inclusions and the improved correlation of the data for individual specimens when data are so combined) but also because it brings the parameters of all the best-fit lines into reasonable agreement. The best-fit lines obtained after combining data in this way all have slopes corresponding to ages in the range 261 Ma to 291 Ma, and all of the intercepts are in

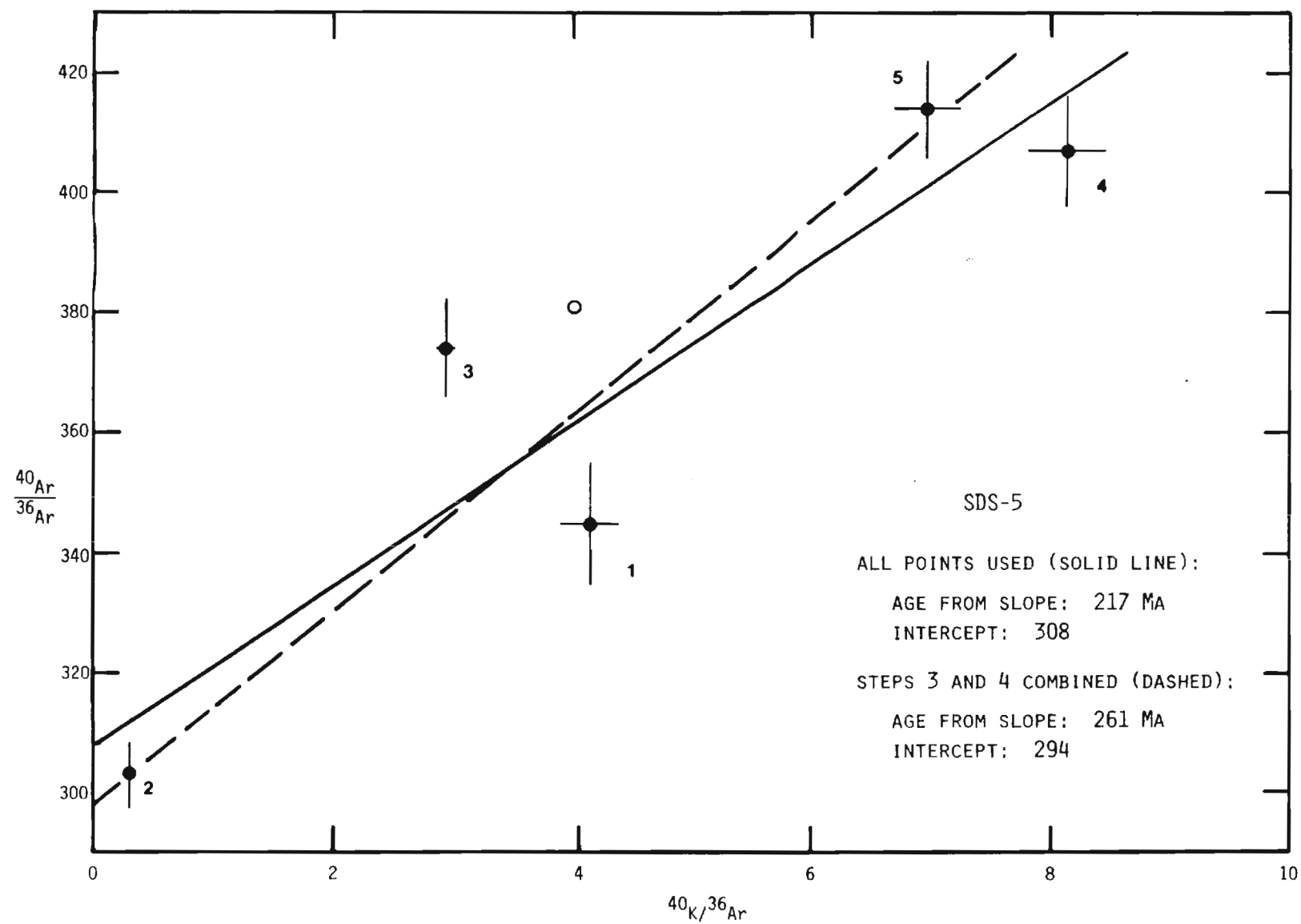


Figure 3-6. Potassium-Argon Isochron Diagram for SDS-5

the range 284 to 298. Because the intercepts do not differ significantly from the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of atmospheric argon, there is no need to be concerned about the possible influence of contamination of the specimens with atmospheric argon during their preparation. Thus, the data from the first step in dissolution of each specimen have been included in computation of the best-fit line for the specimen, even though these data may have been affected by some atmospheric argon recently acquired by the specimen.

3.3.4 Results Obtained by Crushing Specimens in Vacuum

The data obtained in experiments in which six specimens having fluid inclusions were crushed in vacuum are presented in Table 3-6. The data are given in the order in which the experiments were carried out. The first specimen crushed, from a depth of 2599.8 feet, had a few millimeter-size fluid inclusions. In the first crushing experiment, the amount of argon released was so great that it far exceeded the measurement range of the mass spectrometer. Special procedures were used to reduce the amount of argon to a measureable level, but these may have caused some isotopic fractionation of argon within the apparatus. So the fact that the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio measured is slightly below that of atmospheric argon is not likely to be significant. Although the large amount of argon is presumed to have come from the specimen, it is possible that argon was released from the crushing apparatus as a consequence of mechanical strain during the crushing procedure. The specimen was further crushed and the much smaller amount of argon so released was found to be isotopically identical to atmospheric argon. Afterward the crushed material was soaked in absolute ethanol in an attempt to extract the potassium that had been in the fluid inclusions. About 150 mg of salt was dissolved in the ethanol, of which 210 μg was potassium.

Two other specimens from the 2599.8-foot level were crushed. These specimens were selected because they had only very small fluid inclusions, so that the mass spectrometer would not be overwhelmed with argon. The amounts of argon released by crushing these specimens were well within the range of the instrument. One released 52 pmol of argon with an isotopic composition like that of atmospheric argon. The other released only 3.9 pmol of argon, which was slightly enriched in ^{40}Ar .

Table 3-6. Data From Fluid-Inclusion Bearing Specimens Crushed in Vacuum

Depth	Potassium Recovered ^(a)	$^{40}\text{Ar}/^{36}\text{Ar}$	^{40}Ar	$^{40}\text{Ar}^*/^{40}\text{Ar}$	$^{40}\text{Ar}^*$	Seeming Age ^(a)
Specimen	(μg)	$\times 10^{-3}$	(pmol)	(%)	(pmol)	(Ma)
<u>2599.8 feet</u>						
1	213	{ 292.4	5500	-	-	-
		295.4	181	0.0	-	-
2		295.8	52	0.1	0.05	
3		304.0	3.9	2.8	0.12	
<u>2509.8 feet</u>						
1	64	332	165	11.0	18.2	1170
B2	15	304.6	167	3.0	5.0	1310
A2	12	406	7.3	27.2	2.0	770

(a) It is probable that not all of the potassium from the fluid inclusions was recovered. The age values are referred to as "seeming ages" because they are based on inadequate potassium measurements.

Three specimens from the 2509.8-foot depth were selected for crushing. These each contained an inclusion with dimensions on the order of a millimeter. In each case, the argon released was enriched in ^{40}Ar , the maximum enrichment corresponding to 27% radiogenic argon. Ethanol was used in an attempt to extract the potassium from the inclusions opened in these crushing experiments. The amounts of salt dissolved in the ethanol were in the range 63 to 83 mg, and the potassium contents as indicated in the table range from 12 to 64 μg . Apparent ages based on the amounts of potassium recovered are several times greater than the ages associated with the best-fit lines from the isochron diagrams for the stepwise dissolution experiments. The large age values are likely a consequence of incomplete extraction of potassium by the ethanol.

These crushing experiments were actually done prior to the stepwise dissolution work, and they were viewed as preliminary experiments intended to show the typical amount of argon in the fluid inclusions and to identify portions of the core sections where some radiogenic argon is present in fluid inclusions. There is no obvious way to obtain accurate potassium-argon ages from the fluids released in such crushing experiments, short of working with very large inclusions in an apparatus specially designed for such work.

Given the uncertainty in the effectiveness of the potassium recovery and some uncertainty about the source of the argon released during crushing, the data obtained are consistent with the data from the stepwise dissolution work. The points of agreement are as follows:

- (1) Millimeter-size fluid inclusions contain relatively large amounts of potassium, 10 μg or more.
- (2) Radiogenic argon is present in millimeter-size inclusions in sufficient quantities to yield apparent ages of hundreds of millions of years.
- (3) Salt from about 2600 feet deep in the Grabbe #1 well contains more atmospheric argon than salt from about 2510 feet deep, and has correspondingly smaller proportions of radiogenic argon.

3.4 DISCUSSION

According to a current geological time scale (Harland *et al.*, 1982), the rock salt of the lowermost Upper Permian, San Andres Formation should be about 255 million years old. The ratio $^{40}\text{Ar}/^{36}\text{Ar}$ in the Permian atmosphere should have been slightly smaller than that in the modern atmosphere, but models for the isotopic evolution of atmospheric argon, such as that of Ozima (1975), suggest that the difference should be very small. The data obtained by stepwise dissolution of these five salt specimens are, if the data from certain steps are combined as described above, generally very well correlated, having best-fit lines with slopes that correspond to ages in the range 261-291 Ma and intercepts in the range 284-298.

An obvious interpretation of these data is that the best-fit lines correspond closely to the isochrons that would be expected for salt specimens that formed in Permian time with initial argon of atmospheric composition. For the specimens to yield such "internal" isochrons requires that potassium and argon have remained fixed within the specimens on a scale of millimeters (that is, the scale on which different portions of the specimens were separated in the process of stepwise dissolution) for virtually the entire time since the rock was deposited.

An important aspect of the interpretation of the best-fit lines as internal isochrons is that fluid inclusions of significant size are included in most cases. If the combining of data for steps where large fluid inclusions opened with data from one or more subsequent steps, on the assumption that some potassium was carried over, is legitimate, then potassium and argon from these large fluid inclusions are correlated in the same way as they are in the rest of the salt. In other words, these fluid inclusions must have behaved individually as closed systems since Permian time. (One cannot rule out the possibility that there has been some interchange of potassium and argon between the inclusions and the salt immediately surrounding them.) An alternative explanation of the data is to discount the importance of the hypothetical carry-over of potassium. The conventional apparent ages for the steps where fluid inclusions opened are generally well in excess of 260 Ma (not so for the second step for SDS-7 in which a large and apparently potassium-rich inclusion opened, for which the apparent age is 264 Ma), which may suggest that some radiogenic argon has found its way into the inclusions, leaving

behind the potassium from which it had been formed. But even if this is the correct interpretation, there is in each case a corresponding apparent deficit of radiogenic argon in one or two succeeding steps which is usually just right to bring the data for a combination of steps into correlation with the data from the rest of the specimen. If radiogenic argon has migrated preferentially into the large fluid inclusions, it appears to have done so from the salt immediately surrounding the inclusions.

For each of the specimens, the relatively large range of values for the ratio $^{40}\text{K}/^{36}\text{Ar}$ is due mostly to variability in the amount of ^{36}Ar released per unit mass of salt dissolved rather than to variability in the potassium content of the salt. The variability in amount of ^{36}Ar is not surprising, given the non-uniform distribution of small fluid inclusions noted for most of the specimens. An important question is whether the ^{36}Ar is largely from the modern atmosphere or from the Permian atmosphere (or possibly from atmospheric argon incorporated at some intermediate time). Since the Permian atmosphere is not expected to have had a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio appreciably different from that of the modern atmosphere, and since the intercepts of the best-fit lines obtained in this work do not differ significantly from the ratio for the modern atmosphere (295.5), the isotopic data do not provide a direct answer to this question. But consideration of the $^{40}\text{K}/^{36}\text{Ar}$ ratio as a function of step number and of the general correlation of radiogenic argon and potassium released in the dissolution steps suggests an indirect answer.

If most of the ^{36}Ar in the specimens had been from atmospheric contamination introduced artificially (at any time since the drilling began), one would expect that the influence of such argon would be greatest in the first step of dissolution and progressively less in the later steps. Perusal of the step numbers on the figures suggests that there may be such a pattern -- the first step is usually among the leftmost points on the graphs and the last two steps are usually (three out of five cases) the rightmost points. But the step in which the most ^{36}Ar (relative to potassium) was released was the first step in only one case (SDS-6), and in one important case (SDS-9) the amount of ^{36}Ar released in the last step was much greater than in the other steps for that specimen, as well as in any of the steps for all the other specimens. In this particular case the unusually large amount of ^{36}Ar appears to have been associated with a portion of the specimen that was exceptionally rich in mineralogical impurities, an association that is not hard to understand if the

^{36}Ar is from atmospheric argon trapped as the halite crystal grew over the impurities.

The points plotted for the steps in which large fluid inclusions opened (known with reasonable certainty only for specimens SDS-5, -6, and -7) have intermediate $^{40}\text{K}/^{36}\text{Ar}$ ratios but they are well to the left of at least one other point in each case. It is clear that ^{36}Ar is concentrated in the fluid inclusions relative to some portions of the salt, and for those inclusions for which a high potassium content is evident (in SDS-6 and SDS-7) the relative concentration of ^{36}Ar is quite large. Such enrichment would be expected if the inclusions formed from a brine that was in equilibrium with air as the salt crystallized.

Although there are not enough data for a firm conclusion, it seems evident that much of the ^{36}Ar in these specimens was deep within the specimens rather than preferentially near the outer surfaces as one might expect if artificial contamination (for example, by way of temporarily opened fractures) were a major factor. Relatively large amounts of ^{36}Ar appear to have been associated with mineral impurities and with fluid inclusions, as one would expect if such argon had been trapped within the halite crystals as they grew. The good correlation between radiogenic argon and potassium, on a scale of millimeters within these crystals (including the large fluid inclusions), implies that the specimens have in large part been closed systems for about 260 million years (using the best-determined slope, that for SDS-7, as the basis for selecting an age value) but does not rule out the possibility that extraneous argon has permeated the salt more recently along restricted pathways, for example along grain boundaries. But the specimen which had the largest amount of ^{36}Ar , SDS-9, was a fragment of a single crystal having no boundary between large crystals; so was SDS-5, which released an unusually large amount of ^{36}Ar during its second step of dissolution. The specimens that were composites of more than one crystal, SDS-6 and SDS-8, each gave $^{40}\text{K}/^{36}\text{Ar}$ ratios that are generally comparable to the other specimen(s) from the same depth, so there is no indication of a concentration of ^{36}Ar along the boundaries between the (large) crystals. The weight of the evidence is in favor of the idea that most of the atmospheric argon in these specimens is argon trapped from the Permian atmosphere. The data suggest that there has been no significant trapping of extraneous argon that might have permeated the specimens more recently, but the data are not sufficient to rule out this possibility.

In summary, the data obtained in the stepwise dissolution experiments and in the crushing experiments are all consistent with the interpretation that the salt and the inclusions contained within the salt formed in Permian time and have been little disturbed, if at all, since that time. The only disturbances suggested are the possible migration of radiogenic argon from the salt into the fluid inclusions, over distances of not more than a few millimeters, and the possible incorporation of relatively small amounts of argon from the modern atmosphere near the surfaces of the specimens. It is important to emphasize that the data rule out the possibility of any major recrystallization of the salt since the filling of the Palo Duro basin was essentially completed in the Triassic Period. If such recrystallization has occurred, it would be necessary that potassium and radiogenic argon were distributed proportionately in the recrystallized material, a most unlikely possibility given the disparate natures of the two elements and given the presence of a lot of non-radiogenic argon that is distributed quite differently than the potassium.

A final note is necessary because the best-fit lines have slopes that are a little greater than that of an isochron for a rock that is 255 Ma old (although none may be significantly greater). The uncertainties in the time scale from which the 255-Ma age for the San Andres Formation was taken are such that the rock may well be at least 260 Ma old. But it is quite likely that the slopes are a little too high because of analytical error. The very low potassium content of the salt and the experimental nature of the stepwise dissolution procedure, as it was used in this work, both have contributed to making the estimated relative errors considerably greater than normal for geochronometric work. Inspection of the error bars on the isochron diagrams shows that all the data that fit the best-fit lines as drawn (using the combined data -- open circles -- for steps associated with the opening of fluid inclusions) would also fit isochrons with slopes corresponding to 255 Ma. But since three out of five of the best-fit lines have slopes noticeably higher than that of a 255-Ma isochron, one should note the possibility that a systematic error is present. Some error in calibration is possible, which would have affected the data from all specimens equally. Because a positive correction was made to the amount of argon measured in almost every case, on the basis of a following blank run, and because there is a likelihood that there was some degree of overcorrection in this process in cases where the original amount of ^{36}Ar was rather small, it is possible that the slopes are a

little steeper than they should be because of such systematic overcorrection. (The possibility of overcorrection arises because some ^{36}Ar measured in the blank runs may have come from the apparatus.)

There is another reasonable explanation of the tendency of the best-fit lines to be slightly steeper than a 255-Ma isochron. It seems unlikely that rock salt should have formed in a way that meets the criterion of isotopic homogeneity in argon, at the time of closure, to the degree necessary for highly accurate isochrons from rock of very low potassium content. Certainly argon is not distributed homogeneously in the rock, and it seems likely that the rock salt may have been exposed to argon of differing isotopic compositions at different times during deposition and diagenesis. Argon of the Permian atmosphere would have been dominant at the time of initial crystallization of the salt, but argon with a significant radiogenic component may have been migrating through the rock during diagenesis. Such argon may have been derived locally by alteration of detrital biotite in the highly saline environment or of other potassium minerals in the mudstones associated with the salt. If such argon was incorporated into the rock but did not generally mix with atmospheric argon trapped earlier, it would have a greater effect (on average) on the isotopic composition of argon in those portions of the salt having lesser amounts of atmospheric argon. This could have produced a correlated variation in the isotope ratios within the rock at the time of closure that would have been in the correct sense to cause the data measured now to fit a line steeper than a correct isochron. To determine whether or not such a possibility is important would require more accurate data, from more specimens.

4 CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

Silt-size ($>2\ \mu\text{m}$) silicate fractions separated from the lowermost Upper Permian, San Andres Formation, which is about 255 million years old, have illite crystallinity indices that indicate a high-temperature origin and potassium-argon apparent ages of about 345 Ma. These data show that the material is detrital in origin and suggest that potassium-argon ages near 345 Ma are characteristic of the source material.

Mineralogical investigation of clay-size ($<2\ \mu\text{m}$) silicate fractions indicate that potassium is present in at least three minerals -- illite, K-feldspar, and chloritic material. Most of the potassium is in the illite. The sharpness of the illite peaks observed by x-ray diffraction would normally be interpreted as indicating illite formation at temperatures above 200°C , but since little is known about the character of illite that may form in an evaporitic environment, an authigenic origin for this illite cannot be ruled out. The apparent ages obtained for these fractions range from 254 Ma to 322 Ma (discounting one sample, which was mistakenly analysed after a heat treatment), which suggests that they may be mixtures of authigenic illite and detrital material. The x-ray data, which show that these samples are composites of three types of potassium-bearing minerals, and a fairly evident inverse relation between the illite crystallinity index and apparent age for this set of samples are consistent with this concept of mixed ages. But the data available are not sufficient to show conclusively whether or not authigenic illite is present.

Typically, the clay-size fraction of a shale has a potassium-argon age somewhat less than the (depositional) age of the rock, a consequence of the effects of diagenesis or burial metamorphism. That the apparent ages of the clay-size material from the San Andres formation range upward from the depositional age implies a minimum of diagenetic change during burial and rules out the possibility of significant alteration of the illite long after deposition.

Measurement of potassium and argon isotopes released by stepwise dissolution of salt specimens from the San Andres formation show generally good correlation between the ratios $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{40}\text{K}/^{36}\text{Ar}$. If the data from certain steps in the dissolution of samples having large fluid inclusions are

combined, the correlation becomes very good for four out of five specimens analysed and the best-fit lines for all specimens have similar parameters. Interpreted as isochrons, these best-fit lines correspond to ages in the range 261 Ma to 291 Ma and initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in the range 284 to 298. Given the uncertainty in the data and some uncertainty in the date of the beginning of the Late Permian Epoch, none of the best-fit lines differs significantly from an isochron for rock formed at the beginning of that Epoch with atmospheric argon as the initial argon (assuming argon of the Permian atmosphere was not appreciably different from modern atmospheric argon).

Because of the very low potassium content of the salt specimens and because this work is the first in which stepwise dissolution of salt for potassium-argon analysis has been attempted, the data are not as accurate as in normal geochronometric work. But the data are sufficiently accurate to rule out significant alteration of these salt specimens since the filling of the Palo Duro basin was (essentially) completed in the Triassic Period.

Data points associated with the opening of large (millimeter-size) fluid inclusions show more deviation from the best-fit lines than do most other points. Such deviation is thought to be an artifact of the experimental procedure, in which not all of the potassium from a fluid inclusion may be separated from the salt specimen in the step in which argon is released from the inclusion. The effect of this presumed carry-over of potassium from one step to the next may be eliminated by combining the data for the steps involved. An alternative explanation of the data is that some argon has migrated into the fluid inclusions from the surrounding salt. In any case, the good correlations obtained after combining data from selected steps, and the consistency among the parameters for the best-fit lines for all specimens, show that potassium and argon have not moved over distances of more than a few millimeters within these specimens (fluid inclusions and all) since soon after the rock was formed.

Data obtained by crushing specimens that contained fluid inclusions show that such inclusions are enriched in potassium relative to the salt and that some of them contain radiogenic argon in amounts corresponding to apparent ages of hundreds of millions of years. The release of relatively large amounts of atmospheric argon in some cases made it impossible to detect radiogenic argon that may have been present in the inclusions, and the nature of the crushing experiments precluded accurate measurement of potassium from those inclusions that had measureable radiogenic argon.

In summary, all of the data obtained in this study, from silicate materials and from salt specimens, including the fluid inclusions within the salt specimens, are consistent with a conclusion that the rock has not been recrystallized or otherwise appreciably altered since soon after it was deposited in the Permian Period. The data rule out any significant metamorphism of the formation, and for the two horizons from which salt specimens were taken for detailed study they rule out any water-rock interactions that would have affected the bulk of the rock (including the larger fluid inclusions) since the filling of the sedimentary basin was complete.

4.2 RECOMMENDATIONS

In order to determine whether authigenic illite is a significant constituent of the clays present in the San Andres Formation, a follow-up study should include a more detailed study of a smaller number of samples.

^{40}Ar - ^{39}Ar studies of various size fractions could provide information about the apparent ages of the feldspars and the coarser illite (Sedivy et al., 1984). Conventional potassium-argon ages for clay samples separated into narrow size ranges below 2 μm , which may conveniently be obtained by the micro-analytical technique, should show whether there is a major, fine-grained illite component about 255 million years old, which would be evidence of the presence of authigenic illite, or whether there is a continuous range of apparent ages for the finer illite, which would suggest that such illite is detrital material slightly altered by diagenesis. Since an appreciable amount of potassium is present in much of the chloritic material, potassium-argon analyses of isolated chloritic material could indicate whether such material formed by alteration of detrital illite or whether authigenic illite layers formed contemporaneously with the chlorite. Such a study should be complemented by scanning electron microscopy with energy-dispersive x-ray analysis of the materials.

The results obtained by stepwise dissolution of salt show that this new method has great potential for geochronometric study of rock salt of low potassium content. The experience gained in the first set of analyses by this method provides a basis for improved accuracy in future work. The anomalous concentration of argon in recondensed water within the dissolution apparatus, which was a significant problem in the present study, can be avoided by a change in design of the apparatus. The problem of carry-over of potassium from one step to the next can be minimized by not terminating steps immediately after large fluid inclusions open, but rather continuing each step until it is reasonably certain that all potassium from the opened inclusion has been washed from the specimen. Improved precision in the apparent ages calculated from the slopes of the best-fit lines may be obtained by using somewhat larger specimens to ensure that enough ^{36}Ar for accurate measurement is released in each step. It should also be helpful to concentrate work on specimens with particularly large (greater than 1 mm) fluid inclusions. With larger amounts of ^{36}Ar available for measurement and with frequent calibration

runs, the accuracy of measurement of $^{40}\text{Ar}/^{36}\text{Ar}$ could be improved so that the relative error for measured values of this ratio is a few tenths of one percent. (Possibly better accuracy could be achieved with new equipment.) Such an improvement would permit accurate determination of slopes for best-fit lines even in cases where the range of observed $^{40}\text{Ar}/^{36}\text{Ar}$ values is small. It would also allow the intercepts of the best-fit lines to be determined with high accuracy.

As noted in the discussion of the potassium-argon isochron work (Section 3.4), it is not clear whether the differences between the slopes of the best-fit lines obtained in this work and that of a 255-Ma isochron are caused by analytical error or by failure of the specimens to have met precisely the criteria necessary for interpretation of the lines as isochrons (or in part by incorrectness of 255 Ma as the age of the formation). If the problem has been largely a matter of analytical error (and uncertainty in the age of the formation), then the improvements in method suggested above might allow the age of the Palo Duro salt to be determined with an uncertainty of only a few million years. Furthermore, it might be possible to establish a slight difference between the initial argon in the salt and modern atmospheric argon. (Although the difference in $^{40}\text{Ar}/^{36}\text{Ar}$ between the Permian atmosphere and the modern atmosphere is probably not detectable when the error of measurement is about one percent, the difference may well be detectable if the error is reduced to a small fraction of one percent.) Since it appears that some fluid inclusions in the salt are particularly rich in argon, to the extent that their radiogenic argon content is negligible, it would be very useful in interpretation of the age of such inclusions to be able to distinguish between Permian atmospheric argon and modern atmospheric argon.

It would not be surprising to find that more accurate analyses do not improve the way the potassium-argon data fit mid-Permian isochrons, because it seems rather unlikely that the rock salt has been completely undisturbed since shortly after deposition. If post-depositional disturbance has occurred, more accurate data would allow more confident interpretation of the nature of such disturbance. Although the data of the present study rule out any major, recent recrystallization of the salt at the two levels of the Grabbe #1 well from which salt specimens were taken, the possibilities of minor, recent disturbance at these levels and of recent disturbance of salt at other levels cannot confidently be ruled out without more accurate and more extensive analytical work.

The vacuum-crushing experiments of this study show that measureable radiogenic argon is present in some of the fluid inclusions in the Palo Duro salt. If a more sophisticated apparatus were constructed to allow large inclusions to be opened, in vacuum, in a controlled way, very useful potassium argon relations should be revealed. It may be possible to physically separate the salt formed by evaporation of water from a large inclusion (dimensions of at least a few millimeters) from the halite that originally surrounded the inclusion, so that the potassium content of that salt can be measured. Even better would be a device that could withdraw the brine from an inclusion before the water has a chance to evaporate appreciably. Since there are components available commercially that would allow for viewing and manipulation of a specimen within an ultra-high vacuum chamber, it should not be particularly difficult to construct an apparatus for controlled withdrawal, in vacuum, of fluids from relatively large inclusions.

5 REFERENCES

- Bodine, M. W., and T. H. Fernalld, 1973. "EDTA Dissolution of Gypsum, Anhydrite, and Ca-Mg Carbonates", Journal of Sedimentary Petrology, Vol. 43, pp. 1152-1156.
- Cox, A., and G. B. Dalrymple, 1967. "Statistical Analysis of Geomagnetic Reversal Data and the Precision of Potassium-Argon Dating", Journal of Geophysical Research, Vol. 72, No. 10, pp. 2603-2614.
- Dalrymple, G. B., and M. A. Lanphere, 1969. Potassium-Argon Dating, Principles, Techniques and Applications to Geochronology, W. H. Freeman and Company, San Francisco, CA, 258 p.
- Dooley, R. D., and J. M. Wampler, 1983. "Potassium-Argon Relations in Diabase Dikes of Georgia -- The Influence of Excess ^{40}Ar on the Geochronology of Early Mesozoic Igneous and Tectonic Events", Studies Related to the Charleston, South Carolina, Earthquake of 1886 -- Tectonics and Seismicity, Geological Survey Professional Paper 1313, G. S. Gohn, ed., U. S. Government Printing Office, Washington, DC, pp. M1-M24.
- Harland, W. B., A. V. Cox, P. G. Llewellyn, C. A. G. Pickton, A. G. Smith, and R. Walters, 1982. A Geologic Time Scale, Cambridge University Press, Cambridge, 131 p.
- Hayatsu, A., and C. M. Carmichael, 1977. "Removal of Atmospheric Argon Contamination and the Use and Misuse of the K-Ar Isochron Method", Canadian Journal of Earth Sciences, Vol. 14, pp. 337-345.
- Mullin, C. W., 1982. Geology of the Caprock and Salt Stock of the Richton Salt Dome, M.S. Thesis, Georgia Institute of Technology, Atlanta, GA, 157 p.
- Ozima, M., 1975. "Ar Isotopes and Earth-Atmosphere Evolution Models", Geochimica et Cosmochimica Acta, Vol 39, pp. 1127-1134.

Sedivy, R. A., J. M. Wampler, and C. E. Weaver, 1984. "Potassium-Argon", Shale-Slate Metamorphism in Southern Appalachians, C. E. Weaver and Associates, Elsevier, Amsterdam, pp. 153-183.

Steiger, R. H., and E. Jäger, compilers, 1977. "Subcommission on Geochronology: Convention on the Use of Decay Constants in Geo- and Cosmochronology", Earth and Planetary Science Letters, Vol. 36, pp. 359-362.

Wampler, J. M., M. C. Thoroman, and A. Padan, 1985. "A Microanalytical Technique for Potassium-Argon Analysis of Clay", (Abstract), Geological Society of America, Abstracts With Programs, Vol. 17, No. 2, p. 141.

Wampler, J. M., and Y. Yanase, 1974. "Argon Adsorption and Trapping by Cold Trap Ice", (Abstract), EOS, Transactions American Geophysical Union, Vol. 55, p. 472.

Weaver, C. E., and Associates, 1984. Shale-Slate Metamorphism in Southern Appalachians, Elsevier, Amsterdam, 239 p.

York, D., 1969. "Least-Squares Fitting of a Straight Line With Correlated Errors", Earth and Planetary Science Letters, Vol. 5, pp. 320-324.