

# POTASSIUM-ARGON ANALYSIS OF DOMAL SALT BY STEPWISE DISSOLUTION

A. A. Hassanipak<sup>1</sup> and J. Wampler<sup>2</sup>

<sup>1</sup>*Department of Mining Engineering, Faculty of Engineering, University of Tehran,  
Tehran, Islamic Republic of Iran*

<sup>2</sup>*School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta,  
Georgia, USA*

## Abstract

Potassium-argon analysis by stepwise dissolution provides a way to measure in detail the distribution of argon isotopes and potassium in rock salt. The method can be used for salt that contains only trace amounts of potassium, because the potassium and argon in detrital silicates within the salt are not released during the dissolution. Water may be used as the solvent when relatively large amounts (one gram or more) of salt are to be dissolved in each step of the analysis. Methanol may be used when relatively small amounts of salt are to be dissolved in each step, in order to obtain high spatial resolution of the distribution of potassium and argon in the salt. Although preliminary analyses show that potassium-argon relationships in the deformed salt of salt domes can be very complex, analysis of these relationships by stepwise dissolution of properly chosen samples should provide useful isotope correlations in cases where the amounts of atmospheric argon and radiogenic argon in the salt are comparable.

## Introduction

Most radiometric dating work on sedimentary rocks has been directed toward establishing chronometric reference points for the geological time scale. As the Phanerozoic time scale has become well established [1], the emphasis in radiometric dating of sedimentary material has been changing. Radiometric methods can provide important information about the post-depositional history of sediments [2-4]. Evaporites are particularly susceptible to post-depositional change [5,6], and it will be important to establish the degree to which radiometric dating methods can reveal the history of such change.

Sylvite has been considered to be unreliable for radiometric dating because it is especially prone to argon loss [7,8], but in some cases the K-Ar age of sylvite is close to the absolute age corresponding to its stratigraphic position [9, 10]. Cambrian rock salt from the Siberian Platform

containing minor sylvite and carnallite was found by Tarasevich *et al.* [10] to yield K-Ar ages that reflect the age of the sediments in zones where crustal movement has been weak or non-existent. Wampler and Hassanipak [11] demonstrated that halite from bedded salt of the Palo Duro Basin of Texas (U.S.A.) contains small amounts of radiogenic argon even though potassium is only a trace constituent of the salt samples. By using a stepwise-dissolution technique, they were able to show that the radiogenic argon has remained localized within halite crystals for approximately 250 million years. The resolution of the stepwise-dissolution technique was sufficient to indicate that radiogenic argon has not moved within the salt over distances greater than a few millimeters.

These studies indicate that halide salts are satisfactory materials for geochronometric work. The susceptibility of sylvite to argon loss is probably due to its susceptibility to recrystallization rather than to a tendency for existing

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crystals to lose argon readily. Radiometric dating of halides as well as sulfates should be useful in establishing the post-depositional history of salt formations. In particular, it should be possible to establish the chronology of diagenetic recrystallization of bedded salts in cases where there has been no subsequent tectonic disturbance. For salt that has been tectonically disturbed, radiometric dating may provide important information about the timing of recrystallization of the salt.

The stepwise-dissolution technique provides a way to effectively separate a single evaporite specimen into multiple portions for the purpose of potassium and argon measurements. Because detrital silicate minerals that may be present in the salt will not dissolve, and because no heating of the argon-extraction apparatus is necessary during an analysis, the method can be sensitive to extremely small amounts of radiogenic argon in salt and thus can be useful for study of ordinary halite in which potassium is only a trace constituent [11]. The technique allows the analyst to determine the distribution of argon isotopes and potassium within the salt on a scale that is determined by the amount of salt dissolved in each step of the analysis.

### Apparatus and Procedures

There are three essential components of an apparatus for extraction of argon and potassium by stepwise dissolution of salt. These are shown schematically in Figure 1.

1. A *reaction vessel* to hold the salt and in which solvent vapor may be condensed to form a liquid that will dissolve part of the salt. There must be a way to drain the liquid, which will contain the dissolved salt, from the reaction vessel to a "sump" where the dissolved salt may be isolated for later potassium analysis.

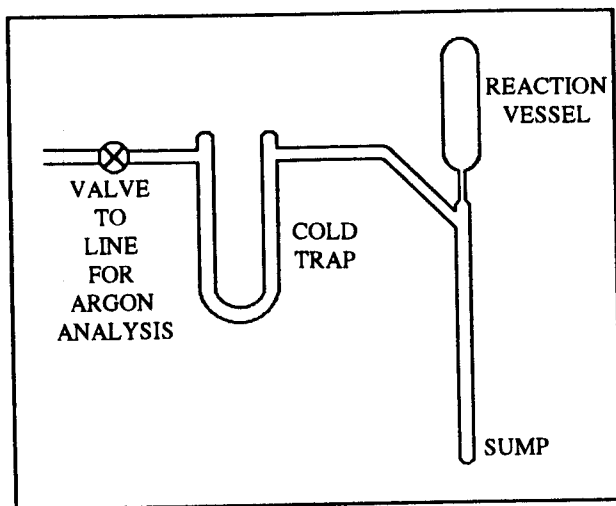


Figure 1. Schematic diagram of an apparatus for potassium-argon analysis of salt by stepwise dissolution

2. A *sump* in which the salt dissolved in the fluid that drains from the specimen may be collected. The design of the sump must allow the solvent to be distilled away from the salt and must provide for the salt dissolved in each step to be separated from that dissolved in the following step.

3. A *cold trap* in which the solvent vapor may be separated, by condensation, from the argon released during dissolution.

Such an apparatus is used in the following way for each step in an analysis. At the beginning of each step the argon and potassium from the previous step are removed from or isolated within the apparatus. A portion of the solvent is distilled to the reaction vessel so that salt may dissolve. The liquid containing the dissolved salt then drains to the sump. Fresh solvent may be redistilled to the reaction vessel as many times as necessary to dissolve the desired amount of salt. The argon is then transferred out of the apparatus for isotopic analysis, and the residual salt within the sump is isolated so that it may be analysed for potassium at a later time. (One way to isolate the residual salt is to distill the solvent to the cold trap and then seal the sump tube above the salt by glassblowing).

The key to separation of argon from the solvent vapor is the proper choice of temperature for the cold trap. The temperature of the trap must be low enough so that virtually all of the solvent vapor will be trapped, but it must be high enough so that argon will not be occluded in the ice formed by the condensing vapor. Liquid nitrogen may not be used as the coolant for the cold trap, because at the temperature of liquid nitrogen (-196°C) argon is occluded within the ice as it condenses [12]. A cold trap temperature of -110°C is sufficient to trap either water or methanol as solids (Fig. 2). The amount of water vapor or methanol vapor that will

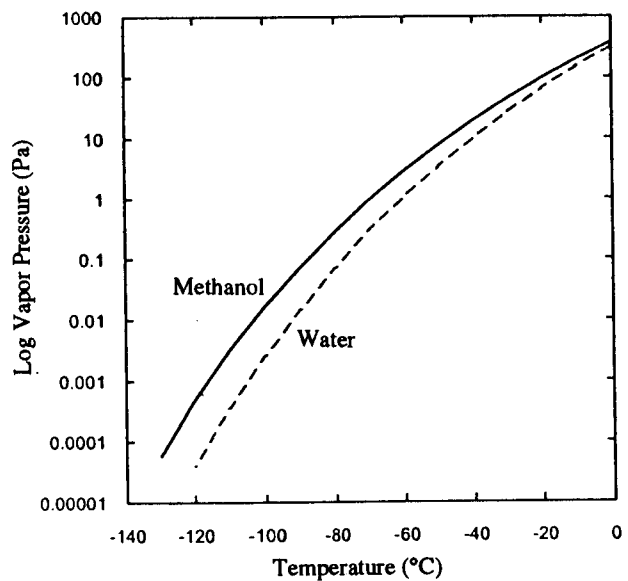


Figure 2. Vapor pressures of methanol and water as functions of temperature

pass through such a trap in the time required for transfer of the argon is negligible.

The use of water as a solvent limits the resolution of the stepwise-dissolution procedure because there is at the end of each step a film of brine that will not drain from the salt specimen. The potassium within such brine contributes to the potassium analysed for the next step, but the argon associated with such potassium is not carried over into the next step. Since the amount of salt in the undrained brine at the end of each step is of the order of 10 mg, water should not be used as a solvent unless the amount of salt to be dissolved per step is of the order of one gram.

Since the solubility of salt in methanol is about 25 times less than its solubility in water [13], methanol may be used as a solvent for potassium-argon analysis in steps involving much smaller amounts of salt. Furthermore, the surface tension of methanol is only about one-third that of water, so the amount of solution that does not drain from the specimen when methanol is the solvent is less than when water is the solvent.

It should also be possible to use a mixture of methanol and water as the solvent for stepwise dissolution of salt. The varying solubility of sodium chloride in methanol-water solutions of varying composition [14] is shown in Figure 3. Clearly, one may choose an appropriate mixture that would dissolve considerably more salt than pure methanol does, but in which salt is not nearly so soluble as in water. Figure 3 also shows the partial pressures (at 25°C) of methanol and of water over solutions of methanol and water of varying composition. The greater partial pressure of methanol allows the analyst to distill to the reaction vessel a portion of the liquid that is considerably

richer in methanol than the liquid remaining in the sump is. In this way, a dissolution step may be ended with a liquid in which salt is considerably less soluble than it would be if all the liquid were distilled to the reaction vessel.

In summary, water is a satisfactory solvent for potassium-argon analysis of salt by stepwise dissolution only if the amount of salt to be dissolved per step is of the order of one gram. Methanol should be used as the solvent when the amount of salt to be dissolved per step is substantially less than one gram. A mixture of methanol and water can be used to dissolve samples more rapidly than pure methanol will. By choosing an appropriate solvent, an analyst can be assured that the desired amount of salt can be dissolved in a reasonable period of time and that virtually all of the potassium dissolved during each step can be transferred from the reaction vessel to the sump.

### Applications to Domal Salt

#### Gibson Dome, Utah

The Gibson Dome area in Utah (U.S.A.) is within the Paradox Basin where there are widespread evaporites of Pennsylvanian (Carboniferous) age. Although there are salt anticlines in the northern part of the Paradox Basin, there are no salt diapirs in the basin [15]. (Gibson Dome is an ordinary structure, not a salt diapir). The Paradox salt represents a kind of rock salt for which potassium-argon studies may be particularly useful because potassium salts are finely disseminated within halite. The amount of potassium in the rock is greater than in many salt rocks, and because the potassium minerals are often present as inclusions within larger halite crystals, radiogenic argon may be retained within parts of the rock in spite of disturbances that have been severe enough to cause argon to move out of the potassium minerals.

Huff and Wampler [6] studied carnallite-rich samples of rock salt from the Gibson Dome No. 1 well using a technique in which argon was released in two steps, first from the carnallite and then from the remainder of the salt, by controlled heating. Their study indicated that radiogenic argon formed within carnallite has in some cases become trapped within the surrounding halite. Study of such rock salt by stepwise dissolution should provide more detailed information about the distribution of potassium and radiogenic argon.

Data obtained by dissolution of four samples of salt from the Gibson Dome No. 1 well are shown in Table 1. In this preliminary work, each sample was dissolved with water in one step rather than in multiple steps. The data show that the samples have been profoundly disturbed, for the apparent ages are discordant and are much less than the age of the Paradox Formation in which the salt occurs. Carnallite is particularly susceptible to argon loss [6], and

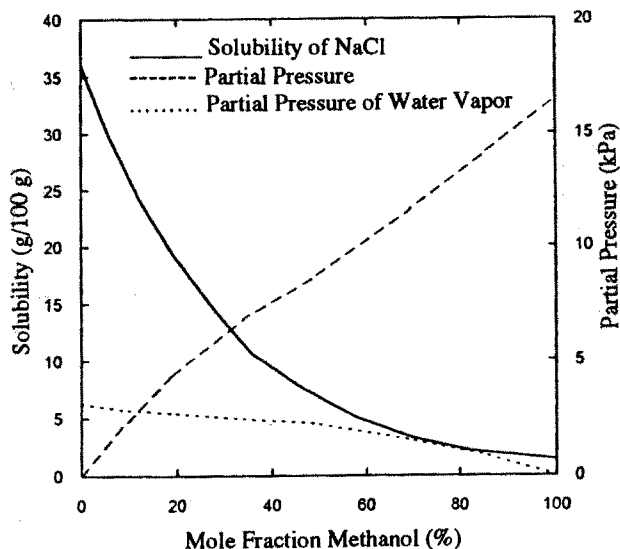


Figure 3. Solubility of sodium chloride in methanol-water mixtures and vapor pressures of methanol and water over such mixtures

**Table 1.** Potassium-Argon Measurements Obtained by Dissolution of Salt Samples from the Gibson Dome No. 1 Well, Utah, U. S. A.

Sample No.	Depth (m)	Potassium Content (%)	Radiogenic Argon % (pmol.g)		Apparent Age (Ma)
1	955	0.118	75.8	18.2	87
2	955	0.125	79.3	>14.2	>64
3	955	0.120	73.4	13.8	65
4	960	1.00	65.0	53.3	31

Note: Some of the radiogenic argon from Sample No. 2 was lost during the extraction of argon.

the especially low apparent age for Sample No. 4 (31 Ma) may be a consequence of the relatively high carnallite content of this sample.

Since the potassium content of the Gibson Dome salt is relatively high, samples of the salt could be dissolved in small increments with methanol to provide detailed information about the distribution of argon isotopes and potassium within the salt. Such a study should provide useful information about the timing of events that have caused recrystallization or other disturbances of this salt.

#### Diapiric Salt

Salt diapirs in southern Louisiana, U.S.A., include anomalous zones (also called shear zones) characterized by extensive shearing and tectonic lensing of the included clastic sediments. Such zones are prone to gas outbursts during mining, and the burst-prone volumes of salt are associated with inclusions containing gas under high pressure [16]. Several samples of rock salt from the Weeks Island Salt Dome have been partially dissolved for the purpose of argon isotopic analysis. The rock consists of deformed halite crystals that contain a multitude of small fluid inclusions and small mineral inclusions. The fluid inclusions contain gas at a pressure considerably higher than atmospheric pressure. The amount of gas evolved by dissolution of the salt is of the order of 0.1 ml per gram of salt. The salt contains a relatively large amount of argon, which has an isotopic composition like that of argon in the atmosphere. The amount of atmospheric argon is so large that any radiogenic argon that may have formed within this salt is negligible in comparison to the amount of atmospheric argon.

Domal salt is virtually impermeable [16] because of the ability of salt to flow under pressure. Deeply buried salt may effectively seal itself against loss of its internal fluids (including argon) and against penetration by fluid of external origin, and such sealing may remain effective during diapirism except where the salt is strongly deformed. In portions of diapirs that have not experienced severe

deformation the radiogenic argon that has been formed within the rock might be preserved. It would be interesting to examine salt diapirs formed from relatively old salt deposits, such as the Cambrian salt in Iran, for the presence of radiogenic argon that might have survived the effects of diapirism.

Initially, potassium-argon studies of diapiric salt should focus on samples that contain disseminated potassium minerals in appreciable quantity, insofar as such samples are available. For dating to be successful, there must be enough radiogenic argon to be detectable in the presence of atmospheric argon that was originally trapped in the salt. Samples from shear zones should be avoided, to minimize the likelihood that pressurized gases that are not indigenous to the salt have been trapped.

When the amounts of radiogenic argon and non-radiogenic argon in salt are comparable, the data obtained by stepwise dissolution may be plotted on an isotope correlation diagram ( $^{40}\text{Ar}/^{36}\text{Ar}$  vs.  $^{40}\text{K}/^{36}\text{Ar}$ ). In a favorable case, such a plot may define an isochron whose slope gives the age of the salt crystals and whose intercept is the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of the argon originally incorporated in the sample. For undeformed salt, the original argon may be that of the ancient atmosphere at the time the salt was deposited [17]. The potassium-argon relationships in tectonically deformed salt are certain to be more complex than those in undeformed salt. The study of such relationships in diapiric salt may prove to be as challenging, and perhaps will be as rewarding, as the study of rubidium-strontium isotope correlations in metamorphic rocks has proved to be.

#### Conclusion

Potassium-argon analysis by stepwise dissolution is a new technique that should prove to be very useful for interpretation of the history of crystallization or recrystallization of rock salt. Water may be used as the solvent when relatively large amounts of salt are to be dissolved. Methanol or a methanol-water mixture may be

used when relatively small amounts of salt are to be dissolved in each step, in order to obtain high spatial resolution of the distribution of potassium and argon in the salt. Preliminary analyses of deformed salt from the Gibson Dome (Utah) and the Weeks Island diapir (Louisiana) show that radiogenic argon may be lost during deformation and that highly sheared salt may have large amounts of gas, including atmospheric argon, under high pressure. Although the potassium-argon relationships in diapiric salt may be very complex, analysis of these relationships by stepwise dissolution of properly chosen samples should provide useful isotope correlations in cases where the amounts of atmospheric argon and radiogenic argon in the salt are comparable.

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