

good internal agreement between the  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  decay systems and by the good agreement with radiocarbon results for the mammal sites. These results indicate that the Del Mar and Sunnysvale skeletons are much younger than was previously estimated and could be derived from the population waves that came across the Bering Strait during the last lowering of sea level about 13,000 years ago (22).

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23. Samples and particulars of the Del Mar, Sunnysvale, Rancho La Brea, and Mountain View sites were graciously provided by R. Tyson, B. Gerow, G. Jefferson, and C. Repenning. We thank T. L. Ku, B. Szabo, and J. Rosholt for advice and instruction on analytical techniques and instrumentation. Special thanks go to R. Shlemon for visiting the Del Mar site with us and sharing his observations and expertise on the local geology and to R. Tyson for arranging and guiding the field visit.

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## Trace Water Content of Salt in Louisiana Salt Domes

**Abstract.** *The trace water content of salt in six Louisiana salt domes has been determined and has been found to be the lowest of any terrestrial rock type. The average water content of normal domal salt is on the order of 0.003 percent by weight, but anomalous zones within salt stocks can have more than ten times this amount. From the average value, the minimum amount of water in liters,  $W$ , available to collect around a radioactive waste repository is given as  $W = 0.28 r^3$ , where  $r$  is the radius in meters of the sphere in which water may be thermally activated to migrate completely to the repository.*

In considering salt domes as repository sites for nuclear wastes, a major question is the significance of brine inclusions, which have been observed to migrate through salt in response to a thermal gradient (1). Salt dissolves from the warmer side of the inclusion and precipitates on the cooler side, and thus the brine inclusion moves toward the heat source. Microscopic brine inclusions are observed in natural salt samples, and it is possible that this brine will migrate to a nuclear waste repository. It is therefore important to assess the total reservoir of trace water within salt domes that might be affected by this process.

In the work reported here, salt samples (3 to 56 g) from six Louisiana salt

domes were heated under high vacuum to volatilization. Water released on heating was reduced quantitatively over uranium metal at  $700^\circ\text{C}$  to produce hydrogen gas. The hydrogen was collected by a Toepler pump and its volume was measured manometrically (2). Less than  $10^{-6}$  mole of water can be measured with this procedure. For an 18-g sample, the water content of salt can therefore be determined to  $\pm 1$  ppm.

Figure 1 illustrates the water release with temperature for salt sample VK-3-49 when it was heated from  $23^\circ$  to  $1000^\circ\text{C}$  at an average rate of  $1^\circ$  to  $2^\circ\text{C}$  per minute. A relatively large water component is released at  $23^\circ\text{C}$  and appears to outgas until  $218^\circ\text{C}$ . Another water component outgasses from  $280^\circ$  to  $800^\circ\text{C}$ . Other salt

samples of various sizes and water contents display similar water evolution patterns, although changes in the rate of heating can affect the pattern somewhat. In particular, exposure of the samples to high vacuum at  $23^\circ\text{C}$  for 30 minutes or longer removes the low-temperature water component entirely. This low-temperature component is interpreted as water adsorbed or condensed on the salt surface and along fractures (3).

To test the interpretation that adsorbed water can be pumped away at room temperature, a 2-g sample of salt from Weeks Island, sample F-2-34, was soaked in an NaCl-saturated aqueous solution for 23 hours to introduce as much adsorbed water as possible. This sample was air-dried in a desiccator and analyzed routinely (2). As shown in Table 1, the amount of water released over the range  $23^\circ$  to  $1000^\circ\text{C}$  was not significantly greater than that from the other Weeks Island samples. In addition, single crystals of halite, samples RK-5, RK-7, and RK-10, were cut dry, in water, and in oil (4), respectively. As shown in Table 2, there was no significant variation in the amounts of trace water measured for these samples. It is concluded that adsorbed water can be removed from domal salt by exposing the samples to high vacuum for at least 30 minutes. Nevertheless, all samples analyzed were taken from freshly broken hand samples or cores and were exposed to air for as short a time as possible. Water evolved from the salt above  $23^\circ\text{C}$  and under high vacuum is trace water within the salt and is considered to have geological significance.

In all salt samples analyzed, gas other than water is evolved during heating. In the case of sample VK-3 (Fig. 1) this gas contains a major  $\text{CO}_2$  component, as determined by mass spectrometer. The pattern of evolution of  $\text{H}_2\text{O}$  is not parallel to that of the  $\text{CO}_2$ -rich gas, suggesting that the water is not derived by pyrolysis of trace amounts of organic matter. The high temperature of the gas release suggests decomposition of trace amounts of solid phases, including carbonate. In any case, the water evolves separately, giving further evidence that it represents an actual water component in the salt.

Table 1 gives the results of the trace water measurements on salt samples from six Louisiana salt domes. The values range from less than 0.001 percent by weight for single crystals to 0.034 percent by weight for certain samples in the Weeks Island dome. The highest water contents are for the salt stalagmites, which formed recently around water seeps or condensation zones in mine

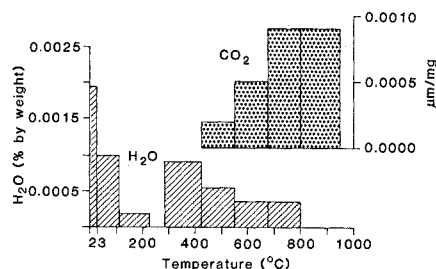


Fig. 1. Evolution of water and CO<sub>2</sub>-rich gas from Vacherie salt dome sample as temperature is raised from 23° to 1000°C under high vacuum. Water evolved below 220°C is interpreted as adsorbed water. Water evolved at high temperature is considered to be trace water in the salt and to have geological significance.

openings. This freshly formed halite with 0.054 to 0.519 percent H<sub>2</sub>O is greatly enriched in water relative to all samples of domal salt. The lower water content of the domal salt is probably due to progressive exclusion of water from the halite crystals by compaction and repeated recrystallization episodes at depth.

Except for the recently formed stalagmites, the water contents of samples from the Jefferson Island, Avery Island, Belle Isle, Rayburn's, and Vacherie domes fall into the narrow range 0.0001 to 0.007 percent. Samples from the Weeks Island salt mine contain 0.011 to 0.034 percent water and are thus significantly enriched in water relative to the other domes. However, all these Weeks Island samples were obtained from anomalous zones within the mine. Sam-

ples from mine room F-2 are near areas where water is seeping from the salt (5). Samples from room C-2 contain even more water (0.032 to 0.034 percent) and represent halite associated with major sandstone inclusions in the salt dome. The trace water content of domal salt appears to be greatest near such anomalous zones.

If the anomalous Weeks Island samples are excluded, the average water content of the salt in these domes is on the order of 0.003 percent. Since the samples were obtained from mines as well as drill cores and from coastal as well as interior salt domes, it seems reasonable to take 0.003 percent as the overall "background" water content of domal salt in the Gulf Coast region. More water-rich portions of the salt stocks exist, but it is unlikely that large volumes of salt will be found with a water content lower than 0.003 percent. Published values for the water content of nominally anhydrous silicates range upward from 0.009 percent by weight (6) and are all larger than the water content of normal salt in salt domes. It is therefore likely that the trace water content of domal salt is the lowest of any terrestrial rock type.

Assuming a water content of 0.003 percent and a salt density of 2.2 g/cm<sup>3</sup>, the reservoir of water around any point in a salt dome is given by  $W = 0.28 r^3$ , where  $W$  is the volume of water (liters) and  $r$  is the radius (meters) of the sphere around the given point. Since sediment

Table 2. Water contents of single crystals of halite from Rayburn's salt dome after samples were cut with dry, wet, and oil saws. The natural variation in water content appears to be greater than any variation due to contamination from the preparation procedure. Single crystals have the lowest water contents of any domal salt samples.

Sample	Preparation	H <sub>2</sub> O (percent by weight)
RK-5	Cut dry	0.0005
RK-5	Cut dry	0.0003
RK-7	Cut with water saw	0.0005
RK-7	Cut with water saw	0.0001
RK-7	Cut with water saw	0.0007
RK-10	Cut with oil saw	0.0004

inclusions and anomalous wet salt zones may occur within this sphere,  $W$  represents a minimum value for the water content of domal salt.

The amount of water that will collect around a radioactive waste repository can be estimated from the equation above if  $r$  is the radius of the sphere of influence in which water will be thermally activated to migrate completely to the repository. The value of  $r$  for a particular repository depends on many factors, including the temperature of the repository and surrounding salt, changes in the thermal gradient with time, and still unknown variables regarding water migration in salt domes. We stress that this equation probably gives a minimum value because salt anomalously rich in water may be encountered in the sphere of influence.

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2. Salt samples are loaded against a stream of dry nitrogen into a quartz furnace tube that has been preheated under high vacuum to 1000°C. The furnace is sealed and the nitrogen pumped out through a liquid nitrogen-cooled trap (−196°C) until high vacuum is again obtained. After 30 minutes at 23°C the evacuated sample is heated progressively to 1000°C. Water and other volatiles evolved from the salt are condensed in liquid nitrogen-cooled traps. At approximately 650°C halite begins to volatilize and condenses at the edges of the furnace tube. Little, if any, water is trapped by the condensing salt, since most of the water outgasses below 650°C (Fig. 1). By 900°C the halite is completely volatilized.

Table 1. Trace water contents of Louisiana salt domes. Core box numbers are given in parentheses.

Sample	Description	H <sub>2</sub> O (percent by weight)	Sample	Description	H <sub>2</sub> O (percent by weight)
<i>Weeks Island mine</i>			<i>Avery Island mine</i>		
F-2-5		0.011	A-2-16		0.004
F-2-9		0.013	A-1-26		0.004
F-2-39		0.012	A-1-77		0.003
F-2-45		0.026	<i>Belle Isle mine</i>		
F-2-34	Soaked in H <sub>2</sub> O prior to analysis	0.024	B1-7-24	Stalagmite	0.519
F-2-75		0.018	BS-3-35		0.003
C-2-7	Salt in sandstone inclusion	0.032	BS-1-43		0.004
C-2-21	Salt in sandstone inclusion	0.034	BS-2-44	Stalagmite	0.501
Z-15-8	Stalagmite	0.054	BS-1-78		0.007
LL-51-29	Stalagmite	0.090	B1-29-10	Stalagmite	0.457
<i>Jefferson Island mine</i>			<i>Rayburn's core</i>		
J-3-40		0.001	RK-4-32(36-22)	Single crystal	0.0004
J-2-19		0.001	RK-4-41(36-22)	Single crystal	0.005
J-2-76		0.004	RK-5-74(31-13)		0.0003
J-1-20		0.003	RK-1-46(5-8)		0.006
			RK-2-47(15-6)		0.006
			<i>Vacherie core</i>		
			VK-3-49(27-6)		0.002
			VK-3-53(27-6)		0.004
			VK-3-70(27-6)		0.004
			VK-5-79(16-4)		0.001
			VK-5-80(16-4)		0.001

Any noncondensable gases are collected by a Toepler pump and measured manometrically. These usually total less than 0.001  $\mu$ mole per milligram of sample. Water is separated from other condensables by warming the trap to  $-78.5^{\circ}\text{C}$ . The amount of noncondensable gas evolved ranges from 0.001 to 0.02  $\mu$ mole per milligram. With this procedure, any  $\text{CH}_4$  and  $\text{H}_2\text{S}$ , present in the salt, would be separated from the water before reaction of the water with the uranium. The sample water is reacted with uranium metal at  $700^{\circ}\text{C}$  as described by J. D. Godfrey [*Geochim. Cosmochim. Acta* 26, 1215 (1962)]. Hydrogen liberated in this reaction is collected into a calibrated volume by a mercury Toepler pump and the amount of gas measured manometrically. Background water yields from the apparatus are less than 1  $\mu$ mole, as determined by repeated analysis of sample blanks. Absolute water yields from the samples ranged from 30 to 950  $\mu$ mole, depending on the sample size.

3. The experiment in Fig. 1 differed from the normal procedure described in (2) in that the salt sample was loaded into the furnace tube under laboratory air rather than under dry nitrogen.

The water released below  $218^{\circ}\text{C}$  undoubtedly included atmospheric water vapor adsorbed on the interior surfaces of the apparatus during loading. Samples loaded under dry nitrogen yield no measurable water between  $23^{\circ}$  and  $218^{\circ}\text{C}$ , provided the samples are exposed to high vacuum for at least 30 minutes.

4. Oil was removed from sample RK-10 after sawing by soaking the sample in organic solvent Furfural (John B. Moore Corp.).

5. The origin of the water responsible for such mine leaks is discussed in L. P. Knauth, M. B. Kumar, J. D. Martinez, *J. Geophys. Res.* 85, 4863 (1980).

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## Clear Air Turbulence: An Airborne Alert System

**Abstract.** An infrared radiometer system has been developed that can alert a pilot of an aircraft 2 to 9 minutes in advance of an encounter with clear air turbulence. The time between the warning and the clear air turbulence event varies with the flight altitude of the aircraft. In turbulence-free areas, the incidence of false alarms is found to be less than one in 3.4 hours of flight time compared to less than one per 10 hours of flight time in areas with turbulence.

Clear air turbulence (CAT) constitutes a hazard to air safety, and a pilot warning in advance of a CAT encounter has become important to the welfare of aircraft passengers and crew. The CAT-related average economic loss of commercial and military aviation worldwide is more

than \$25 million annually (1). Forecasting CAT is difficult, since it is often a microscale phenomenon not usually apparent on synoptic-scale weather charts. An on-board detection device could warn the pilot of this phenomenon.

A high frequency of CAT and large changes in water vapor content are often associated with stable layers in the atmosphere. This is especially true at the tropopause, where dry, ozone-rich, stratospheric air comes in contact with relatively moist, ozone-poor, tropospheric air. Clear air turbulence produces marked variations in the distribution of water vapor, through which its presence can be detected with an infrared sensor that is sensitive to radiation in the molecular water vapor band.

Some atmospheric conditions that foster CAT are predictable—for example, a sloping tropopause or a standing wave in the lee of a mountain. However, there are conditions under which CAT is unpredictable. Vertical wind shear in stable layers can intensify until a critical value is exceeded locally. Spontaneously, Kelvin-Helmholtz waves can form, amplify, become gravitationally unstable, and give rise to CAT (2-4). Under these conditions, an on-board sensor may provide the only warning.

An infrared radiometer system has been developed by the NOAA Environmental Research Laboratories and NASA Ames Research Center that alerts the pilot to the onset of turbulence (2). It

consists of an infrared radiometer with appropriate optics (5) mounted in a fixed forward-looking position on the aircraft. The voltage output response of the radiometer is received by a microprocessor, which computes the standard deviation of the stream of voltages over a prescribed time interval. If the deviation exceeds a certain threshold, a flashing light warns the pilot of the subsequent onset of turbulence. Cloud effects can be eliminated by use of a second channel of the radiometer in the portion of the spectrum from 9.5 to  $11.5\ \mu\text{m}$  ( $870$  to  $1050\ \text{cm}^{-1}$ ), so that the system responds only to CAT.

The system was tested in NASA jet aircraft flying at altitudes ranging from 5.8 to 12.5 km. The distance from which the radiometer can detect atmospheric emission anomalies increases with height, due to the decreased concentration of absorbing gas (water vapor) in the atmosphere at higher altitudes. Figure 1 shows an envelope of the alert time before a CAT encounter. The solid line is the maximum alert time based on experimental data. The dashed line indicates 70 percent values; that is, 70 percent of the alarms are received during the time period up to the curve. Figure 1 was produced empirically from the data for 367 encounters in all types of atmospheres. The edge of the envelope is not linear since atmospheric absorption is not linear.

Table 1 shows the results of compila-

Table 1. Results of CAT alert system tests based on all data obtained during CAT-dedicated missions in 1978 and 1979.

Category	Number	Percent
Total encounters	367	
Alert given	327	89.1
No alert given	40	10.9
Total alarms	380	
True alarms	327	86.1
False alarms	53	13.9

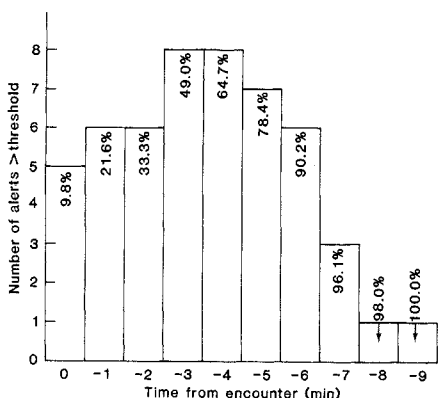


Fig. 1. Time envelope showing alerts preceding CAT encounters.

Table 2. Results of CAT alert system tests in nonturbulent areas with and without clouds.

Date in 1979	Cirrus included		Cirrus excluded	
	Hours	False alarms	Hours	False alarms
20 June	3.5	5	3.0	2
11 July	2.5	0	2.5	0
13 July	6.5	0	6.5	0
29 July	4.0	13	1.5	2
Totals	16.5	18	13.5	4

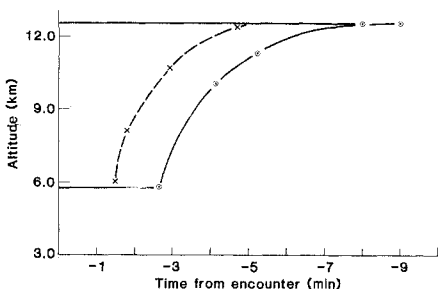


Fig. 2. Time distribution of CAT alerts. Data were obtained at an altitude of 12.5 km. The percentages are cumulative.