Naturally Occurring Radioactive Materials (NORM) in Produced Water and Scale from Texas Oil, Gas, and Geothermal Wells:
Geographic, Geologic, and Geochemical Controls
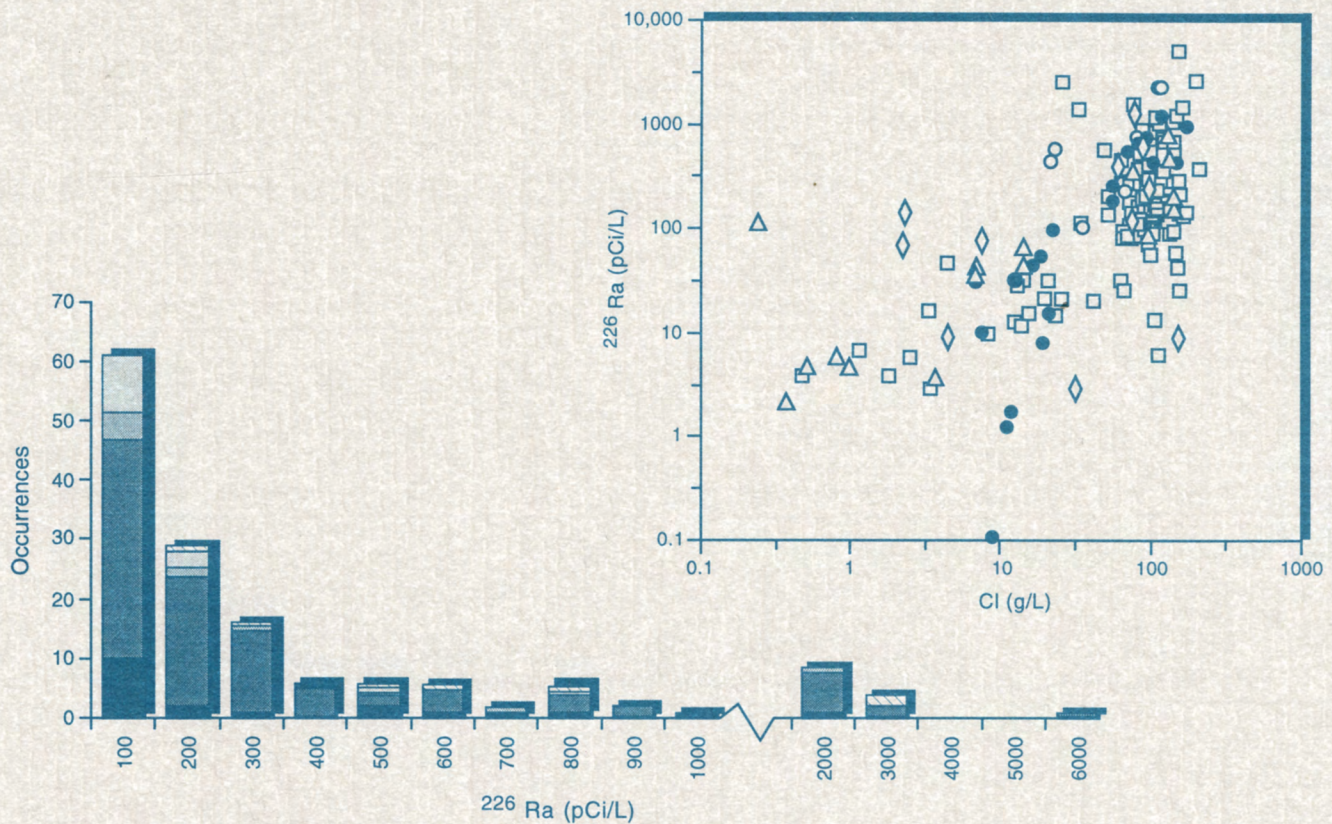
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1995

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ABSTRACT

Water produced from oil, gas, and geothermal reservoirs contains natural radioactivity that ranges from background levels to levels found in uranium mill tailings. Radioactivity in fluids and in the scale that forms in oil-producing and gas-processing equipment increases concerns for worker and public safety as well as costs of handling and disposing of naturally occurring radioactive materials (NORM), which include water, sludge, scale, and affected equipment. This study explored natural controls on such radioactivity to identify screening criteria by which high NORM activity can be anticipated on the basis of geologic or geochemical information. Such criteria can help State and Federal agencies target disposal regulations for situations likely to incur high radioactivity levels and can also prevent operators from making costly measurements if the likelihood of encountering elevated NORM activity is low.

NORM in oil and gas operations is caused mainly by radium-226 (^{226}Ra) and radium-228 (^{228}Ra), daughter products of uranium-238 (^{238}U) and thorium-232 (^{232}Th), respectively, in barite scale. To explore natural controls on radioactivity, we considered the (1) geographic distribution of NORM in oil-producing and gas-processing equipment, (2) geologic controls on uranium, thorium, and radium in sedimentary basins and reservoirs, (3) mineralogy of NORM scale, (4) potential of Texas formation waters to precipitate barite scale, (5) radium activity in Texas formation waters, and (6) geochemical controls on radium isotope activity in barite scale. Our approach combined compilations of published data, collection and analyses of new water and scale samples, and geochemical modeling of scale pre-cipitation and radium incorporation in barite.

We found that (1) elevated NORM levels (90th percentile in both major oil- and gas-producing regions of Texas) occur where volcanic rock fragments are abundant in sandstone reservoirs, (2) lithologic or mineralogic heterogeneities within reservoirs are a major control on NORM activities in produced water, (3) barite scale is the most likely NORM host in sludge and scale, (4) the potential for barite to precipitate from produced water increases with reservoir temperature, (5) high radium activity (> 200 pCi/L) occurs only if water salinity exceeds about 35,000 mg/L total dissolved solids, and (6) the radium activity of barite scale is predicted to vary significantly be-tween major Texas basins. These results suggest that multivariate analysis of geologic and geochemical parameters may be useful in predicting NORM activity in produced water and scale in individual basins, plays, or reservoirs.

INTRODUCTION

Natural Radioactivity in Oil and Gas Production

Since the early reports of NORM (naturally occurring radioactive materials) in Canadian oil fields in 1904 (Wilson, 1994) and in Russian oil fields in the 1930's (Kolb and Wojcik, 1985), awareness has steadily increased that small amounts of radioactive materials are commonly being produced from oil and gas reservoirs along with hydrocarbons. Health, safety, and environmental concerns began to develop during the early 1980's and 1990's as measurable levels of radioactivity were found in oil-producing and gas-processing facilities in the North Sea and along the United States Gulf Coast, in hardware and playground equipment made from recycled oil- and gas-field tubing, and in produced waters discharged into coastal environments (Miller and others, 1991; White, 1992). A recent national survey sponsored by the American Petroleum Institute (API) found radioactivity exceeding background levels in oil-producing and gas-processing equipment in all major oil- and gas-producing states (Otto, 1989). Thus, NORM production and accumulation are natural consequences of extracting hydrocarbons from the Earth's crust.

NORM in oil- and gas-field operations occurs as produced water; as sludges, sands, and mineral scale precipitated in pipes, valves, or gauges; as thin platings on the inner surfaces of gas processing and transporting equipment; or as a gas (Smith, 1987; Baird and others, 1990; White, 1992). Most radioactivity in oil- and gas-field operations is produced by members of the ^{238}U and ^{232}Th decay series (fig. 1). Because the chemical properties and mobility of different elements in the decay series differ under various reservoir and production conditions, only certain radioactive species are transported to surface facilities.

In produced water, scale, and sludge accumulations, most of the radioactivity is caused by radium-226 (^{226}Ra) and radium-228 (^{228}Ra). In gas-processing facilities lead-210 (^{210}Pb), a decay product in the ^{238}U series, can accumulate as thin platings on the inner surfaces of pipes. Radon (Rn) gas (radon-222 [^{222}Rn] or radon-220 [^{220}Rn]), a daughter product of radium (Ra) decay in both the ^{238}U and ^{232}Th series, is also produced but typically escapes to the atmosphere before it reaches hazardous levels (Nazaroff and Nero, 1988). Effective concentrations of radionuclides are generally reported in terms of radioactivity in units of curie (Ci), picocurie (pCi = 10^{-12} Ci), disintegrations per second (dps), Becquerel (Bq, 1 Bq = 1 dps), or disintegrations per minute (dpm), whereas radiation effects are reported in terms of dosages (rad, rem, or roentgen) (table 1). Produced water contains NORM at approximately the same concentrations as formation water in the reservoir. NORM levels in produced water range from essentially background values to activities as high as several thousand picocuries per liter (pCi/L) (White, 1992). Sludge coatings on reservoir grains or other particulates derived from the well system, sands, mineral scale, or pipe platings contain higher levels of NORM than produced water because radionuclides have been precipitated as minerals or coatings on reservoir material or on other particulates derived from the well system. Sludges in production equipment typically contain ^{226}Ra and ^{228}Ra in amounts ranging as high as several hundred picocuries per gram (pCi/g) (Baird and others, 1990). NORM in oil- and gas-field equipment can reach very high activities because Ra isotopes accumulate in scale over long periods of time and are extracted from large volumes of produced water. NORM levels in scale can reach activities as high as several thousand pCi/g (Baird and others, 1990).
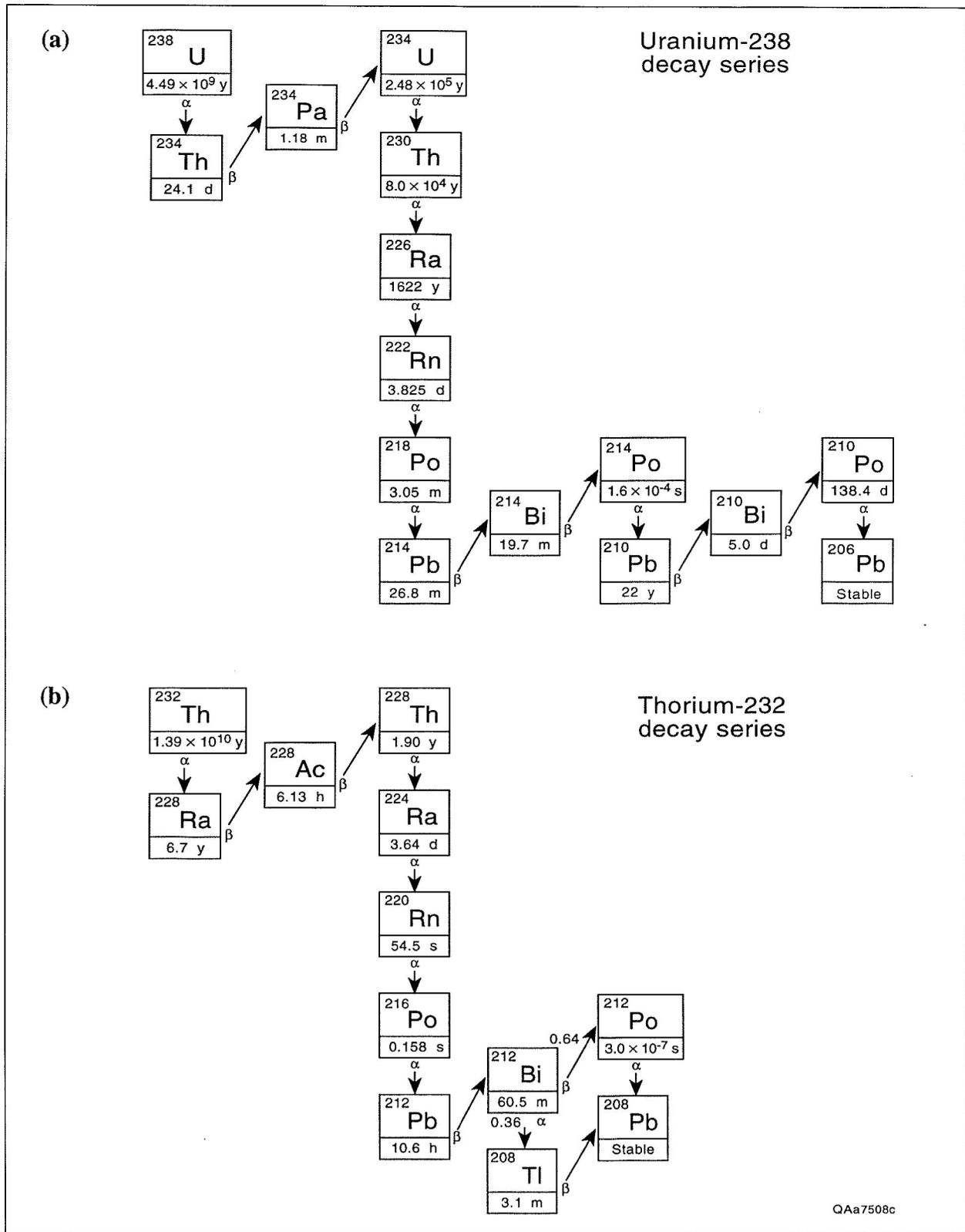
Figure 1. (a) Uranium-238 (^{238}U) and (b) thorium-232 (^{232}Th) decay series and half-lives of isotopes (after Molinari and Snodgrass, 1990). α = alpha decay; β = beta decay; y = years; d = days; h = hours; m = minutes; s = seconds.

Table 1. Units of radioactivity.

Curie (Ci)	The quantity of any radioactive material that produces 3.7×10^{10} disintegrations per second (dps).
Picocurie (pCi)	The quantity of any radioactive material that produces 1×10^{-12} Ci or 3.7×10^{-2} dps.
Becquerel (Bq)	A unit of radioactivity defined as 1 dps. The Bq is the Standard International Unit (SI) of radioactivity; equal to 27.03 pCi.
Rad	A unit of absorbed dose defined as the quantity of radiation or energy absorbed per unit mass. One rad equals 100 ergs per gram of material.
Rem	The dosage of any ionizing radiation that will produce a biological effect equivalent to that produced by 1 roentgen of X-ray or gamma-ray radiation.
Roentgen (R)	The quantity of X-ray or gamma-ray radiation that will produce 1 electrostatic unit (esu) of charge of either sign in 1 cubic centimeter of dry air at 0°C and 760 mm of mercury pressure; equal to 2.58×10^{-4} coulombs per kilogram of dry air.

Health, Safety, and Environmental Issues

Because most of the radioactivity associated with NORM is caused by ^{226}Ra and ^{228}Ra, studies of the potentially hazardous effects of NORM focus on the chemistry of Ra and its progeny in ecosystems and organisms. ^{226}Ra decays by emission of an alpha particle with an energy of 4.79 MeV, whereas ^{228}Ra undergoes beta decay with an energy of 0.012 MeV (Moore, 1972). Radium has an ionic charge (+2) and radius similar to those of other Group 2A elements (1.48 angstroms [Å] in eightfold coordination, versus 1.12, 1.26, and 1.42 Å for calcium [Ca], strontium [Sr], and barium [Ba], respectively, in eightfold coordination) (Shannon, 1976). Of the Group 2A elements, Ca is the most abundant in living organisms, and therefore the effects of Ra substitution for Ca are of greatest concern. Ingested Ra has been associated with bone cancer, bone sarcoma, and cranial carcinoma (Mays and others, 1985). Health and safety issues have been reviewed by Snavely (1989), Baird and others (1990), White (1992), Gundersen and Wanty (1993), and Wilson (1994).

The threat of NORM from oil and gas operations to the general public arises from the way in which produced water or NORM scale and sludge are disposed. If produced water contaminates drinking-water supplies, NORM can be ingested and assimilated into the body. It may be incorporated into the food chain as contaminated plant or animal material resulting from produced-water discharge or uptake of scale, sludge, or dust. If contaminated food is then consumed by humans, Ra is concentrated in the bones. Exposure to radioactive equipment also poses potential low-level but long-term health problems. The exposure to radiation and/or the inhalation of Rn or Po by oil- and gas-field workers during normal operations are limited because radioactivity is shielded by the containing hardware and because Rn gas rarely accumulates to harmful levels. However, maintenance and cleaning of tubing and equipment to remove NORM scale from pipes and tubing generate small particles that can be inhaled and also increase surface area, which promotes Rn emission. Because NORM can present health, safety, and environmental threats, various State and Federal agencies have established or are writing regulations to control NORM production, handling, and disposal. Such regulations were reviewed by Smith (1987), Snavely (1989), Baird and others (1990), and Wilson (1994).

Natural Radioactivity in United States Oil-Producing and Gas-Processing Facilities

Before 1989, few published data existed to quantify the extent of NORM in United States oil

and gas operations. Recognizing this need for basic information, API sponsored a nationwide survey in which participating companies collected radiation measurements at their facilities using standardized equipment and measurement protocols and submitted the results for statistical analysis and aggregation. The results of the API survey (Otto, 1989) showed that highest median readings above background levels (greater than 33 μrems/h) were found along the Gulf of Mexico coast from Florida to South Texas and in southeast Illinois (fig. 2).

Purpose

The nearly universal occurrence of NORM in oil and gas production; the health and safety concerns associated with handling, storing, and disposing of radioactive materials; and the increased costs incurred by oil and gas companies as they comply with health and safety regulations raise fundamental questions about the distribution of natural radioactivity and the controls on NORM accumulation in oil and gas facilities. If the factors that control or influence NORM occurrence and accumulation can be identified, exploration and production geologists and engineers will be better able to anticipate handling and disposal costs. Additionally, regulatory agencies will be better able to establish rules and guidelines for handling, transporting, and disposing of oil- and gas-field NORM. Our goal was to identify screening criteria that could be used to anticipate NORM levels and thereby allow regulators to target specific situations for controls and reduce operating and disposal costs to oil-producing and gas-processing companies.

Approach

Previous investigations of radioactivity in produced water involved specific regions or formations (for example, Adams and others, 1959; Cowart, 1981; Kraemer, 1981, 1985, 1993; Kraemer and Reid, 1984; Kraemer and Kharaka, 1986; Gilkeson and Cowart, 1987; Gascoyne, 1989; Szabo and Zapecza, 1993; Taylor, 1993) and could not

distinguish between local and general controls on radioactivity in oil, gas, and geothermal production. This study addresses controls on Ra in sedimentary basins and formation waters, as well as controls on the precipitation of NORM-containing scale in oil-producing and gas-processing facilities. We focused on the geologic and geochemical properties of Ra, U, and Th isotopes because U and Th in geologic media produce Ra and because Ra is the first mobile daughter product in the decay series that ultimately produces stable lead (Pb) isotopes (fig. 1). We addressed natural controls on U, Th, and Ra through six investigations.

Distribution of NORM in Texas Oil-Producing and Gas-Processing Facilities

We used the data compiled by Otto (1989) to identify counties where oil-producing and gas-processing equipment had high radioactivity. We then combined this information with the atlases of major Texas oil (Galloway and others, 1983) and gas (Kosters and others, 1989) reservoirs to identify geologic basins and structures associated with the high NORM activities.

Geologic Controls on Uranium, Thorium, and Radium in Sedimentary Basins

Radium in solution is not produced by U and Th in solution. Predicting areas most likely to have high NORM potential, therefore, requires consideration of the geologic and lithologic distribution of parent U and Th and the mechanisms by which Ra escapes to the fluid phase. Two hypotheses regarding NORM in produced water and in oil-producing and gas-processing equipment scale can be evaluated. The first is that elevated NORM levels are produced by locally high U and Th concentrations in the reservoir. If this is true, NORM will be controlled largely by geologic formation and lithology. The second hypothesis is that elevated NORM levels accumulate from ordinary geologic media during
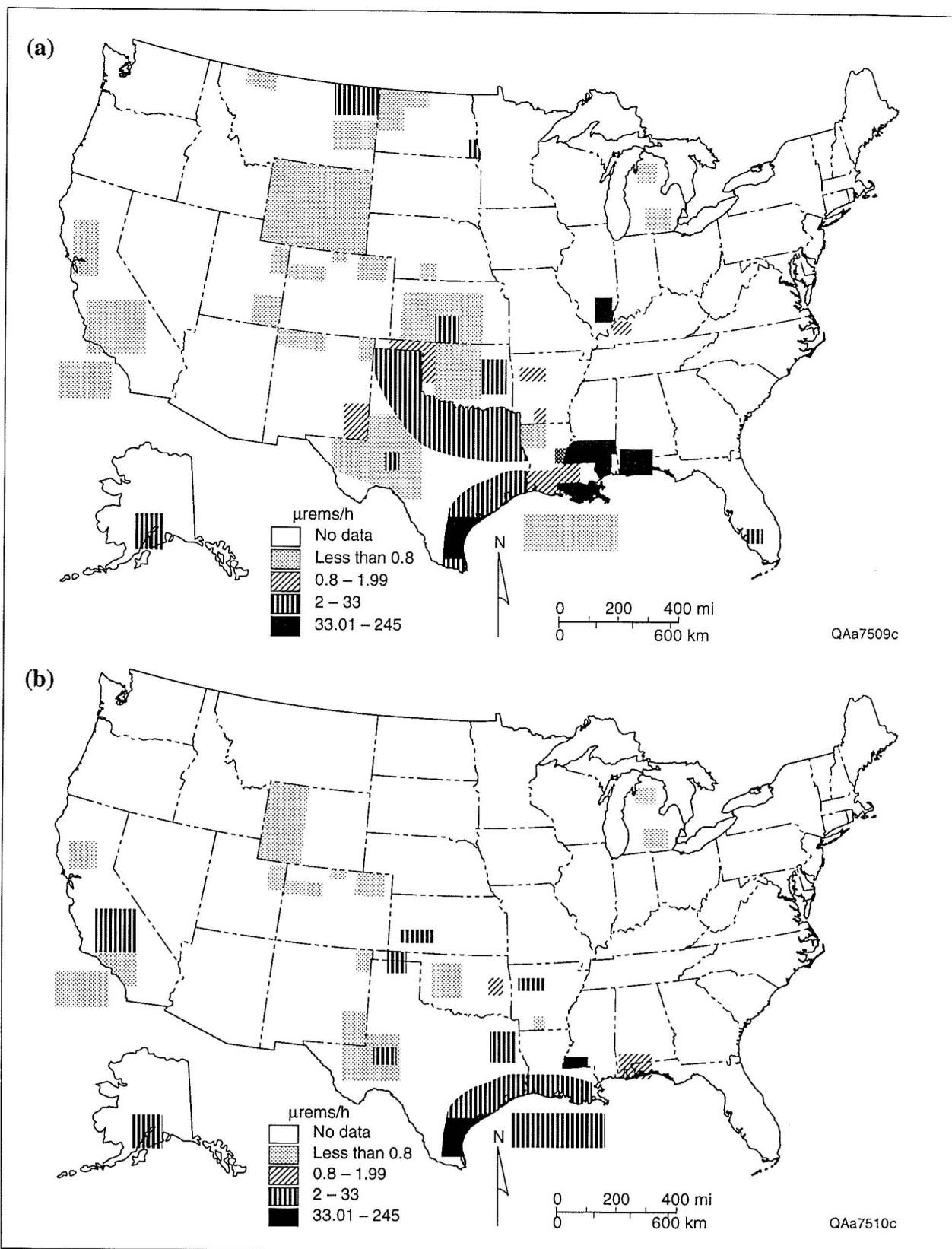
Figure 2. Maps showing regions of high NORM activity in United States oil-producing facilities (a) and gas-processing facilities (b). Values are aggregated median difference over background (Otto, 1989).

normal geologic processes. If this is true, the potential for high NORM activity can be predicted largely from basin history. We evaluated these hypotheses by searching for correlations between Ra activity and geologic or geochemical properties of reservoir and formation water.

Mineralogy of NORM Scale

NORM is incorporated in the mineral scale that precipitates as oil and gas are produced. However, few data quantifying the chemical or mineralogical form of the NORM-containing phases exist. Such information is essential for geochemically predicting NORM accumulations on the basis of reservoir conditions and water chemistry. These data can then be used to geochemically model NORM accumulation. We used literature reports, geochemical evidence, and direct analyses to identify NORM-containing minerals in production scale. Then we obtained a suite of scale samples and performed mineralogical and chemical analyses to determine the NORM-containing phase.

Potential to Form NORM Scale in Texas Reservoirs

The composition of water produced from oil, gas, and geothermal wells varies significantly within Texas. Water chemistry reflects basin lithology and history, affects Ra mobility, and determines the type and amount of scale that will precipitate when formation water is produced. Therefore, regional differences in NORM accumulation could be related to regional variations in water chemistry. To address this issue we compiled available water chemistry data to investigate the distribution of formation water types in the major oil-producing and gas-processing regions of the state. We used the geochemical modeling program SOLMINEQ.88 (Kharaka and others, 1988) to compute the amount of barite that would form as pressure and temperature conditions change from those within the reservoir to those at surface production facilities.

Radium in Texas Formation Water

Some data already exist regarding Ra in water produced from wells drilled for geothermal, hydrocarbon, and nuclear waste isolation investigations. The results of individual studies have been interpreted separately, but the data have not been integrated to infer common parameters that control radionuclide distributions regardless of formation, lithology, or water chemistry. Existing data on Ra in formation water come mostly from wells in the Texas Gulf Coast and Panhandle regions. New data are needed to explore NORM in formation water from other geologic environments and geographic areas throughout the state. We compiled published information and collected and analyzed new samples to provide better statewide coverage of formation water chemistry.

Geochemical Controls on Radium in Formation Water and Scale

Thermodynamic modeling of scale precipitation during production and of Ra coprecipitation with scale provide insights into factors that promote or retard NORM accumulation. We estimated the amount of Ra that would coprecipitate in barite by using formation water chemistry, temperature, and thermodynamic data (Langmuir and Melchior, 1985; Langmuir and Riese, 1985). These results can be used to better anticipate NORM levels in equipment scale. This information will also allow operators to better plan NORM handling and disposal strategies.

Results are used to evaluate whether there are statewide differences in the (1) Ra content of formation water, (2) potential to form barite scale in production equipment, and (3) Ra content of scale. This information also provides a basis for identifying geographic, geologic, geochemical, and production characteristics that are likely to yield high NORM levels in produced water and equipment scale.

RESULTS

NORM in Texas Oil-Producing and Gas-Processing Facilities

The API national NORM survey (Otto, 1989) obtained radioactivity measurements from oil-producing and gas-processing facilities in 123 of the 254 Texas counties. This survey identifies geographic regions where above-background radioactivity in oil-producing and gas-processing operations has been recorded. However, the way in which measurements were collected and reported restricts its usefulness to our study for two primary reasons. First, because the measurements were taken external to pipes, pumps, and other equipment, the readings reflect the total amount of NORM accumulated from unknown fluid volumes passing through the equipment for unknown time periods. Second, because data are aggregated by county, relating NORM activity to a particular well, field, or formation is impossible.

Survey results (Otto, 1989) showed that the highest median radiation values in oil-producing facilities occur along the Gulf Coast from South Texas to the Houston area, in north- and west-central Texas, and in the Texas Panhandle (fig. 3). Highest values for gas-processing facilities occur in the Texas Panhandle and the lower Gulf Coast. The Gulf Coast crescent includes production from Eocene, Oligocene, Miocene, and Plio-Pleistocene strata from the Houston Salt Basin (northeast coast), the central Texas Gulf Coast Basin, and the Rio Grande Salt Basin (southwest coast), as well as production from Cretaceous strata in south-central Texas (fig. 3). The north- and west-central regions include the Hardeman and East Texas Salt Basins, as well as parts of the Eastern Shelf, Central Basin Platform, Midland Basin, and Delaware Basin. The Texas Panhandle area includes the Palo Duro, Dalhart, and Anadarko Basins and the Amarillo Uplift (fig. 3).

Focusing on counties that have NORM levels in the upper 75th or 90th percentiles provides a clearer view of the location of facilities where NORM levels are most likely to cause concern for operators and regulators. Twenty-three counties have median above-background radioactivity values ranging from 2 to 22 µrems/h (75th percentile), and 12 counties have median above-background values greater than 22 µrems/h (90th percentile) in oil-producing facilities (fig. 4a). Eight of these (Hidalgo, Willacy, Jim Hogg, Kenedy, Brooks, Kleberg, Jim Wells, and Nueces Counties) are located in the south Texas Gulf Coast within and adjacent to the Rio Grande Salt Basin. The major oil fields in this basin produce mostly from Frio strata (Oligocene); fields in Vicksburg (Oligocene) and Miocene strata have minor production (Galloway and others, 1983). Major oil fields in Refugio, Calhoun, and Jackson Counties along the central Texas Gulf Coast also produce mainly from Frio strata. In and adjacent to the Houston Salt Basin along the north Texas Gulf Coast, Wharton, Matagorda, Fort Bend, Galveston, Chambers, Orange, and Polk Counties have major oil fields that produce largely from Miocene strata and have subordinate production from Frio strata. Nacogdoches, Smith, and Kaufman Counties are located in and adjacent to the East Texas Salt Basin, where major oil fields produce from the Woodbine and Paluxy Formations (Cretaceous age). Atascosa County is in south-central Texas along the Charlotte Fault Zone; major oil fields there produce from Cretaceous Edwards and Olmos strata. Four counties having NORM levels in the 75th percentile are along the Amarillo Uplift and in the Anadarko Basin of the Texas Panhandle (Roberts, Carson, Gray, and Wheeler Counties). Major oil production here is from Paleozoic strata, as is major oil production in Wilbarger County in the Hardeman Basin, north Texas. Six counties having NORM levels in the 75th or 90th percentile are along and

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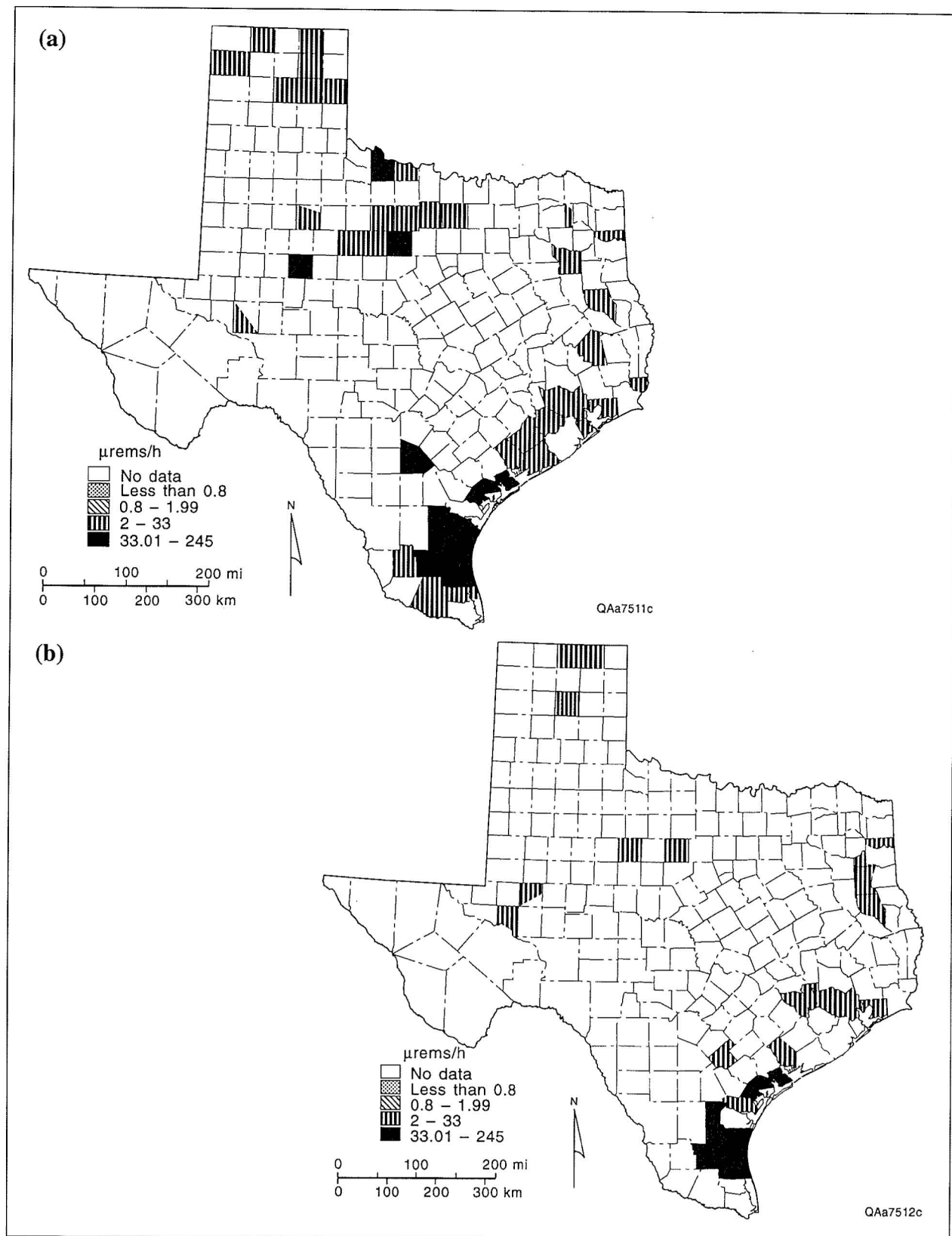
Figure 3. Maps showing regions of high NORM activity in Texas oil-producing facilities (a) and gas-processing facilities (b). Values are aggregated median difference over background (Otto, 1989).

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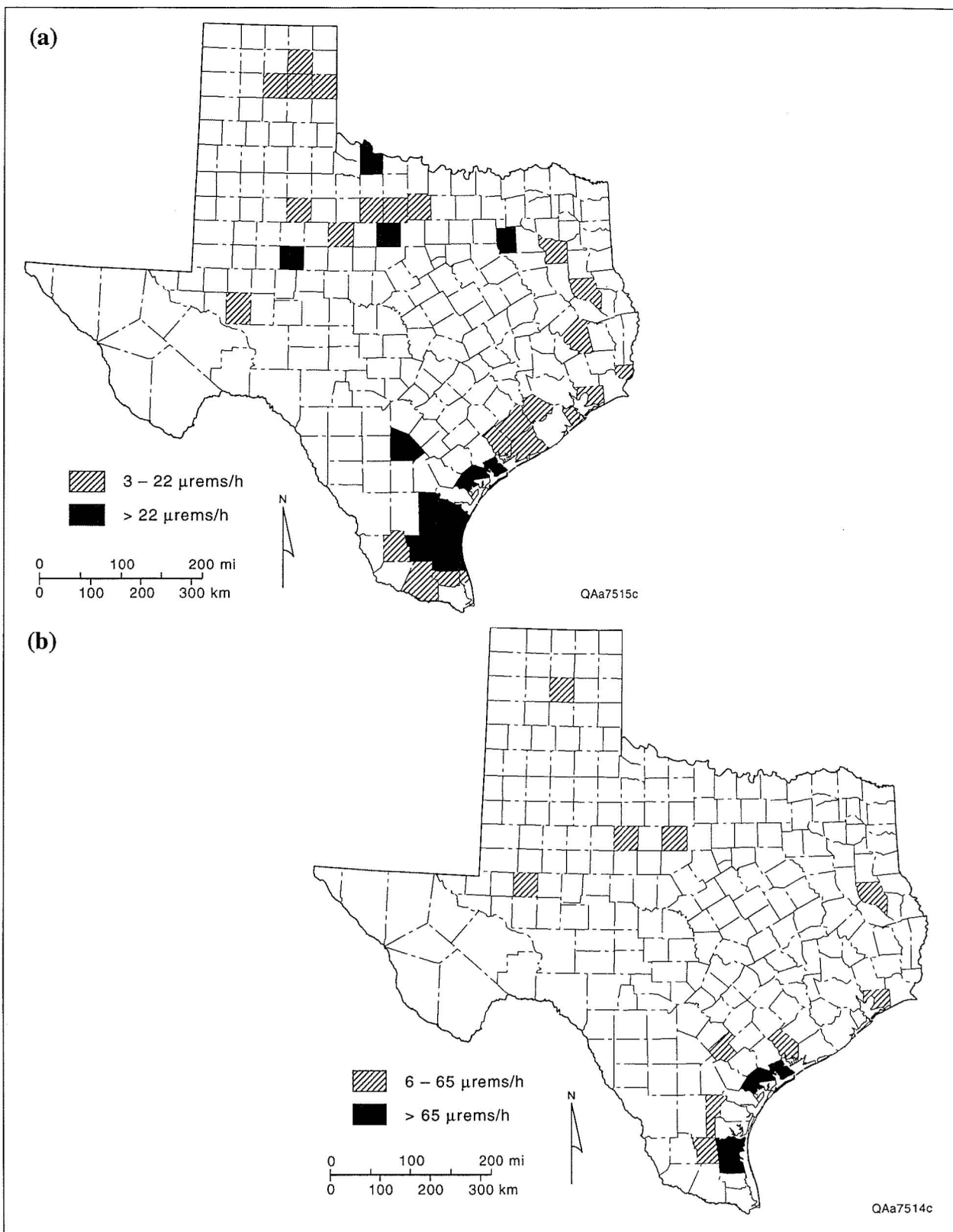
Figure 4. Maps showing counties in which NORM activity in Texas oil-producing facilities (a) is in the 75th (3–22 μrems/h) and 90th (>22 μrems/h) percentiles and in gas-processing facilities (b) is in the 75th (6–65 μrems/h) and 90th (>65 μrems/h) percentiles (data from Otto, 1989).

adjacent to the Bend Arch in either the Fort Worth Basin or the Eastern Shelf, north-central Texas (Jack, Throckmorton, Young, Jones, Stephens, and Wilbarger Counties). Major oil fields in these counties produce from Mississippian–Pennsylvanian strata. The remaining three counties, Mitchell, Kent, and Upton, are in West Texas near the eastern edge of the Midland Basin, the Horseshoe Atoll, and the western part of the Midland Basin, respectively. Various fields in Middle to Upper Pennsylvanian strata provide most of the oil production in these counties.

Fewer counties reported NORM activities in gas-processing facilities. Five counties have NORM levels in the 90th percentile (>65 μrems/h), and nine counties have median readings in the 75th percentile (6 to 65 μrems/h). Four of the counties reporting median values greater than 6 μrems/h and all counties reporting greater than 65 μrems/h are along the Texas Gulf Coast (fig. 4b). Kenedy, Brooks, Kleberg, and Jim Wells Counties in the south Texas Gulf Coast are in or adjacent to the Rio Grande Salt Basin. Production from major gas fields in this basin is mostly from the Frio Formation; additional production comes from Miocene strata (Kosters and others, 1989). Refugio, Calhoun, Jackson, and Karnes Counties are in the central Texas Gulf Coast. Major gas fields in these counties produce primarily from Cenozoic strata (Wilcox, Reklaw, and Frio Formations and Miocene strata) (Kosters and others, 1989). Chambers County, in the north Texas Coastal Plain, lies within the Houston Salt Basin. Major gas fields in Chambers and adjacent counties in the Houston Salt Basin produce from Frio and Miocene strata. An area of salt pillows associated with the East Texas Basin encompasses Nacogdoches County in East Texas. Major gas production here is from Mesozoic strata, chiefly the Pettet and Rodessa Formations. In north-central Texas, gas-processing facilities in Stephens and Jones Counties have NORM levels in the range of 6 to 65 μrems/h. No major gas fields exist in these counties (Kosters and others, 1989). Major gas fields in Midland County in West Texas produce from several Permian stratigraphic intervals. Major gas production in Carson County, Texas Panhandle, is predomi-

nantly from Pennsylvanian and Permian strata associated with the Amarillo Uplift and the adjacent Anadarko Basin.

Assuming that high NORM activity levels in a county reflect the radioactivity produced from the fields and formations that account for major oil and gas production in that county leads to several conclusions. First, elevated NORM activities (75th percentile or higher) are not restricted to reservoirs of a particular geologic age or lithology. Second, many counties that have major oil and gas fields, and in which NORM levels were measured, do not have high radioactivity associated with production and processing equipment. Third, the Rio Grande Salt Basin and the central Texas Gulf Coast are the only regions that have NORM levels in the 90th percentile for both oil and gas facilities. These are also regions in which large quantities of oil and gas are produced from Frio reservoirs that, in south Texas, contain appreciable quantities of volcanic rock fragments (Langford and others, 1994). Such volcanic material is likely to contain high concentrations of U and Th that, along with daughter Ra isotopes, are released to the pore water system during diagenesis (Walton and others, 1981).

Uranium, Thorium, and Radium in Reservoirs and Formation Water

The isotopes ^{226}Ra and ^{228}Ra produce most of the radioactivity in oil and gas facilities. Because the half-lives of ^{226}Ra and ^{228}Ra are geologically short (1,622 yr and 6.7 yr, respectively), Ra incorporated with sediments and original pore water does not survive to be produced. Rather, Ra generated from parent U and Th isotopes in the reservoir leads to NORM accumulations. The short half-lives of ^{226}Ra and ^{228}Ra, combined with typical flow rates of basinal brines (cm/yr in the Texas Panhandle [Wirojanagud and others, 1986] and Gulf Coast Basin [Harrison and Summa, 1991]) indicate that Ra is not transported long distances. For example, in one half-life, ^{226}Ra and ^{228}Ra would move only about 160 and

Table 2. Mean values and ranges of uranium and thorium concentrations (ppm) in selected rocks and minerals.

Rock or mineral	U mean	U range	Th mean	Th range	Reference
Average shale	3.7		12		a
Average shale	3.5	3.0 – 4.0			b
Common shales	3.7	1 – 13	12	2 – 47	c
Black shale	8	3 – 250			b
Black shales		1.4 – 80		2.8 – 28	c
Black shales, metal-rich	20				a
Sandstones (267 samples)	2.4		8		d
Orthoquartzites	0.45	0.2 – 0.6	1.7	0.7 – 2.0	c
Siltstones (52 samples)	2.7		8.8		d
Claystone/shale (176 samples)	4.4		11.5		d
Carbonates	2.2		1.7		e
Bentonites	5	1 – 21	24	6 – 44	c
Carbonate rocks		0.1 – 9	1.7	0.1 – 7	c
Halite	2.2	0.1 – 0.2		0.4 – 0.5	c
Anhydrite		0.1		0.15	c
Phosphate rock		245		3.9	c
Chert		1.9 – 3.3		0.1 – 1.6	c
Minerals from igneous rocks					
Quartz	1.7	0.1 – 10		0.5 – 10	f, g
Feldspar	2.7	0.1 – 10		0.5 – 10	f, g
Biotite	8.1	1 – 60		0.5 – 50	f, g
Muscovite		2 – 8			f
Hornblende	7.9	0.2 – 60		5 – 50	f, g
Pyroxene	3.6	0.1 – 50			f
Olivine	0.05		0.02		f
Allanite	200	30 – 1,000	9,100	1,000 – 20,000	f, g
Apatite	65	10 – 100	70	50 – 250	f, g
Epidote	43	20 – 200	200	50 – 500	f, g
Garnet		6 – 30			f
Huttonite		3,000 – 70,000			f
Magnetite, opaque minerals		1 – 30		0.3 – 20	f, g
Monazite	3,000	500 – 3,000	49,700		f, g
Sphene	280	10 – 700	510	100 – 1,000	f, g
Xenotime		300 – 40,000			f
Zircon		100 – 6,000	560	100 – 10,000	f, g
Other					
Asphaltite	4,000				h

a: Bell, 1978 c: Adams and others, 1959 e: Turekian and Wedepohl, 1961 g: Rogers and Adams, 1969b
b: Swanson, 1961 d: Dypvik and Bue, 1984 f: Rogers and Adams, 1969a h: Pierce and others, 1964

0.6 m, respectively. Flow rates can be much faster during reservoir production, but such conditions are maintained for only a few decades at most. Therefore Ra in produced water must be generated from parent U and Th and released to formation water relatively near the producing well.

Uranium and Th are typically present at parts-per-million (ppm) concentrations in sedimentary

rocks and in the igneous and metamorphic minerals that contribute detritus to clastic sediments (Rogers and Adams, 1969a, b; Gascoyne, 1989; table 2). Sandstones generally contain less than 3 ppm U and less than 8 ppm Th, whereas limestones contain less than 9 ppm of either U or Th. Evaporite strata generally contain less than 0.1 ppm U and less than 1 ppm Th. However, some sedimentary strata and accessory minerals can have parts-per-thousand concentrations (table 2). Uranium concentrations exceeding 100 ppm are found in black shales, phosphates, coals, and asphaltites, whereas Th concentrations greater than 10 ppm are found in shales, bauxite deposits, manganese nodules, and oceanic clays (table 2.2 of Gascoyne, 1989). Uraniferous asphaltite, a U-bearing carbonaceous material found in the Texas Panhandle and in many other geologic and geographic settings (Pierce and others, 1964), may contain several thousand parts per million of U. Accessory minerals such as allanite, huttonite, monazite, and zircon contain U and Th concentrations as high as several thousand parts per million (table 2). In general, therefore, typical reservoir strata can be expected to contain parts-per-million levels of U and Th, whereas organic-rich shales, phosphate deposits, asphaltites, and accessory minerals contain concentrations of U and Th that are several orders of magnitude greater.

Under the reducing conditions present in hydrocarbon reservoirs, both U and Th are essentially immobile, as predicted from thermodynamic data and demonstrated by the exceedingly low concentrations measured in formation waters (for example, Kraemer, 1985). At reservoir pH, Eh, and temperature conditions, aqueous U exists in the +4 valence state, from which it forms the highly insoluble minerals uraninite and coffinite (for example, Kraemer and Kharaka, 1986). Thorium occurs only in the +4 valence state and is insensitive to redox state. The minerals that have Th as a major cation are highly insoluble under reservoir conditions (Rogers and Adams, 1969a). Furthermore, at pH values greater than 3, thorium in solution readily hydrolyzes to form various insoluble hydroxide species (Zukin and others, 1987). Thorium also has a strong tendency

to adsorb onto reservoir materials (Langmuir and Chatham, 1980). For these reasons, the aqueous activities of parent ^{238}U and ^{232}Th are insufficient to support the activities of daughter ^{226}Ra and ^{228}Ra, respectively, present in formation waters and ground waters (for example, Kraemer, 1981; Kraemer and Reid, 1984; Kraemer, 1985; Kraemer and Kharaka, 1986; Kraemer, 1993).

Both ^{226}Ra and ^{228}Ra are produced by alpha decay (fig. 1), and recoil damage to the host mineral is generally regarded as the mechanism by which Ra is released. Fleischer and Raabe (1978), Fleischer (1982), and Rama and Moore (1984) investigated the effectiveness of alpha-decay product removal from mica, feldspar, pyroxene, quartz, and natural glass. They reported that recoil ejection from grains and release by natural etching of alpha-recoil tracks are the two principal mechanisms by which alpha-decay products enter the pore water system. If parent U or Th isotopes are located on grain surfaces, Ra could be ejected directly to pore water. Intracrystalline damage caused by alpha recoil and subsequent removal of Ra from the grain would probably be a more important release mechanism because the amount of daughter product involved is not limited to that produced by parent isotopes situated on mineral or grain surfaces. Conditions that promote escape of alpha-decay products are (1) small size and large surface-to-volume ratio of U- and Th-containing materials; (2) large, well-connected intragranular and intergranular pore spaces; (3) the presence of U and Th near grain surfaces; and (4) water-filled pore spaces (Fleischer, 1982).

Diagenetic processes may either retard or promote Ra mobilization (fig. 5). Precipitation of cement on grain surfaces may retard alpha-recoil release of radionuclides. Essentially no U, Th, or Ra coprecipitates with authigenic phases because of the relatively low temperatures of formation (80° to 120°C) and the absence of U and Th in formation water. Therefore authigenic quartz, feldspar, or carbonate deposited on detrital grains could shield alpha-recoil products from reaching the interface between grain surface and pore water (Kraemer, 1981). Albitization of detrital feldspar and conversion of detrital clays to illite
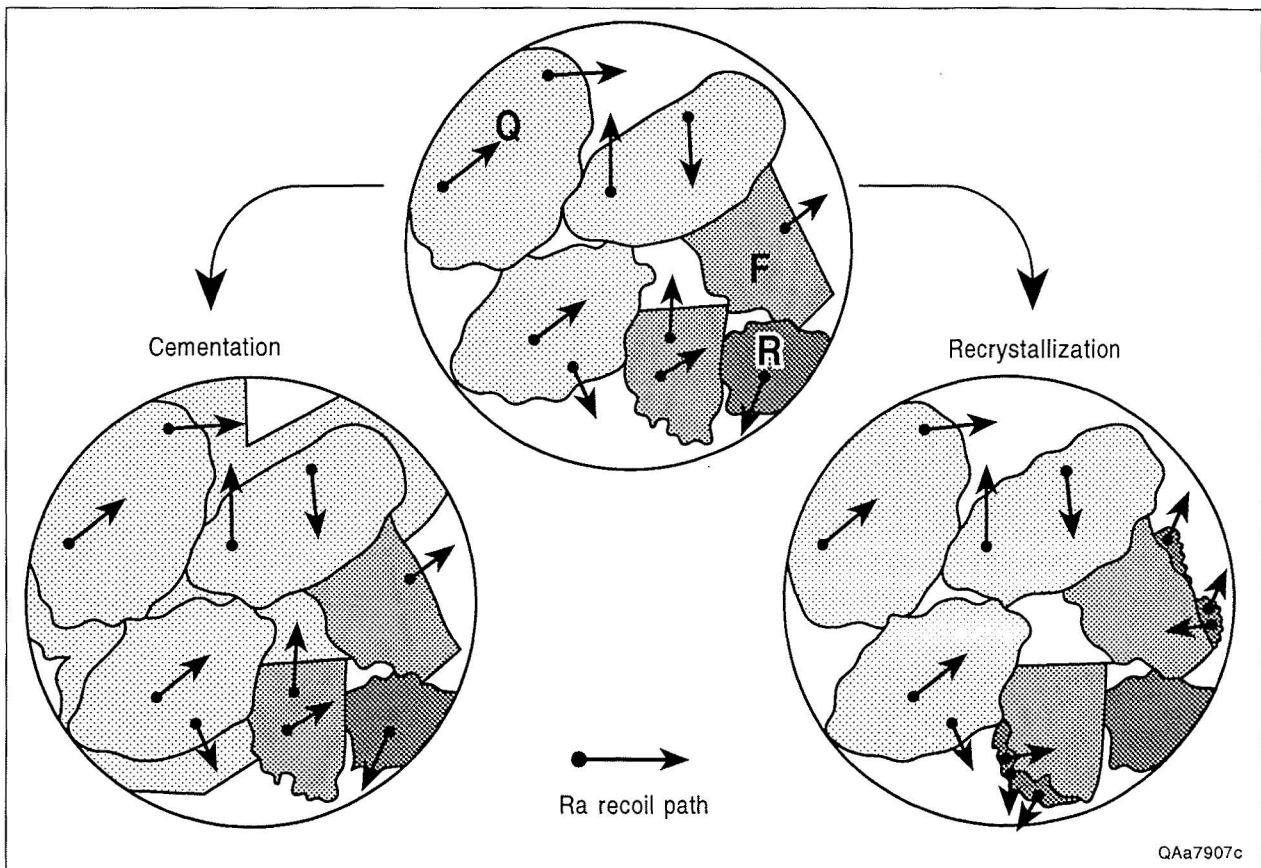
Figure 5. Schematic illustration of the results of diagenesis on Ra mobility. Pore-filling cementation will reduce the possibility that Ra generated from parent Th in the reservoir matrix will escape to the pore water system, whereas mineral dissolution and reprecipitation of more stable phases will mobilize U and Th to sites where the Ra generated has greater access to the pore water system. Q = quartz, F = feldspar, and R = rock fragments.

or chlorite in shales and sandstones, diagenetic reactions that affect nearly all sandstones and shales in Gulf Coast strata at temperatures exceeding about 80°C (for example, Milliken, 1988, 1989), may promote Ra release. Dissolution of detrital feldspars or clays and precipitation of authigenic phases release trace elements into solution. Immobile species such as U and Th would be readily adsorbed onto grain surfaces or could form trace amounts of authigenic U- and Th-rich minerals. Alpha-recoil products from parent U and Th isotopes that are either adsorbed onto grain surfaces (Ames and others, 1983a, b) or included in finely crystalline authigenic minerals would then be closer to the water phase than

before diagenesis, and release to the pore water system would be more likely.

Radium released from host minerals by alpha recoil may be removed from solution by mineral precipitation or sorption onto grain surfaces, or it may remain in solution. Previous studies have shown that Ra concentrations in ground water and formation water are always too low for saturation with respect to a pure Ra phase (for example, Langmuir and Melchior, 1985; Langmuir and Riese, 1985). Radium concentrations in formation waters are sufficiently low that radium sulfate ($RaSO_4$), the least soluble Ra phase, is always undersaturated by several orders of magnitude. Radium concentrations must instead be

limited by solid solution formation (coprecipitation), adsorption, or both.

Langmuir and Riese (1985) evaluated the coprecipitation of Ra in various minerals from both a thermodynamic and an experimental perspective. Their findings can be summarized as an empirical distribution coefficient D:

$$D = (RaX/MX)_N / (Ra^{+2}/M^{+2})_m, \qquad (1)$$

where m indicates the molal aqueous concentration of Ra and the major ion (M) that Ra substitutes for in the crystal, and N indicates the mole fraction of Ra and M in solid solution X. If the value of D is greater than 1, Ra will preferentially replace M in solid solution; if D is less than 1, Ra will be excluded from the solid solution. Langmuir and Riese (1985) investigated Ra coprecipitation in sulfate and carbonate minerals. The value of D decreases in the order anhydrite > celestite > anglesite > barite > aragonite > strontianite > witherite. Coprecipitation of Ra in calcite was not investigated because the large ionic size difference between Ra and Ca in the calcite structure precludes ready substitution. For the minerals investigated, D decreases with increasing temperature. Values of D are greater than 1 for anhydrite, celestite, anglesite, and barite at 25°C and greater than 1 for anhydrite, celestite, and anglesite at 100°C. None of the carbonate minerals investigated showed a preference for Ra over Ca in the crystal structure. These data indicate that the thermodynamically favored NORM scale minerals are anhydrite, celestite, anglesite, and barite, and that for a fixed solution composition, less Ra will be incorporated in scale formed at higher temperatures than at lower temperatures. Whether these minerals actually form, however, depends on formation water composition and whether the phases become oversaturated during production.

Many workers have noted a correlation between Ra concentrations and total salinity in ground water and formation water (for example, Dickson, 1990). Dickson (1990) also observed that in dilute solutions and fresh-to-brackish ground waters, Ra is readily removed from solution by sorption onto grain surfaces. High salinity appears to be a requisite for high Ra concentrations (Dickson, 1990), although not all saline waters support high Ra activities. Experimental data confirm that Ra is extremely efficiently scavenged from dilute water by sorption processes (summarized by Dickson, 1990). In saline waters, however, high concentrations of cations such as sodium, calcium, magnesium, and potassium successfully compete for sorption sites, and high levels of Ra can be maintained in solution.

Mineralogy of NORM Scale

Predicting the conditions that favor NORM scale accumulation requires knowledge of the chemical composition and mineralogy of the phase containing radioactive species. Identifying geologic, geochemical, and production characteristics that can mitigate NORM scale accumulation; developing scale inhibitors; and designing water flooding and commingling strategies that will not promote NORM scale accumulation all depend on an accurate knowledge of NORM scale composition. Unfortunately, most scale is a complex mixture of authigenic minerals, rust, and other contamination from the well equipment. Identifying the NORM-containing phase in such material requires detailed separation and analytical procedures. Furthermore, to quantify NORM scale accumulation under various reservoir and production conditions, the scale must be collected from equipment that produces water from a single, untreated formation for a known amount of time or, more specifically, for a known amount of produced water. For these reasons, little quantitative information exists regarding the chemical or mineralogical form of the NORM-containing phase.

Most literature reports indicate that barite ($BaSO_4$) hosts NORM in production equipment (for example, Gallup and Featherstone, 1983; Matty and others, 1985; Smith, 1987; Waldram, 1988; Snavely, 1989; Baird and others, 1990; Stephenson, 1992; Oddo and Tomson, 1994); NORM associated with calcite is less commonly

mentioned. Geochemical evidence supports the contention that Ra resides in barite. Because Ra forms a solid solution with barite, barite has long been used to remove Ra from mine waters and U mill tailings. Langmuir and Melchior (1985) investigated the ability of Ra to form solid solutions with common sulfate and carbonate minerals, whereas Gnanapragasam (1991) studied Ra partitioning in calcite, gypsum, and brushite, minerals that are likely to form in treated U mill tailings. Because of its ionic radius (1.48 Å in eightfold coordination [Shannon, 1976]), Ra can most readily substitute for Ba (1.42 Å in eightfold coordination) or Sr (1.26 Å in eightfold coordination). Radium substitution for Ca in NORM scale is less likely because in most common carbonate scale minerals, Ca is in sixfold coordination and has an ionic radius of 1.12 Å (Shannon, 1976), significantly smaller than that of the Ra ion. Langmuir and Riese (1985) determined or estimated distribution coefficients for Ra in the minerals anhydrite ($CaSO_4$), celestite ($SrSO_4$), anglesite ($PbSO_4$), barite ($BaSO_4$), aragonite ($CaCO_3$), calcite ($CaCO_3$), strontianite ($SrCO_3$), witherite ($BaCO_3$), and cerussite ($PbCO_3$). On the basis of the measured or estimated distribution coefficients and the abundances of Ca, Sr, Ba, and Pb in typical formation waters, barite and celestite are the scale minerals most likely to preferentially incorporate significant amounts of Ra (Langmuir and Riese, 1985). Geochemical modeling of formation water compositions (following section) shows that most waters are undersaturated with respect to celestite but saturated or nearly saturated with barite under reservoir conditions; thus, barite is the most likely mineral to precipitate Ra in significant quantities.

We analyzed a suite of NORM scale samples to investigate how radioactivity is incorporated in scale minerals. Twenty scale samples were collected from a field in north Texas by Art Rood of EG&G Engineering Idaho, Inc., with the cooperation of the producing company and API. The X-ray diffraction analysis showed that all samples contain barite and as many as four iron oxide or iron oxyhydroxide minerals (goethite, lepidocrocite, akaganeite, and maghemite). All scale samples also contain halite, which precipitated when residual produced water evaporated after sample collection. Total inorganic carbon analyses showed that the scale contained no carbonate minerals. Concentrations of major cations and activities of selected isotopes are shown in table 3. Qualitative correlations between gross radioactivity and scale color showed that the lighter colored scale samples were more radioactive. This suggests that radioactivity is preferentially associated with barite (a white mineral) rather than with the iron-rich phases (red-brown to brown). To quantify this relation we selected 10 scale samples that ranged from nearly white to deep red and measured major cations in each. Results (fig. 6) show a strong positive correlation between Ba and ^{226}Ra activity and a strong negative correlation between Fe and ^{226}Ra activity. These results confirm that in this suite of scale samples, radioactivity is associated with barite scale rather than the other phases present.
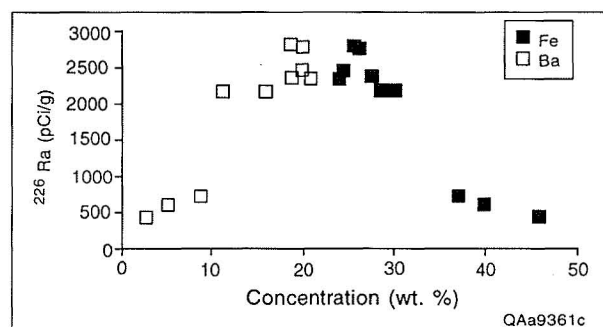
Figure 6. Plots of ^{226}Ra activity versus Ba and total Fe in NORM scale samples. Radium activity correlates positively ($r^2 = 0.866$) with barium content and negatively ($r^2 = 0.901$) with iron content, indicating that barite, not iron oxide, hosts radioactivity.

Formation Water Types and Potential to Form Barite Scale in Texas Reservoirs

Previous studies found significant differences in formation water compositions both along the Texas Gulf Coast and in the Texas Panhandle.

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Table 3. Results of radiometric analyses of scale provided by EG&G Engineering Idaho, Inc., and chemical analyses performed at the Bureau of Economic Geology's Mineral Studies Laboratory (MSL).

Sample number	MSL number	^{226}Ra (pCi/g)	^{232}Th (pCi/g)	Rn (pCi/g)	Fe (μg/g)	Ba (μg/g)	Na (μg/g)	Mg (μg/g)	Sr (μg/g)	Ca (μg/g)	SiO$_2$ (wt. %)
PF002SC001		895.47	1,508.0	0.79							
PF002SC002	94-318	2,150.00	2,955.0	1.60	301,500	112,500	51,840	2,440	14,490	11,470	2.41
PF002SC003		1,977.00	2,991.0	0.47							
PF002SC004		1,941.00	2,789.0	0.82							
PF002SC005	94-319	2,156.00	2,999.0	2.80	287,600	159,000	29,520	1,700	19,600	8,620	1.91
PF002SC006		397.70	512.5	1.00							
PF002SC007	94-320	424.75	534.0	0.90	459,100	27,250	9,900	1,270	3,180	8,170	4.08
PF002SC008	94-321	2,747.00	4,063.0	1.10	262,900	198,000	6,310	460	28,560	3,810	1.50
PF002SC009		1,042.10	1,622.0	0.50							
PF002SC010	94-322	2,321.00	3,619.0	1.10	241,400	208,000	6,610	680	29,760	5,540	1.58
PF002SC011		2,224.00	3,818.0	2.30							
PF002SC012		2,629.00	393.0	2.90							
PF002SC013		716.80	1,313.0	0.60							
PF002SC014	94-323	2,337.00	3,605.0	0.90	277,300	187,200	16,290	1,070	25,600	7,200	1.65
PF002SC015	94-324	2,762.00	4,050.0	2.00	258,100	186,800	15,480	1,170	26,600	6,360	1.77
PF002SC016	94-325	707.30	1,295.0	0.70	369,500	89,340	35,910	2,390	11,350	9,630	3.47
PF002SC017	94-326	2,437.00	3,974.0	1.00	246,000	198,000	6,670	1,070	27,830	5,810	1.69
PF002SC018		658.00	1,363.0	0.50							
PF002SC019		2,256.00	3,359.0	0.90							
PF002SC020	94-327	591.90	1,502.0	0.70	398,900	52,080	41,400	1,930	7,360	6,940	4.37

These differences could affect the presence of NORM in oil- and gas-field equipment in three ways. First, the composition of formation water influences Ra mobility in sedimentary basins. Second, water chemistry, as well as production techniques, controls the type and amount of scale that can form in well-bore and surface equipment. Scale mineralogy in turn affects the amount of NORM extracted from produced water and concentrated in equipment scale. Third, formation water composition records basinal processes and history. Because geologic phenomena such as thermal and diagenetic history may be important in determining Ra release from parent rocks and minerals, formation water chemistry may be a useful predictor of NORM activity in production and processing equipment.

Chemical Composition of Water in Texas Reservoirs

Studies of Texas formation water have focused primarily on the Gulf Coast and the Texas Panhandle. The Gulf Coast has been an area of intense interest both because of the enormous quantities of oil and gas produced and because of the potential for developing geopressured-geothermal energy resources. In addition to being an important energy-producing area, during the 1980's the Texas Panhandle was a candidate in U.S. Department of Energy investigations for a suitable site for high-level nuclear waste isolation. Formation water chemistry was investigated in both Gulf Coast and Panhandle fields to clarify subsurface geochemical conditions, hydrologic flow systems, and basinal diagenetic processes. Published data from other hydrocarbon provinces in Texas are less abundant.

Morton and Land (1987) found four distinct types of formation water in Frio Formation (Oligocene) sandstones along the Texas Gulf Coast: (1) highly saline sodium chloride water, associated with salt domes and pillows; (2) sodium acetate water produced by shale dewatering; (3) calcium-rich water resulting from extensive silicate diagenesis; and (4) low-salinity sodium chloride water of limited distribution. Sodium and

chloride are the predominant cation and anion, respectively, in water from Oligocene sandstones in the salt dome province of the Houston Embayment. Sodium chloride water having generally lower salinity and high organic acid concentrations predominates along the San Marcos Arch in the central Texas Gulf Coast. High-salinity sodium calcium chloride (Ca-rich) water occurs in sandstones in a small area of the south Texas Gulf Coast. Along the Rio Grande in South Texas, low-salinity sodium chloride water prevails. Land and Macpherson (1992) and Macpherson (1992) found the same four water types with the same general distribution in waters from all Cenozoic sandstones that could be sampled along the Texas Gulf Coast. Sulfate concentrations are typically less than 100 milligrams per liter (mg/L) in all these formation water types because of bacterial sulfate reduction at ambient burial temperatures. The origin of these water types is discussed extensively in Morton and Land (1987), Land and Macpherson (1992), and Macpherson (1992) and is not repeated here. Significant to this study are the conclusions that compositionally distinct formation waters exist in oil and gas reservoirs along the Texas coast and that formation water compositions reflect basinal geologic and hydrologic processes.

Bein and Dutton (1993) grouped deep-basinal formation waters from oil and gas wells in the Texas Panhandle into sodium chloride and calcium chloride types. The sodium chloride type brine was interpreted to form as meteoric water dissolves halite. Calcium-rich brines were interpreted to be modified connate seawater. Sulfate concentrations in these waters range from several tens to several thousand milligrams per liter.

Land and Prezbindowski (1981) and Prezbindowski (1981) investigated formation waters from oil and gas wells in the Lower Cretaceous Glen Rose and Edwards Formations, Stuart City Trend, south-central Texas. Chemical and isotopic analyses (Prezbindowski, 1981) indicate that the formation waters are characterized by molal sodium-to-chloride ratios less than 1 and (Cl–Na)/ Mg ratios greater than 1. Sulfate concentrations in these waters range from several tens to several thousand milligrams per liter. Production

depths range from 800 to 4,400 m. Land and Prezbindowski (1981, 1985) and Prezbindowski (1981) interpreted the deep, saline brine to be a product of halite dissolution and diagenetic reactions involving silicate minerals. As the basinal brine moves upward and becomes diluted with meteoric water, additional reactions between fluid and host rock phases produce the less saline waters observed at shallower depths.

Kreitler and others (1987) investigated formation water chemistry as part of a hydrologic characterization of the East Texas Basin. These formation waters are similar to the sodium chloride waters in the Texas Panhandle. The saline waters in this basin are interpreted to have a continental meteoric origin, sodium and chloride are the predominant ions, and salinity is derived primarily from salt dissolution. Sulfate concentrations in these formation waters range from several tens to several hundred milligrams per liter.

Published chemical analyses thus indicate the presence of four volumetrically important formation water types in Texas. These are (1) a sodium chloride water having variable salinity and sulfate concentration that is produced by evaporite dissolution, (2) a sodium acetate water, generally less saline than seawater, that originates as water expelled from thick shales, (3) a calcium-rich sodium chloride water that results from evaporite dissolution coupled with extensive silicate mineral diagenesis, and (4) a calcium chloride water resulting from evaporative concentration of seawater accompanied by diagenesis of carbonate and evaporite minerals. Mixtures of these water types with each other, with seawater, or with meteoric water are possible. Other chemical types may exist locally, but we focused on the principal water types because they are most volumetrically significant in oil and gas production.

Scaling Potential of Texas Formation Water

To investigate natural controls on NORM, we first evaluated whether there are systematic regional or geologic variations in the amount of NORM scale that can precipitate during fluid production. Barite is the primary mineral of concern because Ra substitutes for Ba more readily in the barite crystal structure than in other common scale minerals and because barite is reported to be the principal NORM scale material. Radium also can coprecipitate in celestite (Langmuir and Riese, 1985). However, results of our geochemical modeling show that most Texas formation waters are saturated with barite but not with celestite at reservoir temperatures. Similar results were reported by Macpherson (1989, 1992) for Gulf Coast formation waters.

Oil and natural gas in Texas are produced from a wide variety of reservoirs, having diverse pressures, temperatures, and water compositions. It is not practical to geochemically test all available formation water compositions for barite saturation because the quality of analytical data for some samples is unknown and in situ temperatures and pressures may be missing or inaccurate. Water chemistry data that include high-quality chemical analyses of Ba and SO_4 were available from the Texas Panhandle (Dalhart, Anadarko, Palo Duro, and Hardeman Basins), East Texas Salt Basin, Texas Gulf Coast, Edwards Group, Central Basin Platform, and Delaware Basin (fig. 7). We used SOLMINEQ.88 (Kharaka and others, 1988) to compute the equilibrium solubility constant of barite ($K = [Ba^{+2}]$ $[SO_4^{-2}]$). We chose a model temperature of 100°C because the formation water temperatures in our data set range from about 50° to 150°C. Barite solubility is only slightly dependent on pressure (Templeton, 1960; Blount, 1977; Schulien, 1987); however, pressure effects may be important to our calculations because reservoir depths range from about 1.5 to 4.5 km. Therefore we calculated the saturation concentrations of Ba and SO_4 at pressures equal to the vapor pressure of water at 100°C and at a total pressure of 828 bars (pressure of typical Gulf Coast reservoirs at 3.6 km). Figure 8 shows the Ba and SO_4 concentrations of all samples in our data base and the lines relating Ba and SO_4 concentrations for barite equilibrium under the conditions previously described. The good agreement between Ba and SO_4 in Texas formation waters and those predicted for equilibrium supports the hypothesis that most Texas
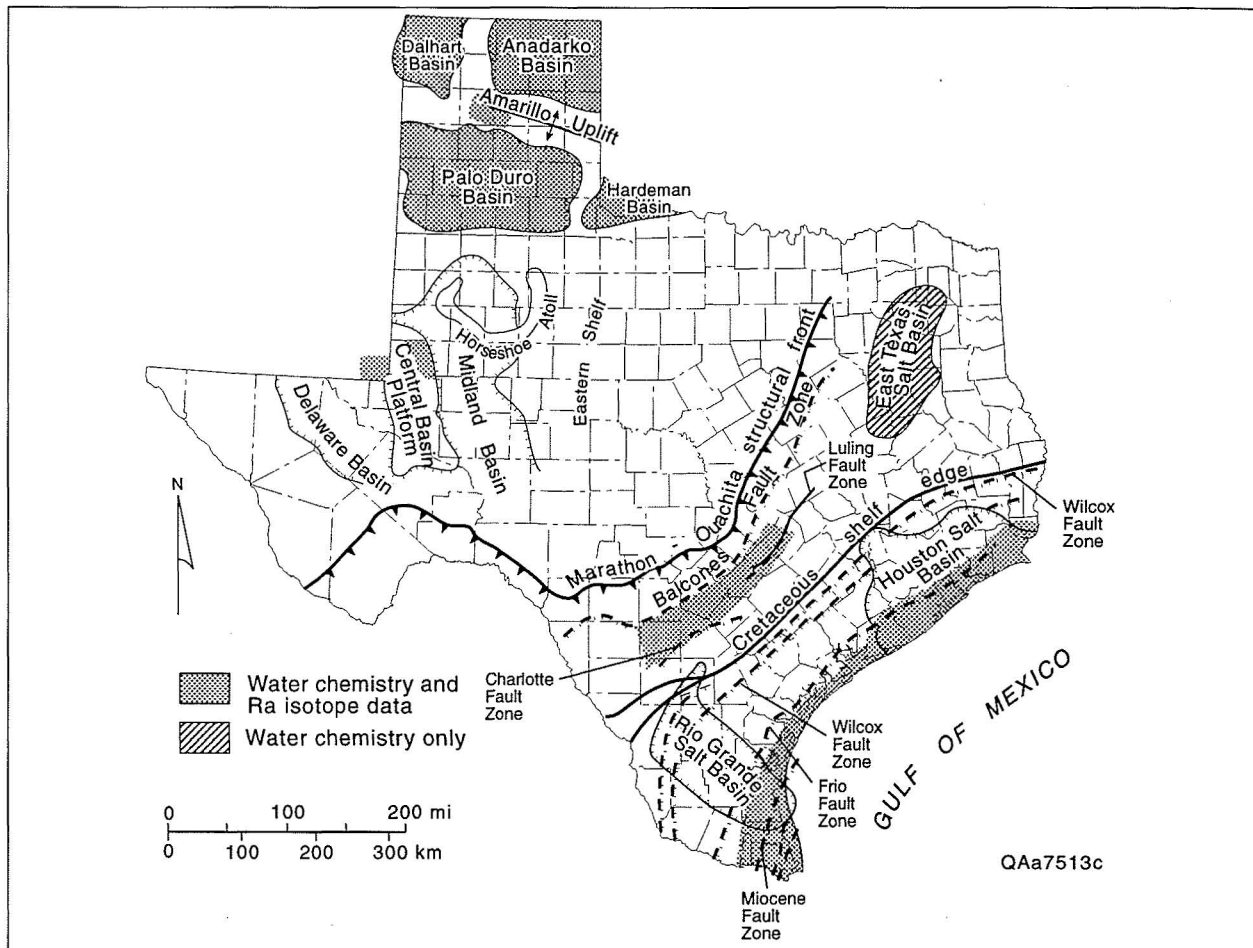
Figure 7. Map showing major structural elements in Texas and basins where water chemistry and water chemistry plus Ra isotope data are available.

formation waters are in or very near barite equilibrium under reservoir conditions. Because the solubility of barite decreases with temperature, barite will precipitate as water moves from reservoir to surface facility, and some Ra will be removed from the water and included in the barite scale.

Mean values (table 4) for the amount of barite scale that can precipitate fall into three groups. Waters from the Central Basin Platform and Texas Panhandle can precipitate less than 10 cubic centimeters of barite scale per 100 barrels of water (10 cm³/100 bbl), waters from East Texas, Frio, and Miocene reservoirs can precipitate 30 to 40 cm³/100 bbl, and waters from the Edwards Group can precipitate more than 60 cm³/100 bbl. Statistical analyses (95-percent confidence interval based on the Student's t-test

for unpaired sample sets with unequal variances [table 4]) show that the mean value of barite precipitated from Central Basin Platform wells is significantly lower than that of any other basin represented. The mean value of barite precipitated from Panhandle wells also is significantly lower than that of any other sample set except the Edwards Group. Barite precipitated from East Texas waters is significantly lower in mean value than that precipitated from Panhandle waters. Other differences in mean values are not significant at the 95-percent confidence level. Results from the Edwards Group, however, are strongly affected by one extremely high value. Although there is no reason to doubt the reported water composition, exclusion of that one sample results in a group mean of 5.6 cm³ barite/100 bbl water

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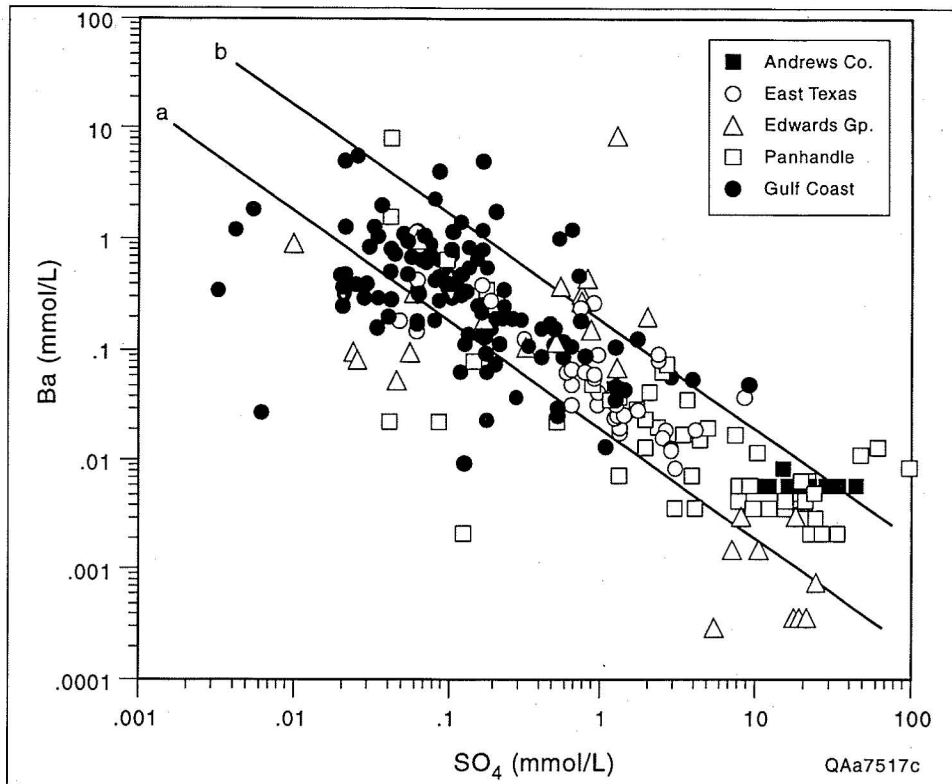
Figure 8. Plot of Ba versus SO_4 concentrations in Texas formation waters. Lines show the relation between Ba and SO_4 for barite equilibrium computed by SOLMINEQ.88 and corrected for typical activity coefficients for (a) pressure = vapor pressure of formation water at 100°C and (b) pressure = 828 bars. "Gulf Coast" samples include waters from Wilcox, Vicksburg, Frio, and Miocene strata. Agreement between predicted and measured concentrations suggests that most formation waters are equilibrated with barite at reservoir temperatures.

Table 4. Results of statistical analysis of amount of barite scale that can form from formation water samples, showing mean values of temperature, volume of scale that can form from 100 bbl water, and results of Student's t-test used to evaluate significance of differences between mean values.

Basin	Temperature (°C)	Barite scale (cm³/100 bbl)	East Texas	Edwards Group n = 21	Edwards Group n = 20	Gulf Coast Frio	Gulf Coast Miocene	Frio and Miocene	Panhandle
Central Basin Platform (12)	41	3.5	y	y	y	y	y	y	y
East Texas (38)	80	32.6		n	n	n	n	n	y
Edwards Group (21)	65	62.4				n	n	n	n
Edwards Group (20)	61	5.6				n	n	n	n
Gulf Coast Frio (37)	107	35.3					n	n	y
Gulf Coast Miocene (43)	93	35.5						n	y
Gulf Coast Frio and Miocene (80)	98	35.4							y
Panhandle (47)	62	9.2							

(n) = number of samples
y = >95-percent probability that mean values are different
n = <95-percent probability that mean values are different

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(table 4). In this case the formation water samples fall into two groups: those that can precipitate less than 10 cm³ barite/100 bbl water (Central Basin Platform, Edwards, and Panhandle waters) and those that can precipitate 30 to 65 cm³ barite/ 100 bbl water (water from East Texas, Frio, and Miocene reservoirs). The change in mean value of barite precipitated from Edwards Group waters does not affect the statistical significance of differences between mean values from the various basins.

The barite scaling potential of formation waters from the studied basins generally reflects mean formation water temperature and the fact that most formation waters are saturated with barite under reservoir conditions. The Central Basin Platform and the Texas Panhandle produce the coolest formation waters, with mean temperatures of about 41°C and 62°C, respectively. Mean reservoir temperatures of water samples from the Gulf Coast are 107°C (Frio), 93°C (Miocene), and 98°C (Frio and Miocene combined). Barite solubility increases with temperature up to about 100° to 125°C, depending on salinity and pressure (Blount, 1977). Over the range of sample temperatures, hotter waters are therefore expected to precipitate greater amounts of barite than cooler waters during production.

Radium in Produced Water from Texas and Adjacent Areas

Data Sources

Some data already exist regarding U, Th, and Ra in wells drilled for geothermal research, hydrocarbon production, and nuclear waste isolation. Although results of these studies have been analyzed individually, common parameters that may control radionuclide distributions regardless of basin or lithology type have yet to be explored.

In addition to the published data, new measurements were needed to study NORM in formation water throughout the state, particularly in areas where the API survey identified high NORM levels in production equipment. Our ob-

jective was to collect all available measurements of Ra and other dissolved species in produced water from oil, gas, and geothermal wells in Texas and adjacent areas so that interpretations and conclusions would not be limited to a single geologic or geographic region, nor to only the number of new samples we could obtain during this study. For this reason, the data base of Ra in produced water contains results from published reports, recent Ra measurements performed on previously collected water samples, and radioactivity measured in samples collected for this study.

Previous studies of Ra in Texas formation water focused on specific fields or wells. Pierce and others (1955, 1964) analyzed water, natural gas, asphaltite, and crude oil for various radioisotopes to investigate sources of U and helium in the Panhandle gas field, Texas Panhandle. Langmuir and Melchior (1985) measured radioisotope concentrations in formation waters from the Texas Panhandle as part of an investigation into the suitability of bedded evaporite strata to host a high-level nuclear waste isolation facility. Kraemer (1981, 1985, 1993), Kraemer and Reid (1984), and Kraemer and Kharaka (1986) measured radioisotopes, including ²²⁶Ra, in test wells along the Texas and Louisiana Gulf Coast as part of a U.S. Department of Energy program to evaluate geothermal energy potential. Taylor (1993) plotted ²²⁶Ra activities in produced-water discharges in Texas coastal waters as part of an investigation conducted by the Railroad Commission of Texas in an attempt to identify parameters that could be used to predict NORM levels.

Chemical compositions of produced-water samples collected as part of this investigation were measured at the Bureau of Economic Geology's Mineral Studies Laboratory (MSL) under an existing quality assurance/quality control program. Concentrations of major and most minor species are reproducible to within 5 percent, whereas trace constituents are reproducible to within 10 percent. The quality of data taken from published reports, some of which date from the mid-1960's or report only partial chemical analyses, is more difficult to evaluate. Where major cation and anion concentrations were reported, we accepted only those samples

for which the charge balance (cations − anions/ cations + anions) in milliequivalents per liter was 10 percent or lower.

In addition to evaluating new samples and data extracted from the literature, we evaluated the possibility of measuring Ra activity in samples previously collected and stored under known conditions. We identified a suite of several hundred produced-water samples that had been collected and analyzed for major, minor, and trace solutes as well as for isotopic composition of oxygen, hydrogen, carbon, and strontium in conjunction with other research at The University of Texas at Austin's Bureau of Economic Geology and Department of Geological Sciences. These produced-water samples were a significant resource for the NORM study because they were collected from a wide variety of geographic areas and geologic formations, they had already been analyzed for a large number of chemical and isotopic constituents, and they represented fields and reservoirs that have since been shut in. The field name, formation, depth of production, and storage history of these samples are well documented. If it could be shown that relevant parameters of brine composition had not changed since sample collection, we could also determine Ra activities in archived waters and thus greatly extend the data base. The high salinity of most formation waters and the fact that samples were filtered and acidified upon collection should prevent the loss of Ra from stored samples caused by sorption onto the container.

The appendix contains the chemical and radiometric data compiled for this study from basins throughout Texas and adjacent areas in New Mexico and the Louisiana Gulf Coast (fig. 7). The following sections describe data quality of samples from each region.

Central Basin Platform, West Texas

For this study, we collected 12 produced-water samples from oil and gas wells in Martin field, Andrews County, Texas. Wells in Martin field produce from stratigraphic intervals ranging from Ordovician to Permian. Limestone,

dolomite, sandstone, and chert lithologies are present. Chemical analyses were performed at the Mineral Studies Laboratory (MSL) of the Bureau of Economic Geology. The ^{226}Ra and ^{228}Ra analyses were performed on seven selected samples by Core Laboratories of Casper, Wyoming, according to methods described by Demorest and Wallace (1992) and established at Core Laboratories as Standard Operating Procedures CA-GLR-06.0 and CA-GLR-07.0. These procedures, designed specifically for saline produced waters, involve chemically separating Ra and then counting ^{226}Ra by alpha scintillation and counting beta emission of ^{228}Ra decay products (Demorest and Wallace, 1992). Analytical errors for this set of samples are approximately 20 pCi/L for ^{226}Ra and ^{228}Ra. Detection limits are approximately 7 pCi/L for ^{226}Ra and 30 pCi/L for ^{228}Ra.

Edwards Group, South-Central Texas

Water samples from the Edwards Group (Lower Cretaceous carbonate strata) were lent to us by Lynton Land, Department of Geological Sciences, The University of Texas at Austin. The sample suite was collected in 1990 as part of a joint U.S. Geological Survey–University of Texas investigation of the saline section of the Edwards aquifer. All samples had been filtered at the time of collection through 0.45-μm membrane filters, and both acidified and untreated aliquots were preserved. Repeat chemical analyses performed at MSL in 1994 duplicated the major and minor ion concentrations determined at the Department of Geological Sciences in 1990 to within the limits of analytical uncertainty. Because Ba and Ra have similar geochemical characteristics and because repeat analyses of Ba concentrations in the acidified aliquots were in good agreement with values originally measured, we considered these samples to have retained representative Ra concentrations. Sixteen samples covering a depth range of 165 to 3,374 m and a salinity range of 1,900 to 227,600 mg/L total dissolved solids (TDS) were analyzed for ^{226}Ra by Core Laboratories. Because only about 0.002 half-lives of ^{226}Ra had passed since the time of sample

collection, we did not adjust ^{226}Ra activities for decay in storage. The ^{228}Ra data were corrected to activities at the time samples were collected.

Delaware Basin, Southeastern New Mexico

Herczeg and others (1988) published Ra data for saline ground waters, lakes, and springs in the Delaware Basin, southeastern New Mexico, adjacent to Andrews County, Texas. Thirteen samples, collected from wells at the Waste Isolation Pilot Project (WIPP) site, oil or gas wells, or saline springs, were judged to be similar to produced water from oil and gas wells. Producing lithologies are anhydrite, halite, carbonate, dolomitic sandstone, cherty limestone, and shaly limestone. We could not evaluate the charge balance of these samples because Herczeg and others (1988) published only partial chemical analyses. However, we have included the reported chemical concentrations and Ra activities in our data base because they augment the sample coverage of a variety of lithologies near an important oil- and gas-producing part of the state.

Texas Panhandle

Radioisotopes in formation water from the Texas Panhandle were previously investigated for two purposes. Investigations during the 1950's and 1960's focused on the origin of helium in the Panhandle gas field, located along the Amarillo–Wichita Uplift. Studies during the 1980's measured U, Ra, and Rn radioisotope activities to interpret the suitability of bedded salt formations for high-level nuclear waste isolation. Related investigations elucidated the origin, age, and movement of formation water in the Texas Panhandle. These various studies provide a large data base of water chemistry, Ra activity, and host rock composition.

Pierce and others (1964) published 75 formation water analyses, including ^{226}Ra concentrations. Of these, 70 had acceptable charge balances and were included in the data base. Producing formations were not identified; however, they noted that "The highly saline brines of the Panhandle field are most likely derived from the evaporites of Leonard age, which overlie the oil and gas reservoir rocks." Leonardian-age strata in the Texas Panhandle include the Wichita Group (anhydrite, dolomite, and shale) and the lower Clear Fork (siltstone and shale interlaminated with dolomite and anhydrite). Pierce and others (1964) found that both Ra and Ca concentrations are highest in formation waters that have high chloride-to-sulfate ratios and high salinities. These relations were interpreted as reflecting the similar geochemical behavior of Ra and Ca and the effects of ion exchange. Pierce and others (1964) also concluded that Ra concentrations are not directly controlled by the U content of encasing strata. Disequilibrium ages, the time since isotopes were in equilibrium with each other, of 4 to 5 days were calculated on the basis of activity ratios for ^{226}Ra and ^{223}Ra (a decay product in the actinium series) and for ^{228}Ra and ^{224}Ra. These short ages suggest that Ra isotopes were derived from parent nuclei in the immediate vicinity of the well bore.

Langmuir and Melchior (1985), Dutton and Orr (1986), Fisher and Kreitler (1987), and Bein and Dutton (1993) investigated the composition and movement of water in strata ranging from pre-Pennsylvanian to Permian in the Texas Panhandle as part of an integrated geologic, geochemical, and hydrologic investigation to evaluate the suitability of bedded evaporite strata for a high-level nuclear waste repository. Radioisotope data for four deep-basin samples were collected as part of this work (Langmuir and Melchior, 1985). Because of the extensive data base, the variety of lithologies and formations previously sampled, and the large collection of formation water samples archived at MSL, we evaluated the chemical stability of selected samples during storage. Repeated analyses of major cations, anions, and Ba indicated that original compositions were preserved in acidified, field-filtered samples. In one case we were able to compare the ^{226}Ra activity of a sample collected and analyzed in 1985 by Langmuir and Melchior (1985) with ^{226}Ra measured in 1994 by Core Laboratories. Good agreement between the original and recent values indicated that ^{226}Ra activities measured as

part of this study are representative of formation conditions. Therefore, 25 formation water samples collected earlier (Fisher and Kreitler, 1987; Bein and Dutton, 1993) were analyzed for [226]Ra, and these results were combined with the data of Langmuir and Melchior (1985) to complement the Texas Panhandle data base.

Texas Gulf Coast

Formation water samples from wells along the Texas and Louisiana Gulf Coast were analyzed for Ra isotope activity as part of geothermal energy tests and as part of a Railroad Commission of Texas NORM investigation. Kraemer and Reid (1984) reported [226]Ra and [228]Ra activities in wells drilled for U.S. Department of Energy geothermal energy tests. Tested intervals were in the Tertiary Frio and Cretaceous Tuscaloosa sandstones at depths ranging from 2,984 to 6,238 m. Chemical data were not presented in Kraemer and Reid (1984) but are available elsewhere (Kharaka and others, 1977; 1978a, b; Kraemer and Kharaka, 1986; Kraemer, 1993). Kraemer and Reid (1984) reported that Ra activity correlates better with total salinity than with any other parameter. A study by the Railroad Commission of Texas (Taylor, 1993) presented [226]Ra values for offshore oil and gas wells without full chemical analyses. Plotted data show that Ra levels in produced waters from offshore wells in the Gulf of Mexico are higher in Oligocene Frio reservoirs than in overlying Miocene reservoirs. In waters from both Frio and Miocene formations, Ra levels increase with increasing salinity. These data suggest that Ra may be more readily mobilized from deeper, hotter formations and that high salinity tends to prevent Ra immobilization by processes such as ion exchange or sorption.

Relations between Radium Activity, Location, and Water Chemistry

For analytical reasons, [226]Ra is more commonly determined than [228]Ra. Even though the two Ra isotopes are members of different decay series, most studies find a close correlation. Our data set (appendix) contains 153 measurements of water chemistry and [226]Ra activity; 20 of these samples were also analyzed for [228]Ra. The correlation between [226]Ra and [228]Ra (fig. 9) is excellent ($r^2 = 0.96$; slope of regression line = 1.03); therefore, the following discussions based on [226]Ra data can be extrapolated to [228]Ra activities.

The [226]Ra activities in formation waters (appendix) range from 0.1 to 5,150 pCi/L (fig. 10). Ninety-five percent of the values fall between 2.0 and 2,290 pCi/L, and 41 percent are less than 100 pCi/L (fig. 10). Fourteen waters (9 percent of samples) have values greater than 1,000 pCi/L, and 17 samples (11 percent of samples) have values between 500 and 1,000 pCi/L. There is little apparent geographic control on [226]Ra activity values. Formation water samples that have more than 1,000 pCi/L [226]Ra are found in the Central Basin Platform (2 samples), Delaware Basin (1 sample), the Gulf Coast (1 sample), and the Texas Panhandle (10 samples), and values greater than 500 pCi/L occur in each of the sample groups (appendix).

Mean values of [226]Ra activity range from 140 pCi/L in water from the Edwards Group to 958 pCi/L in water from the Central Basin Platform (table 5). The Student's t-test was used to determine whether differences in mean Ra activities varied significantly among the sample groups. Results suggest that [226]Ra activity in formation water from wells in the Central Basin Platform is significantly (95-percent confidence level or higher) greater than in water from the other basins sampled and that [226]Ra activity in water of the Edwards Group is significantly lower than in water from the Texas Panhandle (table 5). However, the high mean [226]Ra value for water from the Central Basin Platform reflects the fact that two samples have [226]Ra activities greater than 2,000 pCi/L, whereas the other five samples are all less than 800 pCi/L. If the two exceptionally high values are omitted, the mean value of Central Basin Platform waters is 431 pCi/L, and this mean value is not significantly different from mean values of [226]Ra in the other basins (table 5).

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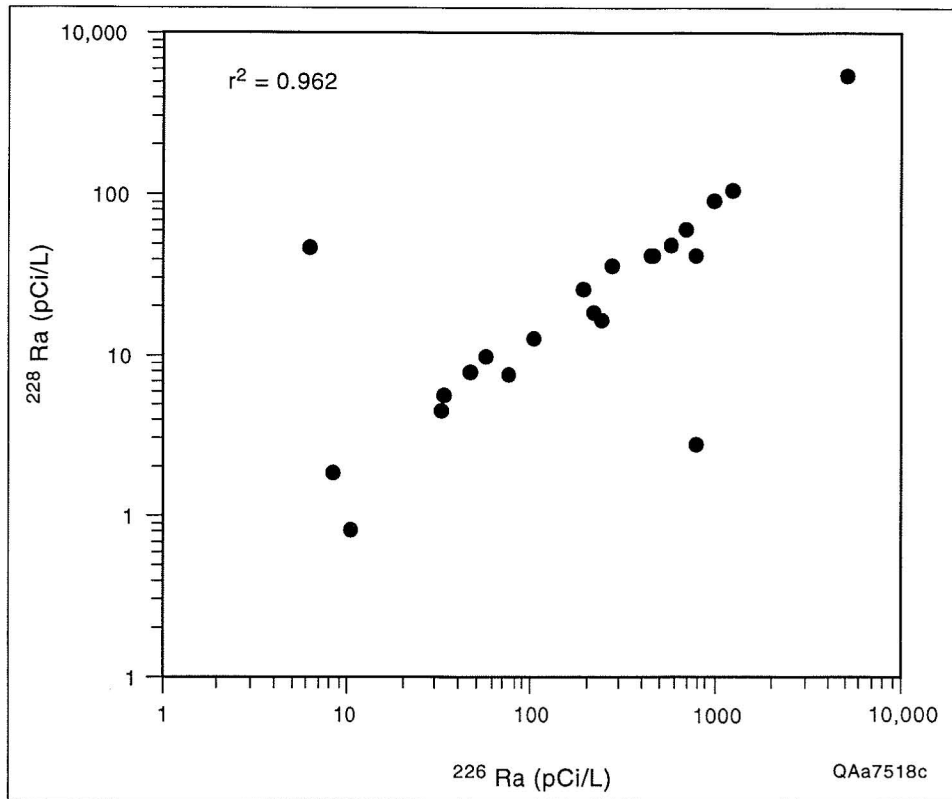
Figure 9. Plot of ^{226}Ra activity versus ^{228}Ra activity. Excellent correlation between the two radioisotopes indicates that activity of the less commonly measured ^{228}Ra isotope can be predicted from the activity of ^{226}Ra.
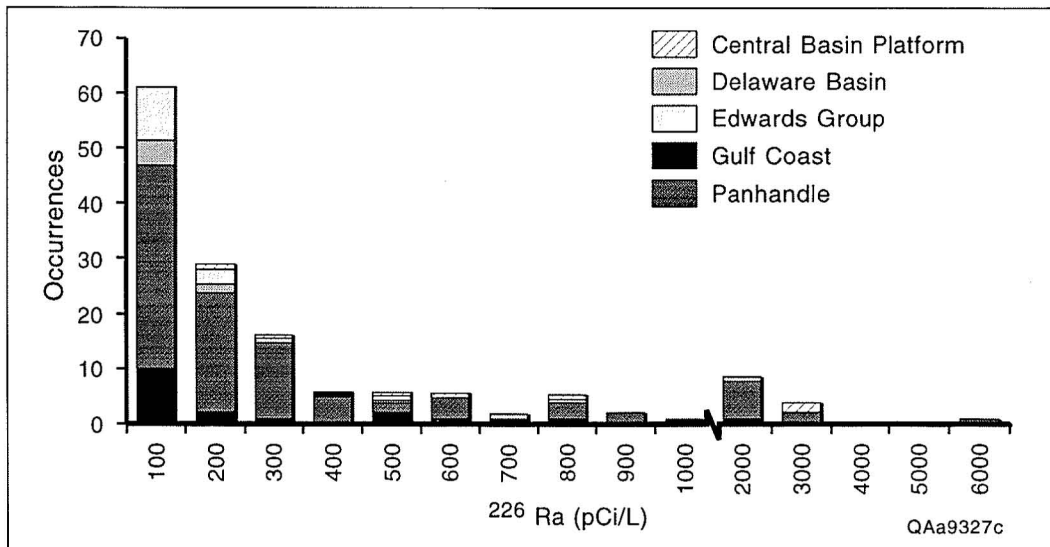
Figure 10. Histogram of ^{226}Ra activity in Texas formation water samples.

Table 5. Results of statistical analysis of [226]Ra activity in formation water samples, showing mean values and results of Student's t-test used to evaluate significance of differences between mean values.

	Mean pCi/L	Delaware Basin	Edwards Group	Gulf Coast	Panhandle
Central Basin Platform (7)	958	y	y	y	y
Central Basin Platform (5)	431	n	n	n	n
Delaware Basin (11)	284		n	n	n
Edwards Group (16)	140			n	y
Gulf Coast (20)	296				n
Panhandle (99)	370				

(n) = number of samples
y = >95-percent probability that mean values are different
n = <95-percent probability that mean values are different

Previous studies reported a general correlation between Ra activity and salinity in formation water; no other correlations between Ra and water chemistry, production depth, or temperature were noted. Kraemer and Reid (1984) found a correlation between Ra activity and TDS for produced-water samples from Gulf Coast reservoirs in Texas and Louisiana. A plot of log [226]Ra activity versus log TDS for water from geopressured-geothermal wells yielded a correlation coefficient (r^2) of 0.81, whereas a similar plot that included data from commercial oil and gas wells yielded an r^2 value of 0.52 (Kraemer and Reid, 1984). Data plots by Taylor (1993) show the same general trend for produced waters from offshore Gulf Coast oil and gas wells that produce from the same formations as the wells sampled by Kraemer and Reid (1984). Pierce and others (1964) reported that Texas Panhandle waters that have high Ra activities

also have high Cl concentrations, although many waters with high Cl have low Ra contents. The correlation coefficient r^2 for log [226]Ra and log Cl for data reported by Pierce and others (1964) is 0.56.

We cannot explore statewide correlations between Ra and TDS because not all samples included in our data base were analyzed for the full suite of major and minor ions. However, in samples with complete analyses, Cl correlates well with TDS ($r^2 = 0.995$) (fig. 11). Thus, correlations that are significant with TDS should also be significant with Cl. Figure 12 shows the relation between [226]Ra activity and Cl for all samples in the appendix; table 6 lists correlation coefficients relating log [226]Ra activity and log Cl content. Clearly the relation between [226]Ra and Cl that holds for Gulf Coast sandstones is not universal. Sample sets with the highest correlation coefficients are those in which all waters were derived from simi-

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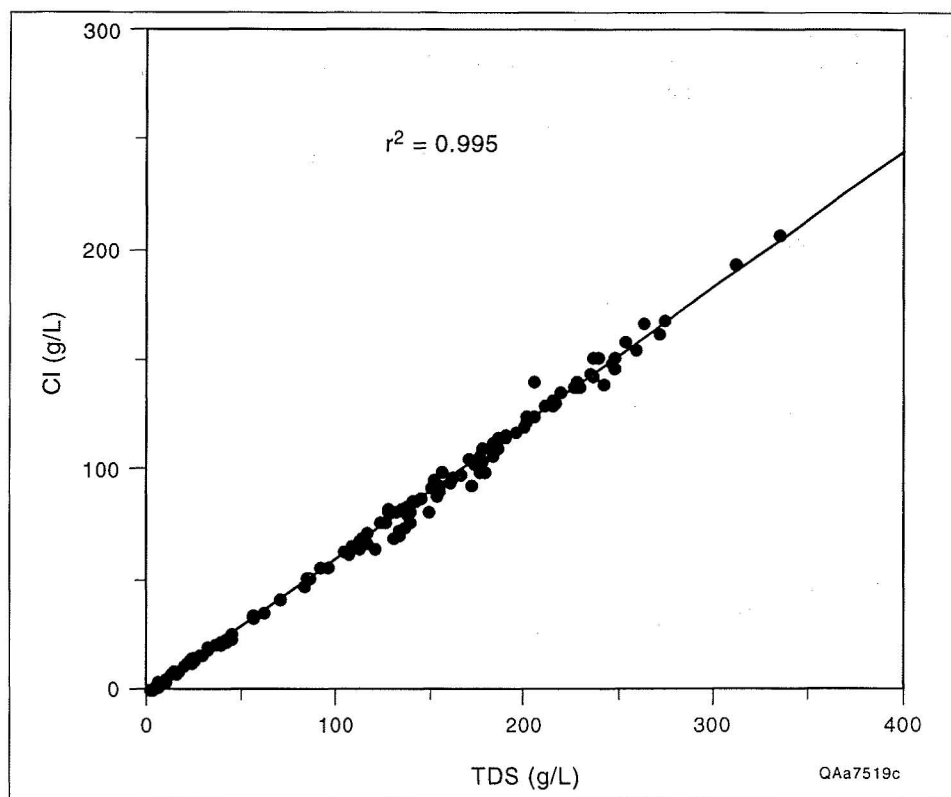
Figure 11. Plot of total dissolved solids (TDS) versus chloride (Cl) concentrations for produced waters that have been analyzed for ^{226}Ra or ^{228}Ra activity. Excellent correlation indicates that relations between ^{226}Ra or ^{228}Ra activity and TDS should also hold for relations between ^{226}Ra or ^{228}Ra activity and Cl.

lar rock types, for example, water samples from Gulf Coast sandstones ($r^2 = 0.71$) and those from Edwards Group carbonates ($r^2 = 0.63$). Data sets that contain different types of water samples (Delaware Basin) or waters hosted by different rock types (Central Basin Platform) have only poor correlations between ^{226}Ra and Cl (table 6). Figure 12 does illustrate that low-salinity waters do not support high Ra activities. The ^{226}Ra activities greater than 200 pCi/L are found only in waters that have more than about 20 g/L Cl (36 g/L TDS).

Statistical correlations between radioactivity and other dissolved constituents were determined to explore hydrochemical controls on ^{226}Ra activity in formation water (table 6). Correlations were considered geologically significant only if they accounted for more than 50 percent of

the variation in Ra activity, that is, only if r^2 was greater than 0.5. Correlations were sought between log Ra activity and the log of major ion concentrations because Ra activity and ionic concentrations fit a log-normal distribution more closely than a normal distribution. Results (table 6) show that there is no strong correlation between depth, temperature, or major ion concentrations for (1) all formation waters examined, (2) formation waters from the Delaware Basin, or (3) formation waters from the Texas Panhandle. We attribute this lack of correlation to the diverse reservoir rock types from which water is produced. Correlations between Ra activity and water chemistry are best for waters from the Edwards Group and the Gulf Coast (table 6). We interpreted this relation to indicate that general water chemistry can be a good predictor of Ra activity if a set of water samples represents

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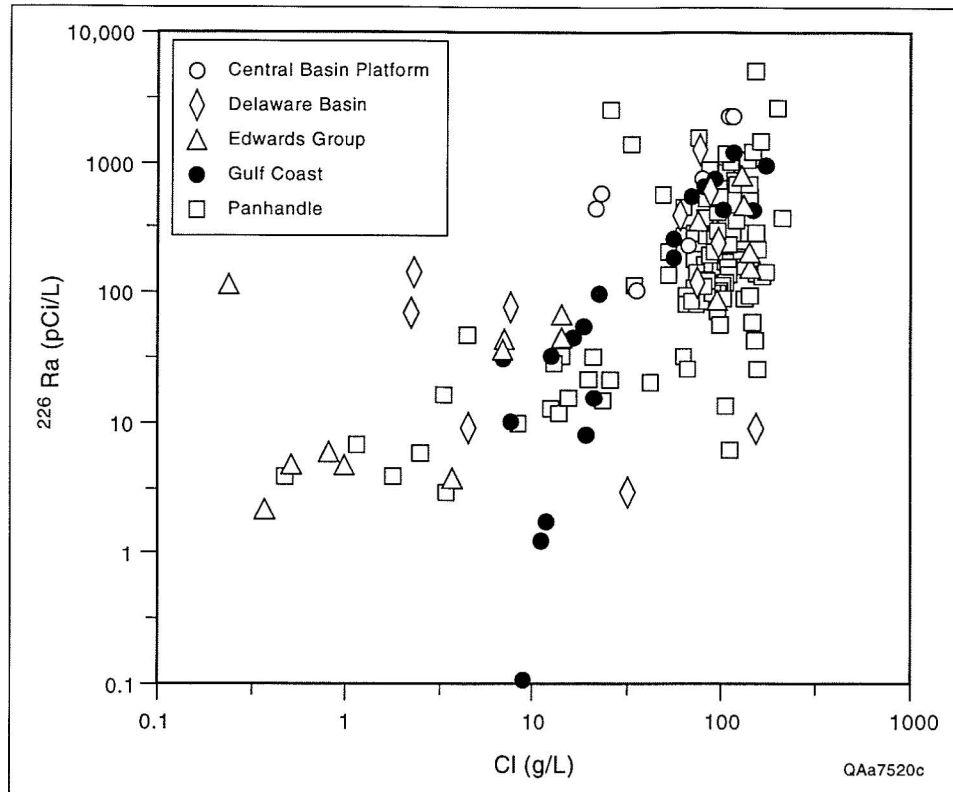
Figure 12. Plot of chloride concentration versus log ^{226}Ra activity for formation waters. Waters having high Ra activity also have high chlorinity. However, the direct correlation between chlorinity or salinity and Ra activity observed by Kraemer and Reid (1984) for Gulf Coast geothermal wells is generally not observed.

similar reservoir rock types or a group of similar rock types. A strong negative correlation was found between log Ra and log alkalinity for Central Basin Platform samples (table 6) but not in any other sample group. However, because the Central Basin Platform data set contains only four analyses of both water chemistry and Ra activity, this correlation is probably not geologically sufficient.

Relations between Ra activity and formation water type were also investigated by calculating correlations between ^{226}Ra and those parameters used by Morton and Land (1987) and Bein and Dutton (1993) to identify the different water types. Results generally show that correlations are better with salinity or chlorinity than with the parameters that define water types. The available data do not suggest that chemically distinct formation water types have systematically different Ra activities.

Geochemical Controls on NORM in Scale

Natural radioactivity of the equipment scale that ultimately accumulates in production and processing equipment is complexly dependent on several variables. One is the capacity of the formation water to precipitate Ra-containing scale when water, oil, and gas are produced. A second is the Ra activity of the formation water or, more precisely, the activity ratio of Ra to major cations for which Ra can substitute in scale minerals. The third major variable is the way in which Ra is included in scale minerals.

Several lines of evidence point to barite as the major scale component that can preferentially incorporate Ra. Because nearly all formation

Table 6. Correlation coefficients (r^2) showing relations between radium activity and other hydrochemical parameters.

	All samples log ^{226}Ra	Central Basin Platform log ^{226}Ra	Delaware Basin log ^{226}Ra	Edwards Group log ^{226}Ra	Gulf Coast log ^{226}Ra	Panhandle log ^{226}Ra
Depth (m)	< 0.5	< 0.5	na	< 0.5	0.556	< 0.5
Temp. (°C)	< 0.5	< 0.5	na	< 0.5	< 0.5	< 0.5
log Na	< 0.5	< 0.5	na	0.648	0.695	< 0.5
log K	< 0.5	< 0.5	na	0.667	0.637	< 0.5
log Ca	< 0.5	< 0.5	na	0.674	0.722	< 0.5
log Mg	< 0.5	< 0.5	na	0.550	0.695	< 0.5
log Ba	< 0.5	< 0.5	na	0.682	0.548	< 0.5
log Cl	< 0.5	< 0.5	< 0.5	0.630	0.709	< 0.5
log SO$_4$	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
log Alkalinity	< 0.5	-0.972	< 0.5	< 0.5	< 0.5	< 0.5
log TDS	< 0.5	< 0.5	na	0.689	0.707	< 0.5

na = not applicable

waters we tested are near or at saturation with barite under reservoir conditions and because barite solubility decreases with decreasing temperature below about 125°C, barite scale will form as most waters are produced. The amount of barite scale that can form depends both on the temperature difference between reservoir and surface and on the proportions of Ba and SO$_4$ in solution. Barite precipitation removes Ba and SO$_4$ in equal molal amounts; thus, a water can be highly oversaturated with barite at surface conditions but will deposit little material because scale precipitation is limited by the amount of the least abundant ion. Radium activity and the Ra-to-Ba ratio in formation water are highly variable in reservoirs throughout the state. Furthermore, although high Ra activity is generally associated with high salinity, there is no systematic relation between the Ra-to-Ba ratio and total salinity. Thus, Ra activity alone cannot be used to predict NORM activity in scale.

Radium incorporation in scale minerals can be estimated on the basis of thermodynamic data. However, much more information regarding NORM scale composition is needed before we can evaluate how accurately such estimations reflect actual conditions in oil and gas fields. Our approach to estimating the amount of NORM scale in Texas oil and gas operations was as follows. First, we assumed that barite is the mineral that hosts Ra and that Ra coprecipitation in barite follows the distribution coefficient (D) equation of Langmuir and Melchior (1985) and Langmuir and Riese (1985) between 0° and 100°C:

$$\log D = (428.2/T) - 1.181, \qquad (2)$$

where T is temperature in degrees Kelvin and D is as defined previously. Note that D increases as T decreases; lower temperatures of barite precipitation favor greater substitution of Ra for Ba. Therefore, barite that precipitates in surface

Table 7. Mean values and results of Student's t-test analyses of the radioactivity caused by [226]Ra incorporated in barite scale from formation waters under different scenarios.

			pCi/100 bbl reservoir T	pCi/100 bbl 25°C	pCi/100 bbl D = 1	pCi/g scale reservoir T	pCi/g scale 25°C	pCi/g scale D = 1
Central Basin Platform		Average	7.21E+06	8.44E+06	4.69E+06	4.82E+05	5.60E+05	3.11E+05
Edwards Group		Average	1.94E+06	2.35E+06	1.30E+06	1.17E+06	1.29E+06	7.16E+05
Gulf Coast		Average	1.34E+06	2.41E+06	1.34E+06	9.06E+03	1.75E+04	9.70E+03
Texas Panhandle		Average	4.29E+06	6.30E+06	3.50E+06	2.69E+05	3.85E+05	2.14E+05
Central Basin Platform	vs.	Edwards	y	y	y	n	n	n
Central Basin Platform	vs.	Gulf Coast	y	y	y	y	y	y
Central Basin Platform	vs.	Panhandle	y	y	y	y	y	y
Edwards	vs.	Gulf Coast	y	y	n	y	y	y
Edwards	vs.	Panhandle	y	y	y	y	y	y
Gulf Coast	vs.	Panhandle	y	y	y	y	y	y

pCi/100 bbl: Picocuries activity in barite scale that forms from 100 barrels of formation water

pCi/g: Picocuries activity per gram of barite scale

Reservoir T: Distribution coefficient calculated for reservoir temperature

25°C: Distribution coefficient calculated at 25°C to represent surface temperature

D = 1: Distribution coefficient set to 1.0

y = >95-percent probability that mean values are different

n = <95-percent probability that mean values are different

See text for discussion.

equipment is predicted to be more radioactive than barite that precipitates in the well bore near the producing interval. We calculated values of D for reservoir temperature and surface temperature (25°C). We also considered the case in which precipitation is so rapid that there is no discrimination between Ra and Ba in the crystal lattice and therefore D = 1. We then used the three values for D, chemical analyses of formation waters, reported or measured [226]Ra activity, reservoir temperature, and the amount of barite scale that would form during production (previously cal-culated using SOLMINEQ.88) to calculate the [226]Ra activity of the barite scale that would form from 100 bbl of produced water. This gives an estimate of the total radioactivity per unit of produced water. Finally, we calculated the [226]Ra per gram of barite scale. This gives an estimate of the radioactivity per unit of scale material or the "intensity" of the NORM activity. We used the mean values of Ra activity for the Central Basin Platform, Edwards Group, Gulf Coast, and Texas Panhandle and performed the calculations for water samples for which the concentrations

of Ba and SO_4 were known and reservoir temperature was known or could be estimated from reservoir depth. Results show the combined effects of statewide differences in formation water composition and Ra activity, reservoir temperature, and potential to precipitate barite during production. These values are upper limits to the amount and radioactivity of scale expected because (1) the scale may be distributed throughout the various equipment components, (2) other scale minerals can also precipitate and essentially dilute the radioactivity caused by Ra in barite, (3) actual scale will probably be less dense than the barite minerals used to obtain the thermodynamic data, and (4) the distribution coefficient (D) may be lower in saline formation waters.

Table 7 presents the results of six calculations. The first three give mean values for the total radioactivity because of ^{226}Ra in the barite scale predicted to precipitate from 100 bbl of produced water when the (1) Ra-to-Ba ratio in barite reflects reservoir temperature, (2) Ra-to-Ba ratio in barite reflects surface temperature (25°C), and (3) Ra-to-Ba ratio in barite reflects formation water composition. Columns 4 through 6 give mean values for the radioactivity per gram of barite scale under the same assumptions. Formation water from wells in the Central Basin Platform produces the greatest total amount of radioactivity, whereas water from wells in the Edwards Group produces the most highly radioactive scale (table 7). Waters from Gulf Coast wells produce the least amount of total radioactivity and the least radioactive scale.

We used the Student's t-test to evaluate whether the differences between basins are statistically significant. Results (table 7) suggest that all differences between basins are significant at the 95-percent confidence level, with the exceptions that total radioactivity in scale from Edwards waters is indistinguishable from total radioactivity in scale from Gulf Coast wells and that scale from Central Basin Platform and Edwards waters has the same activity (pCi/g).

SYNTHESIS

Natural radioactivity is commonly produced from oil, gas, and geothermal reservoirs. In some cases the fluids themselves, or the scale that forms from produced water, may be sufficiently radioactive to cause safety, environmental, or regulatory concerns as well as increased costs for special handling and disposal practices.

This study investigated natural controls on radioactivity in sedimentary basins and produced waters and the accumulation of natural radioactivity in oil-producing and gas-processing facilities. We focused on the isotopes ^{226}Ra and ^{228}Ra because these are the most commonly reported sources of NORM in produced water and on the scale mineral barite because it is the most common form of NORM in production equipment. The goal was to identify screening criteria that could be used by plant operators and health and safety regulators to anticipate special needs in areas where NORM levels are likely to be greater than normal. Although samples and data were collected from Texas and adjacent areas in New Mexico and the Louisiana Gulf Coast, results and conclusions should be generally applicable because the activity, type, and sources of NORM in Texas reservoirs are similar to those reported at other oil and gas operations in the United States and throughout the world.

Data obtained by measuring radioactivity in various types of oil- and gas-field equipment and aggregating values by county revealed elevated NORM activity levels in oil and gas facilities in north, north-central, east, south-central, and Gulf Coast Texas (Otto, 1989). The highest activities

were found along the south Texas Gulf Coast where major oil and gas reservoirs contain volcanic detritus. Survey results cannot be extrapolated to other areas because sample sites were neither randomly selected nor uniformly distributed. However, the results do show that (1) not every major oil or gas field has associated high NORM levels, and (2) no major hydrocarbon-producing basin in Texas is exempt from high levels of natural radioactivity.

A survey of the U and Th content of sedimentary rocks and the minerals typically found in sedimentary basins shows no order-of-magnitude differences in concentrations of Ra-producing elements between siliciclastic and chemical sedimentary rocks. Sandstones, common shales, carbonate rocks, and the individual minerals that compose these strata have mean U and Th contents in the 1- to 10-ppm range. In contrast, black and organic shales, U- and Th-rich accessory minerals, and carbonaceous accumulations can have U and Th concentrations in the 1,000- to 70,000-ppm range. The combination of slow natural transport velocities relative to Ra isotope half-lives and the relatively short production times of most reservoirs makes long-distance Ra transport to well bore highly unlikely. Burial diagenesis can either promote or retard alpha-recoil release of Ra from parent U- and Th-containing solids. Dissolution and reprecipitation or recrystallization can redistribute U and Th from grain interiors to new phases or surface coatings on other grains where alpha-recoil products have greater access to reservoir fluids. In contrast, pore-filling and grain-coating cements can form a barrier between alpha-recoil products and the fluid phase.

To investigate geologic and hydrochemical controls on NORM activity, we assembled a data base of 153 formation water samples for which chemical and Ra isotopic analyses were available. The data included new samples and analyses, results from publications, and new analyses of previously collected formation waters. The samples were obtained from reservoirs in the Texas Panhandle (Dalhart, Anadarko, Palo Duro, and Hardeman Basins and the Amarillo Uplift), the Edwards Group (south-central Texas), the Central

Basin Platform (West Texas), the Texas and Louisiana Gulf Coast, and the Delaware Basin (southeastern New Mexico). Samples in the data base represent widely diverse conditions of salinity; Ra activity; reservoir depth, temperature, and lithology; and geographic location. Mean ^{226}Ra activity ranged from 958 pCi/L in the Central Basin Platform to 140 pCi/L for the Edwards Group. Formation waters were divided into three groups: those from the Central Basin Platform were expected to have a generally high mean ^{226}Ra activity (>400 pCi/L); those from the Texas Panhandle, Gulf Coast, and Delaware Basin were expected to have an intermediate mean ^{226}Ra activity (200 to 400 pCi/L); and those from the Edwards Group were expected to have a low mean ^{226}Ra activity (< 200 pCi/L). Statistical analysis, however, revealed the variability of ^{226}Ra activities and the difficulty of obtaining sufficient samples for confident predictions. Because choosing random data subsets from the smaller sample groups greatly affects the mean value, more data are needed to adequately represent Ra activity in Texas formation waters.

The correlation previously observed between ^{226}Ra activity and total salinity for waters from Gulf Coast reservoirs does not hold for other sample groups nor for the combined set of all analyses. We conclude that factors such as host rock lithology and diagenetic history are as important as water chemistry in supporting high aqueous ^{226}Ra activities. One generalization that can be made is that ^{226}Ra activities greater than about 200 pCi/L require chlorinities greater than 20 g/L; higher ^{226}Ra activities cannot be supported by less saline waters.

To investigate statewide variations in the capacity of formation water to precipitate NORM scale, we assembled a data base that consists of several hundred formation water analyses. Published reports, observations, and thermodynamic relations suggest that barite is the most common NORM scale. We used the geochemical modeling program SOLMINEQ.88 (Kharaka and others, 1988) to predict that amount of barite that could precipitate from formation waters of the Texas Panhandle, Gulf Coast, Edwards

Group, Central Basin Platform, and East Texas Salt Basin. We then used an experimentally derived distribution coefficient that describes how Ra will substitute for Ba in barite to estimate the radioactivity of barite scale in the various basins. These results combine the mean ^{226}Ra activity of each basin with the barite-forming capacity of formation water from each basin. Although the absolute values of ^{226}Ra activity in scale are subject to the effects of errors in water chemistry analyses, reservoir temperatures, lack of pressure values, and uncertainty in the thermodynamic data, the results are useful for ranking the relative NORM-forming potential of produced water from different geographic and geologic settings.

Results are presented two ways. We first calculated the radioactivity of scale that could precipitate from each 100 bbl of produced water. This value reflects the mean Ra-to-Ba ratio in the water, the amount of barite that can form from 100 bbl of water, and the reservoir temperature. These results predict high scale radioactivities in the Central Basin Platform, intermediate activities in the Texas Panhandle, and low activities in the Edwards Group and Gulf Coast reservoirs. We also calculated that amount of radioactivity per

gram of scale. This value reflects the mean Ra-to-Ba ratio in the water and reservoir temperature but not the total amount of barite that can precipitate. These results predict significant differences between the four formation water groups with scale radioactivities decreasing in the order Edwards Group > Central Basin Platform > Texas Panhandle > Gulf Coast.

Information for this study was gathered from all available sources. The resulting data sets included complete chemical analyses of several hundred formation waters from basins throughout the state and 153 formation water analyses that included ^{226}Ra activity. In addition, we obtained chemical, mineralogical, and radiological analyses of 20 scale samples. Although this data base is large, it inadequately represents the number of geographic, geologic, geochemical, and hydrologic variables in Texas oil and gas fields that can affect NORM distributions in production and processing equipment. Chemical, mineralogical, and radiological characterization of NORM scale in particular is sparse. A larger data base of well-characterized water and scale samples might reveal controls on NORM distributions that could not be resolved using currently available data.

CONCLUSIONS

This investigation found that NORM levels in produced fluids and equipment scale are controlled primarily by local geologic variables that determine the abundance of U and Th within a few hundred meters of the well bore. These locally high concentrations of Ra parent isotopes can generally be anticipated on the basis of regional and local geologic information. Other factors that influence NORM levels in oil- and gas-field operations are related to the original reservoir rock, diagenetic modifications, formation water chemistry, and production and disposal practices. Although we find no reliable statewide quantitative predictors of NORM levels, local (reservoir- or field-scale) predictors do exist and can help operators and regulators anticipate special procedures required for the safe handling and disposal of natural radioactivity associated with hydrocarbon or geothermal production.

Geographic and Geologic Associations

The national survey sponsored by API shows general areas and counties where NORM levels in oil-producing and gas-processing equipment are above median values. These statistical data identify the south Texas Gulf Coast as particularly prone to high NORM activities. Without information concerning the reservoir strata and length of time these facilities were in operation, it is impossible to determine why this is an area of high radioactivity. It is highly likely that the NORM levels in the south Texas Gulf Coast reflect the higher abundance of volcanic rock fragments carried to the Gulf of Mexico by the Rio Grande from volcanic source terranes in northern Mexico and Trans-Pecos Texas.

Transport distances are limited by the geologically short half-lives of ^{228}Ra and ^{226}Ra, coupled with the slow natural fluid velocities and the relatively short production times of most

reservoirs. Therefore, long-distance transport of NORM sources is much less likely than local derivation of the radioactivity. Typical reservoir (sandstones, limestones, and dolostones) and associated rock types (siltstones, mudstones, and shales) have U and Th concentrations in the 1- to 10-ppm range. Release of Ra isotopes from these rocks to produced fluids will be favored by small grain size (large ratio of surface area to grain volume), high and well-connected porosity, and water-filled pore spaces.

Much more important are the volumetrically small accumulations of U- and Th-rich strata such as black, organic- and metal-rich shales, lag accumulations of heavy and accessory minerals, and carbonaceous material derived from hydrocarbon deposits. The presence of these accumulations in a play, field, or reservoir setting can be anticipated from basic geologic information. Black organic- and metal-rich shales form from deposition in reducing conditions that develop in deep waters when circulation is restricted. These conditions commonly occur during times of rapid sea-level rise and mark the bases of transgressive sequences. Concentrations of heavy or accessory minerals typically accumulate where transport energy is sufficiently high that less dense grains remain in transport. Accumulations of these minerals are therefore anticipated at the bases of fluvial or distributary channels or in heavily wave- or current-modified beach or shoreface deposits and in sandstones derived from igneous and metamorphic source rocks. Carbonaceous matter such as the Texas Panhandle asphaltite accumulations might be expected to occur near the margins of hydrocarbon deposits.

Diagenetic Associations

Diagenesis of reservoir rocks can either promote or reduce Ra mobility. Pore-filling or grain-coating cements can shield the U- and Th-bearing grains from pore water, thus not permitting alpha-

recoil products to escape the solid material of the reservoir. Conversely, large-scale remobilization of sedimentary materials through feldspar and clay dissolution-reprecipitation reactions of recrystallization of carbonate strata can release trace U and Th from the rock matrix. Because U and Th form highly insoluble phases under reservoir conditions, this remobilization effectively moves the Ra parent isotopes to authigenic phases or grain coatings, where alpha-recoil products have a much greater opportunity to escape to the fluid phase. Which of these diagenetic effects will predominate in a reservoir cannot be predicted statewide but can be readily established by local, field-specific investigations.

Water Chemistry Associations

Although no statewide predictive associations were found between Ra activity and other water chemical parameters, good correlations do exist between Ra activity and total salinity in Gulf Coast geothermal reservoirs. In restricted geographic areas where producing reservoirs have similar lithology and burial history, a semi-predictive relation was found between Ra activity and total salinity (Kraemer and Reid, 1984). Similar relations probably exist within fields but could not be established from our data set. The Texas data base does indicate that Ra activities greater than about 200 pCi/L require chlorinities greater than 20 g/L. Apparently Ra can successfully compete with more abundant cations for exchange or sorption sites in less saline waters, and we would expect high Ra isotope activities only in water that has more than about 20 g/L chloride.

Equipment Scale Associations

Radium substitution for Ba in barite is the main mechanism by which radioactive Ra isotopes are removed from water and concentrated in equipment scale. Because most Texas formation waters are at or near barite saturation under reservoir conditions, the amount of barite scale that can form during production depends on the change in solubility between reservoir and surface conditions. The radioactivity of that scale depends on how much Ra substitutes for Ba in the mineral.

Barite solubility depends on temperature, pressure, and ionic strength of the solution. Under typical reservoir conditions, however, barite solubility is at a maximum at temperatures of about 125°C. Waters near this temperature are capable of precipitating more barite scale than hotter or colder waters. The amount of barite that actually precipitates is limited by the less abundant ion. Therefore, for any degree of oversaturation at surface conditions, waters that have nearly equal molar concentrations of Ba and SO_4 will deposit the greatest amount of mineral scale. Water analyses in the Texas data base generally are abundant in either Ba or SO_4 and depleted in the complementary ion. For this reason, barite precipitation can be significantly increased if waters are mixed during either production or waste disposal. Radium substitution for Ba in barite depends on the solution Ra-to-Ba ratio and temperature of precipitation. High Ra-to-Ba ratios and low precipitation temperatures favor Ra concentration in barite scale.

Screening Criteria for NORM Activity

A major goal of this study was to identify screening criteria or indicator species that could be used by operators and regulators to predict where and under what conditions high NORM activity levels would be encountered. We could not achieve this goal because of the large number of geologic and geochemical variables that significantly affect the sources and mobility of Ra relative to the number of samples and analyses. However, we can identify factors that either promote or diminish the probability of high NORM accumulations.

Factors that will promote high NORM levels in produced water and scale are
  (1) an igneous, metamorphic, or volcanic source terrain for siliciclastic reservoirs;
  (2) local concentrations of accessory minerals, asphaltite, or strata that are enriched in U and Th;
  (3) grain-replacement diagenesis;
  (4) highly saline formation water;
  (5) reservoir temperatures in the range of about 100° to 125°C;
  (6) approximately equal concentrations of Ba and SO_4 in produced water; or
  (7) a high Ra-to-Ba ratio in formation water.

Factors that will promote low NORM levels in produced water and scale are
  (1) sedimentary source terrain for siliciclastic reservoirs;
  (2) pore-filling cementation diagenesis;
  (3) formation water having less saline than seawater;
  (4) reservoir temperatures of less than 100°C or greater than about 125°C;
  (5) vastly unequal concentrations of Ba and SO_4 in produced water; or
  (6) a low Ra-to-Ba ratio in formation water.

In addition, the mixing of formation waters, either through the commingling of fluids or water-flooding, is likely to increase the amount of barite scale formed and hence the amount of NORM scale and sludge that can accumulate.

The relation between each of these factors and Ra activity can be quantified in well-constrained geologic systems. We therefore suggest that some form of multivariate correlation, based on detailed investigation of formation water chemistry and reservoir heterogeneity, could produce a model that would adequately predict high- and low-NORM occurrences and thus be useful to both industry and regulatory agencies.

ACKNOWLEDGMENTS

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Appendix. Sample identifications, radium isotope activity, and chemical compositions (mg/L).

Sample numbers	Formation	Stratal type	Depth (m)	Temp. (°C)	^{226}Ra (pCi/L)	^{228}Ra (pCi/L)	Na	K	Ca	Mg	Ba	Fe	Cl	SO$_4$	Br	Alkalinity	TDS
Central Basin Platform																	
Nellie C. Martin-6	San Andres		1,370		104.0		18,800	773	1,860	804	0.80		34,800	3,270	79.5	1,070	61,500
Nellie C. Martin-21	Tubb		1,930	37.0	2,260.0		58,800	1,050	8,760	2,690	0.80		116,000	854	577.0	87	189,000
ARCO B-6	U. Clear Fork		1,750	29.0	776.0	28.2	46,700	985	5,370	2,150	0.80		80,100	2,380			138,000
Parker-123	L. Clear Fork		2,000	39.0	2,290.0		61,300	1,140	8,110	2,120	0.80		110,000	1,090	481.0	136	185,000
Parker-2	Wichita		2,080	42.0	440.0		13,800	298	1,880	503	0.80		21,700	4,040	50.6	369	42,700
Parker-11	Ellenburger		2,620	64.0	596.0		14,200	373	1,670	514	0.80		23,100	1,930	44.2		41,900
Parker-18	McKee				238.0	171.0	33,800	521	9,010	1,590	0.80		66,600	854	261.0		113,000
Edwards																	
S-01	Edwards	Carbonate	358	27.0	4.5		470	25	550	210	0.05	0.23	970	1,800	4.3	305	4,330
S-02	Edwards	Carbonate	176	26.0	4.5		300	21	150	100	0.04	0.03	510	520	2.4	305	1,910
S-03	Edwards	Carbonate		58.5	63.9		6,500	130	1,900	580	0.40	0.20	14,000	1,700	82.0	500	25,300
S-04	Edwards	Carbonate		65.0	333.0		32,000	1,100	13,000	1,100	123.00	1.30	76,000	1	420.0	329	124,000
S-05	Edwards	Carbonate		40.5	2.0		200	11	690	100	0.05	0.10	360	1,700	2.1	244	3,310
S-06	Edwards	Carbonate	2,210	38.0	732.0		51,000	3,200	18,000	2,900	9.30	2.20	125,000	120	820.0	414	201,000
S-07	Edwards	Carbonate	661	53.5	41.5		3,300	160	840	350	0.20	0.09	6,800	710	42.0	853	13,000
S-08	Edwards	Carbonate	165	25.5	3.6		1,800	80	930	440	0.10	0.07	3,600	2,300	22.0	475	9,630
S-10	Edwards	Carbonate		45.0	192.0		63,000	5,800	17,000	1,600	12.90	3.00	140,000	2	810.0	219	228,000
S-11	Edwards	Carbonate	3,370	79.0	84.1		40,000	1,300	14,000	1,300	11.00	1.70	95,000	3	560.0	268	152,000
S-12	Edwards	Carbonate	502	36.0	108.0		170	14	640	66	0.05	0.17	240	1,800	1.0	219	3,150
S-13	Edwards	Carbonate		43.5	144.0		61,000	4,500	20,000	1,600	7.24	2.70	140,000	5	830.0	268	227,000
S-14	Edwards	Carbonate		57.0	41.4		6,700	270	1,600	540	0.40	0.20	14,000	770	80.0	512	24,400
S-15	Edwards	Carbonate		47.5	34.5		3,400	150	840	400	0.20	0.12	6,700	980	42.0	597	13,100
S-16	Edwards	Carbonate		40.0	448.0		57,000	3,400	18,000	1,500	12.40	2.90	130,000	6	820.0	146	210,000
S-17	Edwards	Carbonate	890	36.0	5.6		400	20	610	210	0.05	0.05	790	2,000	5.3	293	4,320
Delaware Basin																	
DB-01	Rustler	Salt			3.1								31,700	3,820		92	
DB-02	Rustler	Salt			81.0								7,690	5,890		85	
DB-08	Castile	Salt			132.0								75,500	6,970		67	
DB-20	Y-SR-Q	Sandstone			420.0								60,000	2,770		311	
DB-21	Devonian	Carbonate			152.0								2,300	279		366	
DB-22	Wolfcamp	Carbonate			71.4								2,230	2,910		31	
DB-23	Y-SR-Q	Sandstone			261.0								98,400	720		61	
DB-24	Y-SR-Q	Sandstone			634.0								89,500	279		6	
DB-25	Y-SR-Q	Sandstone			1,350.0								78,500	307			
DB-26	Wolfcamp	Carbonate			9.3								4,500	29		12	
DB-05	Salado	Salt			9.6								152,000	3,780		134	
Panhandle USGS																	
2		Evaporite	870		177.0		65,500		2,190	689			104,000	3,770		40	176,000
4		Evaporite	871		90.9		65,900		1,180	584			99,400	10,100		21	175,000
5		Evaporite	858		118.0		67,300		937	500			99,200	10,300		75	178,000
6		Evaporite	846		98.8		64,400		844	475			93,400	11,800		77	171,000
7		Evaporite	858		181.0		48,300		898	494			70,900	13,300		155	134,000
8		Evaporite	875		111.0		49,400		907	628			70,000	12,900		167	134,000
9		Evaporite	884		148.0		48,400		1,070	1,080			72,300	9,840		172	133,000
10		Evaporite	899		87.9		48,200		948	544			68,800	11,900		77	130,000
11		Evaporite	896		11.9		7,420		1,630	342			13,500	2,410		21	25,400
12		Evaporite	883		161.0		68,200		1,930	798			108,000	4,450		53	183,000
13		Evaporite	972		84.0		39,500		1,970	1,120			63,800	5,170		59	112,000
14		Evaporite	970		26.7		40,500		1,900	1,660			66,200	5,990		136	116,000
15		Evaporite	1,620		1,050.0		58,100		9,490	2,030			112,000	120		69	182,000
16		Evaporite	893		98.8		57.300		1.300	699			87.900	6.440		60	154.000

Appendix (cont.)

Sample numbers	Formation	Stratal type	Depth (m)	Temp. (°C)	^{226}Ra (pCi/L)	^{228}Ra (pCi/L)	Na	K	Ca	Mg	Ba	Fe	Cl	SO$_4$	Br	Alkalinity	TDS
17		Evaporite	905		82.0		50,100		1,060	705			73,500	10,400		117	136,000
18		Evaporite	902		88.9		51,600		937	612			76,800	8,360		79	138,000
19		Evaporite	879		33.6		12,500		1,730	428			21,000	3,430		150	39,200
20		Evaporite	881		120.0		60,000		4,410	2,190			105,000	2,130		84	174,000
21		Evaporite	1,010		204.0		49,700		5,180	956			87,100	2,000		46	145,000
22		Evaporite	963		122.0		16,900		18,400	8,500			82,500	895		261	127,000
24		Evaporite	1,020		33.6		7,550		1,540	205			14,200	954		79	24,500
25		Evaporite	1,030		16.8		1,800		364	51			3,320	276		74	5,890
26		Evaporite	1,020		12.8		8,520		706	74			12,500	1,340		328	23,400
27		Evaporite	935		20.7		24,100		1,910	671			40,800	2,130		46	69,900
28		Evaporite	893		4.0		345		49	14			475	119		167	1,170
29		Evaporite	824		125.0		42,700		4,050	3,630			81,900	2,240		22	135,000
30		Evaporite	823		168.0		47,700		2,050	2,600			81,600	4,400		45	138,000
31		Evaporite			711.0		71,000	1,140	4,900	1,600			138,000	1,920		47	229,000
32		Evaporite	977		430.0		51,400	442	4,640	1,470			93,500	2,240	59.0		154,000
33		Evaporite	981		558.0		53,100	507	3,440	4,220			96,900	2,490	72.0		161,000
34		Evaporite	991		568.0		55,100	578	5,860	1,370			140,000	2,080	85.0		205,000
35		Evaporite	1,010		215.0		54,600	471	5,110	1,270			90,700	1,850	82.0		154,000
36		Evaporite	967		5.9		1,290		658	104			2,480	1,090			5,880
37		Evaporite	1,090		14.8		15,300		1,230	320			23,000	4,920			45,000
38		Evaporite	895		119.0		28,100		12,200	5,780			81,000	1,010		63	128,000
39		Evaporite	777		4.0		1,120		771	143			1,770	1,970		505	6,280
40		Evaporite	960		43.5		94,600		1,180	566			146,000	4,210		26	247,000
42		Evaporite	999		314.0		44,000		8,650	3,800			93,200	1,370		153	151,000
43		Evaporite	1,040		3.0		1,530		1,050	222			3,350	1,870			8,250
44		Evaporite	1,080		286.0		36,900		2,620	1,120			61,900	3,830		204	107,000
45		Evaporite	1,100		477.0		32,100		5,260	1,790			62,400	2,100		142	104,000
46		Evaporite	1,150		346.0		44,500		6,700	2,260			86,100	1,290		122	141,000
47		Evaporite	1,100		138.0		27,800		3,790	1,080			50,800	2,480		156	86,100
49		Evaporite	1,100		1,540.0		39,700		6,210	1,860			76,200	1,730		224	126,000
50		Evaporite	1,010		96.8		44,700		1,110	684			64,700	6,220			121,000
51		Evaporite	1,010		124.0		53,800		2,400	1,230			80,900	9,480		342	148,000
52		Evaporite			138.0		63,800		4,700	2,050			107,000	4,490		205	182,000
53		Evaporite			119.0		20,500		1,570	613			33,900	1,410		735	55,800
54		Evaporite			21.7		5,750	94	5,500	580			19,500	654		90	32,200
55		Evaporite			28.7		3,250	95	3,700	900			12,900	1,370		86	22,300
56		Evaporite			21.7		12,300	225	3,800	1,300			25,300	1,850		140	44,900
57		Evaporite			9.9		3,350	224	1,600	240			8,100	617		71	14,200
58		Evaporite			15.8		9,350	138	1,400	270			15,600	1,600		110	28,500
59		Evaporite			13.8		55,000	264	3,400	2,100			105,000	3,350		68	169,000
60		Evaporite	934		57.3		61,600	245	1,690	771			97,900	2,700	30.0		165,000
61		Evaporite	1,040		221.0		34,800	240	5,160	2,470			69,300	845	351.0		114,000
62		Evaporite	1,780		1,160.0		58,300	600	4,810	1,600			104,000	1,300			171,000
63		Evaporite			715.0		65,000		8,700	2,630			117,000	1,740			195,000
64		Evaporite	1,070		145.0		57,700	1,640	14,500	18,800			167,000	493	833.0		262,000
65		Evaporite	742		6.9		419	19	813	162			1,130	1,630	4.0		4,250
66		Evaporite	890		32.6		32,800	1,060	2,560	1,870			62,300	4,140	365.0		106,000
67		Evaporite	824		95.8		88,100	2,330	3,220	5,400			139,000	2,800	692.0		242,000
68		Evaporite	814		61.3		69,500	2,210	2,360	8,400			144,000	7,100	853.0		235,000
69		Evaporite	808		224.0		88,000	2,310	1,670	863			151,000	2,800	146.0		248,000
70		Evaporite	802		148.0		62,500	1,490	8,280	13,100			151,000	754	782.0		239,000
71		Evaporite	838		139.0		92,200	3,650	2,870	7,010			162,000	2,310	1050.0		271,000

Appendix (cont.)

Sample numbers	Formation	Stratal type	Depth (m)	Temp. (°C)	^{226}Ra (pCi/L)	^{228}Ra (pCi/L)	Na	K	Ca	Mg	Ba	Fe	Cl	SO$_4$	Br	Alkalinity	TDS
72		Evaporite	892		285.0		48,300		7,820	1,840			92,700	1,400		52	152,000
73		Evaporite	893		543.0		41,400		7,960	2,230			82,300	1,420		83	135,000
74		Evaporite	845		26.7		97,200		1,650	1,590			155,000	2,930		26	259,000
75		Evaporite	879		47.4		2,280	77	1,550	184			4,350	1,760			10,400
Panhandle BEG																	
PO601	Granite Wash	Sandstone	2,690	73.2	6.1	475.0	55,400	680	9,390	1,480	48.80	39.90	110,000	17	386.0	383	177,000
HT601	Brown Dolomite	Carbonate	963	38.2	73.5	76.0	54,600	490	5,550	2,000	0.70	1.60	94,800	2,200	193.0	268	160,000
DS7	Wolfcamp	Carbonate	1,780	54.3	92.7		72,500	589	8,390	2,160		16.80	130,000	1,370	147.0	205	215,000
RO602	Brown Dolomite	Carbonate	948	37.6	108.0		54,500	500	7,480	2,360	0.50	1.50	98,100	1,800	273.0	326	165,000
DN3	Mississippian	Carbonate	1,370	45.9	159.0		61,000	337	19,400	2,320			132,000	237	554.0	106	215,000
WH601	Hunton	Carbonate	4,900	117.0	184.0		59,700	2,000	15,700	1,820	1,170.00	18.10	125,000	4	540.0	172	204,000
HP602	Morrow Fm.	Sandstone	3,610	90.7	196.0		59,000	900	16,100	1,640	220.00	138.00	123,000	4	504.0	239	200,000
OC603	Cleveland Fm.	Sandstone	2,200	62.6	216.0	186.0	27,500	680	3,320	850	10.60	279.00	51,300	14	263.0	575	84,200
OC602	Marmaton Fm.	Sandstone	1,970	58.7	234.0		37,900	300	2,890	780	4.90	91.70	65,600	105	438.0	364	108,000
KG601	Strawn Reef	Carbonate	1,630	51.1	241.0		55,200	580	10,200	2,420	0.80	10.10	106,000	740	571.0	115	176,000
FO601	Cisco	Carbonate	1,160	41.8	280.0		43,800	430	8,300	1,830	0.80	168.00	82,900	764	352.0	86	138,000
KG602	Mississippian	Carbonate	1,640	51.4	294.0		35,800	590	7,280	1,430	0.60	26.20	70,900	744	259.0	67	117,000
SW3	Wolfcamp	Carbonate	1,670	52.1	372.0		69,300	339	6,240	1,820			120,000	1,650	512.0	94	199,000
SW4	San Andres	Carbonate	889	36.8	381.0		68,200	3,300	47,100	8,110			207,000	187	800.0	147	334,000
KT602	Cisco	Carbonate	1,800	54.5	396.0		44,200	290	7,660	1,540	1.80	47.20	81,700	180	400.0	374	136,000
HK601	Clear Fork	Carbonate	2,000	58.6	579.0		26,400	640	3,760	930	0.30	0.50	47,500	2,680	108.0	872	82,800
SH602	Marmaton	Sandstone	1,660	51.8	754.0		64,500	490	6,500	1,840	2.30	4.70	115,000	670	125.0	117	189,000
DA601	Penn.	Carbonate	2,740	73.4	852.0		60,200	560	6,770	1,690	2.10	11.80	103,000	405	645.0	144	173,000
OC605	Hunton	Carbonate	2,760	73.7	1,100.0		60,500	1,500	19,300	2,540	10.20	24.80	135,000	240	456.0	115	219,000
TR601	Wolfcamp	Carbonate	3,030	79.2	1,230.0		82,300	2,600	4,750	1,230	1.60	11.50	143,000	960	1,390.0	230	23,5000
KT603	Ellenburger	Carbonate	2,320	64.8	1,450.0		18,800	520	2,130	570	0.40	0.50	32,400	2,200	44.0	48	56,700
CO601	San Andres	Carbonate	1,460	48.2	1,490.0		55,200	4,400	23,900	10,200	0.50	1.00	158,000	390	1,180.0	460	25,3000
TR602	Fusselman	Carbonate	3,920	97.0	2,660.0		14,500	400	1,970	390	0.60	0.70	25,200	1,800	31.0	718	45,000
HK603	Clear Fork	Carbonate	1,910	57.2	2,680.0		65,700	4,330	40,300	8,210	1.00	15.60	193,000	118	1,900.0	498	312,000
DS1	Penn. carbonate	Carbonate	2,490	68.4	5,150.0	5490.0	77,900	620	15,700	2,110			149,000	440	161.0	35	245,000
L&M Sawyer 1 zone 5	Wolfcamp	Carbonate	970	32.0	900.0		43,500	118	6,760	2,490	0.01	6.40	86,300	2,010	330.0	144	141,000
L&M Sawyer 1 zone 4	Wolfcamp	Carbonate	1,310	38.0	290.0		63,400	332	18,300	2,180	1.51	41.00	151,000	336	551.0	78	235,000
L&M Mansfield #1 zone 1	Wolfcamp	Carbonate	1,480	41.0	290.0		78,400	369	5,960	1,320	9.05	3.70	138,000	1,220	107.0	131	225,000
L&M Mansfield #1 zone 2	Wolfcamp	Carbonate	1,400	40.0	220.0		76,100	380	6,020	1,600	0.22	13.30	131,000	1,320	118.0	161	217,000
Gulf Coast																	
KK01	Frio	Sandstone	4,280	117.0	437.0	428.0	78,000	1,070	10,300	1,140	185.00	84.00	143,000	6	419.0	450	236,000
KK02	Frio	Sandstone	4,840	135.0	986.0	914.0	84,600	1,080	15,800	1,500	310.00	162.00	168,000	7	595.0	320	274,000
KK03	Frio	Sandstone	3,370	116.0	1.3		7,500	62	101	18	3.70	34.00	10,700	59	30.0	1,610	20,300
KK04	Frio	Sandstone	3,220	113.0	0.1		6,500	52	42	10	1.00	0.10	8,700	54	24.0	1,960	17,500
KK05	Frio	Sandstone	3,260	110.0	1.8		8,000	5	83	16	9.00	3.00	11,600	25	31.0	1,310	21,200
KK06	Frio	Sandstone	3,620	128.0	15.6		13,300	72	330	48	13.00	1.60	21,000	42	45.0	1,180	36,000
KK07	Frio	Sandstone	3,690	131.0	8.2	18.6	11,800	44	370	56	11.00	6.00	18,700	26	29.0	1,140	32,400
KK08	Frio	Sandstone	5,730	159.0	1,240.0	1090.0	51,700	467	14,800	920	370.00	116.00	115,000	1	65.0	430	185,000
KK09	Frio	Sandstone	3,780	107.0	45.0	79.3	10,900	73	97	21	6.20		16,100	24	28.0	2,040	29,600
KK10	Frio	Sandstone	4,690	148.0	454.0	427.0	42,000	1,740	11,000	670		59.00	99,400	2		251	156,000
KK11	Frio	Sandstone	4,830	132.0	785.0	431.0	48,300	988	7,670	623		56.00	91,400	1		208	150,000
KK12	Tuscaloosa	Sandstone	5,110	166.0	55.9	98.6	11,000	97	460	39	3.50	20.00	18,200	10		2,090	32,200
KK13	Frio	Sandstone	4,450	141.0	265.0	373.0	31,200	510	3,090	270	300.00	10.00	55,100	542		420	91,900
KK14	Frio	Sandstone	4,510	134.0	32.4	56.8	8,710	43	115	17	2.00	0.10	12,400	591		1,370	23,400
KK15	Frio	Sandstone	2,980	149.0	31.5	45.9	4,800	26	42	7	5.10	0.05	6,740	23		1,530	13,300
KK16	Frio	Sandstone	4,510	146.0	101.0	131.0	14,900	111	832	84	4.40	83.60	21,800	166		740	38,900
KK17	Frio	Sandstone	4,470	138.0	692.0	613.0	38,000	840	9,100	660	760.00		80,600	5		365	132,000
KK18	Frio	Sandstone	3,570	127.0	10.2	8.2	5,450	61	27	6	7.20	0.05	7,280	32		2,410	15,300
KK19	Frio	Sandstone	3,930	114.0	570.0	496.0	40,000	265	1,860	270	8.20	0.40	67,900	220	63.0	1,050	112,000
KK20	Frio	Sandstone	4,080	109.0	190.0	266.0	33,000	320	3,310	246		0.00	55,300	526		2,380	95,100

Blanks indicate not analyzed.