P-III and taken from the Ono Menyanthes bed (*7*).

The counting rate of the alpha rays from Th^{228}, which is required to compute R_{β}' by Eq. 3, was not always equal to that from the Th^{232}, even when the contribution from Ra^{224} to the 5.4-Mev peak of the Th^{228} spectrum was eliminated. The radioactive disequilibrium between Th^{228} and Th^{232} may result from difference in chemical behavior between these nuclides. A prominent excess amount of Th^{228} in O-1 (Table 1) seems to indicate that Th^{228} atoms were selectively extracted from the minerals during the acid treatment. The disequilibrium may support the view that recoil atoms produced by alpha decay in the solid are more soluble in the chemical treatment than are the atoms that have remained intact in the rock.

The occurrence of this chemical effect on recoil atoms is a disadvantage in a method based on separation, by acid extraction, of portions having different uranium:thorium ratios. When an extraction is used as a source of a portion from the total rock sample, the isotopic composition of thorium in the portion from which a part of thorium was extracted must be represented in the extracted solution. The chemical effect on the atoms, of disintegration products of uranium, possibly makes observed Th^{230}:Th^{232} or Th^{234}:Th^{232} ratios in the extracted solution different from the ratio in an analyzed portion of the rock sample. However, since in that portion Th^{234} and some Th^{230} are grown *in situ* by alpha decays of nearly equal energy, these nuclides may behave in about the same manner: that is, the ratio of extracted Th^{230} to Th^{230} grown *in situ* in that portion may be the same as the ratio of extracted Th^{234} to total Th^{234}. If these two ratios are the same, a plot of R_{4i} versus R_{0i} gives a point on a straight line given by Eq. 1.

In the cases of O-2, O-3, and O-4, there was no distinct difference between the counting rates of Th^{232} and Th^{228}. Although O-1 showed significant difference between the counting rates of Th^{232} and Th^{228}, all four points O-1, O-2, O-3, and O-4 (Fig. 2) lie on a straight line. Thus it is shown that, in the acid-extraction process for O-1, the chemical behavior of Th^{230} grown *in situ* was just the same as that of Th^{234}.

When this dating procedure is used with separated minerals, there should be no complex problem in regard to the basis of the dating. Separations by partial dissolution or extraction probably involve the recoiled-atom effects when the observed Th^{228} and Th^{232} activities are not equal. Fortunately in the case of this pumice (*6*) these effects appear to have been the same for Th^{234} and Th^{230}. Because of a great difference between the half-lives of Th^{234} and Th^{230}, it is also plausible that in the other rocks only a feeble effect is left on the recoiled Th^{230} atoms; further studies are necessary to establish a general conclusion.

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Iodide Abundance in Oilfield Brines in Oklahoma

Abstract. *Samples of subsurface water, oil, and rock from strata of Mississippian and Pennsylvanian age in the Northern Oklahoma Platform area were analyzed. Several of the water samples contained iodide at more than 500 parts per million. Analyses of the brines and rock indicated that the iodide originated organically.*

Samples of water, oil, and rock were obtained from various strata in the marine-sedimentary Anadarko Basin, coming from primary production wells; they should represent connate data as closely as possible. Some of the water samples were analyzed at the wellhead for unstable properties and constituents; others were stored in plastic bottles and transported to the laboratory for analysis. Each sample was in duplicate; one half was acidified immediately to *p*H 1.5 with HCl. They were analyzed by reported methods (*2*). The oil samples were transported to the laboratory in metal containers and analyzed by reported methods (*3*), except for the iodide analysis which was done by a neutron-activation technique.

Concentrations of iodide exceeded 500 ppm in several samples of water from various oil wells; the highest were in brines taken from rocks of Mississippian and Pennsylvanian age in the Northern Oklahoma Platform area (Fig. 1). These brines contained some of the highest concentrations of iodide on record. Most oilfield brines contain less than 10 ppm of iodide; some approach 100 ppm, but few contain more.

The data indicate that the heaviest concentration of iodide is in the Oklahoma Platform area east of the Nemaha Ridge; here the top of the Mississippian sediments is about 1830 m deep. Table 1 gives the pertinent data for six brines high in iodide content and the iodide and bromide contents of some seaweeds and corals. All these brine samples were taken in Oklahoma from depths exceeding 1800 m, and the associated rocks were Mississippian or Pennsylvanian in age. Sample 5 (Table 1) is obviously a meteoric water containing relatively high concentrations of iodide and bromide; it cannot be relict sea water because of its low content of chloride.

The brines were depleted in magnesium and relatively rich in calcium (up to 16,000 ppm), indicating that they are very old and that diagenetic dolomitization could have occurred. Other constituents detected were lithium, up to 25 ppm; potassium, up to 2100 ppm; rubidium, up to 5 ppm; cesium, up to 2 ppm; strontium, up to 1500 ppm; barium, up to 15 ppm; boron, up to 220 ppm; and sulfate, up to 900 ppm.

Some of the brines were analyzed at the wellhead for ferrous iron, ferric iron, thiosulfate, sulfite, sulfide, dissolved carbon dioxide, bicarbonate, and ammonium. Thiosulfate, ammonium, dissolved carbon dioxide, bicarbonate, and traces of sulfite were present; hydrogen sulfide was absent.

High ratios of ferrous iron to ferric iron indicate a reducing environment. The $Fe^{2+}:Fe^{3+}$ ratios varied from 5.0 to 40.0; *p*H, from 5.9 to 6.5. The measured *Eh* (*4*) ranged from 270 to 300 mv. A reducing environment is characteristic of a petroleum-bearing formation.

It is often assumed that, in brines in which the I:Cl and I:Br ratios are much greater than those of sea water, marine concentrators of iodine are

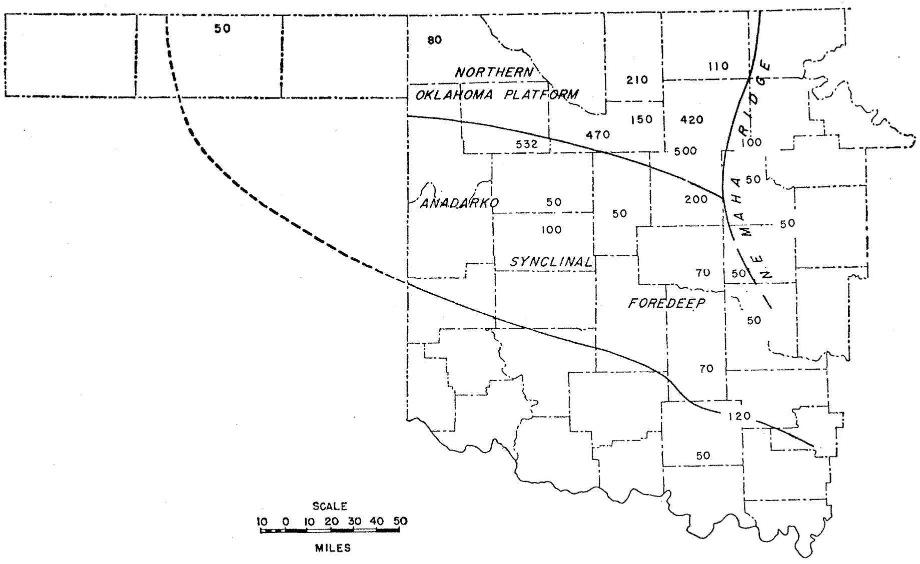

Fig. 1. Western Oklahoma: sources of brine samples, with approximate contents of iodide (parts per million).

the source of the iodide and bromide in excess of the amounts provided by sea water. Our investigation indicates that this may be so in Oklahoma.

The I:Cl ratio is 1000 to 10,000 times greater for the Oklahoma waters than for sea water. The seaweeds and corals (Table 1) are present-day species. The I:Br ratios of these organic concentrators are remarkably similar to those found in the brines: from 0.2 to 8.9 for the brines and from 0.37 to 5.9 for the seaweeds and corals. Therefore the present composition of the brines with respect to iodide and bromide is equivalent to possible equilibria in leaching of the residue of the organic iodide-bromide-concentrating organisms with brackish water or sea water.

For additional evidence concerning the biologic source of the iodide and bromide, core samples were obtained from formations of interest. Some of these samples were leached with water for several hours at a temperature slightly above ambient to remove entrapped brine or solids from evaporated brine; the amount of iodide thus leached ranged from 0.1 to 1.0 ppm. The samples were then dissolved in acid and analyzed for total iodide, which ranged from 4.2 to 14.0 ppm. Therefore the water-insoluble iodide ranged from 4.1 to 13.0 ppm. This iodide was organically bound.

A thin section of a core sample was inspected by a micropaleontologist; it was a bryozoan limestone, with bryozoan debris, calcified algae, and organic matter present. Bryozoa grow rapidly and abound in well-circulated marine waters rich in microorganisms. If deposition were sufficiently rapid these microorganisms could have supplied much of the organic matter in such an environment.

Table 1. Halogens in Oklahoma brines, sea water, and organic concentrators.

Sample	County	Formation	Depth (m)	Sp. Gr.	Content (ppm)		
					Chloride	Bromide	Iodide
Brine 1	Alfalfa	Mississippi	2164	1.148	115,531	768	215
Brine 2	Garfield	Mississippi	2377	1.086	70,124	552	464
Brine 3	Kingfisher	Oswego	1910	1.137	111,552	817	133
Brine 4	Major	Mississippi	2225	1.046	37,677	319	443
Brine 5	Stephens	Springer	1829	1.001	28	450	145
Brine 6	Woodward	Chester	2438	1.026	21,341	58	519
Sea water				1.026	18,500	63	0.05
Seaweed (9)							
Laminaria digitata (dry matter)						1380	510–8000
L. saccharina (dry matter)						340	2000
Desmaresta (ash)						6800	5200
Coral (9)							
Gorgonia verrucosa						16,200	69,200
Gorgonellidae						19,800	22,100
Isididae						7400	20,300

The associated petroleum is a light oil of about 43° API gravity and brownish-green in color. It contains about 0.1 percent sulfur, 0.05 percent nitrogen, 11 percent light gasoline, 27 percent naphtha, 44 percent other distillates, and 18 percent residuum. Some of the petroleum samples were analyzed for iodide, but none was detected; the sensitivity of the method used was 0.05 ppm.

It is known that iodine has a strong coefficient of fixation in organic matter (*5*) and that iodine in various states of oxidation is absorbed by carbon, clays, and rocks (*6*). The absorption rate increases with temperature and acidity (*7*), and decreases in the presence of naphthenic acids and mineral salts, especially calcium chloride (*8*).

Together the data on the brines and cores strongly suggest that the source of the iodide was organic because: (i) it is known that iodine has a strong coefficient of fixation in organic matter; (ii) seaweeds, algae, and corals are known to concentrate iodine; and (iii) analysis of the core samples indicated the presence of organically bound iodide in the environment.

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