SOURCE OF HIGH-FLUORIDE GROUND WATER WEST-CENTRAL COMANCHE COUNTY, OKLAHOMA

by

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ABSTRACT

Water withdrawn from wells in west-central Comanche County, Oklahoma, is characterized by high fluoride concentrations (15 to 28 mg/L). In order to identify the source of fluoride in the ground water, fluoride contents in 105 samples representative of the Carlton Rhyolite, Mount Scott Granite, Quanah Granite and Post Oak Formation were determined by a selective ion-electrode method. A correlation between fluoride levels in ground water and distribution of fluoride in Post Oak sediments strongly suggests that granitic detritus in these conglomerates and sandstones is the primary source of fluoride ions. Most of the fluoride in Post Oak sandstones was probably adsorbed on clay minerals during diagenetic modification. Fluoride ions F^- are released to bicarbonate enriched ground water through exchange with hydroxyl ions which were accumulated in this solution during hydrolysis reactions. As the water percolates downdip, fluoride may have been concentrated by membrane effects resulting from the intertonguing of Post Oak sandstones with shales, siltstones and sandstones of the contemporaneous Wellington, Garber and Hennessey Formations.

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INTRODUCTION

Fluoride concentrations of 1.0 to 1.5 mg/L in drinking water have been shown epidemiologically to prevent tooth decay. However, higher concentrations of fluoride in domestic water supplies can cause dental fluorosis (tooth mottling) in young children. The U.S. Environmental Protection Agency has determined that when fluoride is naturally present in ground water, the concentration should not average more than two times an appropriate upper limit based on the average maximum daily air temperature (Hem, 1970). An average fluoride concentration greater than two times the optimum value constitutes grounds for rejection of a ground-water supply.

Based on Environmental Protection Agency guidelines, the Oklahoma State Department of Health has designated a 1.6 mg/L maximum concentration limit (MCL) for fluoride in public water supplies in west-central Comanche County (Lawton-Wichita Mountains area) of southern Oklahoma (Fig. 1). However, water withdrawn from private and municipal wells in the area commonly have higher fluoride contents (2.5 to 28 mg/L; Havens, 1975, 1977).

The principal aquifers in west-central Comanche County are the Post Oak Formation (Permian) and the Arbuckle Group (Lower Paleozoic). The source of fluoride in waters withdrawn from these aquifers has been a matter of conjecture, but most researchers have speculated that a relationship exists between the mineralogic composition of the aquifer

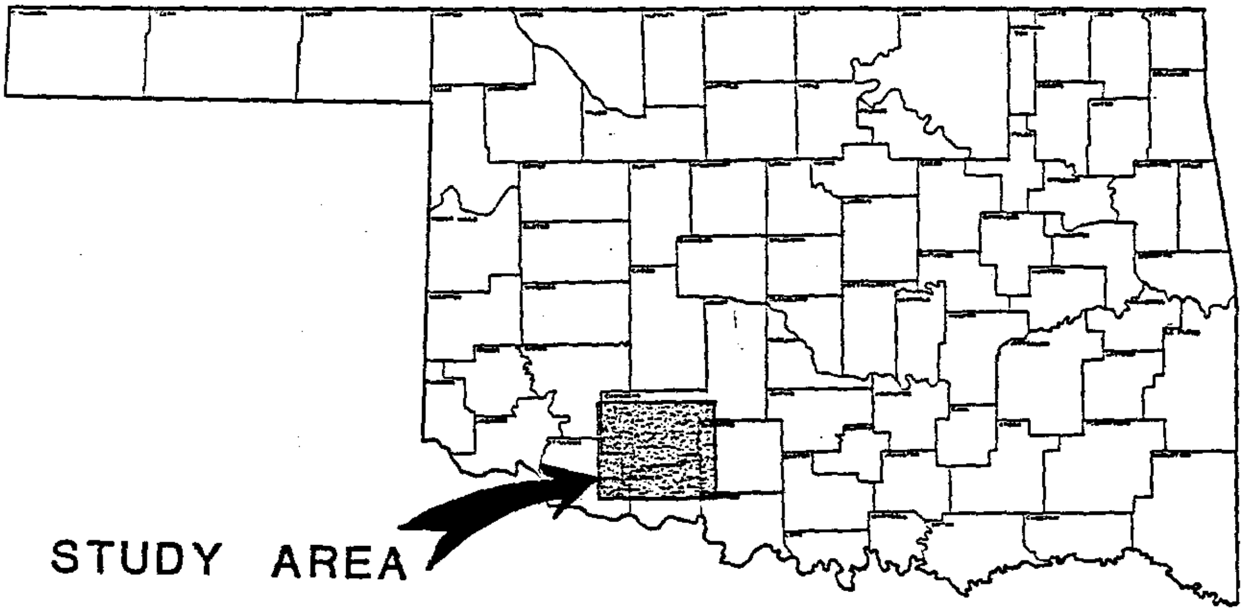

Figure 1. Map showing location of the study area.

sediments and the amount of fluoride in the ground water. Geochemical evidence presented in this report strongly suggests that granitic detritus in conglomerates and sandstones of the Post Oak Formation is the primary source of fluoride ions.

GEOLOGIC FRAMEWORK

Late Precambrian to Cambrian igneous rocks form the uplifted, northwest-trending massif of the Wichita Mountains (Fig. 2). In Comanche County, the igneous complex is divided into (1) troctolites, anorthosites and gabbros of the Raggedy Mountain Gabbro Group, (2) rhyolitic flows, ignimbrites and related pyroclastic rocks of the Carlton Rhyolite, and (3) the calc-alkaline Mount Scott and peralkaline Quanah Granites of the Wichita Granite Group (Ham and others, 1964; Al-Shaieb and others, 1977; Powell and others, 1980). The granites, both as epizonal plutons and as sills, intrude into and above the Raggedy Mountain Group and into the lower part of the Carlton Rhyolite. Riebeckite-aegerine pegmatite dikes cut the granites in the western part of the Wichita Mountains, and are considered to be cogenetic with the Quanah Granite (Merritt, 1967).

South of the Wichita Mountains, the Arbuckle Group is faulted against the igneous complex (Fig. 3). With exception of four inliers exposed just north of Lawton, the 370 to 1800 meters of limestone, dolomite and shale is covered by flat-lying Permian rocks of the Wellington, Garber, Post Oak and Hennessey Formations. Solution of the carbonate rocks along bedding planes and fractures has formed openings and porous zones within which water may be transmitted below the regional water table (Havens, 1975). The aquifer is apparently recharged along the southern flank of the Wichitas and through the overlying Post Oak Formation (Fig. 3).

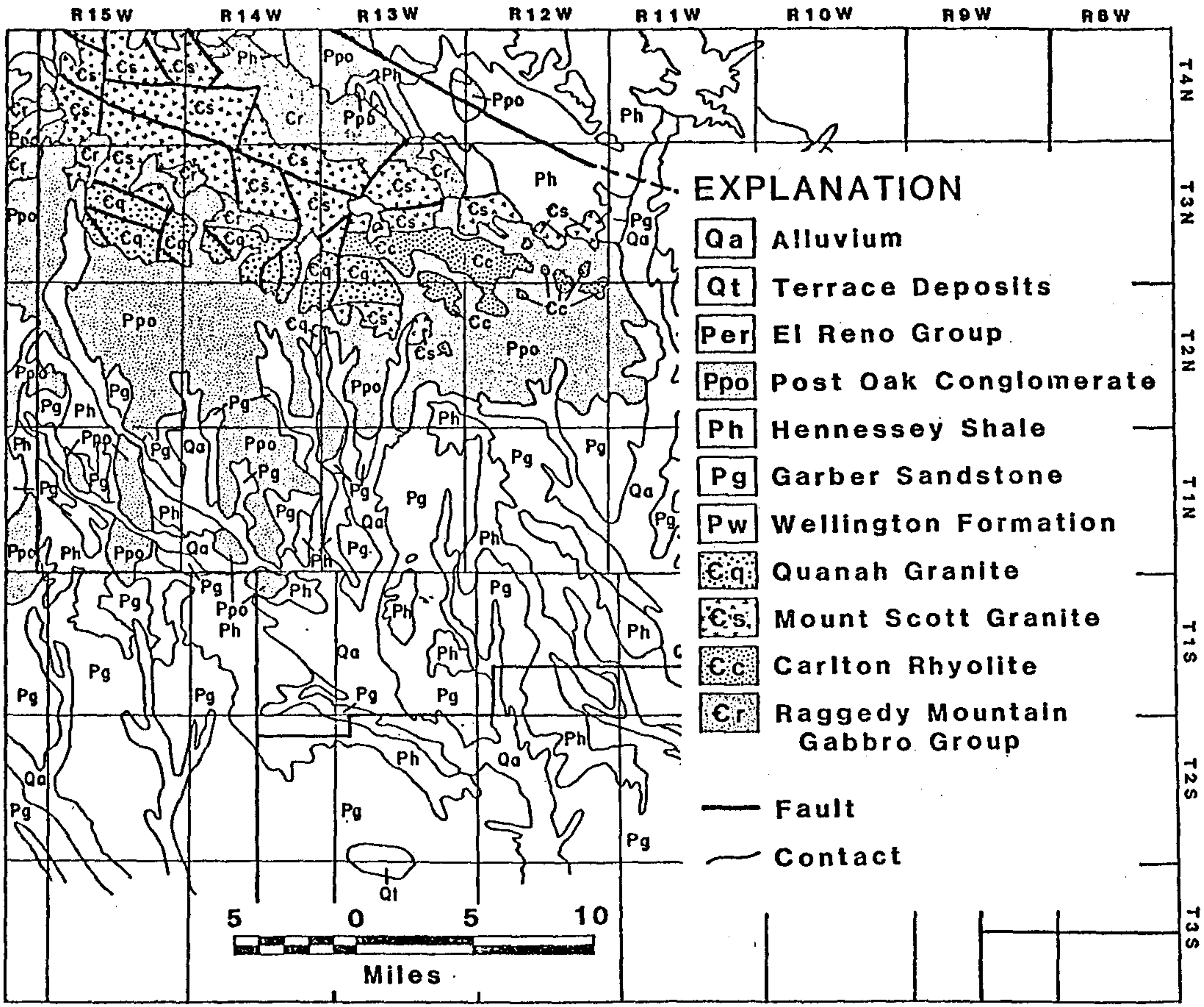

Figure 2. Geologic Map of west-central Comanche County, southwestern Oklahoma.

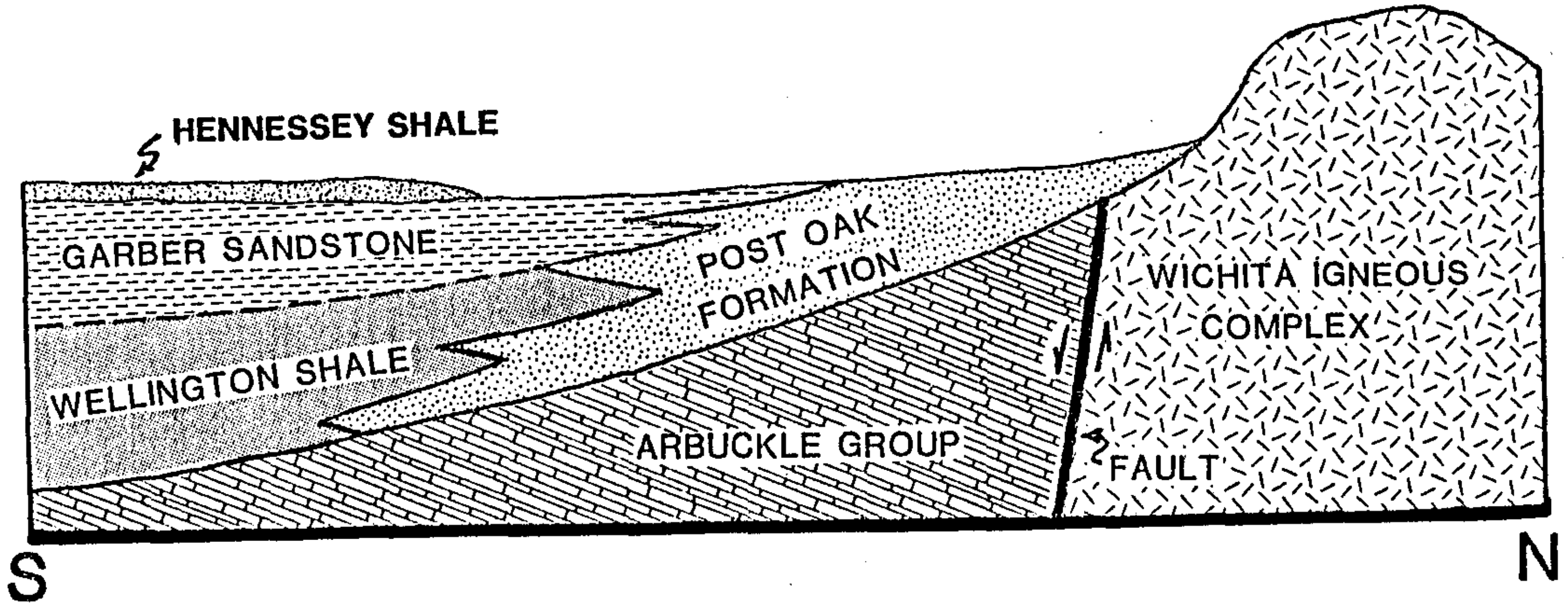

Figure 3. Schematic N-S geologic cross-section of west-central Comanche County, southwestern Oklahoma.

The Post Oak Formation represents a thick sequence of clastic debris derived from the Wichita uplift. Within and adjacent to the mountains, the formation consists of massively-bedded conglomerates that contain 15 to 45 cm clasts of granite and rhyolite set in a coarse-grained sand matrix. Chase (1954) mapped distinct granite and rhyolite conglomerate facies on the basis of clast composition, but Al-Shaieb and others (1980) noted that sandstones associated with both facies exhibit a dominance of granitic over rhyolitic sand-sized fragments. Although the feldspathic litharenites and lithic arkoses contain detrital quartz, feldspar and rock fragments derived from the Mount Scott and Quanah Granites, the Mount Scott Granite is the dominant source.

The Post Oak conglomerates display a decrease in average clast size and a gradual increase in the proportion of sandstone and mudstone away from the mountains. The conglomerates grade laterally into beds of shale, siltstone and sandstone of the Hennessey, Garber and Wellington Formations.

ANALYTICAL PROCEDURE

In order to identify the source of anomalous fluoride concentrations in ground water of west-central Comanche County, fluoride contents in 105 samples representative of the Carlton Rhyolite, Mount Scott Granite, Quanah Granite and Post Oak Formation were determined by a selective ion-electrode method. The procedure was similar to that described by Kesler and others (1973). Solution potentials were measured using an ORION model 94-09 fluoride-ion electrode and a slieve type calomel reference electrode with an ORION model 601A ion meter. Analytical errors were checked with some geochemical standards (G-2, GSP-1 and AGV-1). Standard deviation was less than 10% (av. 5%). The location of fluoride contents of analyzed rocks are given in Tables 1 and 2.

TABLE I
FLUORIDE CONTENT WICHITA IGNEOUS ROCKS

Sample	Location	F(ppm)	Sample	Location	F(ppm)
Quanah Granite					
E-1	SE¼ S26 T3N R14W	85	WG-44	SE¼ S21 T3N R14W	273
E-4	SW¼ S26 T3N R14W	226	WG-52	NW¼ S28 T3N R14W	760
E-18	SE¼ S27 T3N R14W	366	WG-56	NE¼ S29 T3N R14W	970
FS-4	SW¼ S7 T2N R13W	316	WG-77	SW¼ S32 T4N R14W	1070
H-1-1C	SE¼ S4 T3N R15W	1660	WG-121	NE¼ S30 T3N R14W	445
H-6-1C	NE¼ S4 T3N R15W	1366	WG-124	SW¼ S24 T3N R15W	260
OS-2	SE¼ S22 T3N R14W	138	WG-127	NE¼ S9 T3N R15W	838
Q-3	SE¼ S16 T3N R15W	760	WG-131	SW¼ S30 T3N R14W	596
Q-8	NW¼ S21 T3N R15W	43	WG-134	SE¼ S15 T3N R15W	176
Q-9	NW¼ S21 T3N R15W	168	WG-139	NW¼ S21 T3N R14W	66
Q-11	NE¼ S21 T3N R15W	28	WG-141	SE¼ S20 T3N R14W	1070
Q-14A	NE¼ S21 T3N R15W	332	WG-148	SE¼ S28 T3N R13W	301
S-1	NE¼ S12 T2N R13W	880	WG-151	SW¼ S34 T3N R13W	1922
S-4	SE¼ S33 T3N R13W	1434	WGQ-1	SE¼ S21 T3N R13W	838
S-7	SW¼ S32 T3N R13W	138	Z-5	NE¼ S21 T3N R15W	1660
W-4	NE¼ S23 T3N R13W	515			
W-6	SE¼ S23 T3N R15W	515	Carlton Rhyolite		
W-12	NE¼ S13 T3N R15W	1581	W-126	NE¼ S28 T3N R13W	224
W-14	NW¼ S13 T3N R15W	690	W-131	SW¼ S27 T3N R13W	625
WG-21	NE¼ S23 T3N R14W	1743	W-129	NE¼ S34 T3N R13W	798
WG-22	NE¼ S20 T3N R14W	1180			
WG-24	SW¼ S25 T3N R14W	924	Mount Scott Granite		
WG-25	SE¼ S22 T3N R14W	567	WG-1A	SE¼ S11 T3N R13W	204
WG-32	SE¼ S21 T3N R14W	1505	WG-28	SE¼ S8 T3N R13W	567
WG-34	NE¼ S18 T3N R14W	1019	WG-73	NW¼ S4 T3N R14W	1070
WG-36	NW¼ S25 T3N R15W	1123	WG-103	NW¼ S10 T3N R14W	690
WG-38	NE¼ S10 T3N R15W	567	WG-154	NW¼ S10 T2N R13W	798
WG-40	SW¼ S11 T3N R15W	490			

TABLE 2
FLUORIDE CONTENTS OF POST OAK SEDIMENTS

Sample	Location	F(ppm)	Sample	Location	F(ppm)
Bulk Rock					
41/2	SE¼ S22 T2N R15W	348	56/30	NW¼ S4 T1S R14W	5622
42/1	SW¼ S15 T2N R14W	4195	56/31	NW¼ S8 T1N R14N	322
42/2	SE¼ S13 T2N R14W	798	57/7	SE¼ S28 T2N R13W	3995
43/4	SE¼ S16 T2N R13W	287	57/8	SE¼ S4 T1N R13W	1070
55/7	SW¼ S36 T1N R16W	970	57/11	NE¼ S13 T1N R14W	248
55/8	NE¼ S3 T1S R15W	838	57/12	SE¼ S13 T1N R14W	2018
55/10	NW¼ S27 T2N R15W	1180			
55/11	NE¼ S33 T2N R15W	1660	Matrix Sandstone		
55/18	SW¼ S25 T1N R15W	1301	2-39	SE¼ S12 T1N R14W	384
55/19	NE¼ S31 T1N R15W	1239	2-20	NW¼ S13 T2N R15W	168
55/21	NW¼ S26 T1N R15W	838	3-14	NW¼ S19 T2N R13W	125
55/22	NW¼ S23 T1N R15W	970	2-52	NW¼ S2 T2N R12W	176
55/25	SW¼ S11 T1N R15W	3805	3-20	NE¼ S34 T2N R14W	445
56/1	NW¼ S29 T2N R15W	236	2-25	NE¼ S24 T2N R12W	2839
56/2	NE¼ S36 T2N R15W	1581	3-5	NE¼ S29 T2N R12W	2335
56/6	NW¼ S27 T2N R14W	138	2-56	NW¼ S31 T3N R11W	1506
56/8	NW¼ S13 T1N R14N	332	3-4	NE¼ S14 T1N R15W	131
56/10	NE¼ S15 T1N R14W	1660	2-6	NW¼ S27 T3N R12W	224
56/9	NW¼ S14 T1N R14W	160	2-22	SW¼ S27 T4N R13W	248
56/13	NE¼ S4 T1N R14W	3130	3-8	NE¼ S3 T2N R14W	176
56/15	NW¼ S11 T1N R14W	1301	2-11	NE¼ S14 T2N R13W	131
56/16	SW¼ S36 T2N R14W	1434	2-61	SW¼ S27 T3N R12W	273
56/18	SE¼ S27 T2N R14W	2839	2-17	SE¼ S4 T2N R15W	204
56/21	NW¼ S29 T2N R14W	2453	3-17	NW¼ S7 T2N R13W	138
56/23	NW¼ S25 T2N R15W	224	2-58	SE¼ S35 T3N R12W	85
56/24	SE¼ S25 T2N R15W	1922	2-60	SE¼ S3 T2N R15W	138
56/27	NE¼ S24 T1N R15W	838	2-14	NE¼ S31 T3N R14W	145
56/28	SW¼ S32 T1S R14W	4833	2-21	NW¼ S28 T3N R13W	131

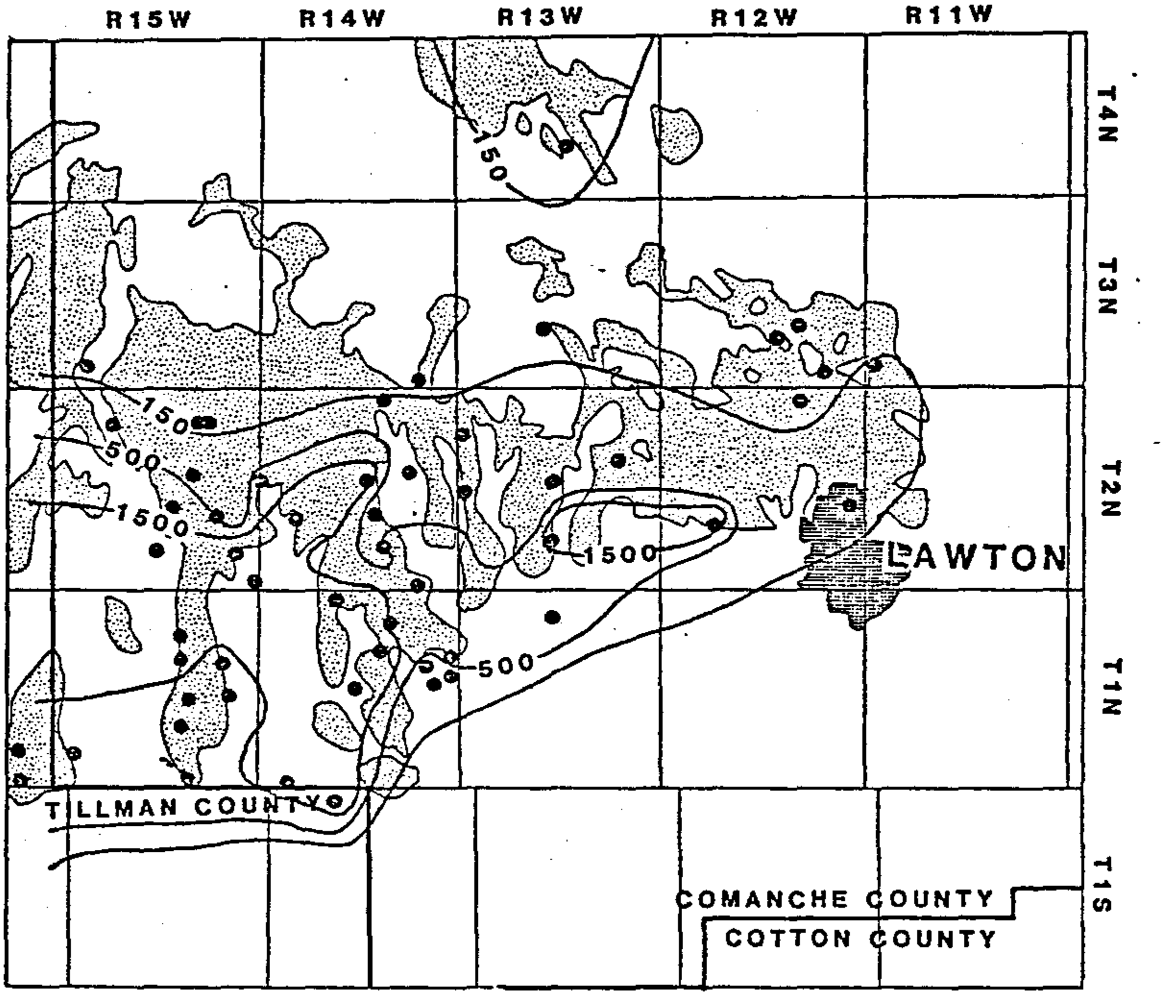

Figure 4. Distribution of fluoride in the Post Oak Formation. Stippled area represents the extent of Post Oak outcrop, solid dots indicate the location of analyzed samples. Concentrations are continued in parts per million.

2839 ppm) are encountered in conglomerates that outcrop immediately north and west of Lawton.

The sediments probably contain F-bearing minerals in sufficient quantities to account for the observed F abundances. Although amphiboles are a major ferromagnesian constituent of Wichita granitic rocks, they are not present as detrital minerals in Post Oak sandstones. Furthermore, the amphiboles in granitic clasts are commonly altered to iron oxides and clay minerals. Brown biotite occurs as rare detrital grains that also show variable degrees of oxidation to iron oxides. Apatite is found in minor amounts in some arkosic channel sandstones near the southwestern edge of the outcrop area, but is only a trace component in other Post Oak sandstones. Fluorite has not been observed in any rock examined in thin section. It is therefore considered that most of the fluoride in Post Oak sediments may be adsorbed on mineral surfaces. Appreciable amounts of both allogenic and authigenic clay are present in many of the poorly-sorted sandstones (Al-Shaieb, 1978). Kaolinite, the most common clay mineral in the sandstones, has a high F adsorption capacity (Bower and Hatcher, 1967).

Al-Shaieb and others (1980) concluded that during an early stage of burial, diagenesis involved partial dissolution of feldspar and formation of authigenic kaolinite as a pore-filling. Intrastratal solution of amphibole (and oxidation of biotite) probably provided a source of iron for iron-oxide cement that formed at this stage (Al-Shaieb, 1978). It is suggested that solution of riebeckite and other F-bearing minerals in the granitic detritus also may have released fluoride ions, which were absorbed on the pore-filling (and detrital) kaolinite.

Discussion

The fluoride content of ground water in west-central Comanche County increases from 0.1 to 0.8 mg/L in water withdrawn from wells near the Wichita Mountains, to between 15 and 28 mg/L in water withdrawn from wells at the southern limit of Post Oak outcrop. South of the Post Oak, fluoride concentrations in ground water are less than 1.6 mg/L (Fig. 5). The maximum fluoride contents are encountered in water from wells located where the Post Oak sandstones are characterized by high F abundances (compare Figs. 4 and 5). Three spot samples of water from a test well, which penetrated the Post Oak (cased interval) and Arbuckle Group aquifers, further show fluoride increasing from 8.3 mg/L at 997 feet below land surface (lower Arbuckle aquifer) to 16 mg/L at 560 (upper Arbuckle aquifer) feet below land surface (Havens, 1975, Table 1). These observations combine to suggest that high fluoride levels in ground water of west-central Comanche County originate in the Post Oak aquifer rather than in the underlying Arbuckle Group aquifer.

From a study of ionic association of fluoride with other species in available water-quality data, it is evident that fluoride concentration is closely associated only with the bicarbonate content and to a lesser extent, total hardness of the water. The highest levels of fluoride correspond with the highest bicarbonate concentrations (except in water drawn from alluvium; Fig. 6). Total hardness increases gradually with fluoride content within the Post Oak outcrop area, but thereafter continues to increase southward as fluoride content decreases (Fig. 7).

A mechanism that may explain the close association of maximum fluoride and bicarbonate concentrations in ground water with high levels of fluoride in Post Oak sandstones involves the dissolution of pore-filling carbonate cement, and release of fluoride adsorbed on clay minerals. The field pH of high-fluoride water samples withdrawn from wells of west-

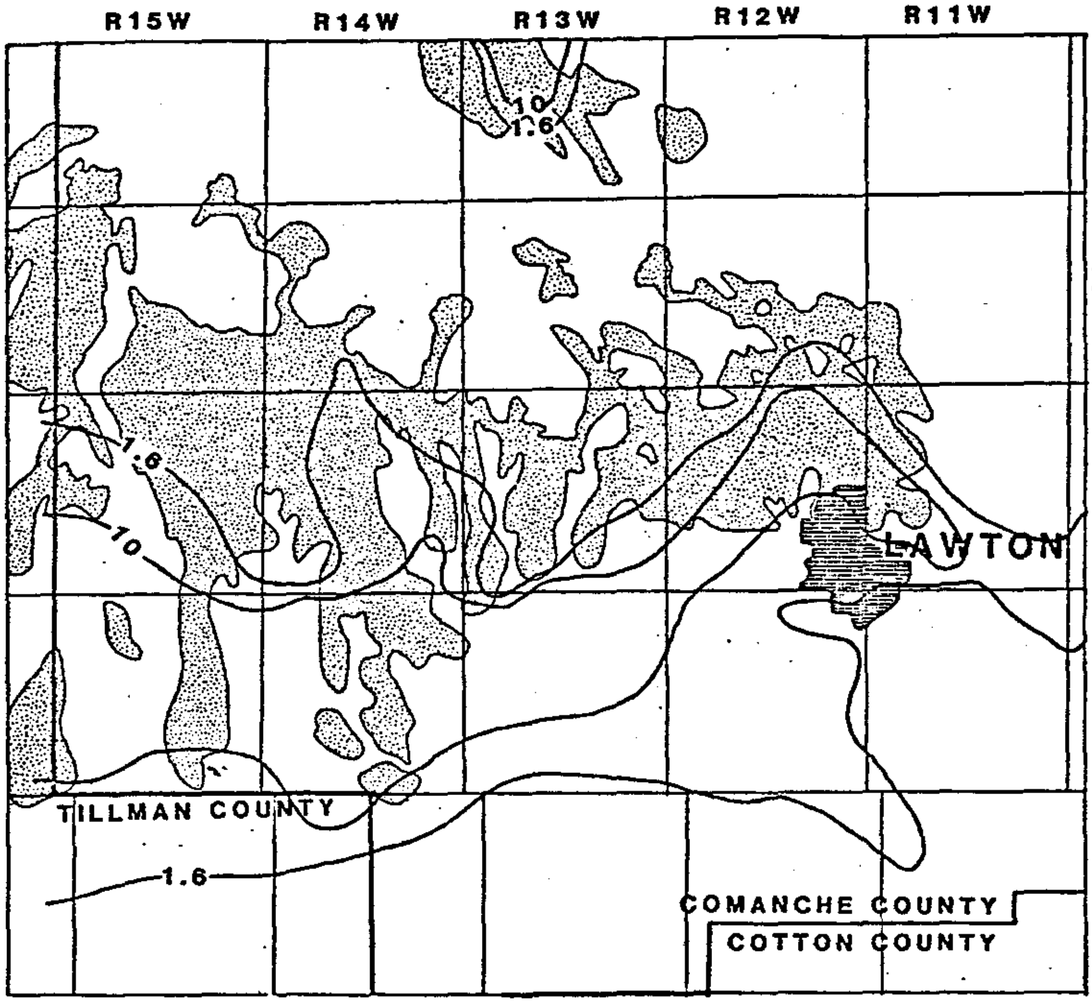

Figure 5. Distribution of fluoride in ground water of west-central Comanche County. Stippled area represents the extent of Post Oak outcrop. Concentrations are contoured in milligrams per liter.

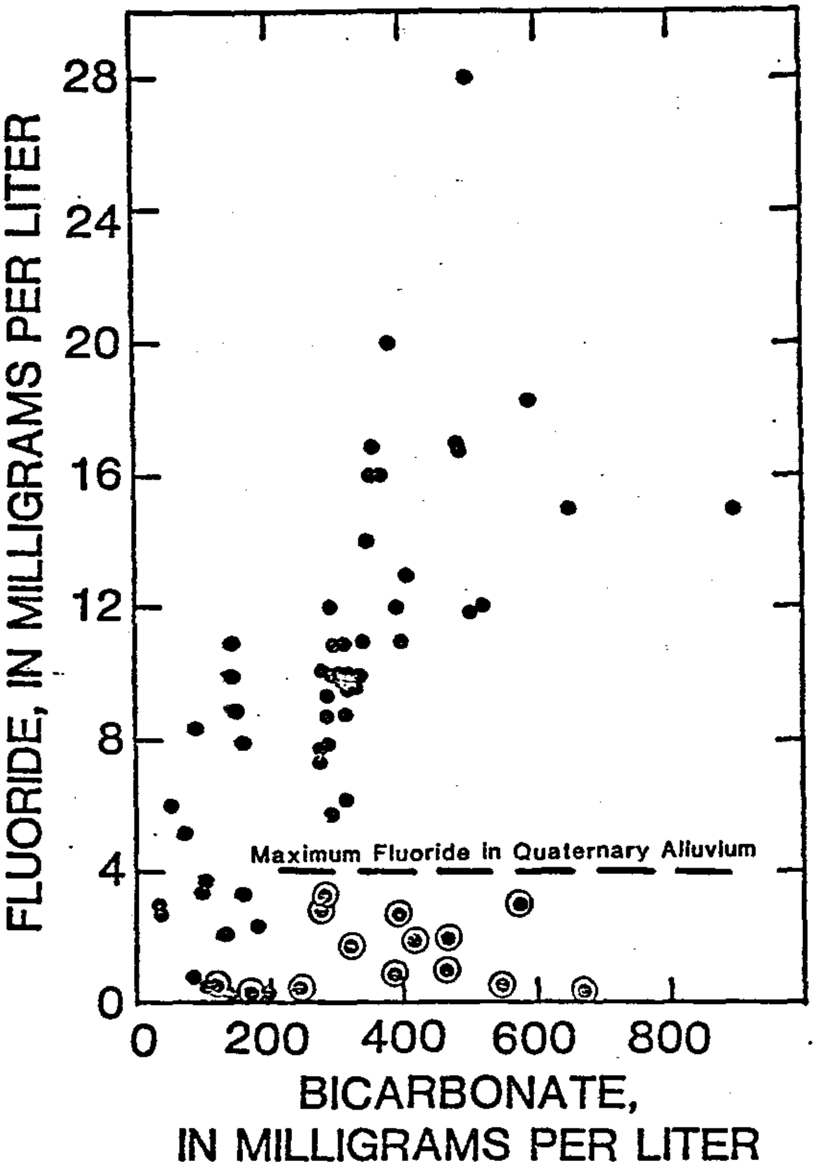

Figure 6. Relation of fluoride and bicarbonate in ground water drawn from the Post Oak and Arbuckle aquifers (solid dots) and from alluvium (circled dots). Note the generally low concentration of fluoride in water withdrawn from alluvium.

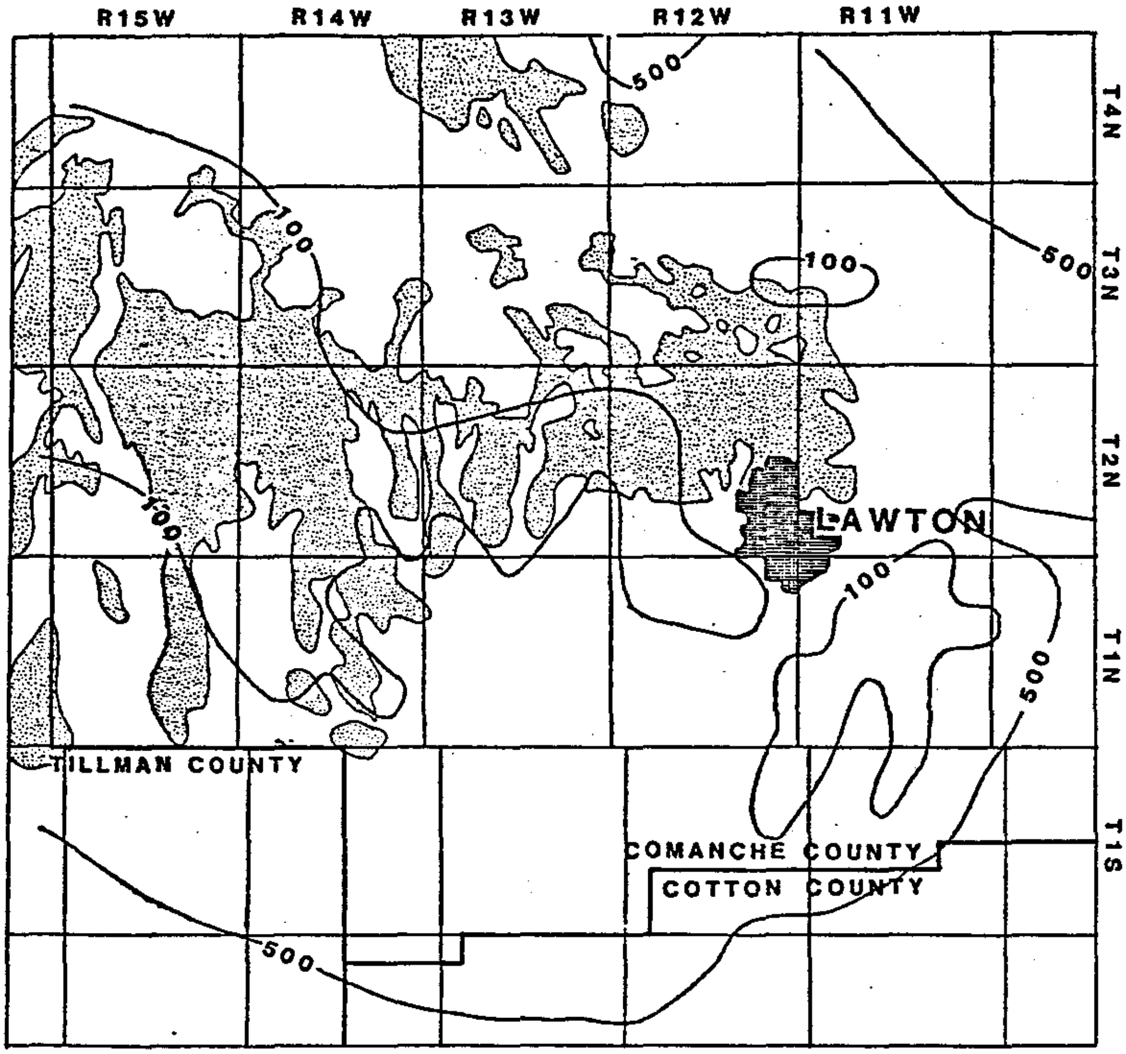

Figure 7. Total hardness of ground water in west-central Comanche County. Hardness values are contoured in milligrams per liter computed by multiplying the sum of milligrams per liter of calcium and magnesium by 50.

central Comanche County ranges between 8.4 and 10.1 (Havens, 1975, Table 1). Garrels and Christ (1965) have shown that bicarbonate ion HCO_3^- is the predominant carbonate ion under these pH conditions. Bicarbonate ions may be produced by the dissociation of calcium carbonate and feldspars in water according to the hydrolysis reactions:

$$CaCO_3 + HOH = HCO_3^- + OH^- + Ca^{++}$$

$$2KALSi_3O_5 + 2H_2CO_3 + 9H_2O_L = AL_2Si_2O_s(OH)4 + 2K^+ + 4K_4SiO_4 + 2HCO_3^-$$

Therefore, ground water will be enriched in bicarbonate and hydroxyl ions from dissolution of early stage carbonate cements and hydrolysis of feldspars (Al-Shaieb, 1980). When this solution comes in contact with clay minerals of the Post Oak formation, fluoride ions F^- adsorbed on clay particles, will be released to the ground-water system through exchange with hydroxyl ions. Fluoride ions F^- will be very stable under existing pH conditions (Pourbaix, 1966). Locally, additional fluoride may be released from apatite through anion exchange.

In some places, fluoride concentrations in the ground water may result from direct anion exchange between the aquifer sediments and water of high pH. However, it is suggested that the anomalous fluoride levels in water pumped from wells located along the southern margin of Post Oak outcrop reflect primarily membrane effects resulting from the interfingering of Post Oak sandstone with the Wellington, Garber and Hennessey Formation. Where fluoride concentrations in ground water are highest, the Post Oak consists of thin beds of coarse-grained arkosic channel sandstones intercalated with yellow-red and green shales (Al-Shaieb and others, 1977). These shale interbeds may act as semipermeable membranes, and therefore may be a major factor in determining the fluoride composition of the ground water. When water and solutes are driven through such a semipermeable membrane under an external gradient, the passage of ionic solutes across the membrane is restricted relative to water (Hem, 1970). Unbalanced surface charges on the clayey material result in adsorption of ions onto the clay particles. Because cations are the dominant adsorbed species, pore fluids develop a net positive charge, which repels cations in solution as the aqueous solution moves through the pore-space. Anions may also be restricted passage through the membrane in order to maintain electrical neutrality across the membrane. If such a process operates within the Post Oak sediments, fluoride ions held back as water passed through the shale interbeds may have accumulated until the observed concentrations were reached.

CONCLUSIONS

High levels of fluoride (15 to 28 mg/L) characterize water withdrawn from the Post Oak and Arbuckle aquifers of west-central Comanche County, Oklahoma. A correlation between fluoride concentrations in ground water and distribution of fluoride in Post Oak conglomerates and sandstones strongly suggests that the high fluoride levels originate within the Post Oak aquifer rather than within the underlying Arbuckle aquifer. Most of the fluoride in Post Oak sediments is probably adsorbed on clay minerals. Hydrolysis of carbonate cement and feldspars releasing adsorbed fluoride through exchange with hydroxyl ions played an important role in associated ground water. It is suggested that as water percolated downdip, fluoride is concentrated by membrane effects resulting from the interfingering of Post Oak sandstones with shales, siltstones and sandstones of the contemporaneous Wellington, Garber and Hennessey Formations.

RECOMMENDATIONS

The Post Oak conglomerate and the underlying "granite wash" form extensive wedge-shaped clastic deposits that lie both north and south of the Wichita Mountains. These alluvial fan deposits extend from the southern part of the Anadarko Basin in the north to the Red River in the south and are the major source of fluoride in ground water. A comprehensive program should be initiated to investigate the areal distribution of the fluoride-rich ground water in the granitic-rhyolitic facies which is derived from the Wichita Mountains. Water samples should be collected and analyzed from fluoride-rich ground, in order to determine changes in concentration as the water moves down gradient from recharge areas.

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