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

by

Nathan L. Green

and

Zuhair Al-Shaieb

Department of Geology
OKLAHOMA STATE UNIVERSITY
Stillwater, Oklahoma 74078

E-002

Submitted to
the
WATER RESEARCH INSTITUTE
OKLAHOMA STATE UNIVERSITY

September, 1981
SOURCE OF HIGH-FLUORIDE GROUND WATER, 
WEST-CENTRAL COMANCHE COUNTY, OKLAHOMA

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Water withdrawn from wells in west-central Comanche County, Oklahoma, is characterized by high fluoride concentrations (15 to 28 mg/L).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.
ACKNOWLEDGEMENTS

This investigation was funded by a grant to Wayne A. Pettyjohn from the Water Research Center at Oklahoma State University.

Chemical analyses of rock samples and geochemical interpretations were carried out by N. L. Green¹ and Z. Al-Shaieb.

¹Present address: Department of Geology, University of Alabama, University, Alabama 35486.
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, north-
west-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 silve 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>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>F(ppm)</th>
<th>Sample</th>
<th>Location</th>
<th>F(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quanah Granite</td>
<td></td>
<td></td>
<td>WG-44</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S21 T3N R14W</td>
<td>273</td>
</tr>
<tr>
<td>E-1</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S26 T3N R14W</td>
<td>85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-4</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S26 T3N R14W</td>
<td>226</td>
<td>WG-52</td>
<td>NW&lt;sub&gt;E&lt;/sub&gt; S28 T3N R14W</td>
<td>760</td>
</tr>
<tr>
<td>E-18</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S27 T3N R14W</td>
<td>366</td>
<td>WG-56</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S29 T3N R14W</td>
<td>970</td>
</tr>
<tr>
<td>FS-4</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S7  T2N R13W</td>
<td>316</td>
<td>WG-77</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S32 T4N R14W</td>
<td>1070</td>
</tr>
<tr>
<td>H-1-1C</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S4  T3N R15W</td>
<td>1660</td>
<td>WG-121</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S30 T3N R14W</td>
<td>445</td>
</tr>
<tr>
<td>H-6-1C</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S4  T3N R15W</td>
<td>1366</td>
<td>WG-124</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S24 T3N R15W</td>
<td>260</td>
</tr>
<tr>
<td>OS-2</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S22 T3N R14W</td>
<td>138</td>
<td>WG-127</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S9 T3N R15W</td>
<td>838</td>
</tr>
<tr>
<td>Q-3</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S16 T3N R15W</td>
<td>760</td>
<td>WG-131</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S30 T3N R14W</td>
<td>596</td>
</tr>
<tr>
<td>Q-8</td>
<td>NW&lt;sub&gt;E&lt;/sub&gt; S21 T3N R15W</td>
<td>43</td>
<td>WG-134</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S15 T3N R15W</td>
<td>176</td>
</tr>
<tr>
<td>Q-9</td>
<td>NW&lt;sub&gt;E&lt;/sub&gt; S21 T3N R15W</td>
<td>168</td>
<td>WG-139</td>
<td>NW&lt;sub&gt;E&lt;/sub&gt; S21 T3N R14W</td>
<td>66</td>
</tr>
<tr>
<td>Q-11</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S21 T3N R15W</td>
<td>28</td>
<td>WG-141</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S20 T3N R14W</td>
<td>1070</td>
</tr>
<tr>
<td>Q-14A</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S21 T3N R15W</td>
<td>332</td>
<td>WG-148</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S28 T3N R13W</td>
<td>301</td>
</tr>
<tr>
<td>S-1</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S12 T2N R13W</td>
<td>880</td>
<td>WG-151</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S34 T3N R13W</td>
<td>1922</td>
</tr>
<tr>
<td>S-4</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S33 T3N R13W</td>
<td>1434</td>
<td>WGG-1</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S21 T3N R13W</td>
<td>838</td>
</tr>
<tr>
<td>S-7</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S32 T3N R13W</td>
<td>138</td>
<td>Z-5</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S21 T3N R15W</td>
<td>1660</td>
</tr>
<tr>
<td>W-4</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S23 T3N R13W</td>
<td>515</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-6</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S23 T3N R15W</td>
<td>515</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-12</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S13 T3N R15W</td>
<td>1581</td>
<td>W-126</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S28 T3N R13W</td>
<td>224</td>
</tr>
<tr>
<td>W-14</td>
<td>NW&lt;sub&gt;E&lt;/sub&gt; S13 T3N R15W</td>
<td>690</td>
<td>W-131</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S27 T3N R13W</td>
<td>625</td>
</tr>
<tr>
<td>WG-21</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S23 T3N R14W</td>
<td>1743</td>
<td>W-129</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S34 T3N R13W</td>
<td>798</td>
</tr>
<tr>
<td>WG-22</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S20 T3N R14W</td>
<td>1180</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WG-24</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S25 T3N R14W</td>
<td>924</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WG-25</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S22 T3N R14W</td>
<td>567</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WG-32</td>
<td>SE&lt;sub&gt;E&lt;/sub&gt; S21 T3N R14W</td>
<td>1505</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WG-34</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S18 T3N R14W</td>
<td>1019</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WG-36</td>
<td>NW&lt;sub&gt;E&lt;/sub&gt; S25 T3N R15W</td>
<td>1123</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WG-38</td>
<td>NE&lt;sub&gt;E&lt;/sub&gt; S10 T3N R15W</td>
<td>567</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WG-40</td>
<td>SW&lt;sub&gt;E&lt;/sub&gt; S11 T3N R15W</td>
<td>490</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 1**

FLUORIDE CONTENT WICHITA IGNEOUS ROCKS

Carlton Rhyolite

Mount Scott Granite
### TABLE 2
**FLUORIDE CONTENTS OF POST OAK SEDIMENTS**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>F(ppm)</th>
<th>Sample</th>
<th>Location</th>
<th>F(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk Rock</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41/2</td>
<td>SE: S22 T2N R15W</td>
<td>348</td>
<td>56/30</td>
<td>NW: S4 T1S R14W</td>
<td>5622</td>
</tr>
<tr>
<td>42/1</td>
<td>SW: S15 T2N R14W</td>
<td>4195</td>
<td>56/31</td>
<td>NW: S8 T1N R14N</td>
<td>322</td>
</tr>
<tr>
<td>42/2</td>
<td>SE: S13 T2N R14W</td>
<td>798</td>
<td>57/7</td>
<td>SE: S28 T2N R13W</td>
<td>3995</td>
</tr>
<tr>
<td>43/4</td>
<td>SE: S16 T2N R13W</td>
<td>287</td>
<td>57/8</td>
<td>SE: S4 T1N R13W</td>
<td>1070</td>
</tr>
<tr>
<td>55/7</td>
<td>SW: S36 T1N R16W</td>
<td>970</td>
<td>57/11</td>
<td>NE: S13 T1N R14W</td>
<td>248</td>
</tr>
<tr>
<td>55/8</td>
<td>NE: S3 T1S R15W</td>
<td>838</td>
<td>57/12</td>
<td>SE: S13 T1N R14W</td>
<td>2018</td>
</tr>
<tr>
<td>55/10</td>
<td>NW: S27 T2N R15W</td>
<td>1180</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>55/11</td>
<td>NE: S33 T2N R15W</td>
<td>1660</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Matrix Sandstone</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>55/18</td>
<td>SW: S25 T1N R15W</td>
<td>1301</td>
<td>2-39</td>
<td>SE: S12 T1N R14W</td>
<td>384</td>
</tr>
<tr>
<td>55/19</td>
<td>NE: S31 T1N R15W</td>
<td>1239</td>
<td>2-20</td>
<td>NW: S13 T2N R15W</td>
<td>168</td>
</tr>
<tr>
<td>55/21</td>
<td>NW: S26 T1N R15W</td>
<td>838</td>
<td>3-14</td>
<td>NW: S19 T2N R13W</td>
<td>125</td>
</tr>
<tr>
<td>55/22</td>
<td>NW: S23 T1N R15W</td>
<td>970</td>
<td>2-52</td>
<td>NW: S2 T2N R12W</td>
<td>176</td>
</tr>
<tr>
<td>55/25</td>
<td>SW: S11 T1N R15W</td>
<td>3805</td>
<td>3-20</td>
<td>NE: S34 T2N R12W</td>
<td>445</td>
</tr>
<tr>
<td>56/1</td>
<td>NW: S29 T2N R15W</td>
<td>236</td>
<td>2-25</td>
<td>NE: S24 T2N R12W</td>
<td>2839</td>
</tr>
<tr>
<td>56/2</td>
<td>NE: S36 T2N R15W</td>
<td>1581</td>
<td>3-5</td>
<td>NE: S29 T2N R12W</td>
<td>2335</td>
</tr>
<tr>
<td>56/6</td>
<td>NW: S27 T2N R14W</td>
<td>138</td>
<td>2-56</td>
<td>NW: S31 T3N R11W</td>
<td>1506</td>
</tr>
<tr>
<td>56/8</td>
<td>NW: S13 T1N R14N</td>
<td>332</td>
<td>3-4</td>
<td>NE: S14 T1N R15W</td>
<td>131</td>
</tr>
<tr>
<td>56/10</td>
<td>NE: S15 T1N R14W</td>
<td>1660</td>
<td>2-6</td>
<td>NW: S27 T3N R12W</td>
<td>224</td>
</tr>
<tr>
<td>56/9</td>
<td>NW: S14 T1N R14W</td>
<td>160</td>
<td>2-22</td>
<td>SW: S27 T4N R13W</td>
<td>248</td>
</tr>
<tr>
<td>56/13</td>
<td>NE: S4 T1N R14W</td>
<td>3130</td>
<td>3-8</td>
<td>NE: S3 T2N R14W</td>
<td>176</td>
</tr>
<tr>
<td>56/15</td>
<td>NW: S11 T1N R14W</td>
<td>1301</td>
<td>2-11</td>
<td>NE: S14 T2N R13W</td>
<td>131</td>
</tr>
<tr>
<td>56/16</td>
<td>SW: S36 T2N R14W</td>
<td>1434</td>
<td>2-61</td>
<td>SW: S27 T3N R12W</td>
<td>273</td>
</tr>
<tr>
<td>56/18</td>
<td>SE: S27 T2N R14W</td>
<td>2839</td>
<td>2-17</td>
<td>SE: S4 T2N R15W</td>
<td>204</td>
</tr>
<tr>
<td>56/21</td>
<td>NW: S29 T2N R14W</td>
<td>2453</td>
<td>3-17</td>
<td>NW: S7 T2N R13W</td>
<td>138</td>
</tr>
<tr>
<td>56/27</td>
<td>NE: S24 T1N R15W</td>
<td>838</td>
<td>2-14</td>
<td>NE: S31 T3N R14W</td>
<td>145</td>
</tr>
<tr>
<td>56/28</td>
<td>SW: S32 T1S R14W</td>
<td>4833</td>
<td>2-21</td>
<td>NW: S28 T3N R13W</td>
<td>131</td>
</tr>
</tbody>
</table>
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 $\text{HCO}_3^-$ 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:

$$\text{CaCO}_3 + \text{HOH} = \text{HCO}_3^- + \text{OH}^- + \text{Ca}^{++}$$

$$2\text{KAlSi}_3\text{O}_8 + 2\text{H}_2\text{CO}_3 + 9\text{H}_2\text{O} = 2\text{Al}_2\text{Si}_2\text{O}_8(\text{OH})_4 + 2\text{K}^+ + 4\text{K}_2\text{Si}_2\text{O}_5 + 2\text{HCO}_3^-$$

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 $\text{F}^-$ adsorbed on clay particles, will be released to the ground-water system through exchange with hydroxyl ions. Fluoride ions $\text{F}^-$ 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 interfinger ing 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 semi-
permeable 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.
REFERENCES


