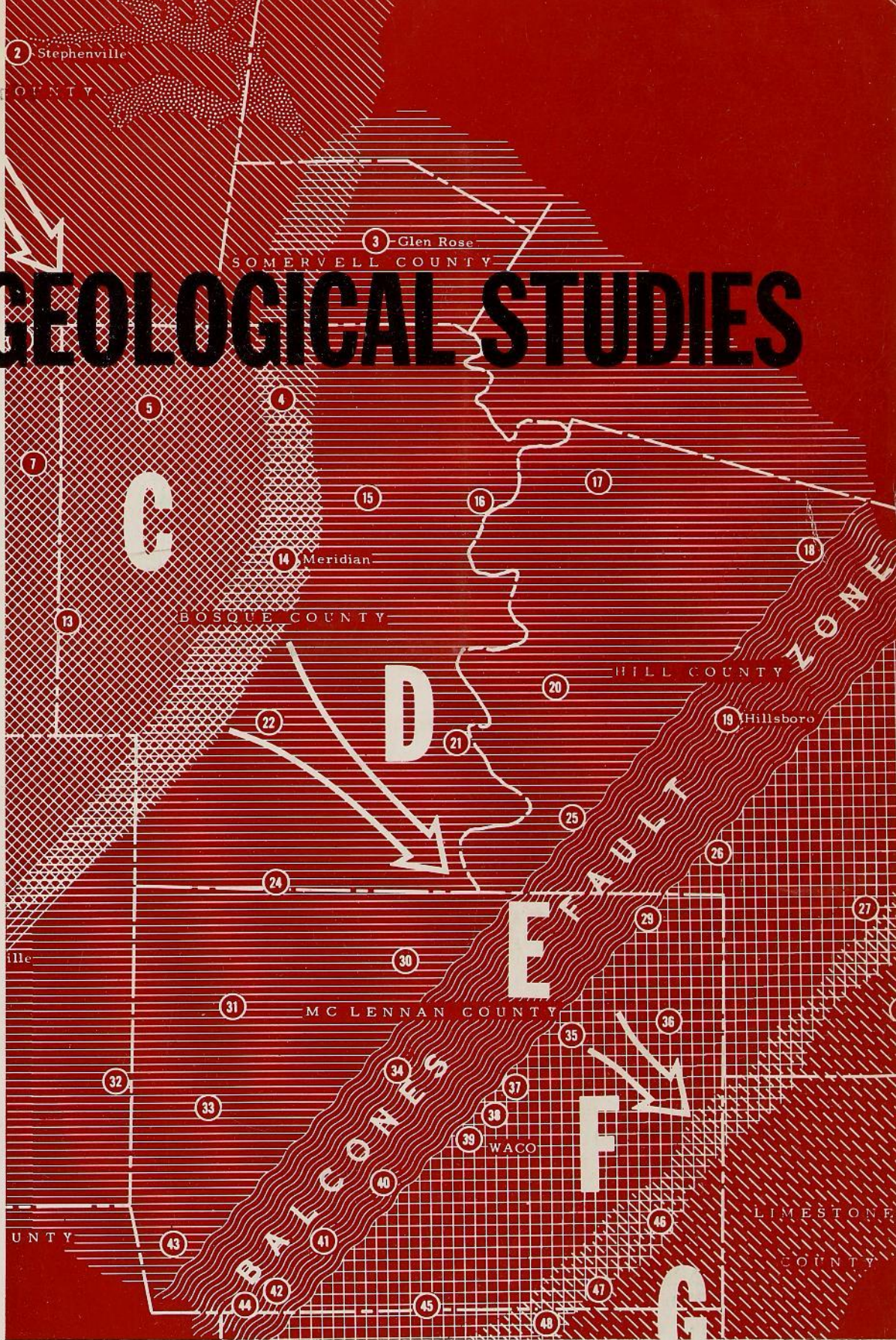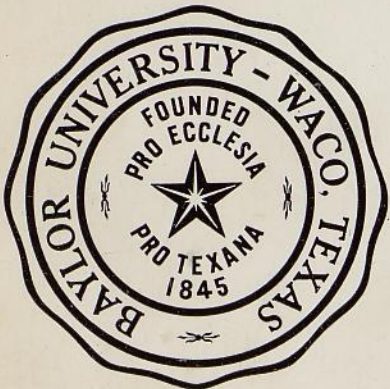# BAYLOR GEOLOGICAL STUDIES

FALL 1962

Bulletin No. 3

Water Diagenesis in Lower Cretaceous Trinity Aquifers of Central Texas

E. ROBERT HENNINGSEN

"Creative thinking is more important than elaborate equipment--"

Frank Carney, Ph.D.
Professor of Geology
Baylor University
1929-1934

Objectives of Geological Training at Baylor

The training of a geologist in a university covers but a few years; his education continues throughout his active life. The purposes of training geologists at Baylor University are to provide a sound basis of understanding and to foster a truly geological point of view, both of which are essential for continued professional growth. The staff considers geology to be unique among sciences since it is primarily a field science. All geologic research including that done in laboratories must be firmly supported by field observations. The student is encouraged to develop an inquiring objective attitude and to examine critically all geological concepts and principles. The development of a mature and professional attitude toward geology and geological research is a principal concern of the department.

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Baylor Geological Studies

The Baylor Geological Studies Bulletin is published semi-annually, Spring and Fall, by the Department of Geology at Baylor University. The Bulletin is specifically dedicated to the dissemination of geologic knowledge for the benefit of the people of Central Texas. The publication is designed to present the results of both pure and applied research which will ultimately be important in the economic and cultural growth of the Central Texas region.

Additional copies of this bulletin can be obtained from the Department of Geology, Baylor University. Waco, Texas. $1.00 postpaid.

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ABSTRACT

The concentration and distribution of chemical elements (ions) and other chemical factors such as pH and alkalinity in water from wells producing from the Lower Cretaceous Trinity aquifers (Hosston and Hensel sands) of central Texas, are used to interpret the diagenesis of the water and its effects upon the aquifer, as well as provide areal data to predict the quality of water at any point in the region.

The present study includes Erath, Bosque, McLennan, Hill, Hamilton, Somervell and parts of Coryell and Falls counties in central Texas.

Chemical variations in the Trinity water are related to the chemical composition of the influent water in the recharge area, reactions between the water and minerals of the host rock, chemical reactions among ions in solution which were introduced from various sources or recharge areas, and physical properties of the rock such as porosity and permeability. Temperature variations in the water reflect porosity and permeability, as well as normal geothermal increase with depth.

The Hosston and Hensel sands of the Trinity group are laterally continuous sand bodies that underlie the central Texas area near the base of the Cretaceous section. Wells producing from the Trinity aquifers in this region display artesian properties since water rises above the sands and in some cases wells flow because of high hydrostatic pressure represented by a shallow piezometric surface for the Trinity system. In the Waco area the sands are approximately 250 and 70 feet thick respectively; the top of the Hensel sand is about 2040 feet deep and the top of the Hosston sand is about 2260 feet deep. The two sands are separated in the Waco area by about 150 feet of section composed of the Pearsall and Sligo formations. The sands crop out west of the area in Parker, Hood, Erath, Eastland, Comanche, Brown, Mills, Lampasas, and Burnet counties where the formations are recharged with surface water.

The chemistry of the Trinity water and its relationship to the mineralogy and physical properties of the aquifer is interpreted in the light of the following six basic factors: ionic potential of dissociated salts, oxidation-reduction potential of ions, hydrogen ion concentration or pH, base exchange between cations and aquifer material, temperature of the water, and reactions of certain ions with minerals in the rocks. These factors are used to interpret the geologic significance of values and distribution of the following fifteen variables from 51 water wells in the area: total solids, hydrogen ion concentration, alkalinity, silica residue, total hardness, temperature, and ions of calcium, magnesium, sodium, iron, manganese, sulfate, chloride, fluoride, and nitrate. These chemical variables change downdip as meteoric water migrates eastward from the outcrop into the basin. The quantitative areal distribution of 13 variables is shown by isopleth maps.

The geochemical interpretation of the chemical variables in the water is used to develop a composite picture of the central Texas Trinity aquifer system including hydrologic data, approximate direction and relative rates of migration, source or recharge areas, individual distinctive water masses or facies, permeability and porosity information, and effects of Balcones faults upon water chemistry.

Two dominant sources for the Trinity water in the study area were delineated—a northwestern or Stephenville source and a southwestern or Llano source. Water masses from these two recharge areas can be distinguished by their distinctive chemical compositions, which reflect the minerals of each source area. These two water masses enter the area through Erath and Coryell counties respectively, and mix in Hamilton and western Bosque counties to produce a third water mass or facies where chemistry reflects reactions between water from the two primary sources. Eastward and downdip from the zone of mixing in eastern Somervell, Bosque, Coryell and western Hill and McLennan counties, is a fourth water mass typified by uniform basinward concentration gradients for most variables; this area of uniform change is related primarily to reactions resulting from increasing depth and temperature. Along the Balcones fault zone extending north-south through central McLennan and Hill counties, a fifth water mass represented by erratic ionic concentration values and locally high salinities is due principally to mixing and subsequent reactions between Trinity water and overlying saline Glen Rose water along faults of the Balcones system. Downdip to the east in eastern Hill, McLennan and western Falls counties, is a
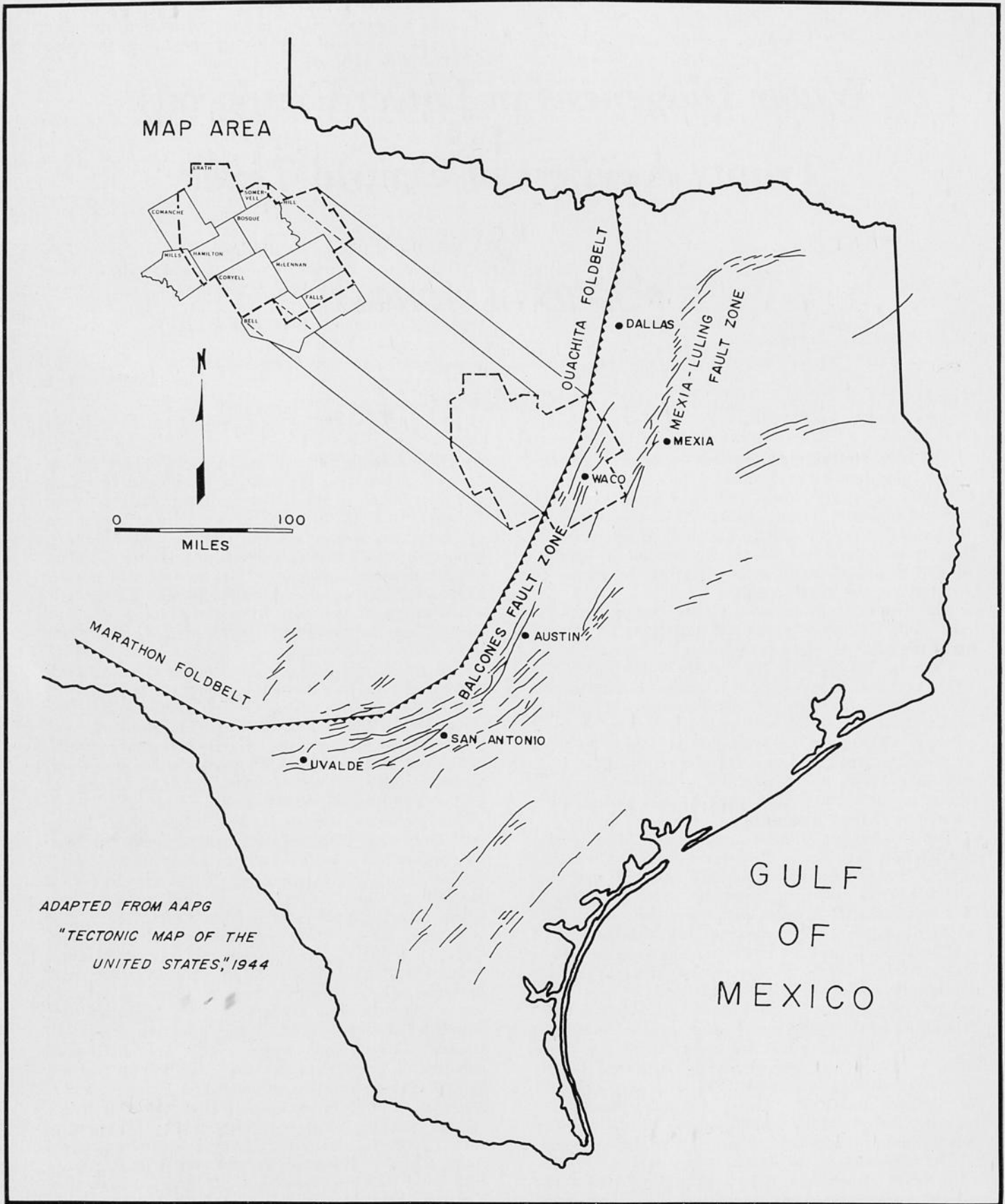
Fig. 1. Index map.

sixth water mass displaying erratic and increasing salinity; prediction of potable water in the Trinity sands in this area is difficult. In this sixth zone ionic concentrations increase because of the contamination by Glen Rose water in the Balcones fault zone to the west, and because of mixing with highly saline water downdip to the east. The chemistry in this zone reflects reactions due to greatly increased ionic concentrations and temperatures; temperature increases rapidly downdip since the aquifers dip more steeply east of the Balcones system. In the extreme eastern part of the area in western Limestone, eastern Falls and Hill counties, a seventh water mass composed of hot, highly mineralized water is gradational with connate water downdip beyond the eastern boundary of the map area. Chemical content of water in this facies reflects the effects of high temperature on highly mineralized water. The areal position of the interface between the sixth and seventh water masses is critical in producing potable water in eastern McLennan, Hill and central Falls counties.

High temperature and ionic concentration anomalies indicate low permeability since the movement of water is retarded, cooling effect is reduced and the "flushing action" of the less saline meteoric water is restricted. Conversely, anomalously low temperatures and ionic concentrations reflect high permeability. Permeability and porosity of the aquifer depend in part upon a balance between solution and deposition. Solution may cause collapse of the pore space with decreased permeability and porosity; abnormal deposition may in turn seal the interstices with impermeable cement. Reactions between ions in solution and minerals of the aquifer are important in the long-range history of the system.

Studies of this nature can be applied to other aquifers in water conservation programs in recharge areas, and in conservation practices in the producing areas. Contamination problems at the interface of water masses or facies, and along fault zones can be better predicted and controlled. Ionic concentration values throughout large hydrologic basins can be predicted by contouring available chemical data, and, thus, provide information for both present and future public and industrial needs of the area. Future studies should include investigation of vertical chemical variations within aquifers, migration rates and trace element concentrations as an aid in better delineating water facies, source areas, and rates of chemical changes in aquifers.

INTRODUCTION[1]

In central Texas, potable water is produced from the deep aquifers of the Cretaceous Trinity group. Although the water is produced from laterally continuous sands, salinity varies from place to place in a predictable manner. In this study, the salinity variations are described in terms of individual ionic concentrations, and an attempt is made to interpret the significance of the changes. The chemistry of each ion is considered independently, and its effect upon other ions and the surrounding rock material is discussed.

The Trinity sands of central Texas (fig. 1) were defined by R. T. Hill in 1901 as the basal sands of the Cretaceous system, which rest upon Paleozoic rocks. Holloway (1961) included in the Trinity division [group] the following formations (fig. 2) from the base to top: Hosston sand, Sligo limestone, Pearsall formation, Hensel sand, and Glen Rose limestone. The shallower water-producing Trinity sand is the Hensel formation, and the deeper aquifer is the Hosston sand. The Hosston sand rests upon impervious Paleozoic rocks in the northwestern portion of the mapped area (fig. 1) and upon Jurassic rocks southeast of Marlin. The aquifer section is everywhere capped by thick Glen Rose limestone. The eastward regional dip varies from approximately 30 feet per mile west of the Balcones fault zone to 90 feet per mile east of the fault zone.

The basal sand section in central Texas crops out over a wide region (figs. 4-17) in Parker, Hood, Erath, Eastland, Comanche, Brown, Mills, Lampasas and Burnet counties. The Trinity outcrop is the recharge area of the aquifer section. The water migrates slowly downdip by percolation at a rate that is presently unknown. It is estimated, however, to be only a few tens of feet per year. The rate of migration should be determined.

The influent water at the outcrop has a chemical composition radically different from water downdip at Marlin (fig. 3). As the water migrates through the sands from the outcrop to downdip wells, definite salinity patterns are established, which can be used to interpret water masses and source areas (fig. 4). Not only is the salinity of the water altered, but there are related effects on the aquifers caused by the ionic exchange and chemical reactions between materials in solution and mineral grains within the aquifer.

Salinity is generally predictable downdip within the aquifers until faults of the Balcones system (fig. 4) are encountered. Throughout the Balcones fault zone water analyses reflect contamination of Trinity water by water from overlying and underlying formations. For this reason it is difficult to predict aquifer conditions or predict salinities of water in the faulted areas. Faults may be detected and suspected faults may be confirmed by anomalous ionic concentrations in the Trinity water.

PURPOSE

Water in basal sands of the Trinity group varies in composition throughout central Texas. The principal purpose of this investigation is to determine if compositional changes are predictable and to what extent the pattern of these variations could add to the interpretation of the geologic history of the aquifer. A second purpose is to provide data with which to predict the quality of water at any point in the area before wells are drilled. Such information would point out quality problems and treatment costs before expensive drilling is initiated.
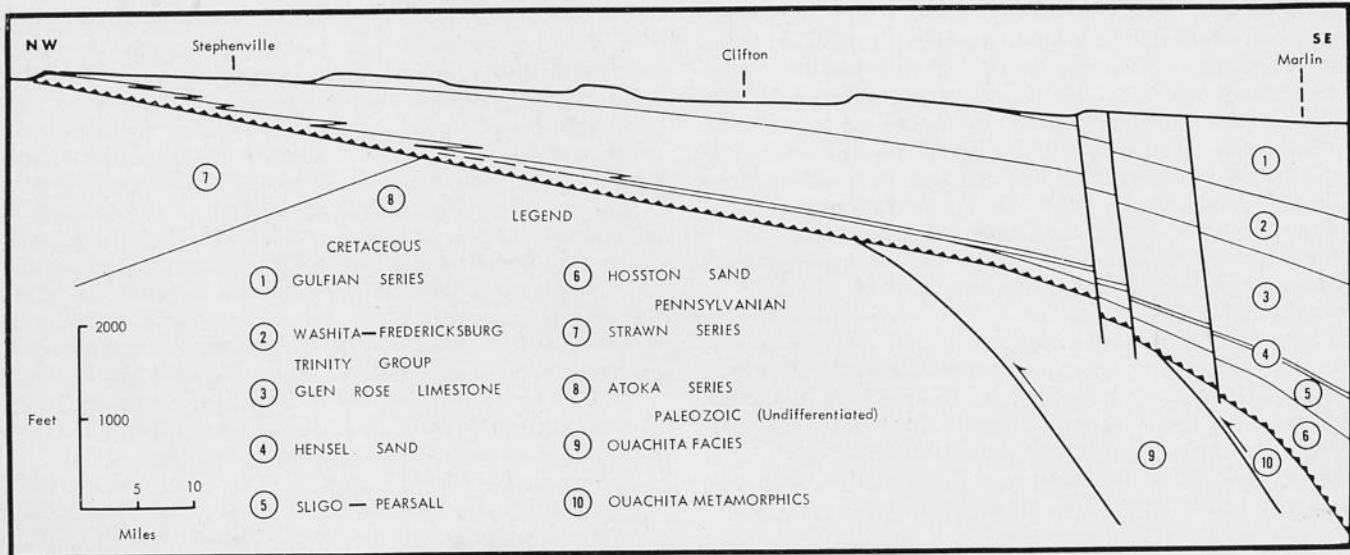
Fig. 2 Diagrammatic facies cross section of Trinity group, central Texas. Ouachita foldbelt data *after* Flawn *et al.* (1962).

Chemical changes in the water are related to physical changes in the aquifer. In part these chemical changes are evidenced by changes in porosity and permeability which one day may have a profound effect upon the productive potential of the aquifer. The need for basic studies of subsurface water becomes more critical each year. With increasing population and migration of industry to the central Texas area, adequate information on the water supply becomes essential.

LOCATION

The area of this study includes Erath, Bosque, McLennan, Hill, Hamilton, Somervell, and parts of Coryell and Falls counties in central Texas.

PROCEDURES

The Bureau of Sanitary Engineering of the State Department of Health in Austin regularly publishes analyses (Table 1) of public supplies in Texas. These readily available analyses of water samples for 51 communities[1] within the area of investigation are the basic data for this study. Cost prohibited specific analyses for the investigation. In this report, therefore, only those ions and radicals regularly reported by the Bureau of Sanitary Engineering are considered. More closely spaced data and analyses for ions not presently considered may yield information of potentially greater geological significance. The most recent analyses of water from each community were used, but some of these were made as early as 1943. If the migration rate of water through the aquifers is as slow as it appears, changes in chemical content from 1943 to 1962 are insignificant. Water temperature at each well was determined by the writer. Pertinent data on the history of each well were obtained from local water company officials.

_____
[1]Refer to Table 1 for number representing water well at each community in the area; well number is located on each map (figs. 4-17).

Isopleth maps (figs. 5-17) were prepared from the chemical and temperature data. These maps show regional variations in concentration of various ions and in water temperatures.

PREVIOUS INVESTIGATIONS

An extensive search of the geologic literature discloses few reports on ground water and ground water chemistry similar to the present study. William Back (1959, and written communication, 1959) recently completed a similar study in Cretaceous and Tertiary formations along the northern Atlantic coastal plain. I. I. Chebotarev (1955) of Australia discussed the metamorphism of natural waters in the earth's crust. His studies were much broader, utilizing approximately 10,000 analyses from several continents. Chebotarev's work did not involve detailed studies of individual artesian basins.

Henri Schoeller (1948) made comparable studies in France in which he described changes in chemical composition of water within a single formation with increasing depth and distance from the outcrop. Schoeller's investigation was perhaps most similar to the present study.

Other research involving individual ions or specific chemical changes are more common, although there is a great need for work on the chemistry of ground water.

ACKNOWLEDGMENTS

GENERAL FEATURES

The climate of the map area lies within the modified Köppen region, *Caf*—subtropical humid climate, though this area is near the dry margin of the belt. The mean annual precipitation in the recharge area is approximately 31 inches. Maximum precipitation occurs in the spring, normally in April, when most water enters the aquifer. Daily temperatures average 70°F during maximum precipitation, thus, limiting the amount of water lost by evaporation. Plant growth is not abundant in early spring, permitting more water to percolate into the aquifer. Inasmuch as soil temperature is lower than the average air temperature in the spring, the soil lowers the temperature of the water entering the aquifer, which probably results in lower salinity near the outcrop than downdip in the basin.

The migration rate near the outcrop and for some distance downdip must be appreciably higher than at greater depth. This is due to higher porosity and permeability of the shallow sands not subject to the greater compaction characteristic of the deeper parts of the basin. This higher migration rate accommodates a maximum influent seepage. Flowing wells occur within a few miles of the outcrop.

It has been estimated that each square mile of the outcrop area of the aquifer receives precipitation amounting to about 521,000,000 gallons of water per year, or 1,400,000 gallons per day (Fiedler, 1934, p. 45). This figure is based on an estimated average rainfall of 30 inches per year. Only a small amount of this precipitation augments the ground water supply in the artesian reservoir. Loss by evaporation, run-off, and transpiration by plants accounts for most of the rainfall. Although the intake of water is small, the large outcrop area provides for yearly recharge of the aquifer.

The dip of the rock strata in the area is east-southeast at a slightly greater angle than the slope of the piezometric surface of the basal Trinity artesian system. The piezometric surface displays about the same slope as the regional topography. Thus, flowing wells are found at successively lower elevations from northwest to southeast across the area. Flowing wells are now normally confined to valley floors, although early in the history of artesian production, flowing wells also occurred at higher topographic elevations.

The chief industries in the area are farming and ranching; however, the greatest water production is in the vicinity of Waco. With the exception of the Rocketdyne plant at McGregor, which utilizes a million gallons of well water per day, heavy industry is centered around Waco. The Waco General Tire and Rubber Company Plant daily withdraws approximately one million gallons of water from the basal Trinity aquifers. Since 1951 the Texas Power and Light Company and James Connally Air Force Base each have used approximately a million gallons daily from the Trinity aquifers, and except for decreasing pressure, the effect of the heavy production has not been established. A detailed aquifer study of the effects of heavy production would be desirable and possibly aid in predicting the future of this central Texas water supply. The combined production of other smaller wells near Waco is approximately a million gallons per day; this quantity, coupled with the large-volume commercial production, makes the future artesian water supply in the Waco area a critical problem.

GEOLOGY

The principal subsurface water supply in central Texas is from sands of the Trinity group (fig. 2), Comanchean series (Lower Cretaceous). Some water is produced from all rock units of this group, but potable water is produced in quantity only from the Hosston and Hensel sands (Holloway, 1961, p. 16). The Hosston and Hensel sands are the only continuous sand bodies of the Trinity group in central Texas. The Hosston and Hensel sands are seldom differentiated by drillers, particularly in the area west of Waco. Therefore, it is difficult to determine which sand is producing in a particular well. However, most commercial and municipal wells produce from both sand sections, and in the western half of the area the two sands are in contact, allowing free communication throughout the sand section.

STRUCTURE

Cretaceous rocks of the map area dip eastward at less than 1 degree, a slightly greater angle than the gulfward slope of the coastal plain surface. West of a north-south line passing through Waco is the Texas craton, a structurally stable area where eastward dip ranges from 10 to 30 feet per mile. East of this line is the Tyler basin, an area of Cretaceous-Tertiary subsidence where dip increases to approximately 100 feet per mile. The boundary between these two structural provinces in the Balcones fault zone (fig. 1), a zone of *en echelon,* down-to-the-coast faults extending northward through Temple, Waco and Hillsboro.

West of the Balcones fault zone in the map area, Comanchean rocks are exposed at the surface, while east of the Balcones zone, surface rocks are of Gulfian (Late Cretaceous) age. Steepening of the eastward dip and the down-to-the-coast displacement along the Balcones system increase the depth to the Hensel and Hosston sands in the eastern part of the area.

HOSSTON SAND

Comanchean seas transgressed the central Texas region northwestward, first depositing thick Comanchean strata in the Tyler basin and then slowly encroaching northwestward across exposed Paleozoic rocks of the Texas craton. Near the transgressing Comanchean shoreline were deposited basal sand and finer land-derived clastic sediments now called the Hosston formation. The near-shore Hosston sand is equivalent in age to marine shales and limestones of the Trinity Sligo and Pearsall formations, deposited eastward in the Tyler basin.

The Hosston sand, which was deposited during initial Cretaceous marine transgression in central Texas, was called the Sycamore sand member of the Travis Peak formation by Hill (1901) and is the lower part of the "Basal sands" of Adkins (1923). The Hosston sand has been the principal producer of artesian water in the central Texas region since the early 1900's; it has be-

come particularly important in the eastern part of the map area.

The near-shore, time-transgressive Hosston sand rests unconformably upon underlying rocks. Near Mart in the eastern part of the map area it rests upon Jurassic rocks of the Cotton Valley group (Imlay, *in* McKee, *et al.,* 1956); in a north-south belt passing beneath the Waco area, the Hosston sand overlies complexly folded, faulted and truncated rocks of the late Paleozoic Ouachita foldbelt. Northwestward from the Ouachita foldbelt to the outcrop northwest of Stephenville, the basal Hosston sand overlaps successively younger Pennsylvanian rocks ranging in age from Atoka to Strawn.

HENSEL SAND

The Hensel sand is equivalent to the upper part of the Travis Peak formation of Hill (1901). In the subsurface it has been designated the T_2 sand by Hill (*idem*) and the T1 sand by Adkins (1923). Recent work by Robert W. Rodgers (oral communication, 1961) indicates that the Hensel sand of the central Texas subsurface may be equivalent to the Bluffdale sand of the outcrop area near Stephenville.

Throughout most of the map area the Hensel sand overlies the Pearsall formation in what may be an unconformable relationship, and is overlain conformably by the lower Glen Rose limestone. The Hensel sand is an important water producer throughout the central Texas region, particularly in the western part of the map area.

The Hensel sand is a near-shore deposit of a post-Pearsall transgression. In the western Tyler basin the lower Glen Rose limestone and the "massive anhydrite" are probably time-equivalent to the Hensel sand in the western part of the map area between Waco and Stephenville.

REGIONAL STRATIGRAPHY

In northern Erath County the Hensel and Hosston sands (Trinity group) crop out as a single sand body about 160 feet thick, with a minor shale and limestone break near the middle. Near Waco the Hensel sand is separated from the Hosston sand by 150 feet of rocks assigned to the Sligo and Pearsall formations, and the Hensel sand is overlain by more than 2000 feet of Comanchean and Gulfian strata. In the southeastern part of the area at Chilton, the top of the Hensel sand is 2150 feet deep, and the top of the Hosston sand is 2600 feet deep. At Chilton the Hensel sand is 40 feet thick and the Hosston sand is 300 feet thick.

Although the Hosston and Hensel sands thicken to the southeast, the permeability of the sands decreases southeastward with decreasing grain size. Both sand units interfinger eastward with shale and limestone strata in the Tyler basin, and ultimately disappear as traceable sand bodies.

GEOCHEMICAL FACTORS

The chemical composition of the water in the Trinity aquifers varies regionally. To explain this variability and its effect upon the aquifer, it is necessary to consider independently each ionic constituent and then interpret its relationship to other ions and to the aquifer.

Customarily, fourteen variables are reported in each analysis by the State Department of Health. These include (1) total solids, (2) hydrogen ion concentration, (3) alkalinity, (4) silica residue, (5) total hardness, and ions of (6) calcium, (7) magnesium, (8) sodium, (9) iron, (10) manganese, (11) sulfate, (12) chloride, (13) fluoride, and (14) nitrate. For this study, water temperature at the well head has also been included.

There are six basic factors which control the salinity of water. These are the (1) ionic potential of dissociated salts, (2) oxidation-reduction potential of ions, (3) hydrogen ion concentration or pH, (4) base exchange between cations and aquifer material, (5) temperature of the water, and (6) reaction of certain ions with minerals in the rocks. The last factor is dependent on one or more of the other basic factors.

The common abundant cations in ground water are sodium, calcium, magnesium, iron, potassium, and aluminum. Small amounts of manganese are reported. The common abundant anions are chloride, sulfate, and carbonate; fluoride and nitrate are less abundant. Changes in salinity occur with exchange of ions as water moves through the aquifer. The exchange of ions is brought about by one or more of the following factors to be discussed.

IONIC POTENTIAL

The ionic potential of an ion is a measure of the intensity of the charge per unit area of the surface of the ion. This is referred to as Z/R where Z is the charge of the ion and R the radius of the ion. This factor is significant, not only for the hydration of an ion, but for many other of its properties in the presence of water. Following is a list of ionic potentials for various cations (Mason, 1958, p. 156).

$$Na^+ \text{ ------------} 1.00$$
$$Ca^{++} \text{ -----------} 2.00$$
$$Mg^{++} \text{ ----------} 3.00$$
$$Mn^{++} \text{ ----------} 2.50$$
$$Fe^{++} \text{ -----------} 2.70$$
$$Fe^{+++} \text{ ----------} 4.70$$
$$Si^{++++} \text{ ---------} 9.50$$

It has been shown that the migration energy of the sodium ion, which depends on ionic size, charge and amount of hydration, is lower than that of the calcium ion; therefore, the sodium ion is more mobile than the calcium ion, particularly at higher temperatures. Elements with lower ionic potentials thus tend to remain in solution under the conditions of the aquifer, and higher concentrations are, therefore, detected by analyses.

Elements with intermediate ionic potentials are precipitated by hydrolysis, their ions being associated with hydroxyl groups in the water. Elements with very high ionic potentials form anions containing oxygen; these

elements are normally soluble (Mason, 1958, p. 156).

Iron in the ferrous state has a relatively low ionic potential of 2.7; therefore, it is relatively stable in acid solution (*idem*). To be precipitated, oxidation to the ferric state with a much higher ionic potential of 4.7 must occur. Divalent manganese with a potential of 2.5 is stable in solution. To be precipitated manganese must undergo transformation to the quadrivalent form with the much higher ionic potential of 6.7. Elements with lower ionic potential in the minerals are most capable of being exchanged with elements of higher ionic potential in the solution, and variability in concentration is greater among these ions. Ions with higher potentials and, thus, lower concentrations commonly occur in natural water. Tetravalent silicon ion, for example, with an ionic potential of 9.5 is not readily dissolved.

OXIDATION-REDUCTION (Eh)

A second factor controlling salinity of water is the oxidation-reduction potential of elements. The loss of one or more electrons by an atom or a group of atoms is termed oxidation. On the other hand, the gain of electrons is known as reduction. Some elements in nature occur in different oxidation states which directly influence the solubility and mobility of their ions. The stability of an element in a particular oxidation state depends upon the energy involved in changing its oxidation state.

Change in oxidation state of various elements (hence changing the ionic potential of the ion) is important in the solution, transportation, and ultimate redeposition of the ions. The reactions may involve hydrogen ions; therefore, the oxidation potential is strongly affected by pH. For many reactions, the oxidation potential decreases rapidly with an increasing pH. Generally speaking, for the type of oxidation-reduction reactions under consideration, oxidation proceeds more readily with increasing alkalinity. Ferrous iron is moderately stable in an acid solution, since its oxidation potential is 0.77 volt (Mason, 1958, p. 164). As the pH rises, the oxidation potential drops sharply to a negative value and spontaneous oxidation to the ferric state occurs. The transformation is attended by a sharp rise in the ionic potential from 2.7 to 4.7, and precipitation results, probably as hydrous ferric oxide. The oxidation potential normally decreases as temperature increases.

Oxidation-reduction reactions of this type commonly are controlled by changes in pH and temperature. Concentration also is significant in chemical reactions. These factors result in variations in the iron concentration in the water of the aquifer.

HYDROGEN ION CONCENTRATION (pH)

The pH of a solution is a measure of the acidity expressed as the negative logarithm to the base 10 of the hydrogen ion concentration in moles per liter. The pH of water has a profound influence upon solubility and precipitation of compounds.

Table 1. Chemical analyses of Trinity water, central Texas.*

Well No.	Location	Total Solids	pH	Alk. CaCO$_3$	Si Res.	Total Hard.	Ca^{++}	Mg^{++}	Na$^+$	Fe^{+++}	Mn^{++}	SO$_4^=$	Cl$^-$	F$^-$	NO$_3^-$	Temp. °C	Analysis date
1	Dublin	399	7.2	290	12	300	74	28	10	.06	.05	25	20	.2	1.1	24	
2	Stephenville	464	6.8	290	14	329	79	32	46	.12	.05	46	64	.2	.4	23	4-1-49
3	Glen Rose	400	7.4	308	11	125	26	15	106	.04	.05	26	19	.1	.4	20	2-2-59
4	Walnut Springs	388	7.5	294	15	235	42	31	55	.16	.05	43	23	.3	.4	21	10-29-56
5	Iredell	388	8.4	- -	14	242	44	32	49	.12	- -	42	16	.2	- -	21	2-10-43
6	Hico	430	6.9	276	14	305	63	35	25	.04	.05	48	30	.3	.4	20	3-4-59
7	Fairy	571	7.9	- -	9	118	24	14	158	1.70	- -	158	52	1.0	2.2	20	
8	Pottsville	678	7.7	- -	12	256	63	24	147	3.60	.05	144	74	.6	2.5	17	3-19-46
9	Priddy	649	7.4	338	14	424	114	34	71	2.00	.05	140	67	.6	.4	21	5-26-44
10	Hamilton	998	8.0	360	12	60	12	7	312	.28	.05	119	134	1.0	.4	26	4-16-58
11	Evant	627	7.6	- -	10	279	54	35	117	1.50	- -	194	50	1.6	3.5	24	6-4-46
12	Aleman	462	7.7	297	- -	270	55	32	100	2.80	.05	160	26	.8	.4	26	4-1-59
13	Cranfills Gap	488	7.7	280	10	108	20	14	135	.42	.05	70	26	1.0	1.3	22	9-10-57
14	Meridian	415	7.5	305	10	68	13	8	144	.82	.05	45	23	.2	.4	27	4-3-57
15	Morgan	414	8.3	- -	11	115	23	14	106	.05	- -	45	12	.4	.2	26	2-10-43
16	Kopperl	468	8.4	- -	11	28	6	3	163	.26	- -	70	14	.3	- -	26	2-10-43
17	Blum	572	8.6	315	10	42	9	5	194	.09	.05	106	25	.6	.4	28	7-10-52
18	Itasca	700	8.6	460	53	123	9	13	199	1.10	.05	68	21	.5	.4	37	8-1-53
19	Hillsboro	704	8.3	- -	18	16	3	2	254	.07	- -	116	59	.3	.4	39	
20	Whitney	590	8.4	330	12	12	3	1	230	.10	.05	108	50	.5	.4	33	4-19-55
21	Laguna Park	543	8.4	340	14	9	2	1	215	.10	.05	88	32	.4	.4	30	6-21-54
22	Clifton	504	8.4	350	12	12	3	1	208	.03	.05	75	25	.5	.4	27	1-12-56
23	Gatesville	1140	7.7	377	14	113	7	4	425	.08	.05	188	300	2.0	.4	25	11-6-52
24	Valley Mills	574	8.2	351	12	13	3	1	221	.04	.05	108	35	.6	.4	28	4-28-58
25	Aquilla	2215	- -	415	50	348	37	62	620	.30	.05	1114	85	6.5	.4	35	11-25-49
26	Abbott	594	8.0	364	- -	11	3	1	213	.01	.05	75	57	.8	1.1	36	2-17-59
27	Malone	3560	7.3	205	34	753	180	74	851	7.00	.05	2200	78	1.8	.4	35	2-1-53
28	Hubbard	1285	8.5	560	30	22	7	1	458	.70	.05	272	124	1.8	.4	60	9-25-55
29	West	705	8.0	343	16	13	3	1	215	.04	.05	80	50	.7	.4	42	
30	China Springs	985	8.4	440	15	48	7	7	348	0.0	.05	307	69	1.8	.4	28	1-7-43
31	Crawford	570	8.3	360	12	15	4	1	226	.10	.05	85	26	.8	.4	29	1-21-57
32	Oglesby	- -	- -	- -	- -	- -	- -	- -	- -	- -	- -	138	- -	- -	- -	- -	
33	McGregor	740	8.3	375	12	18	4	2	280	.05	.05	131	82	1.2	.4	29	1-21-56
34	Speegleville	1410	8.2	- -	9	90	13	14	472	.06	.05	585	63	3.3	.4	31	1-6-43
35	Elm Mott	558	8.4	344	- -	13	4	1	232	.24	5.05	140	46	.7	1.3	46	11-5-59
36	Leroy	- -	7.8	- -	18	64	19	4	550	1.20	- -	98	564	- -	- -	50	
37	Lacy-Lakeview	716	8.4	360	27	19	6	1	260	1.70	.05	152	46	1.3	.4	49	8-8-55
38	Beilmead	600	8.1	355	- -	11	3	1	224	.08	.05	97	43	1.8	.4	47	2-20-57
39	Waco	638	8.6	360	18	48	14	3	244	.04	.05	38	53	1.0	2.2	42	4-1-52
40	Hewitt	1050	8.2	- -	12	62	14	6	367	.14	- -	327	93	1.8	.4	32	1-9-43
41	Lorena	904	8.4	385	14	27	6	3	321	.29	- -	234	69	1.6	1.5	35	1-9-43
42	Bruceville	1810	8.0	- -	6	104	17	15	611	35.0	- -	719	198	3.2	.4	36	1-19-43
43	Moody	864	8.3	395	13	13	2	2	334	.15	.05	108	163	1.4	.4	35	12-15-55
44	Eddy	1040	8.4	- -	12	36	7	5	372	.02	- -	284	131	1.8	1.0	36	1-9-43
45	Golinda	478	8.2	387	- -	18	0	4	235	0.0	- -	125	63	- -	- -	43	9-11-57
46	Mart	700	8.2	420	20	44	6	7	260	.08	.05	114	50	1.6	.4	61	11-1-52
47	Riesel	3800	- -	180	12	530	148	20	1040	1.1	- -	2270	198	1.1	.4	59	2-20-49
48	TP&L	1278	8.1	- -	22	44	9	5	348	.07	.05	229	76	- -	- -	43	11-23-51
49	Chilton	786	7.8	408	34	20	6	1	289	.41	.05	155	50	2.3	.4	55	12-4-58
50	Lott	1560	8.1	- -	30	268	78	18	415	2.40	- -	749	83	2.3	- -	59	6-13-44
51	Marlin	3770	7.5	380	35	502	84	71	1141	1.20	.05	1539	710	4.0	.4	64	8-28-47

*Data from State Department of Health, Austin, Texas. Certain magnesium, calcium and silica residue values have been rounded to nearest whole numbers. All chemical values are reported in parts per million (ppm); pH (acidity) is reported in pH units.
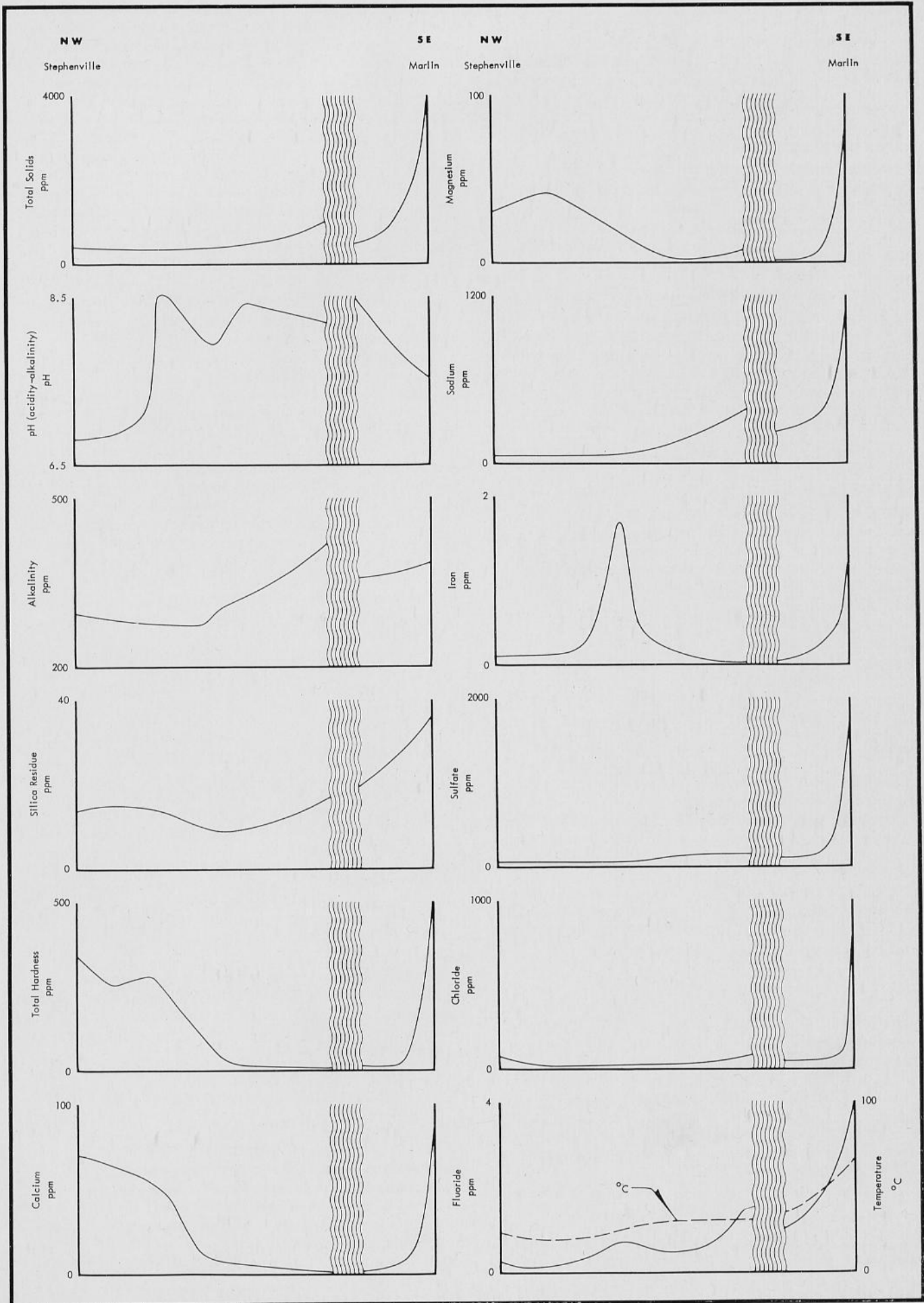
Fig. 3.   Chemical profiles of Trinity water, central Texas.

The pH of ground water commonly ranges from 6 to 8 (Rankama and Sahama, 1950, p. 228). A neutral solution at 20°C has a pH of 7; thus, most natural water is weakly acidic or basic. The effect of pH on solubility varies with the elements. For example, slightly acidic water (pH 6) is more capable of dissolving calcite than is a basic solution (pH 8). As the pH increases, the solubility of calcium carbonate decreases and less is taken into solution. Conversely, other compounds are more stable at a low pH than at a high pH, and much of the marked variability of salinities is attributed to changes in pH. The solubility of silica, for example, increases with an increase of pH; therefore, higher concentrations are found in alkaline water (Krauskopf, 1959, p. 10).

The primary controlling factor of pH in ground water is the amount of carbon dioxide in solution. At shallow depths and near the recharge area, a supply of carbon dioxide is readily available. This carbon dioxide is obtained by meteoric water from the atmosphere and during percolation through the soil. At shallow depths the pH is slightly acidic because of the reaction:

$$CO_2 + H_2O \rightarrow CO_3 = + 2H^+$$
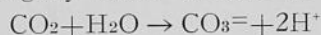
However, the carbon dioxide supply decreases with distance from the outcrop and with depth, bringing about an increase in pH. The depletion of the available carbon dioxide is attributed to reactions with various ions in the aquifer such as the calcium ion.

The influence of pH on the oxidation-reduction potential of those ions capable of occurring in different oxidation states brings about further changes in the salinity of the water within a given system. Of the many variables, the hydrogen ion concentration probably has the greatest influence upon the solution, transportation, and subsequent redeposition of the various ions.

BASE EXCHANGE

The property of base exchange or cation exchange is the ability of a mineral to exchange adsorbed cations for other cations in solution. Clay minerals in particular have the ability for base exchange.

It has been determined that the base exchange capacity of some clays increases as the particle size decreases. Exchange depends also on the state of hydration of the ions, on the solubility of the compounds that may form at the phase boundary, and on the ionic charges of the cation being exchanged. The replacement series of common cations for montmorillonite clay has been established (Rankama and Sahama, 1950, p. 242) as follows:

$$Li^+ < Na^+ \ll H^+ < K^+ < Mg^{++} < Ca^{++}$$
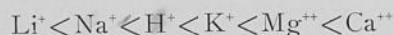
This series shows that under a given set of conditions, calcium ion will preferentially exchange for sodium ion on montmorillonite.

Clays occur within the Trinity aquifers but specific clay minerals have not yet been identified. Since the clay mineral group has base exchange capacity, in all probability the salinity of the water in the aquifers is affected by this phenomenon. The most probable exchange is calcium in solution for exchangeable sodium adsorbed by the clay.

TEMPERATURE

The effects of changing temperature on migrating natural water affects the salinity both directly and in-

directly. Reaction rates are directly related to temperature. For most chemical reactions, the application of heat increases the rate of reaction. As temperature increases within an aquifer, the rate and variety of chemical reactions should normally increase.

Temperature also influences the amount of material which can be contained in solution. For example, cold water, because it can absorb more carbon dioxide, is capable of holding more calcium bicarbonate in solution than is hot water. When calcium bicarbonate concentration is high, precipitation of some of the calcium as a carbonate may occur as a result of the loss of carbon dioxide as temperature increases. The solubility of other compounds, such as sodium sulfate, is likewise affected by changes in temperature. The solubility of sodium sulfate, for example, increases with an increase of temperature; therefore, warm water commonly has a higher sodium ion content.

The indirect influence of temperature may be observed in its effects on the oxidation potential, which normally decreases with an increase in temperature. This decrease in the oxidation potential results in the deposition of those minerals capable of occurring in different oxidation states. For example, iron in the ferric and ferrous states occurs in ground water, and may be influenced by the indirect effect of temperature on oxidation potential.

Temperature may also be an indirect indicator of the porosity and permeability of a formation. When porosity and permeability are high, the migration of water is faster, and, therefore, the flow of water over long periods of time has served to "cool" the rocks of the aquifer below the predicted value for a normal temperature gradient.

A dominant effect of increasing temperature is an increase in the rate of chemical reactions. Deep hot water, though potable, is normally more saline than shallower water within the same aquifer.

AQUIFER-WATER REACTIONS

Solubility of the rock material is affected by the pH of the water. Temperature of the environment accelerates or retards reactions depending upon the ions involved; for most ions an increase in temperature increases the rate of reaction. The amount of time that the water is in contact with rock material is an important factor; for example, in rocks of high porosity and permeability (high migration rate), reactions are less likely to go to completion than in rocks of lower porosity and permeability.

Furthermore there is the tendency for base exchange between cations and clay minerals in the aquifer. Such reactions change as the composition of the aquifer changes, bringing about a change in the salinity of the contained water.

MIGRATION OF GROUNDWATER

The migration rate of ground water influences the salinity of the water. Hydraulic gradient, porosity, and permeability control the rate of migration. Each of these controls must be considered. Water in the interstices of permeable rocks in the zone of saturation normally moves very slowly and continuously in laminar flow. This is a constant procession of "particles" of water following the same paths, propelled by differential
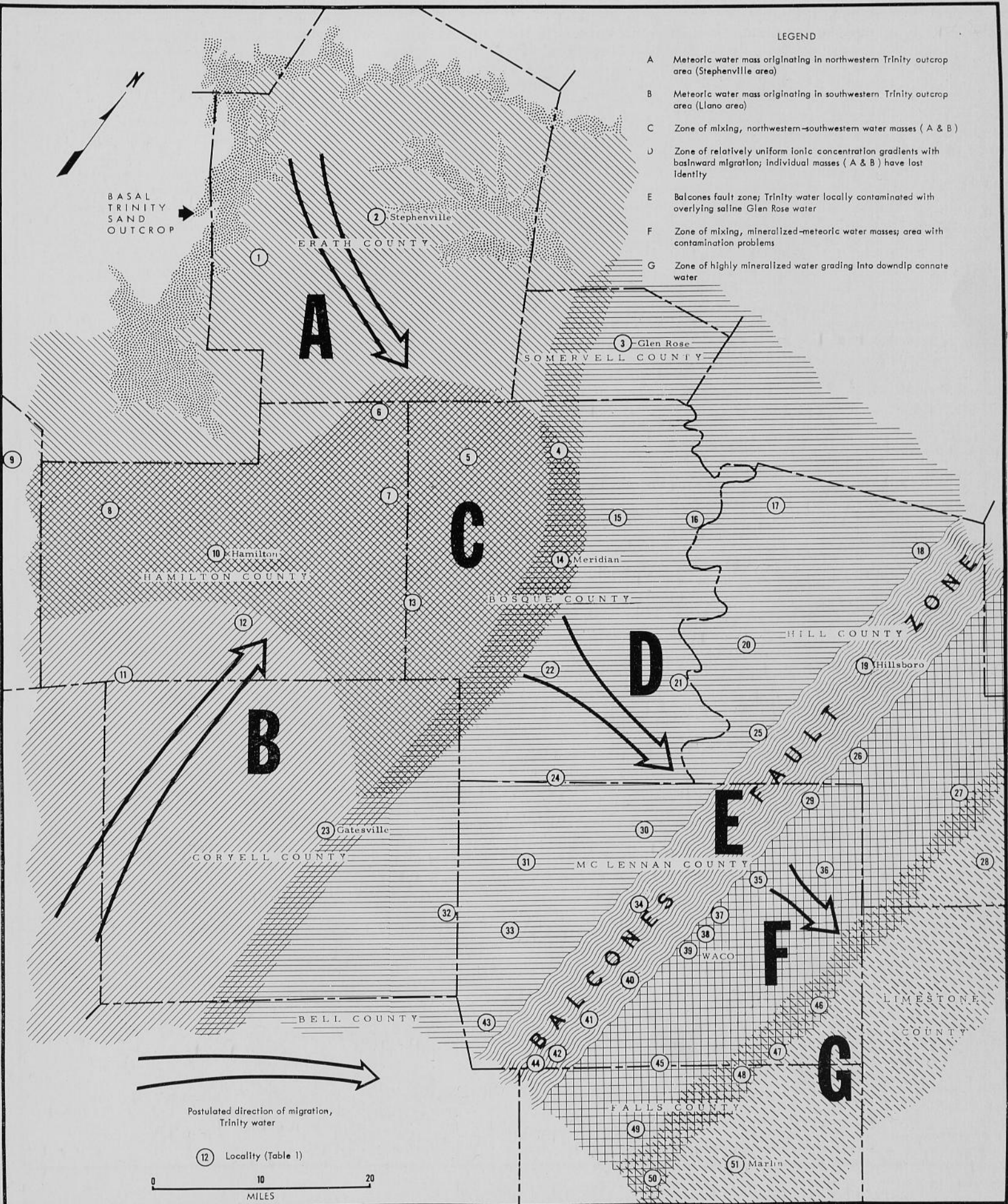
LEGEND

A   Meteoric water mass originating in northwestern Trinity outcrop area (Stephenville area)

B   Meteoric water mass originating in southwestern Trinity outcrop area (Llano area)

C   Zone of mixing, northwestern–southwestern water masses (A & B)

D   Zone of relatively uniform ionic concentration gradients with basinward migration; individual masses (A & B) have lost identity

E   Balcones fault zone; Trinity water locally contaminated with overlying saline Glen Rose water

F   Zone of mixing, mineralized–meteoric water masses; area with contamination problems

G   Zone of highly mineralized water grading into downdip connate water

Fig. 4. Diagrammatic representation of water masses and migration routes, Trinity aquifers, central Texas.
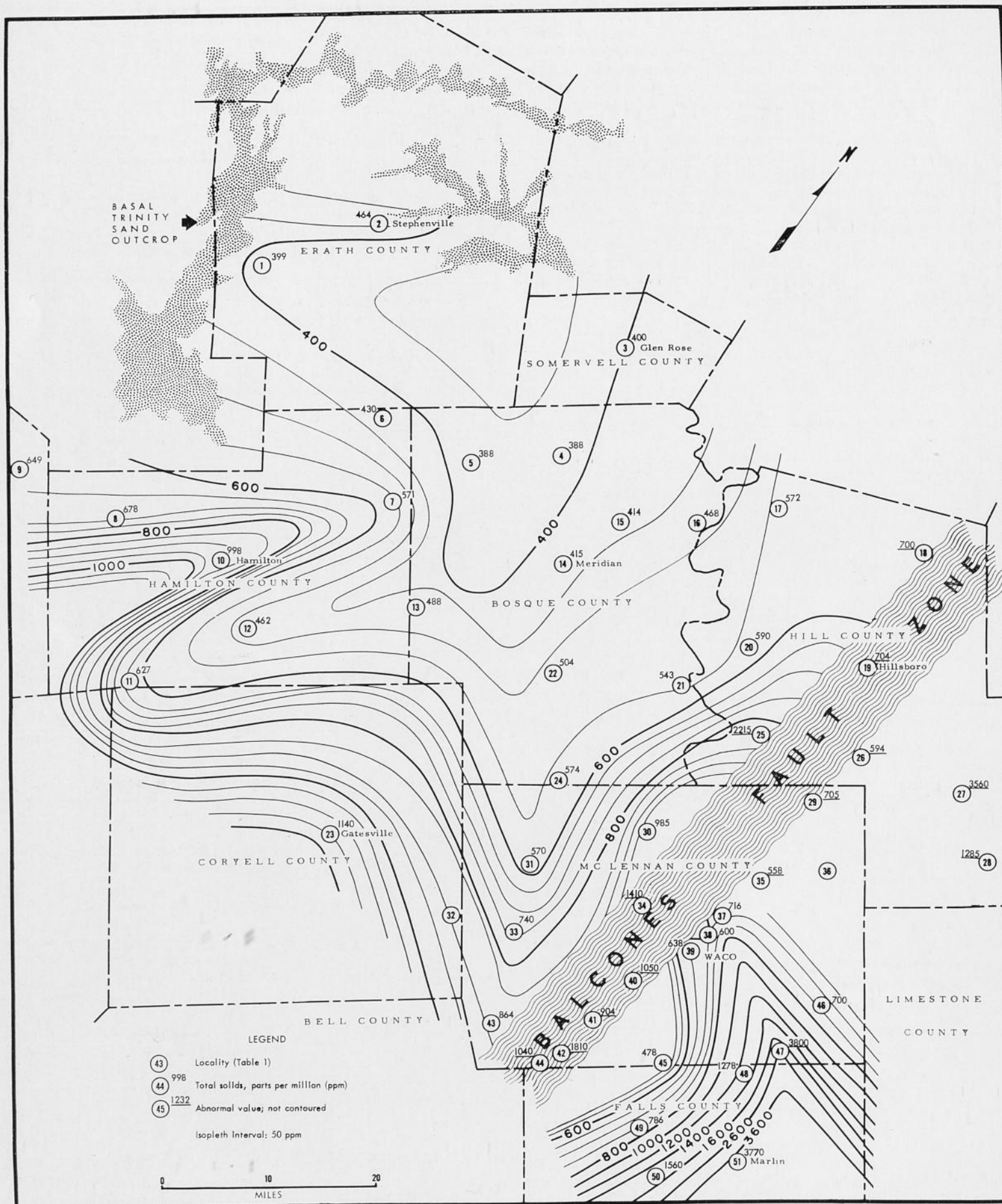
Fig. 5. Total solids isopleth map.

head that overcomes friction between moving water and walls of the medium through which it flows. The rate of flow in pipes and channels varies approximately as the square root of the hydraulic gradient. Studies of flow through very small tubes show that the flow rate varies directly with the hydraulic gradient. Darcy verified this law and applied it to water percolating through the interstices of filter sand (Wisler and Brater, 1959, p. 147). Darcy's law is expressed by the formula $v=Ph/l$, where v is the velocity (commonly expressed as feet per day or year) of the water through a column of permeable material, h is the difference in head (commonly expressed in feet) at the ends of the column, l is the length of the column (commonly expressed in feet or miles), and P is a constant that depends on the character of the material, especially on the size and arrangement of the grains (Meinzer, 1942, p. 445).

The hydraulic gradient of ground water records the head reduced by friction of flow between any two selected points along the gradient profile. The slope is expressed by h, where h is the difference in elevation between any two points (normally expressed in feet), and l is the distance between the points; h/l is commonly expressed in feet per mile.

The porosity of a rock is defined as the percentage of open spaces in the total volume of the rock *i.e.*, the space not occupied by solid mineral matter. In fragmental rocks this property depends upon (1) shape and arrangement of the particles, (2) sorting of the particles, (3) cementation and compaction of the unit, and (4) removal or deposition of minerals by percolating water. Aquifers with well rounded particles normally have high porosity, while angular fragments tend to fit together closely and reduce porosity. Well sorted material has a higher porosity than poorly sorted material. In a mixture of sand, silt, and clay size particles, the silt and clay particles tend to fill the openings among the sand grains and reduce porosity. The degree of cementation and compaction of the unit further influences porosity. If water migrating through the aquifer is of such chemical nature that solution of the constituents in the rock results, a collapse of the pore spaces may result in reduced porosity. Where deposition exceeds solution, porosity is reduced. Porosity depends partly upon delicate balance between solution and deposition within the aquifer.

Permeability is a property of rock which permits it to transmit fluids. A rock may have high porosity, but lack permeability if the interstices are too small or not connected. Permeability is expressed by Darcy's law.

The best aquifer is a rock composed of well-rounded, well-sorted insoluble grains with minimum cementation and compaction.

CONCLUSIONS

The six dominant factors—ionic potential, oxidation-reduction potential, hydrogen ion concentration, base exchange, temperature, and reaction of certain ions in solution with aquifer material—affect the salinity of natural water. Salinity is influenced also by the rate of migration, which is in turn controlled by hydraulic gradient, porosity and permeability. Each of these factors exerts its own influence to produce the diversity of ions in ground water.

The presence or absence of an ion may result from one or more factors. The many variables involved are so closely interrelated that it is difficult, if not impossible, to isolate a principal controlling factor. Where the dominant control can be determined, however, the behavior of the ion in the aquifer may be predicted. Since conditions within an aquifer can not be duplicated in the laboratory, interrelationship of ions can not definitely be established. Interpreted relationships, however, are based on sound theoretical and experimental chemistry.

The theory of water migration is based on the application of laboratory procedures to the solution of the ground water problem. To date, however, various methods of studying migration are unsatisfactory. Some means of dating ground water should be devised. The Carbon-14 method might be applied to organic carbon (such as bacteria) in the aquifer. Although tritium has been used as an indicator, its half-life is so short (12.5 years) that it is useful only in problems involving short migration distances or high migration rates. Through more study and research, a satisfactory dating method may be devised to study fluid migration.

SOURCES OF ERROR

In a study of this type, utilization of many analyses not made especially for the study may lead to errors. If specific analyses had been made, and if all analyses were made by the same chemist, there would naturally be less error in the reported concentrations. Indeterminate errors in measuring ionic concentrations in ground water can result from improper sampling techinques, contaminated containers, or analytical errors.

GEOCHEMISTRY OF TRINITY WATER

TOTAL SOLIDS (SALINITY)

Total solids or salinity reported here in parts per million is a measure of the abundance of all dissolved substances. The value reported may in some instances include organic matter and water of crystallization, although these would represent a very small portion of the total solids in a sample. The dominant fractions of the total solids of most ground water are sodium bicarbonate and sodium sulfate; other important constituents are compounds containing calcium, iron, magnesium, and fluorine.

A general increase in total solids (fig.5) occurs from the outcrop area downdip to connate water east of Marlin. Water from the Stephenville area has a lower total solids content than water derived from the southwest (fig.4) due mainly to the low concentration of sodium in the northwest. As distance from the outcrop and depth of the aquifer increase, more sodium and sulfate ions are present. This increase continues southeastward and is the probable cause for the steady increase in total solids.

A "tongue" of water high in total solids (fig. 5) enters the area from the southwest near Hamilton and Evant. This water apparently originates in the Llano area (fig. 4) where igneous rocks are abundant. Because most minerals present in igneous rocks are unstable under surface conditions, weathering releases much soluble material. Each mineral has a specific solubility product; when a solution becomes saturated with a given ion, the solution can accommodate no more of that ion and the excess precipitates. Although the water may be highly charged with one ion, in general ions of another soluble mineral may be dissolved essentially without regard to the concentration of other ions. Thus, the greater the variety of minerals present in an area, the greater the variety of salts which dissolve to increase the total solids content. In cases where highly saline water is brought into contact with relatively insoluble minerals, such as calcite, the solubility of the calcite is actually increased as a result of the "salt effect."

Throughout the Balcones fault zone (fig. 4), which traverses the map area from north to south near Waco, reported ionic concentration values are highly irregular. Water in overlying rocks (Glen Rose limestone) is high in sulfate ion; therefore, the mixing of water from other formations along faults is probably responsible for abnormally high total solids values. Wells at Malone and Hubbard have anomalously high total solids content, due perhaps to minor faults or to faulty casing in the wells. Faults or casing leaks permit mixing of high sulfate water from overlying rocks with "normal" Hosston water.

A steep concentration gradient (fig. 5) representing a sharp increase in total solids, occurs between Waco and Marlin. This apparently indicates connate water (fig. 4) high in dissolved solids in the basal Trinity sands east of Marlin.

HYDROGEN ION CONCENTRATION (pH)

The pH is a measure of acidity of a solution. The pH is of great importance in chemical reactions which occur between water and the aquifer material. The pH for most ground water normally does not deviate more than two pH units from neutral (pH 7). The pH of Trinity water ranges from an acid 6.8 to a basic 8.6.

The pH of water is directly affected by the amount of dissolved carbon dioxide in the water. Water combines with carbon dioxide to form carbonic acid which ionizes to release hydrogen ions, thus, reducing the pH. Meteoric water is highly charged with carbon dioxide, and additional carbon dioxide is acquired in percolation through the soil. Therefore, water in the aquifer near the recharge area has the lowest pH values.

The hydrogen ion concentration influences transportation and ultimate redeposition of ionic constituents. For example, iron in the ferric and ferrous states is present in ground water. The solubility of iron at pH 6 (when iron is in the ferrous state) is about 10^5 times greater than at pH 8.5, when iron is in the ferric state (Mason, 1958, p. 159). Therefore, iron-bearing minerals are dissolved in environments of low pH. As the pH increases, the solubility decreases and iron is deposited, probably as hydrous ferric oxide.

An increase in pH within the aquifer occurs as a result of reactions between the water and various compounds in the aquifer, such as carbonates of sodium and calcium. Carbonates are converted to bicarbonates, utilizing carbon dioxide in the reaction, which depletes the supply of carbon dioxide in the water and raises the pH. For example,

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

Similarly,

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

Water from the Stephenville well, 8 to 10 miles from the Trinity outcrop, has a low pH (fig. 6). Upon entering the aquifer, the water is highly charged with carbon dioxide, thus, lowering the pH. As distance from the outcrop and depth of the aquifer increase, carbon dioxide is exhausted through reactions with the carbonates to produce bicarbonates. Carbon dioxide is also lost from solution as a result of increasing temperature with depth. Loss of carbon dioxide results in an increase in pH southeastward across the map area; exceptions occur at three control points. In the Iredell area there is a sharp increase in pH, which may reflect local variations within the aquifer, an erroneous analysis report, or a contamination problem. Should the pH reflect local variations within the aquifer, excess carbonate may be the cause. As water circulates through the enriched carbonate zone, carbon dioxide would be used in transforming carbonate to bicarbonate, increasing the pH. The influence of water from the Llano outcrop area (fig. 4) may also affect the pH at Iredell. If water at Iredell is from the more distant Llano outcrop area, the pH will be higher than water from the northwest,
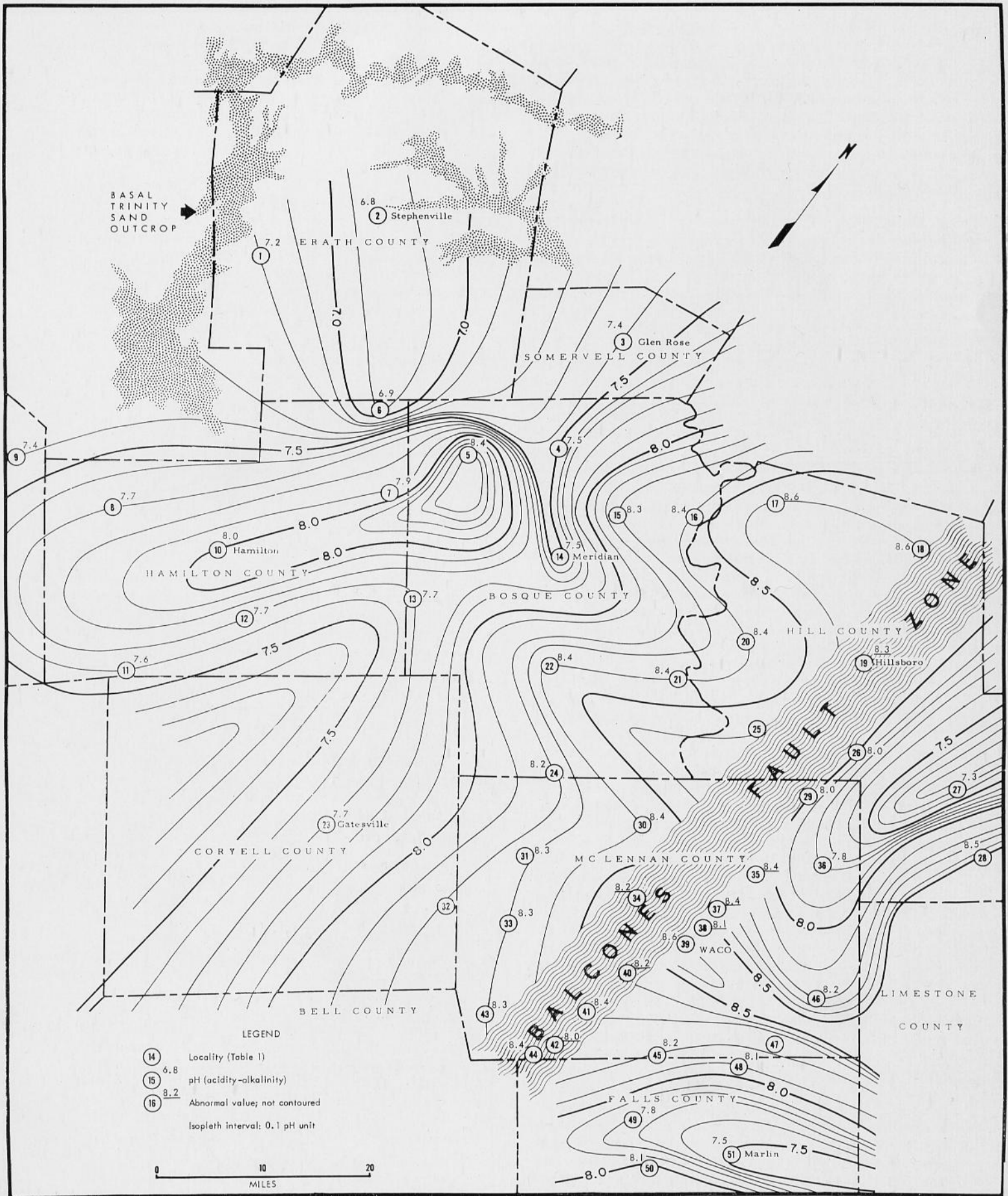
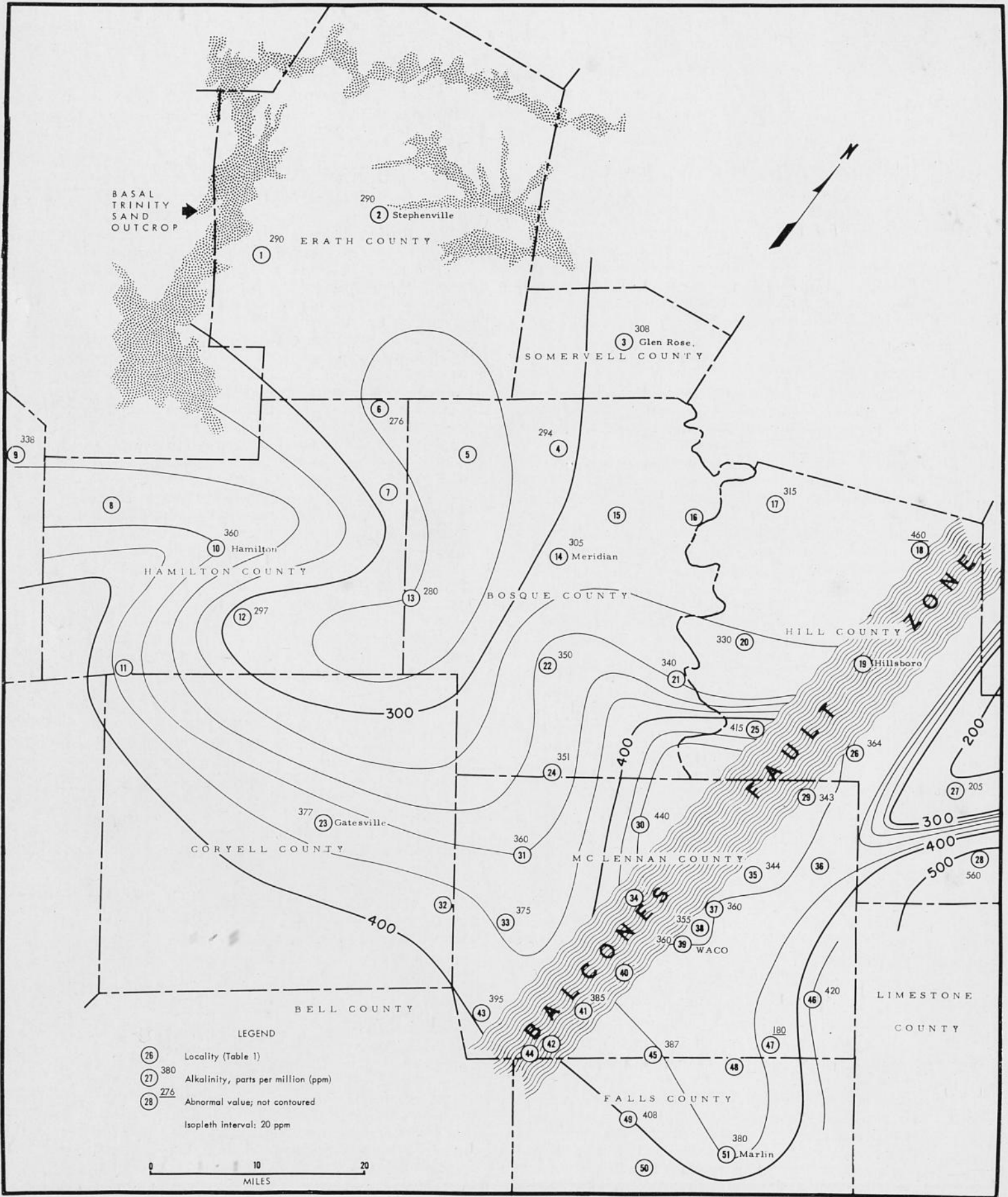Fig. 6.   Hydrogen ion concentration (pH) isopleth map.

Fig. 7. Alkalinity isopleth map.

since more carbon dioxide is lost through reaction during the longer migration period.

In the eastern part of the map area (fig. 6) at Malone and Marlin, an anomalous lower pH occurs. A low pH at Marlin is probably caused by the influence of highly mineralized connate water (fig. 4) downdip from Marlin. At Malone, the low pH may result from mixing of water along minor faults of the Balcones system. The reported sulfate content at Malone is very high (2200 ppm); this indicates a reduction in amount of bicarbonate ion present and a consequent reduction in pH. In the hydrolysis of salts of the less active metals such as iron, pH is reduced as the result of the hydrolysis of the cation. However, all mapped concentration values at Malone deviate from values normally expected in the area, strongly suggesting contamination through faulting or faulty well casing. Sampling and analytical errors also may be factors.

ALKALINITY

The alkalinity of ground water is actually a measure of its bicarbonate ion, with perhaps a trace of carbonate ion that is present. Because the State Department of Health reports total alkalinity in parts per million of calcium carbonate, the concentration of the individual ions is not available.

Ground water with a pH above 8.3 contains some carbonate ion, but the pH of alkaline water is largely controlled by the bicarbonate ion. Water containing appreciable quantities of bicarbonate ion will have a pH of 8.3. As the water absorbs free carbon dioxide the pH will drop below 8.3.

Alkalinity (fig. 7) increases from the outcrop downdip to Marlin. The increasing alkalinity can be attributed to hydrolysis of the carbonate ion yielding bicarbonate and hydroxide ions; *i.e.,*

$$CO_3^= + H_2O \rightleftharpoons HCO_3^- + OH^-$$

High alkalinity (pH greater than 8.3) is associated with the presence of the sodium ion and the absence of the calcium ion.

The calcium-sodium ion ratio can be used as an indicator of alkalinity. Calcium carbonate is essentially insoluble, and when the calcium ion is present, the pH cannot rise because the carbonate ion is precipitated with calcium as calcium carbonate. If the sodium ion is present in solution the pH will rise since sodium and carbonate ions can exist together in solution; the carbonate ion is the one responsible for the increase in alkalinity (pH above 8.3).

At the town of Hubbard (fig. 7) an abnormally high total alkalinity (as calcium carbonate) of 560 ppm is reported. Calcium carbonate reaches saturation at 14 ppm in pure water at 25°C, thus the alkalinity reported must largely result from bicarbonate ions (and carbonate ions where the pH is above 8.3). At Malone total alkalinity (as calcium carbonate) is 205 ppm. This low anomaly is attributed to high sulfate concentration which does not affect pH rather than to the bicarbonate ion which does. The unusually low alkalinity for the Riesel well is considered to be erroneous due to faulty sampling or analysis.

SILICA RESIDUE

Most silicate ions in ground water are monomeric silicic acid (Krauskopf, 1959, p. 15). Some silica may exist as colloidal particles. Analysts invariably find that silicate ion determined colorimetrically coincides with total silica (*idem,* p. 15). The principal sources of dissolved silicate ion are probably the direct solution of silica and the decomposition of silicate minerals. Varying concentrations would be reported, depending upon the form of silica present in the aquifer material. Quartz and chalcedony contribute very little silicate ion to solution, while gelatinous silica available at the outcrop area should dissolve readily up to its equilibrium value at aquifer conditions (*idem,* p. 15).

The solubility of silica and silicates remains low for acidic water and shows only a slight increase for slightly alkaline solutions. In solutions with a pH greater than 9, however, the solubility increases abruptly (Krauskopf, 1959, p. 17). A second significant factor in the solubility of silica is temperature. Not only does solubility increase with temperature, but also the rate of attaining solubility equilibrium increases (*idem.* p. 7).

If pH were the sole controlling factor of the solubility of silica within an aquifer where the pH ranges from 6.9 to 8.6, there would be little variation in silica concentrations. The effects of increasing temperature from 20° to 64°C (fig. 17) probably have greater effect on solubility of silica than pH within the system. Little change in silica content (fig. 8) occurs from the outcrop area to the Balcones fault zone. In the central part of the map area at Cranfills Gap and Meridian, lower concentrations of silicate ion are reported. This decrease probably results from low solubility of silica and silicates in an environment of moderate to low temperature and only slightly alkaline pH. East of the Balcones fault zone, concentration of silica is from two to three times greater than west of the zone. Undoubtedly the higher temperature, coupled with the increasing influence of connate water (fig. 4), is responsible for the great increase in silicate ion in solution east of the fault zone.

TOTAL HARDNESS

Ground water containing certain cations in solution (chiefly calcium and magnesium ions), which form insoluble compounds with soap, is said to be "hard." Carbon dioxide in water increases the solubility of calcium and magnesium carbonates to form bicarbonates. If carbon dioxide is removed from the water by increasing the temperature, bicarbonate is decomposed and calcium and magnesium are precipitated as carbonates. The amount of calcium or magnesium carbonate which water can hold in solution depends on the concentration of carbon dioxide, which in turn depends on the temperature of the water and the amount of carbon dioxide available in the environment. When the carbon dioxide is removed from the water by boiling during analysis, some calcium and magnesium carbonates are precipitated, and the total hardness of the water is reduced. The portion of the hardness thus removed is called "temporary hardness." The hardness remaining after boiling is due mainly to calcium and magnesium ions remaining with sulfate, chloride, nitrate and residual carbonate ions, and is referred to as "permanent hardness." Permanent hardness is caused by cations which form insoluble soaps. The cations include practically every cation except the monovalent ones. The commonest contributors to permanent hardness are ions of calcium and magnesium. The most accurate method in determining total hardness is the measurement of total calcium
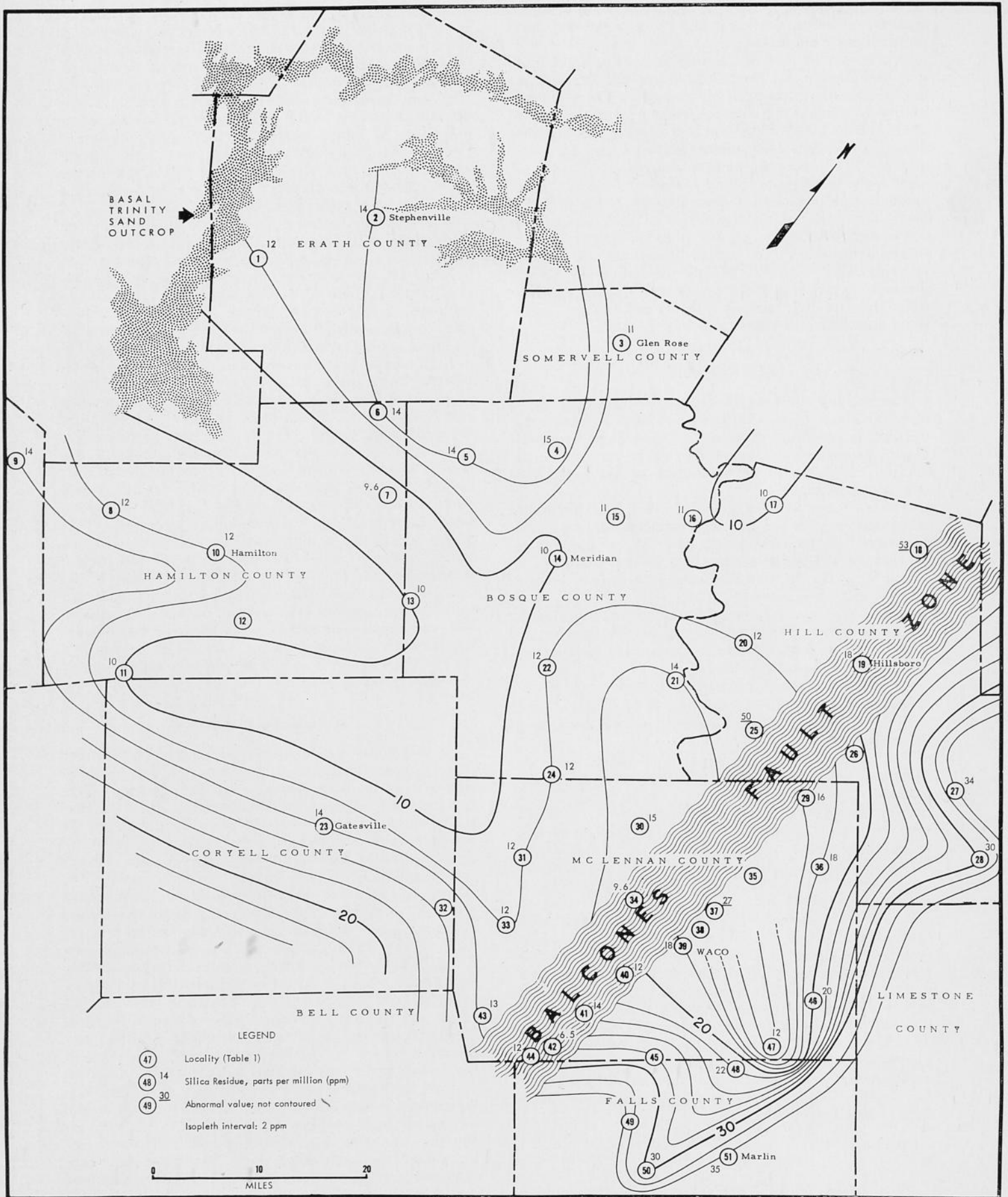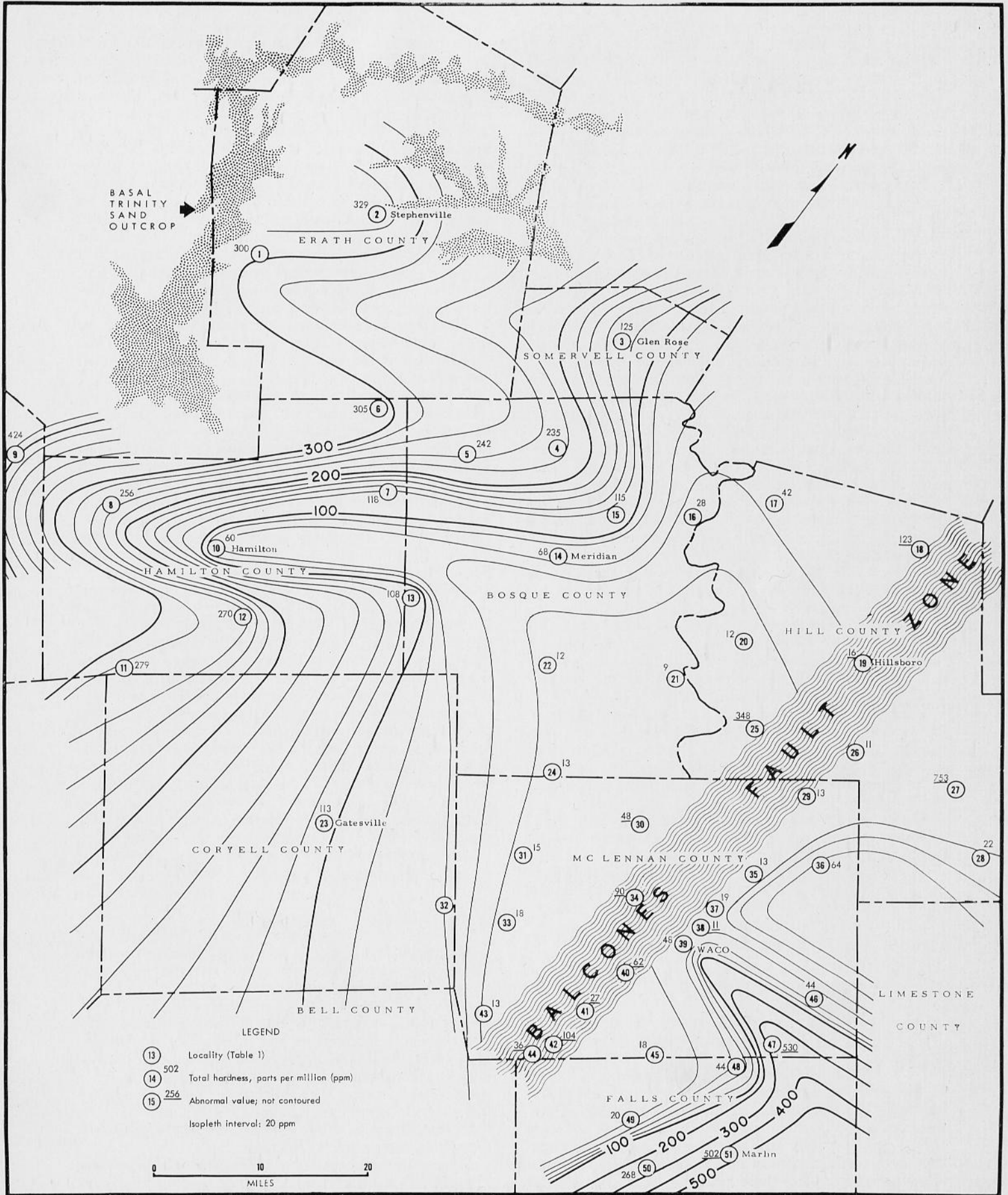
Fig. 8.   Silica residue isopleth map.

BASAL
TRINITY
SAND
OUTCROP

329 ② Stephenville

ERATH COUNTY

300 ①

125
③ Glen Rose

SOMERVELL COUNTY

305 ⑥

424

⑨

242
235
⑤ ④

200

256
⑧ 118 ⑦

115
⑮

42
28 ⑰

16

123
⑱

60
⑩ Hamilton

68 ⑭ Meridian

HAMILTON COUNTY

BOSQUE COUNTY

270 ⑫

108 ⑬

12 ⑳

HILL COUNTY

11 279 ⑪

22 ⑳

12

9
㉑

16
⑲ Hillsboro

348
㉕

26 11

753
㉗

113
㉓ Gatesville

CORYELL COUNTY

24 13

48
㉚

MC LENNAN COUNTY

29 13

31 15

35 13

36 64

22
㉘

32

33 18

90 ㉞

19
㊲

38 11

39 WACO

44
46

LIMESTONE

COUNTY

BELL COUNTY

62
㊵

44 104

42

47 530

43 13

41 27

45 18

44 48

FALLS COUNTY

LEGEND

⑬ Locality (Table 1)

502
⑭ Total hardness, parts per million (ppm)

256
⑮ Abnormal value; not contoured

Isopleth interval: 20 ppm

20 ㊾

502 �51 Marlin

268 ㊿

BALCONES

FAULT ZONE

100 200 300 400 500

0 10 20
MILES

Fig. 9. Total hardness isopleth map.

and magnesium ions in the sample. Traces of nickel or cobalt, or cations of any other metal except alkali metal cations will be reported as total hardness.

Total hardness is reported by the State Department of Health in parts per million of calcium carbonate. Thresh, et al. (1958, p. 22) recognize six degrees of hardness. Water having less than 50 ppm of calcium carbonate is soft; 50 to 100 ppm, moderately soft; 100 to 150 ppm, slightly hard; 250 to 350 ppm, hard; and over 350 ppm, excessively hard.

Water withdrawn from an aquifer near the recharge area is normally hard to excessively hard. This results from higher concentrations of carbon dioxide near the outcrop area and normally low temperature. Inasmuch as the solubility of calcium and magnesium carbonate increases with higher carbon dioxide content, more calcium and magnesium salts are dissolved from rocks in these areas. Carbon dioxide is readily depleted in converting carbonate to bicarbonate; therefore, as carbon dioxide content decreases downdip from the outcrop, less calcium and magnesium carbonate go into solution. As water migrates through the aquifer, a two-fold water-softening process occurs. First and probably most important is the base exchange of sodium ions attached to clays for calcium and magnesium ions in solution. Secondly, the increase in temperature within the aquifer probably causes some precipitation of calcium and magnesium carbonate through loss of carbon dioxide.

Hard to excessively hard water occurs at all control points near the outcrop (fig. 9), but farther downdip lower total hardness is noted. Trinity water is very soft in the central part of the map area near Clifton and Laguna Park. In the southeast part of the map area, a sharp gradient occurs from soft water at Golinda to excessively hard water at Marlin. This is probably due to the influence of the hot, highly mineralized water in the Marlin area. The hardness at Marlin is probably caused by calcium and magnesium sulfates. Inasmuch as all other constituents increase toward the eastern area, hard water naturally would be encountered.

A comparison of the calcium, magnesium and chloride ion concentrations (figs. 10, 11, 15) reveals a decrease downdip from the outcrop area. Iron concentration (fig. 13) for the most part is low; therefore, its effect on hardness is negligible, even though iron content may have an appreciable local effect.

The uniform trend toward softer water downdip from the outcrop increases until highly mineralized water is encountered near Marlin. The regional trend in hardness variation is interrupted at Malone, probably because of contamination of water from overlying rocks along minor faults. Water analyses from Malone (Table 1) show anomalously high concentrations of most ions, and, therefore, an increase in hardness.

CALCIUM

Calcium in ground water is largely in the form of the bicarbonate as a consequence of the following reaction:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

In this reaction calcium carbonate, which is relatively insoluble, is converted to the soluble bicarbonate by the action of water and carbon dioxide.

Water in contact with limestone, dolomite, calcareous sand or gypsum is characterized by high concentrations of calcium ion. All of these minerals occur in overlying rocks and/or within the aquifer. In the low pH environment near the outcrop (fig. 6) where carbon dioxide content is high, calcium carbonate is taken into solution as calcium bicarbonate. As water migrates downdip an exchange of ions occurs between calcium in solution and exchangeable sodium on clays. Calcium ion is thus extracted from solution and replaced by sodium ion. The ionic potential plays a major role in this exchange. The ionic charge of calcium is 2.0, while that of sodium is 1.0, yet their radii are similar. In an environment where both are present, sodium ion will go into or remain in solution and calcium ion will be exchanged. If sodium-rich clays are present within the aquifer, the exchange of calcium ion in solution for sodium ion on the clays occurs by base exchange.

In the southeastern portion of the map area (fig. 10), near the zone of mixing between mineralized and meteoric water, both calcium and sodium ions increase. The average calcium ion concentration in normal sea water is 400 ppm. Thus, where meteoric water and connate water intermix (fig. 4), a higher calcium ion concentration can be expected.

Concentration of calcium ion becomes very low in the central part of the map area, where the influence of the outcrop is at a minimum and connate water has not been encountered. In all probability the importance of base exchange in controlling the water chemistry is at a maximum in this area.

The influence of the recharge area is greatest in the northwest, west and southwest parts of the region. From here it is possible to delineate different water masses (fig. 4) as they migrate through the aquifer. The effects of the outcrop area north of Stephenville are believed responsible for high calcium ion concentration (fig. 10) at Hico. Southward at Pottsville and Priddy, the effect of water from the Llano outcrop area to the southwest is shown by higher calcium ion concentrations. Hamilton, however, occupies a position where the influence of water from outcrop areas has decreased, and the base exchange of calcium ion for sodium ion exerts a greater effect on the water chemistry. Except for analyses within the fault zone, in areas of mineralized water near Marlin, and in the anomalous area near Malone, there is a regional eastward decrease in calcium ion content. The Malone anomaly is probably of local origin; inasmuch as hardness also increases near Malone (fig. 9) the calcium content is probably real and not due to an analytical error. Contamination from water of other formations as a result of faulting or poor well casing may cause the anomaly.

MAGNESIUM

Magnesium carbonate is relatively insoluble, although in the presence of water and carbon dioxide some magnesium bicarbonate is produced:

$$MgCO_3 + H_2O + CO_2 \rightarrow Mg(HCO_3)_2$$

Magnesium bicarbonate is readily soluble and is taken into solution. Magnesium and calcium are similar ions both capable of exchanging positions in some mineral lattices. Magnesium has an ionic charge of 2.0, but a smaller ionic radius than calcium. Magnesium in solution tends to replace calcium in some minerals, and thus, normally magnesium does not migrate as far downdip within the aquifer as calcium.

Magnesium concentration throughout the map area (fig. 11) is relatively low. Higher concentrations oc-
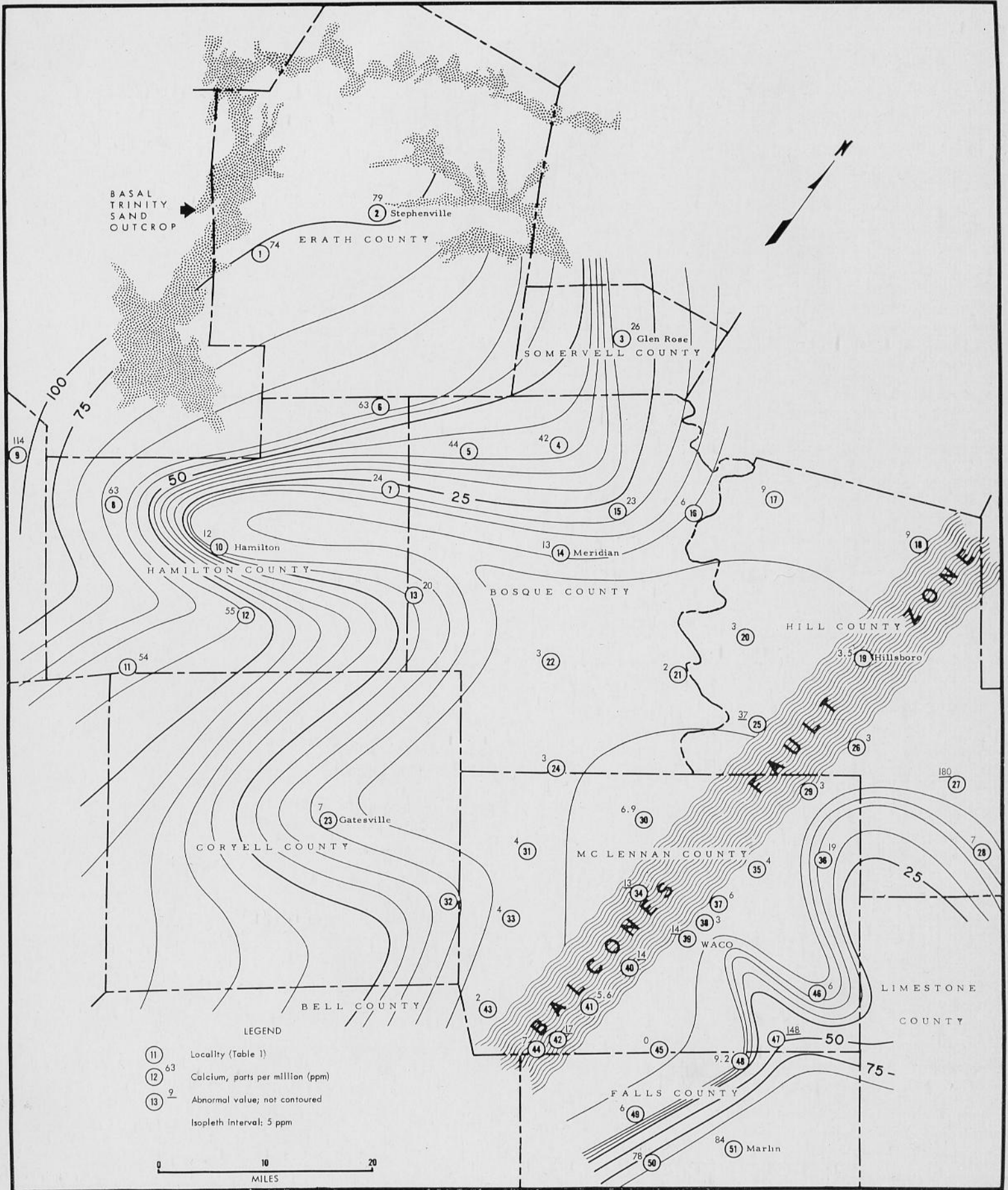
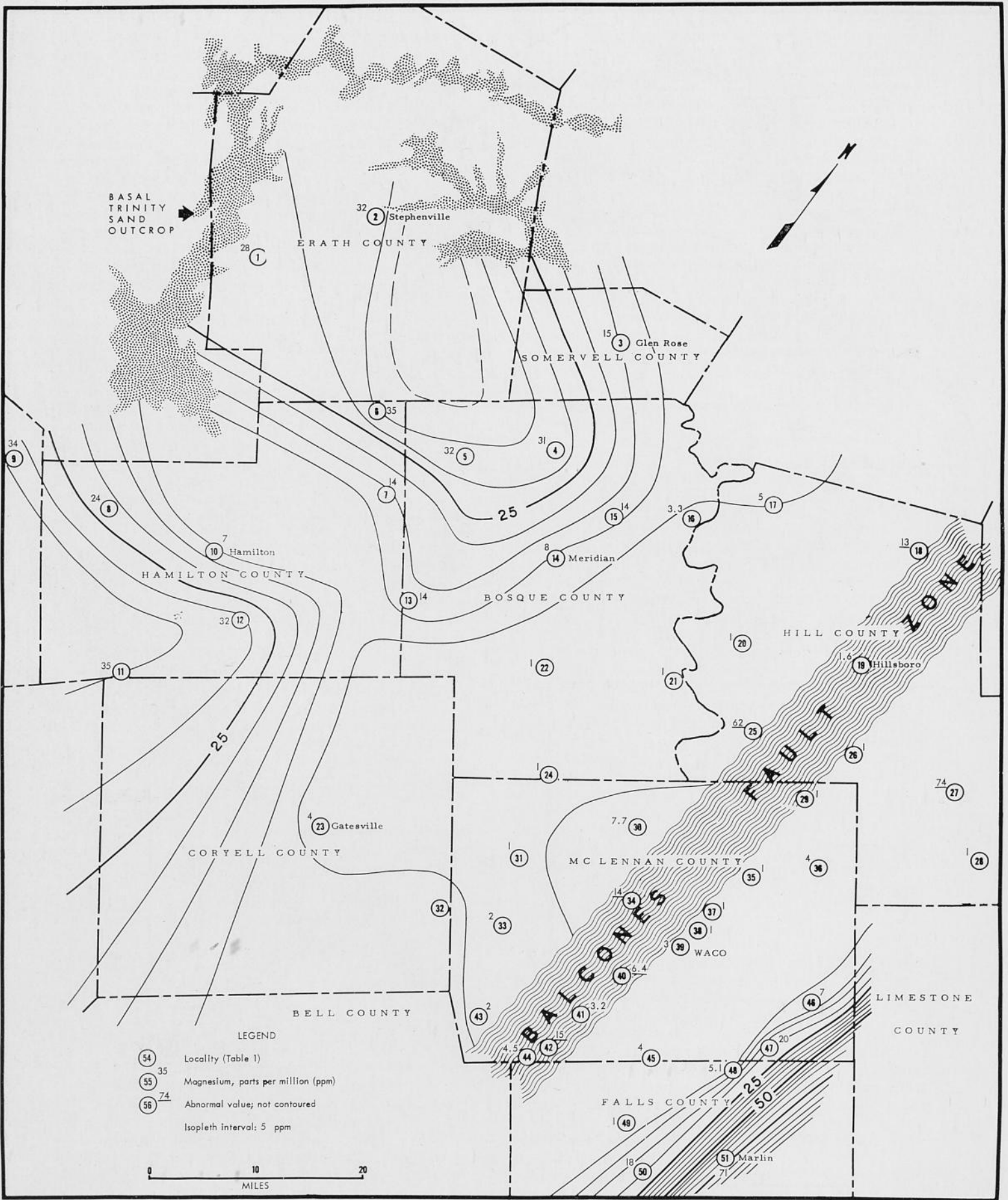Fig. 10. Calcium isopleth map.

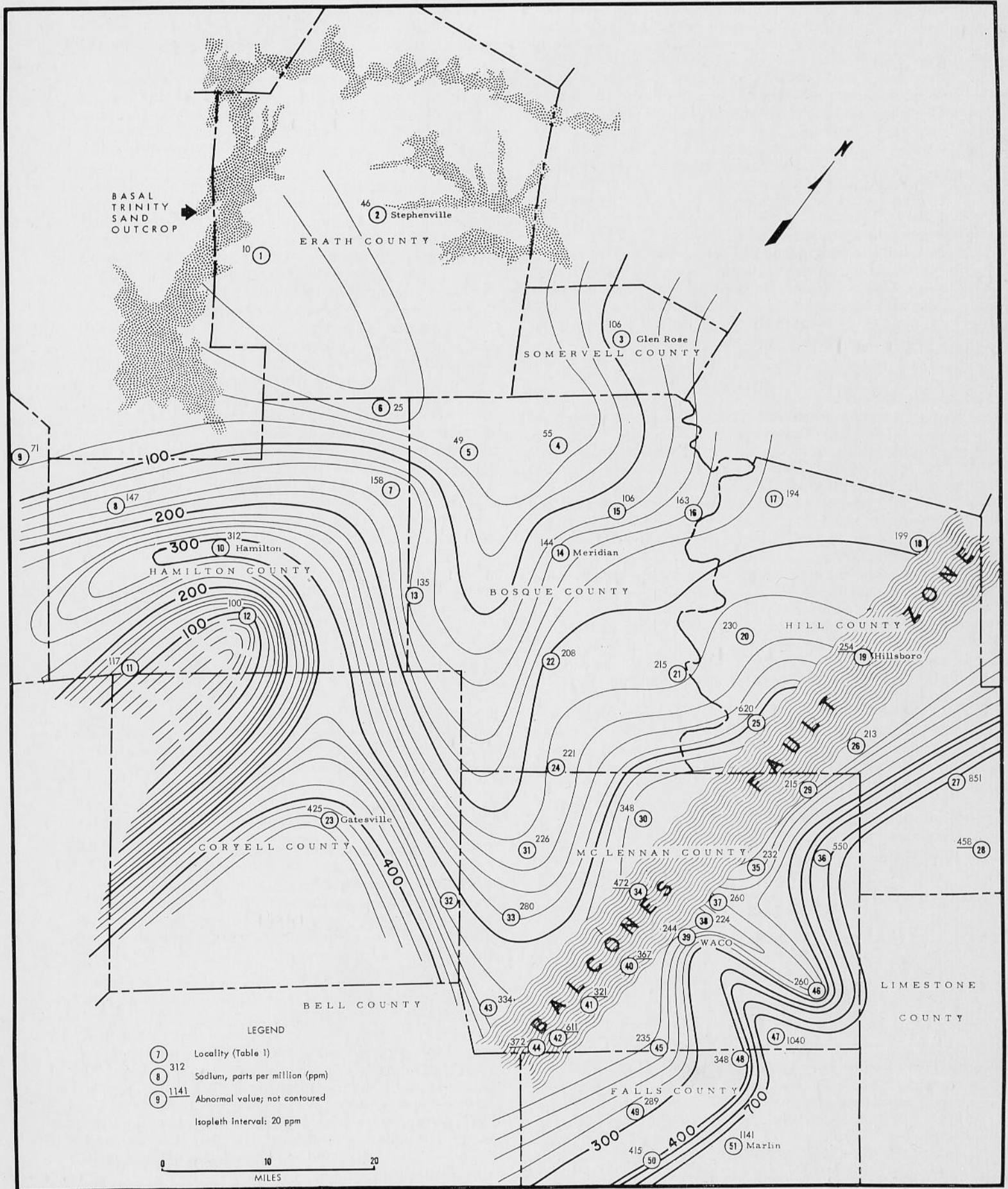Fig. 11.   Magnesium isopleth map.

Fig. 12. Sodium isopleth map.

cur near the outcrop in the northwest and southwest parts of the area probably as the result of more carbon dioxide in the water near the outcrop. Progressively lower magnesium ion values occur downdip. Loss of magnesium ion probably occurs by base exchange of magnesium ion in solution for sodium ion attached to clay minerals within the aquifer and by replacement of calcium in minerals; *i. e.* magnesium carbonate is less soluble than calcium carbonate.

Very low concentrations of magnesium ion occur in the central part of the map area (fig. 11) as the magnesium supply in the water is exhausted. In the area between Mart and Marlin the magnesium content rises sharply to a maximum of 71 ppm at Marlin, probably because of the influence of connate water (fig. 4).

Except in the Balcones fault zone the only control point deviating from the regional pattern of downdip decreasing magnesium ion concentration is at the town of Malone. Contamination by water from overlying rocks is the probable cause of the anomaly.

SODIUM

The relative solubility of most sodium compounds is high. The ionic charge of sodium is 1.0, and the radius is 1.0A (Mason, 1958, p. 71). The sodium ion has the lowest ionic potential of the three ions—sodium, calcium and magnesium have ionic charges of 1.0, 2.0 and 2.0 respectively. It has been established that bivalent cations of small ionic radius are more securely held in their crystal lattices than univalent cations of equivalent radius. Sodium salts are more soluble than the divalent calcium and magnesium salts of the same anion. Sodium minerals in the recharge area and in the aquifer, therefore, readily contribute sodium ion to percolating ground water. In addition, sodium ion on clay minerals exchanges for calcium and magnesium ions in solution, resulting in progressively higher sodium concentrations in water downdip from the outcrop.

Sodium salts are rapidly leached in the outcrop area. In the northwestern part of the map area (fig. 12) near Stephenville, only a limited supply of sodium compounds remains available in the soils and outcropping rocks. Although surface rocks in the area are of marine origin, the sodium salts have been largely removed by leaching. Trinity water originating in this area is low in sodium ion as far southeast as Iredell and Walnut Springs. Water originating in the Llano region (fig. 4) in the southwestern part of the map area contains abundant sodium ion, since the recharge area is adjacent to outcropping igneous rocks rich in sodium compounds.

A sharp increase in sodium ion concentration (fig. 12) occurs near Marlin where meteoric water mixes with connate water, which is commonly high in sodium ion.

IRON

Iron occurs in ground water both as ferrous (Fe^{++}) and ferric (Fe^{+++}) ions. The solution, transportation, and deposition of elements which occur in two or more oxidation states, are directly influenced by the oxidation potential and the pH of the environment. For many reactions the oxidation potential decreases rapidly with an increase of pH (Mason, 1958, p. 163). Thus, the more basic the solution, the more rapidly oxidation proceeds. Iron clearly exhibits a good example of this chemical relationship. In an environment of low pH (pH 1-4), the oxidation potential of ferrous iron is 0.77 volt. As pH increases above 4, the oxidation potential decreases rapidly to a negative value and hydrous ferric oxide is precipitated. By increasing the temperature and pH, the oxidation potential assumes a negative value and deposition of hydrous ferric oxide results.

The iron concentration in the map area (fig. 13) decreases eastward until connate water is encountered. This decrease is a result of decreasing solubility of ferric iron with increased pH, and the subsequent change from ferrous to ferric ion with precipitation of hydrous ferric oxide. Iron in solution may also be exchanged for sodium attached to clay minerals.

The influence of iron rich rocks of the Llano area on Trinity water is illustrated in Figure 13. The lower pH of water near the outcrop increases solubility of the iron and the ferrous ion goes into solution. Water from the Llano area (fig. 4) can be easily recognized a considerable distance downdip from the outcrop by its high iron content. The Llano "tongue" of higher iron concentration (fig. 13) is "deflected" southeastward in the vicinity of Iredell by the effect of higher pH (fig. 6) resulting in a low iron concentration at Iredell.

In the central part of the map area where the influence of water from the outcrop areas is minimum and connate water is distant (fig. 4). iron concentration is very low. Water in this area is basic (fig. 6) ranging from pH 8.2 to 8.4; hence, iron is deposited either through base exchange or precipitation as hydrous ferric oxide. Presumably both processes are involved in extracting iron from solution, resulting in low iron concentration.

Connate water near Marlin increases iron concentration. In this area the pH decreases (fig. 6) resulting in increased solubility of iron compounds such as the iron sulfides, which are also more soluble at the higher temperatures (fig. 17). Iron-bearing sulfides are sensitive to oxidation; sulfides undergo subsequent chemical changes, and colloidal sulfur and hydrogen sulfide are then found in the water supply.

SULFATE

Sulfate ions may be derived from decomposition of gypsum, from oxidation and hydrolysis of metallic sulfides, and from fertilizers. Fertilizer sulfate would chiefly affect the composition of water entering the aquifer and would be detected in shallow wells near the outcrop. The main source of sulfate probably comes from gypsum by the reaction

$$CaSO_4 + H_2O + CO_2 \rightarrow CaCO_3 + 2H^+ + SO_4^=$$
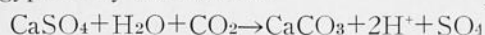
in which calcium carbonate and sulfuric acid are products.

Water originating in the northwest part of the area (fig. 14) is low in sulfate ion, while water from the southwest contains abundant sulfate ion, apparently the result of more sulfate minerals in the Llano region. Sulfate ion concentration increases rapidly in short distances where the aquifer is influenced by Llano derived water. Sulfate ion concentration increases downdip from the area where the northwest and southwest derived water masses (fig. 4) mix.
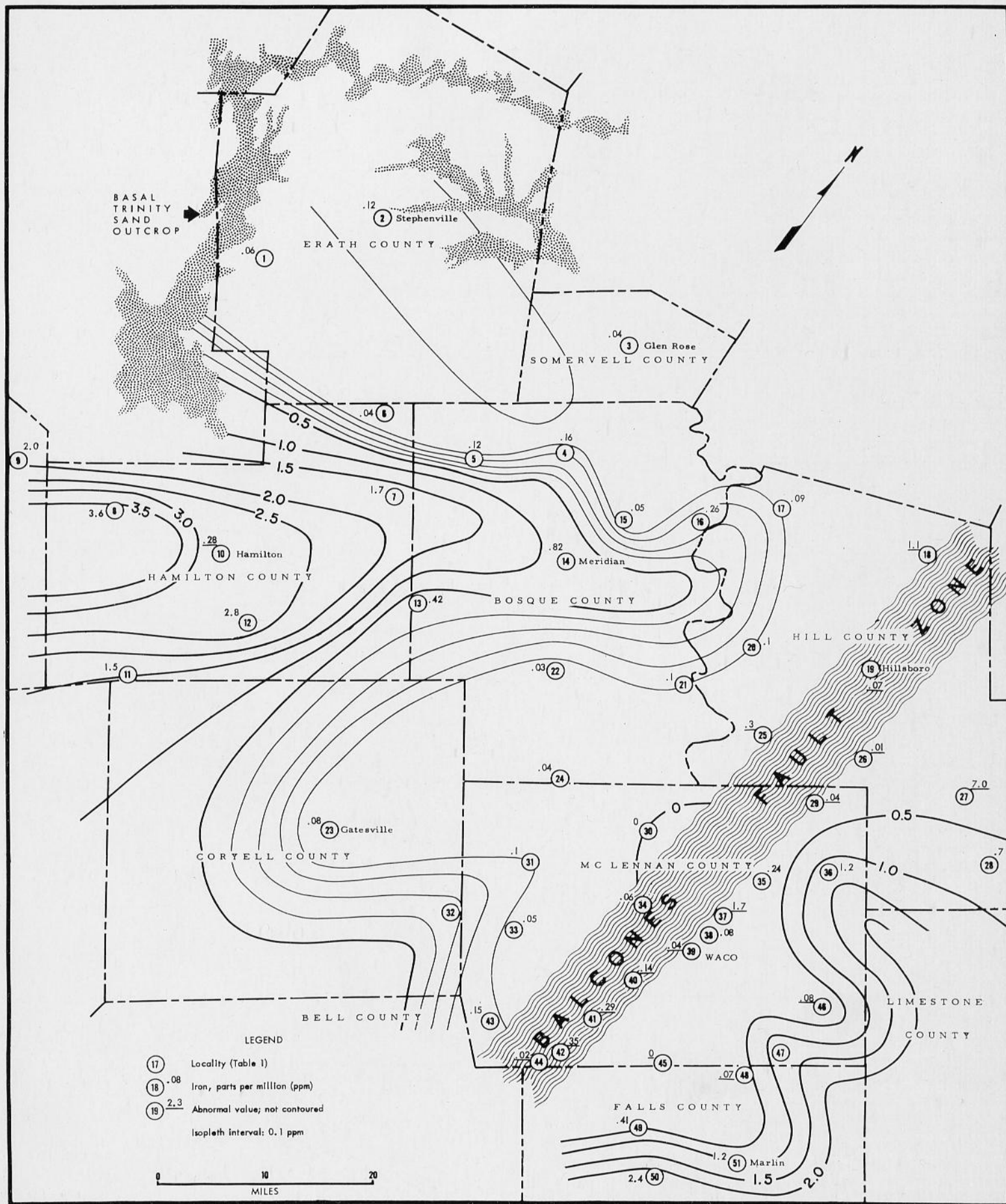
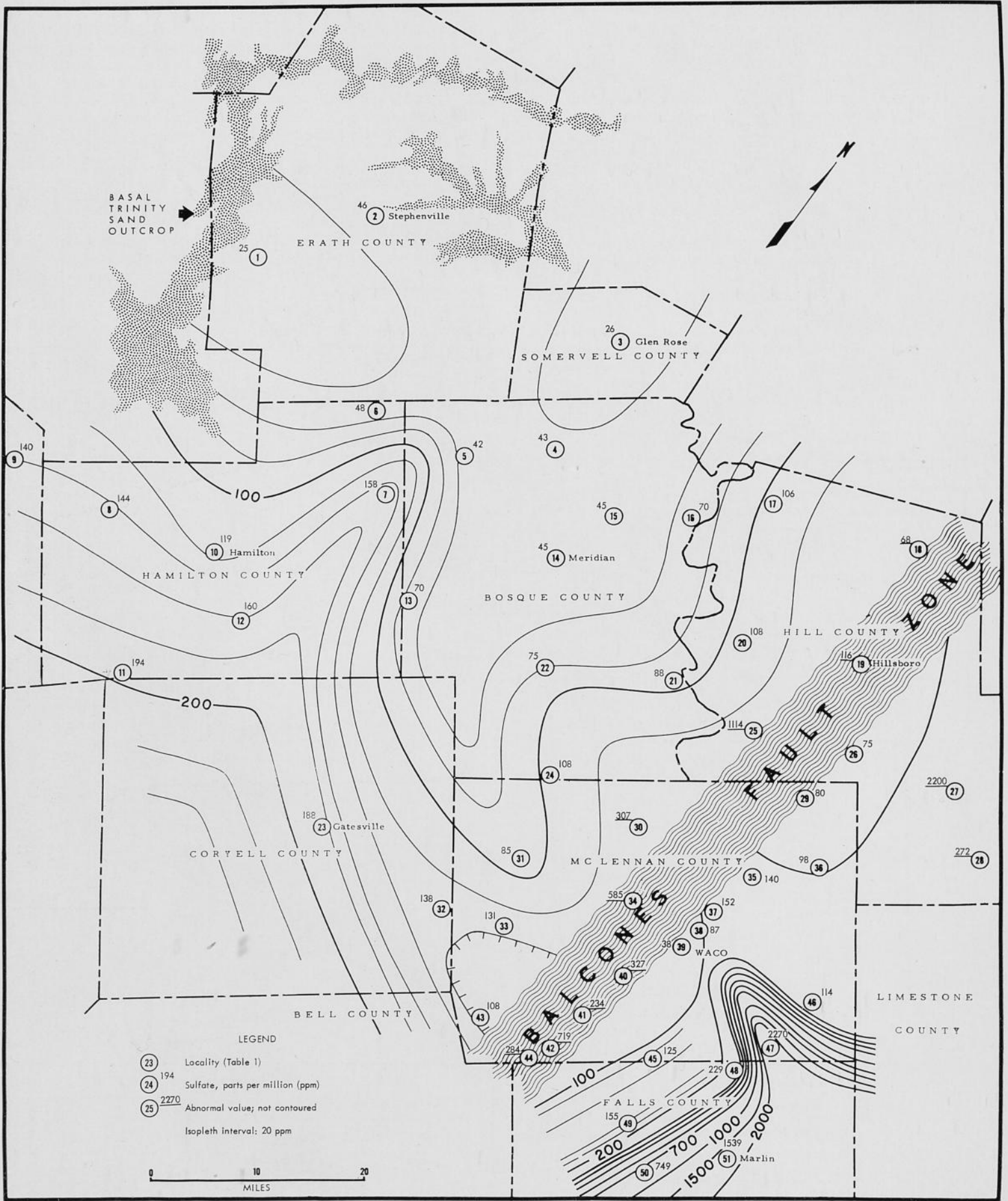Fig. 13.   Iron isopleth map.
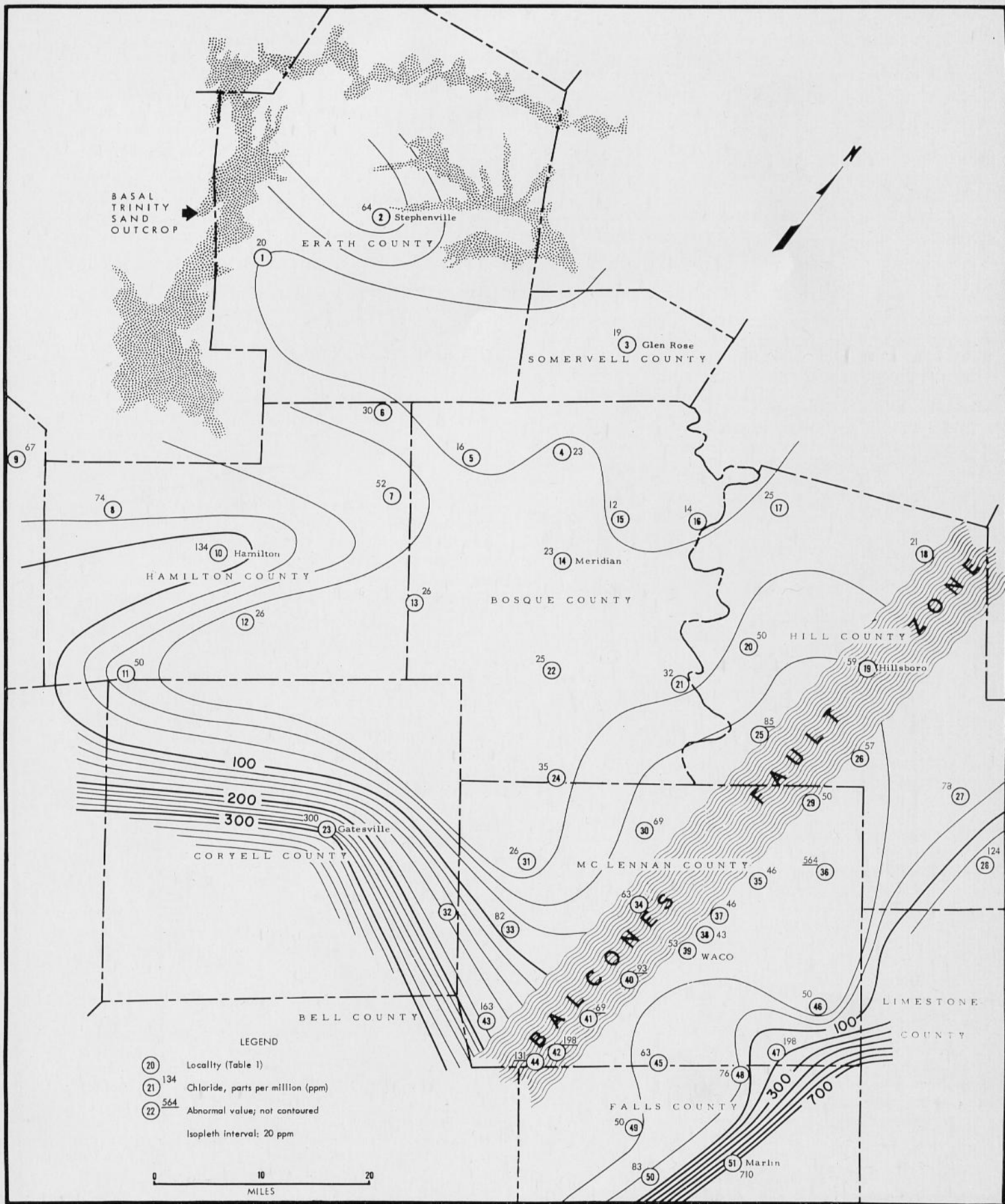
Fig. 14. Sulfate isopleth map.
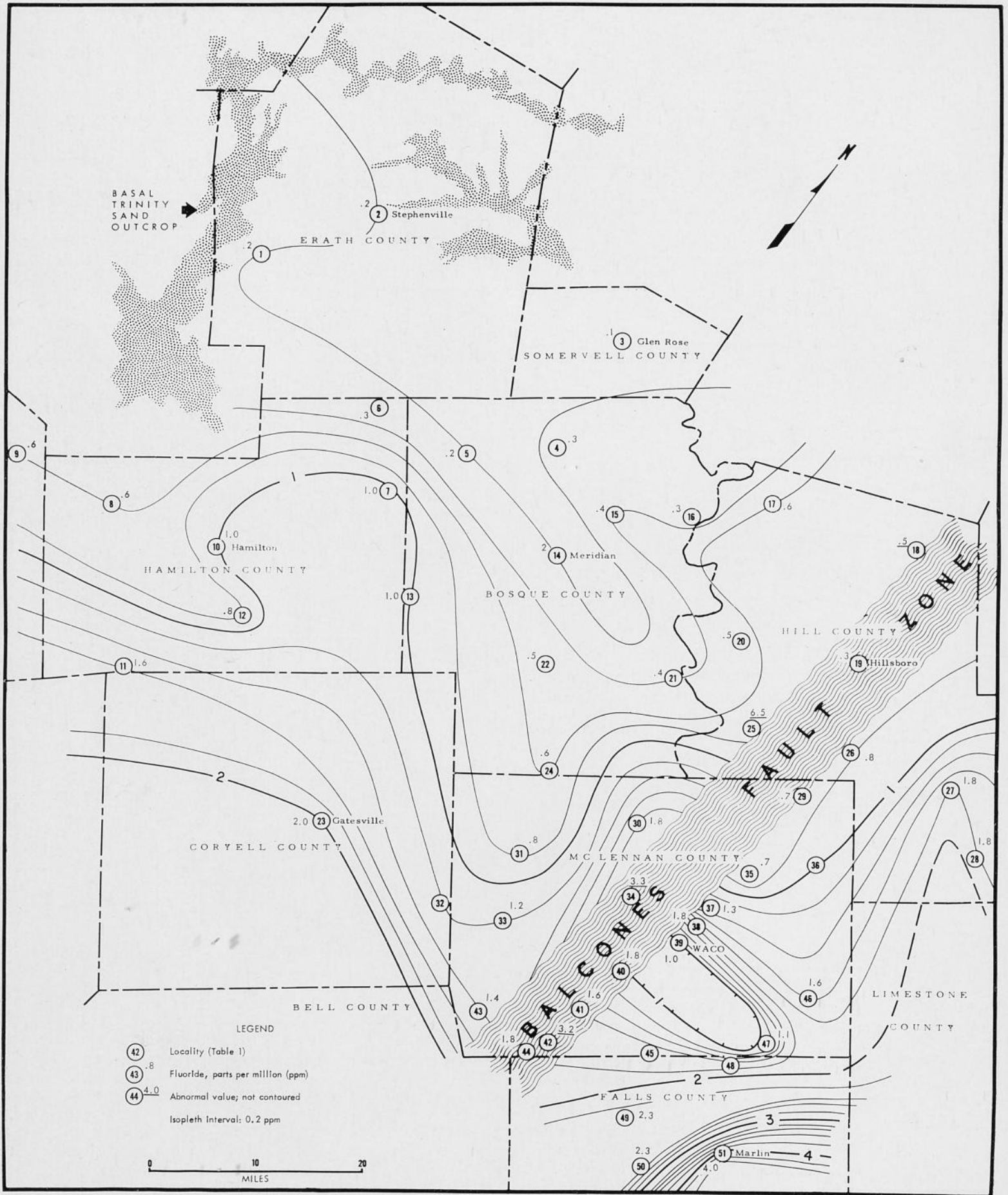
Fig. 15.   Chloride isopleth map.

Fig. 16.   Fluoride isopleth map.

In the southeast part of the map area, where meteoric and connate water mix, sulfate ion content (fig. 14) is extremely high. A steep concentration gradient occurs between Waco and Marlin. Water in overlying rocks is high in sulfate and is commonly called "gyp" water. Higher sulfate ion concentrations occur wherever there is contamination of water in the Hosston aquifer by Glen Rose water due to faulting or poor casing. Aquilla, in the Balcones fault zone, reflects this sulfate ion contamination from overlying formations. Malone is also exceptionally high in sulfate ion, presumably due to minor faults.

CHLORIDE

Chloride ion content averages 314 ppm in igneous rocks, a trace in sandstone and 200 ppm in limestone (Rankama & Sahama, 1950, p. 226). Some chlorides occur in household and barnyard drainage, which may be detected in shallow wells near the outcrop. Chloride ion content increases downdip in the aquifer along with the increasing concentration of sodium ion. Except for silver, lead and mercurous chlorides, chloride salts are very soluble; therefore, chloride compounds in the recharge area or within the aquifer are readily taken into solution.

The primary source of chloride ion in the recharge areas is igneous rocks of the Llano region. Water entering the aquifer from the Llano to the southwest (fig. 4) contains more chloride ion than water derived from the northwest. The northwestern recharge area is composed of sedimentary rocks, thus less chloride ion is available to be introduced into the aquifer system. At Stephenville (fig. 15) an abnormally high chloride ion concentration (64 ppm) occurs, which may be attributed to the use of fertilizers on the nearby Trinity outcrop. Pollution from sewage or an erroneous analysis also may have caused the anomaly.

Regionally, the chloride ion concentration (fig. 15) increases downdip. Sharp increases in chloride ion content occur in the vicinity of water masses (fig. 4) migrating from the southwest. Chloride and sodium ions have similar concentration patterns; both sodium and chloride ions are abundant in modern sea water. The aquifer is composed of sedimentary marine deposits, which probably trapped a high salt content in pore spaces at the time of deposition. This connate water provided a supply of both sodium and chloride ions which was later disseminated by migrating meteoric water. The effect of highly saline connate water is most pronounced in the deeper parts of the aquifer where water movement is slow and mixing with meteoric water has been negligible.

FLUORIDE

Fluoride ion is derived mainly from minerals of igneous origin. The common minerals fluorite (CaF_2), cryolite (Na_3AlF_6), apatite ($Ca_5F(PO_4)_3$), and topaz ($Al_2(F,OH)_2SiO_4$) may be the source for the fluoride ion in ground water. The minerals fluorite, apatite, and topaz occur as accessory minerals in the basal Trinity sands. These minerals are relatively insoluble, but minor amounts of fluoride ion may be contributed to the water of the aquifer. The solubility of fluoride increases in the presence of carbon dioxide; therefore, surface water rich in carbon dioxide can contain more fluoride ion. Water near an igneous source is normally higher in fluoride ion than water some distance from igneous rocks.

In the Trinity aquifers, fluoride ion concentration (fig. 16) is low, ranging from 0.1 ppm at Glen Rose, to 4.0 ppm at Marlin. Fluoride ion concentration is low in the northwest portion of the area where sedimentary rocks contain a limited supply of fluorine-bearing minerals. Fluorite has a higher specific gravity (3.2) than most common rock-forming minerals and is, therefore, considered a "placer" mineral, which may be locally concentrated during deposition. Such "placer" deposits within the aquifer could supply considerable fluoride ion in local areas. A heavy mineral study of Trinity sands from the outcrop and from deep wells near Waco reveals the presence of fluorite, but its abundance is unknown.

Higher concentrations of fluoride ion in the aquifer occur in the Hamilton-Evant area, which is under the influence of water derived from the Llano igneous and metamorphic region (fig. 4). The average fluoride ion content of igneous rocks is 600 to 900 ppm (Rankama and Sahama, 1950, p. 226). Igneous rocks in the outcrop area provide a continuous supply of fluoride ion to the recharge water, and apparently water from the Llano area is responsible for the increasing fluoride ion content along the southern boundary of the map area.

Fluoride ion content increases sharply in the southeastern part of the area. This increase is normal where hot, highly mineralized connate water mixes with meteoric water. Fluoride ion content is lower in the Waco area (1.0 ppm) than in surrounding areas; for example, Bellmead and Lacy-Lakeview have 1.8 and 1.3 ppm respectively.

TEMPERATURE

The average temperature gradient in the outer crust of the earth is approximately 1°C per 100 feet of depth. There are, however, radical local departures from this gradient. The temperature gradient for the map area (fig. 17) approximates the average of 1°C per 100 feet of depth. At Stephenville the temperature is 23°C at a depth of about 300 feet, and at Marlin the temperature is 64°C at a depth of approximately 3400 feet. This represents 41°C variation in 3100 feet of depth, or a gradient in the map area of 1°C for every 75.6 feet increase in depth. This temperature increase undoubtedly effects the salinity of the water within the aquifer.

Where permeability is high, migration of the water is accelerated; subsequently a lower temperature is expected with higher permeability, since the water has over long periods acted as a cooling medium on the surrounding rocks. Prolonged pumping of a well also causes a decrease in temperature, presumably due to the increased migration rate resulting from the drawdown of the well and by exsolution of dissolved gases. Conversely, where porosity and permeability are lower, water temperature consistent with the normal geothermal gradient results.

Temperature has a direct influence upon ionic exchange within the aquifer. Temperature affects the solubility product of compounds, and, therefore, the amount of material taken into solution is a function of the temperature. If a solution is saturated at 25°C and the temperature is increased to 30°C, more solute dissolves until a new equilibrium is established. For some
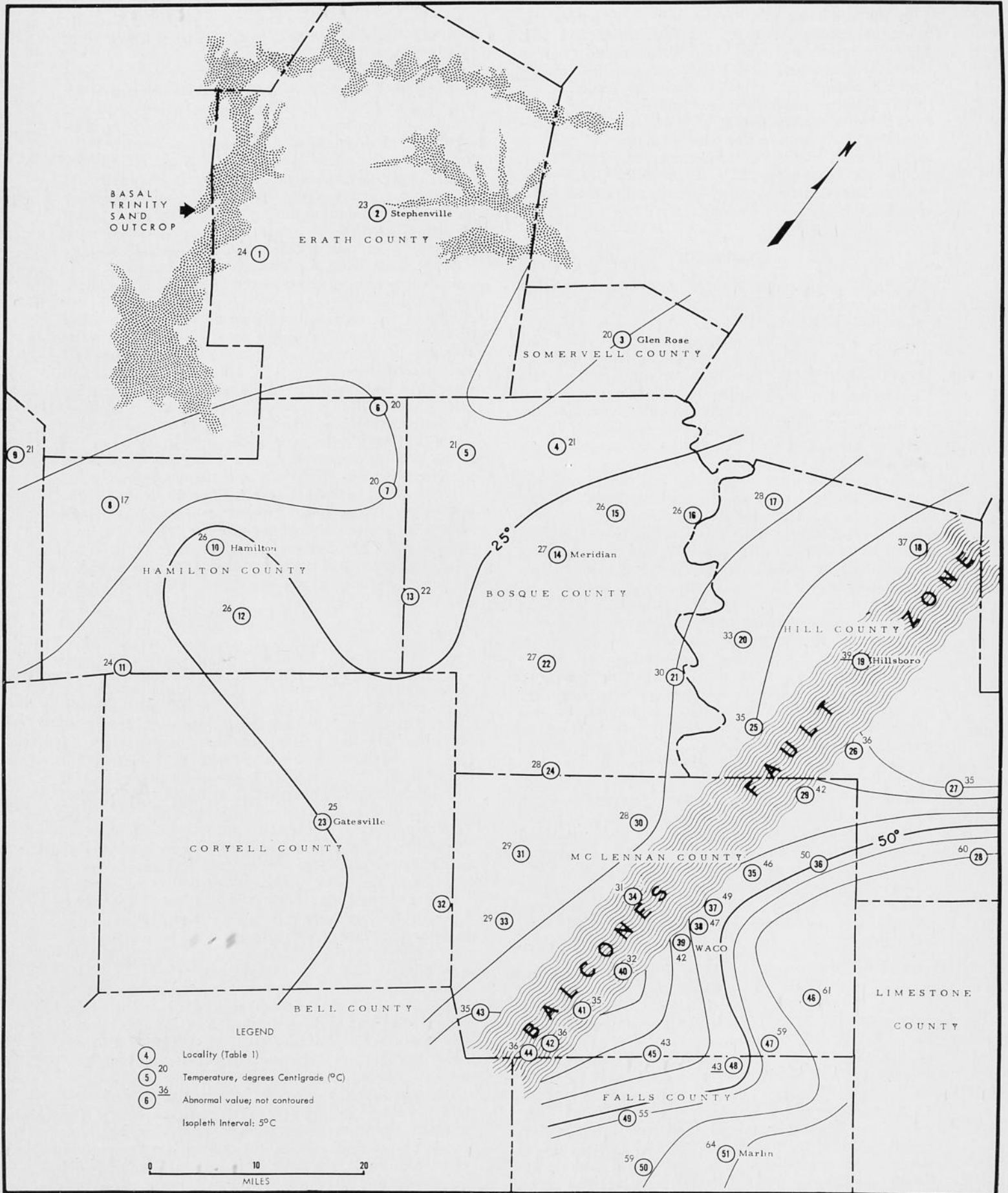
Fig. 17.   Temperature isopleth map.

compounds the amount that can be held in solution varies greatly with the temperature. For example, though this reaction is not one of direct control of solubility by temperature, more calcium carbonate can be dissolved in ground water at low temperatures, and as temperature increases the amount of carbon dioxide in solution decreases and the pH rises with corresponding precipitation of calcium carbonate.

However, as temperature increases, the solubility of most elements increases. Temperature also effects the rate of ionic exchange. In addition, the oxidation potential may decrease slightly with increasing temperature, which may cause precipitation of those elements which occur in different oxidation states in nature.

A zone of highly porous and permeable sands probably trends north-northeast from Pottsville to Glen Rose (fig. 17) where temperatures are consistently low. Water originating in the Llano area apparently migrates northeastward through this more permeable zone, as evidenced by the distinctive "tongues" of water, rich in numerous ions. Iron concentration (fig. 13) best delineates this "tongue" of higher permeability.

Except for the "Pottsville-Glen Rose tongue" temperature gradients west of the Balcones fault zone follow the aquifer temperature gradient of 1°C per 75 feet of depth. East of the fault zone is a sharp increase in average temperature, particularly between Waco and Mart, and Waco and Marlin. This sharp thermal increase probably results from increasing depth of the aquifer by down-to-the-coast faulting, as well as steeper dip east of the Balcones fault zone. At Waco the Trinity sands are approximately 2200 feet deep (Holloway, 1961, p. 9), but 25 miles east depths increase to 3400 feet. High temperatures in the deep sands and the strong influence of connate water, result in an abrupt downdip increase in salinity.

MANGANESE

Throughout the area manganese ion concentration is below 0.05 ppm; therefore, variations are not detected in the analyses. Manganese is less abundant in nature than iron, although it is chemically similar to iron. A high manganese ion content occurs only in ultra-basic rocks such as dunites and hornblendites. Since ultra-basic rocks are not abundant in the Llano area, little manganese is available in this recharge area.

NITRATE

Except for nine control points the concentration of nitrate ions is less than 0.4 ppm.

The nitrate ion may be leached from rocks, although few rocks contain abundant nitrate ion. In natural unpolluted water the nitrate ion is, therefore, usually negligible. Near the outcrop, ground water could acquire nitrate ion by pollution from sewage or commercial fertilizers. Another source may be caliche which contributes a small amount of nitrate to the aquifer.

CONCLUSIONS

(1) Studies utilizing readily available chemical analyses can be applied to any aquifer. Such investigations are important to the field of water conservation and sedimentary geochemistry. Studies of this nature develop better conservation practices since the recharge area(s) of an aquifer can be more clearly defined. Continued comparison of water analyses from wells in the critical mixing zone at the interface of meteoric and connate water, provides data to prevent contamination of potable water.

(2) In the map area at least two sources or recharge areas (fig. 4) can be differentiated—one from the northwest and one from the southwest. These water masses can be traced until mixing erases or masks individual identity. Additional study might lead to improved conservation practices in the two watersheds.

(3) As connate water is displaced by meteoric water, the connate-meteoric interface migrates downdip. This migration results from high hydrostatic pressure existing in the artesian aquifer. In a "closed basin" system, the loss of connate water through seepage, springs, and uncapped wells, allows the downdip migration of the connate-meteoric water front. If fresh water wells of high capacity are permitted to produce near this zone, however, updip migration of this interface will occur. Fresh water production becomes critical near the connate-meteoric water interface.

(4) Permeability of the aquifer is reflected by ionic concentrations and temperature variations of the aquifer water. Where ionic concentrations and temperatures are high, permeability is low; low permeability retards water flow, reducing the effect of dilution and cooling by meteoric water. Conversely, where lower ionic concentrations and temperatures are measured, the permeability is normally high. In areas of high ionic concentration some chemical precipitation undoubtedly occurs; simultaneously, however, some minerals in the aquifer go into soultion resulting in fluctuating porosity and permeability of the aquifer. When deposition in the aquifer exceeds the solution of aquifer minerals, porosity and permeability decrease, but when solution exceeds deposition, support may be removed and pore spaces may collapse, again resulting in a decrease of porosity and permeability. Deposition and solution of the minerals within the aquifer must remain in a delicate balance; should this balance be upset, the Trinity sands will cease to function as efficient aquifers.

(5) An important immediate practical application of an investigation of this nature is knowledge of the chemical composition of the water before drilling. For domestic use, minor chemical variations are not critical; for industry, however, where the water must meet certain specifications, water composition is very important. By using maps similar to the ones in this study (figs. 5-17), well sites can be selected and the chemical composition of the water can be predicted before drilling. These predictions should be relatively accurate except in areas of faulting. Analyses in a fault zone do not show definite patterns since fracturing of the aquifer permits the intermingling of formational waters; analyses in such areas deviate from analyses in nearby unfaulted areas.

(6) As the demand for water supplies grows, further research is needed in the geochemistry of ground water. First, identification of water from a single unit of the aquifer should be attempted to determine vertical as well as lateral changes in composition. A study of individual aquifer units will lead to more accurate predictions of chemical composition. Future studies should include sampling and analyses made specifically for salinity mapping.

Second, some method of dating the water in an aquifer should be attempted. This may be done by the Carbon-14 method, utilizing filterable bacteria as a carbon source, or by radioactive trace elements such as tritium. Dating water will provide a check on the rate of migration which would provide a key to maximum permissible production of wells in any area.

Third, a test for trace elements, particularly heavy metals (because of the ease of detection), should be made. Such research might result in more accurate methods of predicting chemical content, as well as revealing the local mineralogy of the aquifer and underlying Paleozoic section.

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