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DISPERSION OF NATURALLY OCCURRING IONS IN GROUNDWATER FROM VARIOUS ROCK TYPES IN A PORTION OF THE SAN PEDRO RIVER BASIN, ARIZONA*

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Abstract: The groundwater in an alluvial basin in southern Arizona was analyzed for concentrations of Ca^{++}, Mg^{++}, Na^{+}, and Cl^{-}, ions.

The variety of rock types in the area, plus the undisturbed state of the groundwater basin, make comparative rock mineralization-groundwater ionization interpretations possible. Ionic dispersion in groundwater eminating from source areas composed of differing rock types is plotted as isogram maps. These isolated areas of differing mineral composition each exhibit a unique ionic contribution to groundwater. The ion concentrations in groundwater were then used as naturally occurring tracers to determine source areas of recharge and to delineate subsurface barriers to the normal basin flow net. Ion dispersion plots reveal the carbonates of the Dragoon Mountains to be a major contributor of Ca^{++} and Mg^{++} to the deep alluvial portion of the basin. Cl^{-} dispersion patterns show the granitic intrusives of the Tombstone Hills produce a barrier effect in the normal flow pattern of the basin as well as being a contributor of Cl^{-} to groundwater.

Introduction

The alluvium-filled valleys of the Basin and Range Province of the Southwest are huge natural storage reservoirs for groundwater. They typically are filled with a great depth of detrital material containing groundwater in storage. Various rock types make up the fault block mountains forming the boundaries of these basins. These mountainous ridges may be separated by great expanses of alluvium, thus isolating them and permitting the influence of the individual areas on the groundwater within the basin to be studied. Many of the basins are virtually undisturbed by groundwater withdrawal. The low permeability of the formations promotes slow movement of groundwater in the alluvium. This slow rate of groundwater movement permits a long period of contact with the various rock forming minerals; thus, their maximum

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influence on groundwater ionization will be effected. The deep section of unsaturated alluvium above the water table reduces chances of contamination from surface sources. These combined factors make rock mineralization-groundwater ionization analysis possible in basins of this type.

Groundwater movement in the basin was studied using dispersion of selected ions from isolated parent rock sources. Water quality analysis from wells in the basin revealed subsurface barriers and recharge areas.

Geology and groundwater

The upper San Pedro River Valley extends northward from the state of Sonora, Mexico, across the International Boundary, for approximately 45 miles along the San Pedro River (Fig. 1). The area is typified by fault-block

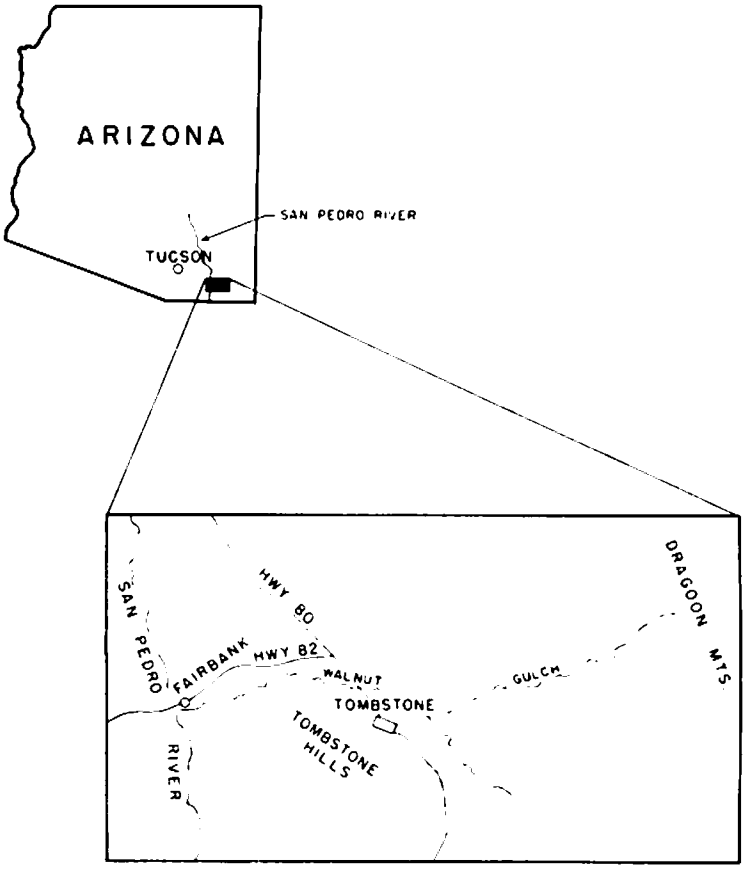

Fig. 1. Location map of study area.

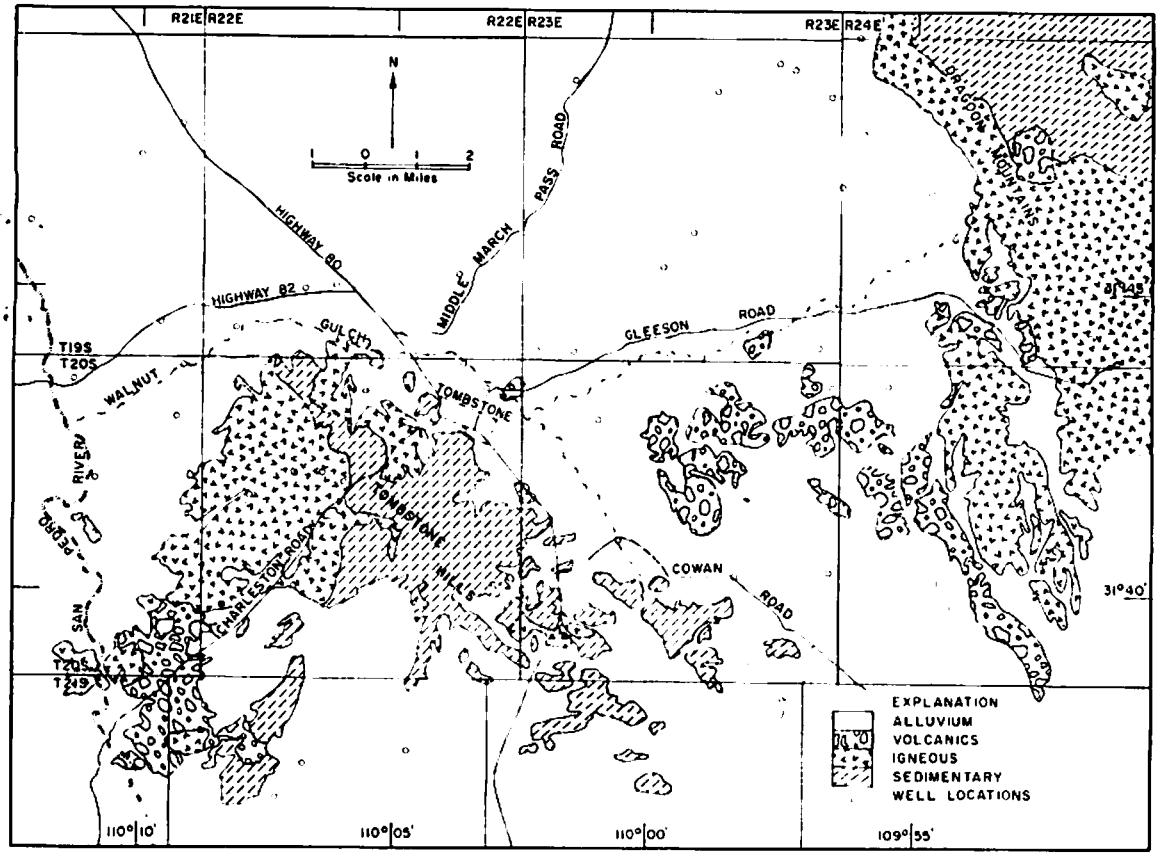

Fig. 2. Map of rock type distribution in study area.

mountains on either side of a deep alluvium-filled trough. The sloping pediment surface is interrupted in numerous locations by igneous intrusions.

The Dragon Mountains, which contain the highest peaks of the area, form the eastern boundary of the study basin (Fig. 2). Deep alluvium fills the major part of the basin, with the Tombstone Hills disrupting the pediment surface near the southern and western edge of the area.

The alluvial portion of the valley, as determined by gravimetric methods, varies in depth from less than thirty feet near the rock outcrops of the perimeter to a maximum depth of 3300 to 3400 ft. This huge volume of alluvium, with mountainous areas contributing recharge to it from locations around its outer edge, is the major aquifer of the study area. Drainage patterns in the alluvium are youthful and drain westward to the San Pedro River.

Section A–A′ (Figs. 3 and 4) shows the characteristic Basin and Range type faulting and igneous intrusions which produce the deep alluvial valleys associ-

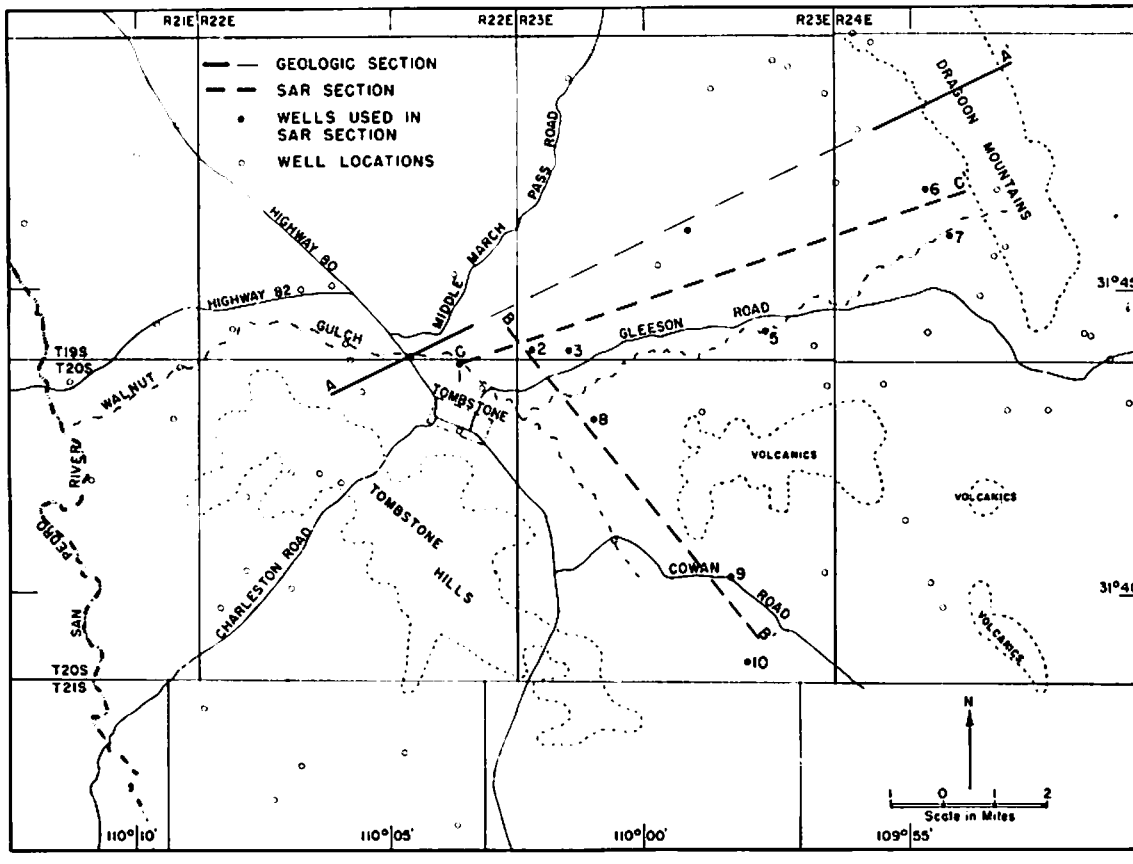

Fig. 3. Map showing well locations; also location of geologic section AA′ and sodium-absorption-ratio sections BB′ and CC′. Numbered wells represent wells used to compile SAR sections.

ated with this type of topography. The primary influence of the faulting on groundwater movement in the area is as a barrier, or partial barrier, to water movement. A large displacement fault east of Tombstone, in conjunction with the granitic intrusion northwest of the section, exerts considerable control on the direction of flow of groundwater. It was impossible to separate the influence each structure exerts on water movement and direction. However, their combined influence can be readily seen (Fig. 5) as groundwater contours near Tombstone deviate from their normal downslope trend in the valley.

By dividing the study area into generalized sedimentary, igneous, volcanic, and alluvial areas (Fig. 2), specific areas and rock types were isolated as contributors of certain representative ions to groundwater.

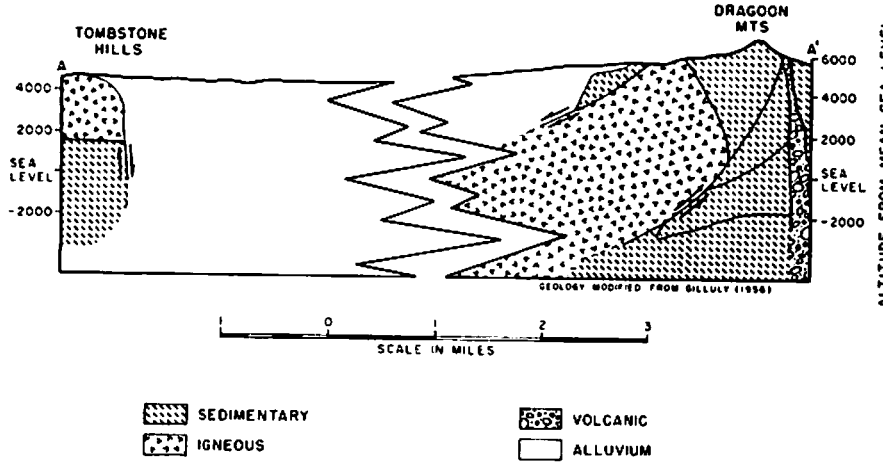

Fig. 4. Geologic section AA′, illustrating intrusive and fault-block boundaries of study basin.

The Tombstone Hills area, which borders the deep alluvium on the southwest, holds tremendous potential as a groundwater storage area. Highly shattered rock formations, cut by numerous dikes and intrusions, form an area which promotes infiltration and storage of groundwater. Due to this complexity of structure and the many perched water levels encountered in the vicinity, mapping of groundwater movement in the Tombstone Hills was impossible on anything except a regional scale.

A groundwater surface contour map compiled from well logs and structural geology maps is shown in Fig. 5. The water table exhibits a normal downslope gradient from the upland areas toward the axial river of the valley. The gradient increases considerably near the foothills of the Dragoon Mountains. The flow pattern is interrupted by a granodiorite intrusive which forms the northern part of the Tombstone Hills. This intrusive mass causes a north and westward deviation from the normal downslope trend.

A structural divide produced by limestone and andesite formations is located south and east of the Tombstone Hills. These formations lie at shallow depths here and create a subsurface barrier to water movement. Northward-moving groundwater drains toward Walnut Gulch and southward-moving groundwater drains toward a different drainage network to the south. Both drainages eventually lead to the San Pedro River.

In the deep alluvial area northeast of Tombstone, the sediments are stratigraphically nonuniform. Many of the formations are lensatic and reworked by changing drainage patterns and cyclic erosion and deposition. Thus, the alluvium has developed into a heterogeneous mass of sand layers,

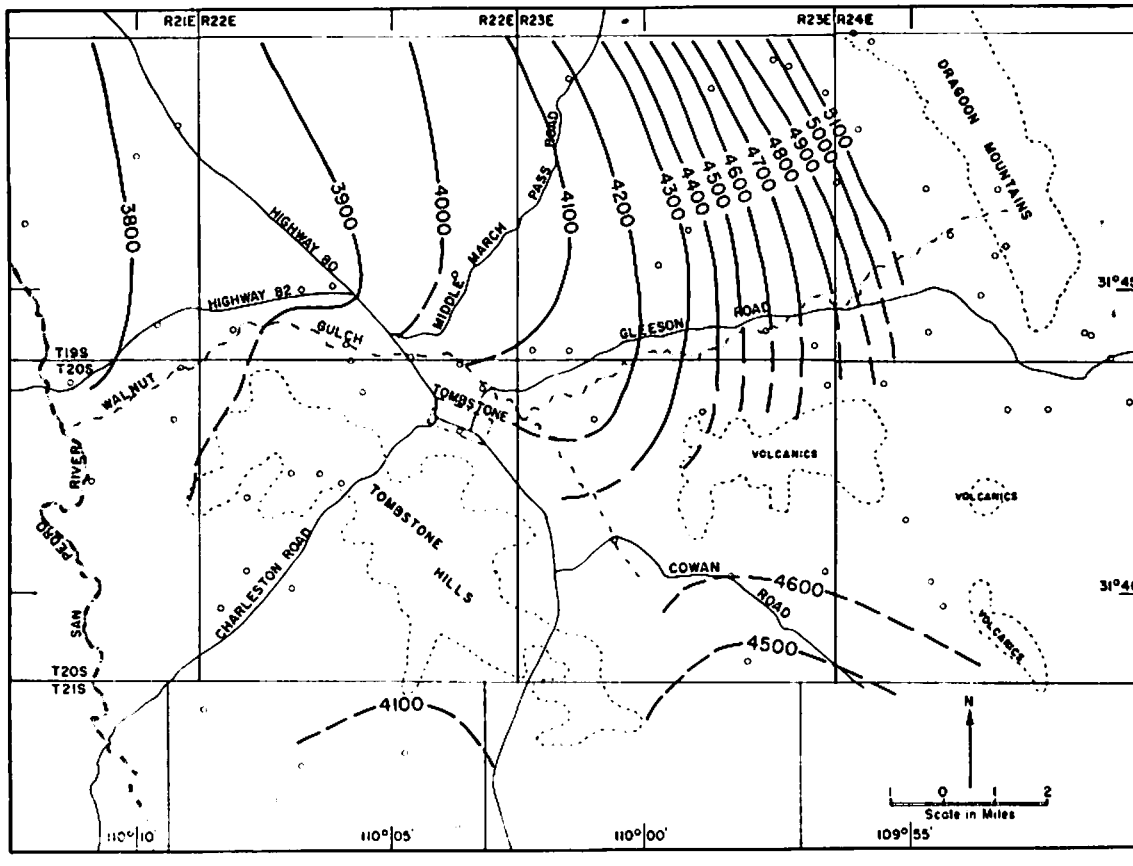

Fig. 5. Generalized groundwater contour map. Contours represent elevation above mean sea level.

gravel lenses, clay beds, and conglomerates. Of 82 available well logs, only two wells with an artesian head were noted. The largest was a 58-foot rise in water-table elevation after penetrating a conglomerate layer in the upland part of the basin. Thus, for studies of regional magnitude, the regional water table is considered as unconfined throughout the alluvial area.

For eight years of record observation wells have indicated an essentially static water table elevation in the basin. A small amount of recharge has been observed beneath ephemeral streambeds near the central portion of the valley. Here the regional water table is less than 160 ft, and mounding of transmission loss water on the water table has been recorded[1,2]). Although exact quantities of recharge from this source are not yet avilable, it is small when compared to the total volume of water in storage within the alluvium.

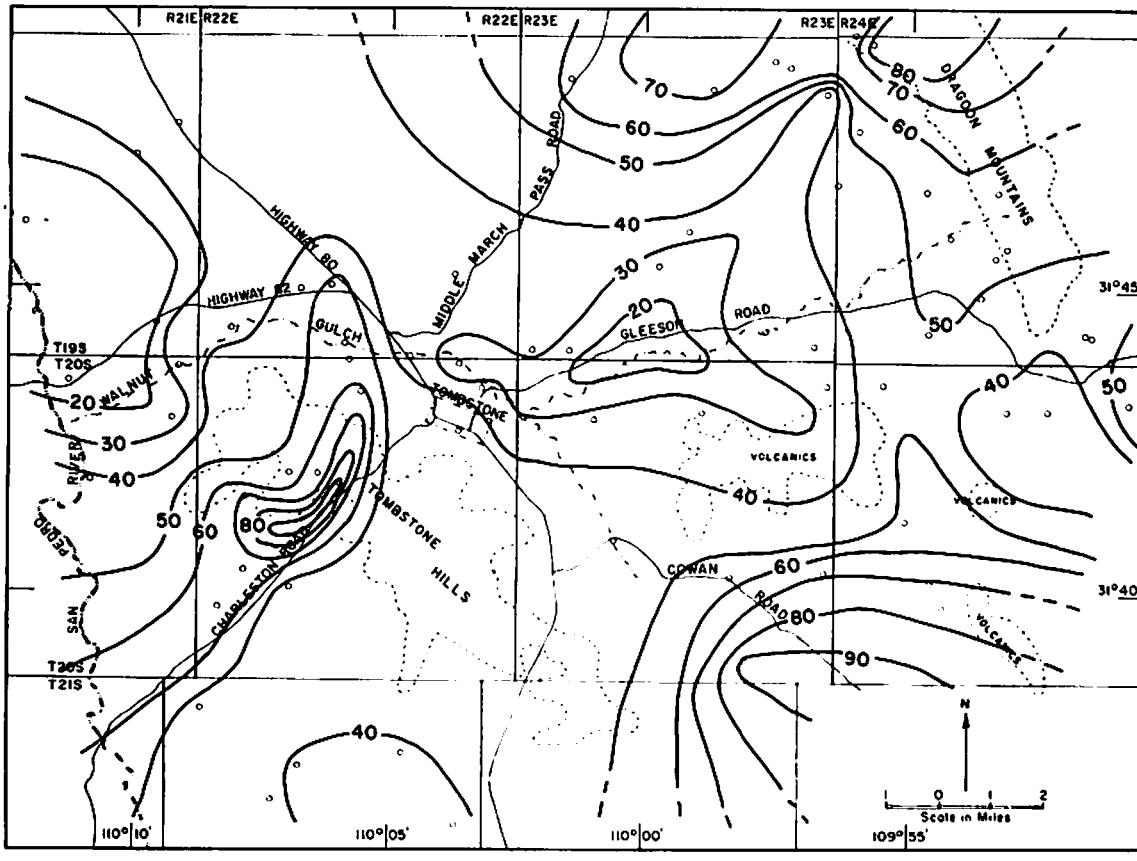

Fig. 6. Map showing Ca^{++} distribution (ppm) in groundwater.

Analysis of ionic concentration and distribution in groundwater

SAMPLING PROCEDURE

Seventy-nine water samples were collected and analyzed during this investigation. Sampling sites are shown on Fig. 3. Samples from open wells were taken with a shop-built sampler consisting of a short tube with check valves at both ends. This tube was lowered into the well and oscillated up and down to collect a water sample. Samples were collected from pumping wells whenever possible; if this was not possible, a dip sample was taken from the storage tank in connection with the well, or the sampler was used. Forty-three of the samples were pumping samples, 22 were dip samples, and 17 were taken by the well sampler. The locations of all wells sampled are shown in Fig. 4.

All samples were collected in sterile plastic bottles, which were tightly sealed until the laboratory analysis was made.

CALCIUM (Ca^{++})

Calcium ion concentration in groundwater decreases in relation to increasing distance from the source areas in the Dragoon Mountains and Tombstone Hills (Fig. 6). This isogram map closely follows the groundwater contour map for the basin. Drainage from the upland recharge areas moves downward into the deep alluvium of the basin where mixing of waters of differing ionic concentration tends to reduce the Ca^{++} concentration. Intermingling of recharge water from the volcanics south and west of the limestone areas also lessens the Ca^{++} concentration, as the andesite-rhyolite formations are resistant to weathering and contain few readily soluble sources of calcium. An increased Ca^{++} concentration to the south and east is due to groundwater being diverted southward by the volcanic formations and migrating through an underlying highly-fractured and jointed limestone.

The Ca^{++} high centered in the Tombstone Hills first appears to be eminating from an igneous mass, as indicated by the rock type map. However, percolation of water through the shattered limestones near the contact of the two rock types is the source of the high Ca^{++} content water. The water

TABLE 1

Sodium-absorption-ratio values for wells from sections BB′ and CC′

SECTION BB′ (Values in equivalents per million)					SECTION CC′ (Values in equivalents per million)				
Well No.	Na	Ca	Mg	SAR	Well No.	Na	Ca	Mg	SAR
1	6.2	13.0	0.54	2.38	10	0.39	47.3	0.63	0.08
2	5.2	16.3	1.1	1.76	9	0.69	30.0	1.20	0.17
3	6.1	14.6	1.0	2.18	8	0.69	16.2	0.66	0.24
4	5.1	16.3	0.79	1.76	3	6.10	14.6	1.00	1.00
5	7.5	17.5	0.52	2.50	2	5.20	16.3	1.10	1.10
6	0.8	27.9	2.34	0.21	1	6.20	13.0	0.54	0.54
7	2.5	30.6	1.09	0.62					

then continues downslope along fracture planes and jointing in the granitic intrusion. Apatite, an abundant accessory mineral of the intrusion, may contribute small amounts of Ca^{++} as a product of rock alteration.

In water quality studies in arid or semiarid areas, base exchange reactions

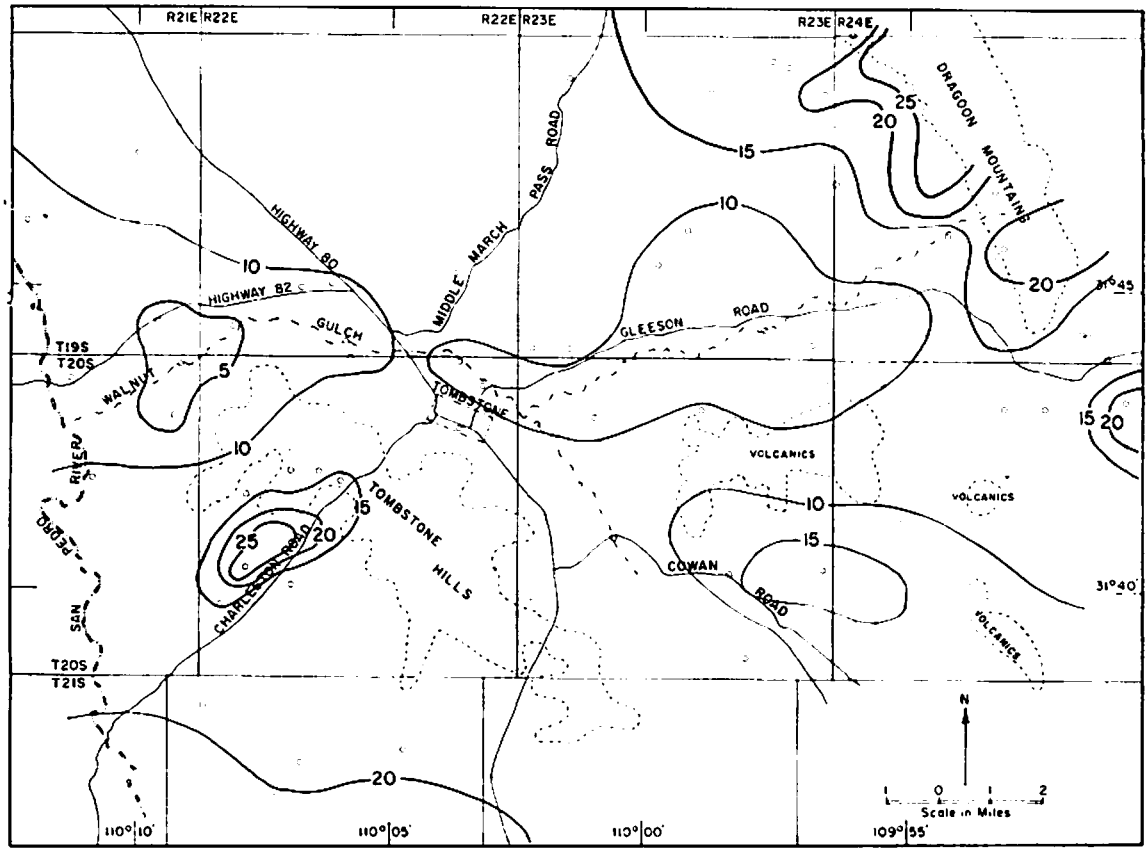

Fig. 7. Map showing Mg^{++} distribution (ppm) in groundwater.

must be carefully considered. Water containing calcium and bicarbonate can be altered to one containing sodium and bicarbonate[3]). Certain clay minerals such as montmorillonite have high capacities for base exchange. Thus, when dealing with waters containing variable amounts of calcium, sodium, and magnesium, base exchange reactions must be suspected.

Sodium-absorption-ratios (SAR) sections were constructed traversing the recharge areas in the mountains and continuing outward into the deep alluvial fill of the central basin (Fig. 3). These sections, computed using the standard sodium-absorption-ratio (SAR) formula:

$$SAR = \frac{NA^{+}}{\sqrt{\frac{1}{2}(Ca^{++} + Mg^{++})}}$$

indicated very little base exchange reaction. As shown in Table 1, SAR varies from .08 to 2.5 for all sections constructed.

MAGNESIUM (Mg^{++})

Mg^{++} distribution in the groundwater, in expected lesser quantities closely paralleled the Ca^{++} concentration patterns (Fig. 7). Subsurface limestones and andesites to the south and west of the Dragoons produce some concentrations of Mg^{++}. The highest Mg^{++} concentrations, however, are in areas in which limestones and granitic rocks coexist. A biotite-augite quartz-monzonite has been implaced along the western edge of the lower Dragoon Mountains. A similar situation exists in the Tombstone Hills, with a hornblende-biotite granodiorite intruding limestones. Both igneous intrusives are coarse grained and susceptable to alteration of the mafic minerals by hydrometamorphism. Biotite and olivine alteration to serpentine is prevalent in both rock types[4]). This alteration of mafics, combined with the Mg^{++} derived from the associated limestones, tends to increase the Mg^{++} concentration in these areas above that derived from areas in which limestone alone is the source of Mg^{++} in the groundwater. Thus, the granitic rock types of the study area are classified as significant contributors of Mg^{++} to groundwater.

SODIUM (Na^{+})

Three major concentrations of Na^{+} are present in the study area (Fig. 8). In the eastern portion of the isogram map, the coarse-grained quartz-monzonites of the lower Dragoon Mountains are the Na^{+}-producing rock type. The large feldspar crystals are decomposed by water containing carbon dioxide to give silica, sodium carbonate and clay minerals[5]). This alteration of feldspars, along with development of chlorite and epidote after the mafic minerals, is also found in core samples from a granitic intrusive northwest of Tombstone. This intrusive is responsible for the minor concentration high, directly west of the city of Tombstone.

An area of greater Na^{+} concentration and much larger areal extent lies north and west of Tombstone. Highly altered volcanic rocks are present at varying depths throughout the area. The formation is almost exclusively andesitic flow breccia, with the dominant primary minerals being plagioclase and hornblende. Alteration has progressed to such an extent that only pseudomorphs of these primary minerals are left. These volcanics underly the alluvium at shallow depths near the San Pedro River in the area directly north of Fairbank. A lessening of Na^{+} concentration in a northeasterly direction is a direct reflection of a deep trough in the basement complex (deter-

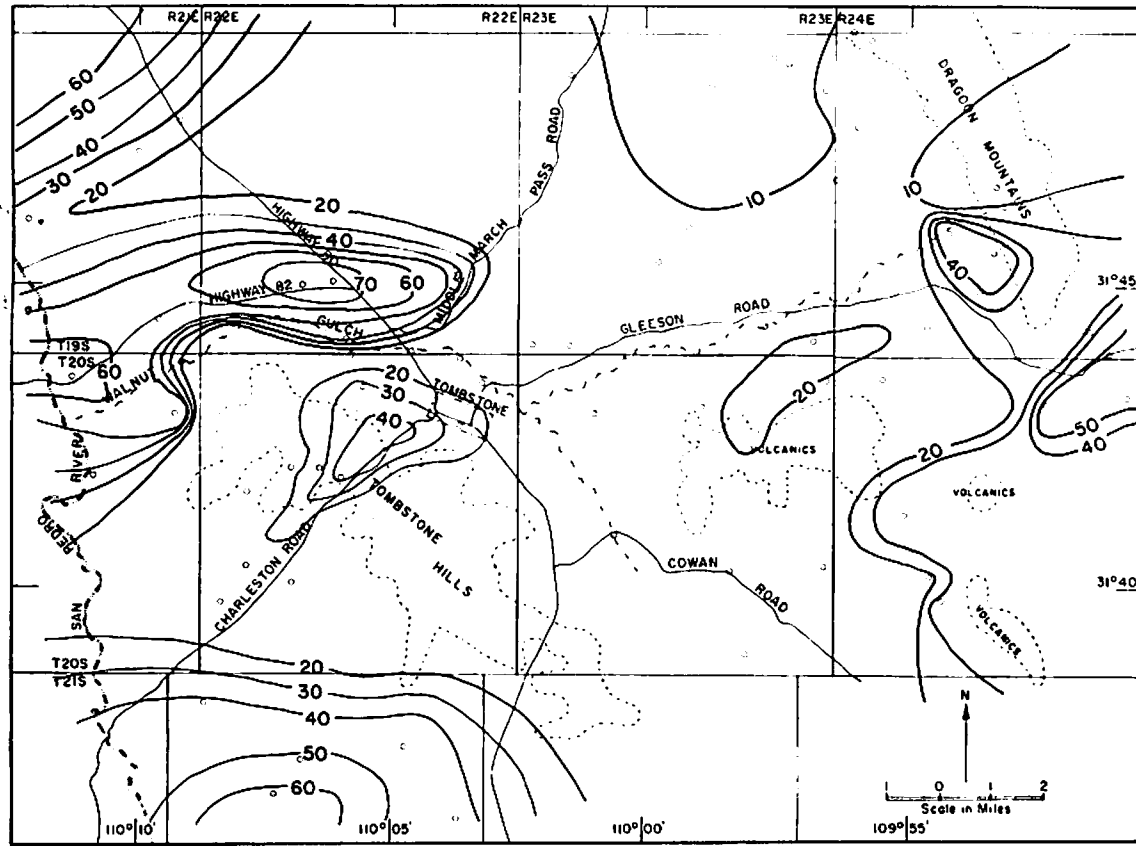

Fig. 8. Map showing Na^+ distribution (ppm) in groundwater.

mined by prior seismic work) extending from near the river outward into the basin. Subsurface flow from the river thus dilutes the Na^+ concentration along the axis of the trough.

The third area of higher Na^+ concentration is in an area south of the Tombstone Hills. This area is underlain by the previously mentioned volcanic formation. The volcanics are at shallow depths along the east side of the river which effectively prevents recharge from the river and also creates a partial confining effect on normal downslope draining of groundwater. Thus, groundwater is forced to flow nearly parallel to the river until out of the influence of the volcanics.

CHLORIDE (Cl^-)

Cl^- concentration of more than 5 ppm is unusual in natural waters from humid areas. Groundwater associated with igneous rocks is generally low in

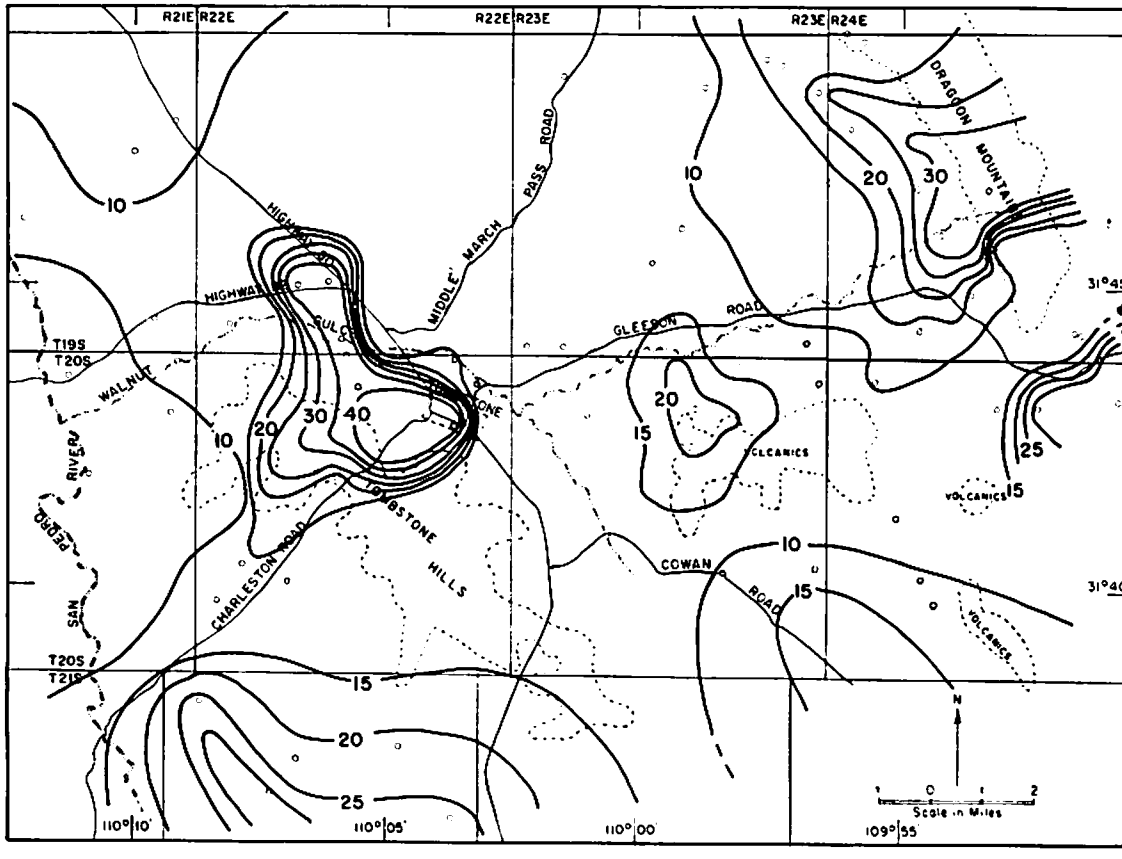

Fig. 9. Map showing Cl^- distribution (ppm) in groundwater.

Cl^- [6]). One area in the Tombstone Hills, however, gives chloride values in groundwater of up to 40 ppm (Fig. 9). This area is coincidental with two large granitic intrusions, a granodiorite and a quartz-latite porphyry. Both rock types are rich in hornblende, biotite, and augite. The granodiorite is especially susceptible to alteration processes, with the quartz-latite porphyry altering on a much lesser scale [4]). Hydrothermal alteration has altered many of these mafic minerals to chlorite and epidote [7]). Alteration has penetrated to considerable depth along jointing planes and fractures in the intrusions, as determined from core-drilling logs of the area. This breakdown of the rock-forming minerals is the major source of Cl^- from this area. Sedimentary rock type areas were observed to be lower in Cl^- concentration than the igneous complexes. The rather complete breakdown of the associated feldspars can be observed in the trend of Ca^{++}, K^+, and Na^{++} concentrations. Movement of groundwater down the subsurface slopes of the dome-like

intrusion carries these ions north and west, which results in the high Cl^- concentrations being recorded in wells northwest and west of the intrusion.

Results

The study area can be divided into two major divisions: one in which the ion concentration of the groundwater is controlled by igneous rock types; and the other which is influenced mostly by sedimentary rocks. The igneous classification includes the granodiorites, quartz monzonites, and quartz latite porphyrys of the area. The granodiorite, which is one of the two major igneous intrusions of the Tombstone Hills, is rich in augite, hornblende, and biotite, and is the major source of chloride ion in the area. The other igneous intrusion in the Tombstone Hills is a quartz latite porphyry, which appears to contribute chloride ions to a lesser degree than the granodiorite due to different compositional and weathering characteristics.

The chloride-rich water from the granodiorite area has migrated north and westward from its source. It seems to be a movement controlled by the natural groundwater gradient, with the chloride ion concentration decreasing due to mixing with the groundwater in the deeper alluvium. This is again evidenced in the eastern portion of the valley. There, quartz monzonite is the major source of chloride, with concentrations decreasing with increasing distance from the source. Geochemical dispersion in the groundwater, plus some recharge through the alluvial fan material near the mountains, both contribute to the lessening of the Cl^- concentration.

An area of high cloride ion concentration that appears to be unrelated to these igneous rock types occurs in the southwestern part of the area studied. Here, chloride is believed to be derived from evaporites with some contribution from volcanics underlying the area.

Sedimentary rock types that influence ion concentrations in the study area consist largely of limestones, with lesser amounts of dolomite and limestone alteration products.

Calcium ion is widespread throughout the valley, and massive formations of limestone are found in many portions of the area under study. Because of its stronger tendency to remain in solution, magnesium ion is present in concentration below that of calcium.

The concentration of calcium is greatest in and near the outer portions of the basin, decreasing in quantity as the groundwater proceeds outward into the alluvium of the central part of the valley and northwestward around the Tombstone Hills. Here, mixing due to recharge from surrounding areas, as well as the formation of caliche conglomerates, lessens the Ca^{++} concentration. Base exchange reactions in the alluvium were not involved to any

extent, as sodium-absorption-ratio data from the basin (Table 1) indicated very little ratio change as groundwater moves outward from the mountainous areas into alluvium. Concentrations of calcium and magnesium serve as excellent tracers for the groundwater flow pattern in this particular case.

An isolated area in the Tombstone Hills exhibits an abnormally high concentration of calcium and magnesium. As stratigraphic logs are not available for wells in this area, it is hypothesized that a local bed or formation is responsible for these higher concentrations of calcium and magnesium. The area is highly shattered and faulted, thus making correlations difficult with the limited data available.

Sodium concentrations are difficult to correlate with a particular rock type in this area. It appears that the granitic rocks in the Dragoon Mountains and Tombstone Hills are sources of sodium. In the isolated basin area south of the Tombstone Hills the higher concentration of sodium is attributed to contact with subsurface volcanics plus the possibility of contact with evaporites, particularly sodium chloride.

Conclusions

Naturally occurring ions in the groundwater of an alluvium-filled basin were usable in determining subsurface flow patterns. The isogram maps of calcium and magnesium exhibited the best evidence of ionic concentration diminishing in strength from source areas. The lower Dragoon Mountains and limestones in the south-central portions of the area studied are the major calcium and magnesium ion contributors. Groundwater movement diffuses the ion concentration as the water proceeds outward from the mountains. Near the Dragoon Mountains recharge through the coarser alluvial material helps diminish the ion concentration of groundwater derived from the massive limestone areas. The influence of the Tombstone Hills on the subsurface flow pattern was also confirmed by tracing the diminishing calcium and magnesium ion concentration in the water.

The influence of the granodiorite was clearly evident in the isogram map of chloride concentration. This intrusion is the major source of chloride ion in the Tombstone Hills; subsurface water movement through the basin alluvium lessens the ion concentration as distance from source areas increases.

The geochemical survey data, combined with structural geologic interpretations, indicate a barrier to subsurface flow in an area south and east of the Tombstone Hills. Here, massive limestones and volcanics lie at shallow depths beneath the alluvium. These formations create a disconnected basin with groundwater flow interrupted and ionic concentration determined

by subsurface flow from the northwest through volcanics and from the north and east through shattered limestones.

Acknowledgements

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