Aqueous Geochemistry of the Magothy Aquifer, Maryland

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Abstract

The Upper Cretaceous Magothy Formation of the Atlantic Coastal Plain is a seaward-dipping strand-zone deposit of fluviomarine origin that crops out in an irregular belt in Maryland. Southwest of the outcrop, the Magothy Formation is overlain by younger strata. Chemical analyses of water samples from the Magothy aquifer, Maryland, indicate several hydrochemical facies. The origin of these hydrochemical facies is related to the source of recharge and the chemical processes that occur as water flows downgradient.

Region I contains the outcrop of the formation. In Region I, ground water is derived from precipitation on the outcrop and is characterized by dissolved calcium, bicarbonate, sulfate, and iron. These ions are the products of reactions among H_2O, CO_2, O_2, and minerals in the aquifer; these reactions include incongruent dissolution of potassium feldspar, plagioclase, and mica, oxidation of pyrite, and oxidation-reduction reactions involving lignite and dissolved iron and sulfur species. The ground water in Region I travels relatively short distances (less than 30 mi) and discharges into Chesapeake Bay and its tributaries.

Region II is underlain by the buried Magothy aquifer; the sole source of water to the recharge area of the Magothy aquifer in this region is downward leakage of calcium bicarbonate water from the Aquia aquifer. Dissolved CO_2 and O_2, commonly associated with recharge from atmospheric precipitation, react with minerals in the Aquia aquifer and are consumed before reaching the Magothy aquifer. As water moves downgradient, calcium replaces sodium on clay-mineral exchange sites and the water takes on a sodium bicarbonate character. In the downgradient part of Region II where CO_2 is added to ground water by anaerobic microbial activity, carbonate dissolution may occur; however, dissolution of silicate minerals is more likely. Ground water in this region travels relatively long distances (up to 50 mi) and discharges through upward leakage into overlying units.

INTRODUCTION

Purpose and Scope

This report describes the partial results of a study by the U.S. Geological Survey to define the geology, hydrology, and geochemistry of the northern Atlantic Coastal Plain aquifer system (Meisler, 1980). The study is part of a national program entitled "Regional Aquifer-System Analysis (RASA)." As part of this study, water-quality data were analyzed to document the distribution of dissolved chemical constituents and hydrochemical facies in the Magothy aquifer, Maryland, and to demonstrate their relation to aquifer recharge, mineralogy, and ground-water flow patterns. Where applicable, reactions are formulated to explain the observed changes in water chemistry.

The majority of the chemical analyses of ground water used in this report were taken from the National Water Data Storage and Retrieval System (WATSTORE) maintained by the U.S. Geological Survey. Most of the analyses were previously published by the Maryland Geological Survey (Woll, 1978) and were collected using standard U.S. Geological Survey methods (Brown and others, 1970; Wood, 1976). Additional sampling was accomplished during the summer of 1982, and field measurements were made of ground-water temperature, pH, alkalinity, specific conductance, and concentrations of total iron (Fe_T) and dissolved oxygen (O_2).

Activities, molalities, and log activity ratios of dissolved constituents in water from the Magothy aquifer were calculated using the computer program WATEQF (Plummer and others, 1978).

Geographic and Geologic Setting

The northern Atlantic Coastal Plain is underlain by a wedge-shaped body of interbedded clay, silt, sand, and gravel that thickens to the southeast. The beds dip gently seaward. The unconsolidated sediments are of marine and nonmarine origin and range in age from Jurassic(?) to Holocene.

The Magothy Formation in Maryland is a strand-zone deposit of fluviomarine origin. It crops out in an irregular belt in Prince Georges, Anne Arundel, Kent, and Cecil Counties. South of central Prince Georges County, it is entirely overlain by younger strata (Hansen, 1972, p. 49). The outcrop of the formation and the boundary of the aquifer, along with location of the ground-water sampling sites, are shown in figure 1.
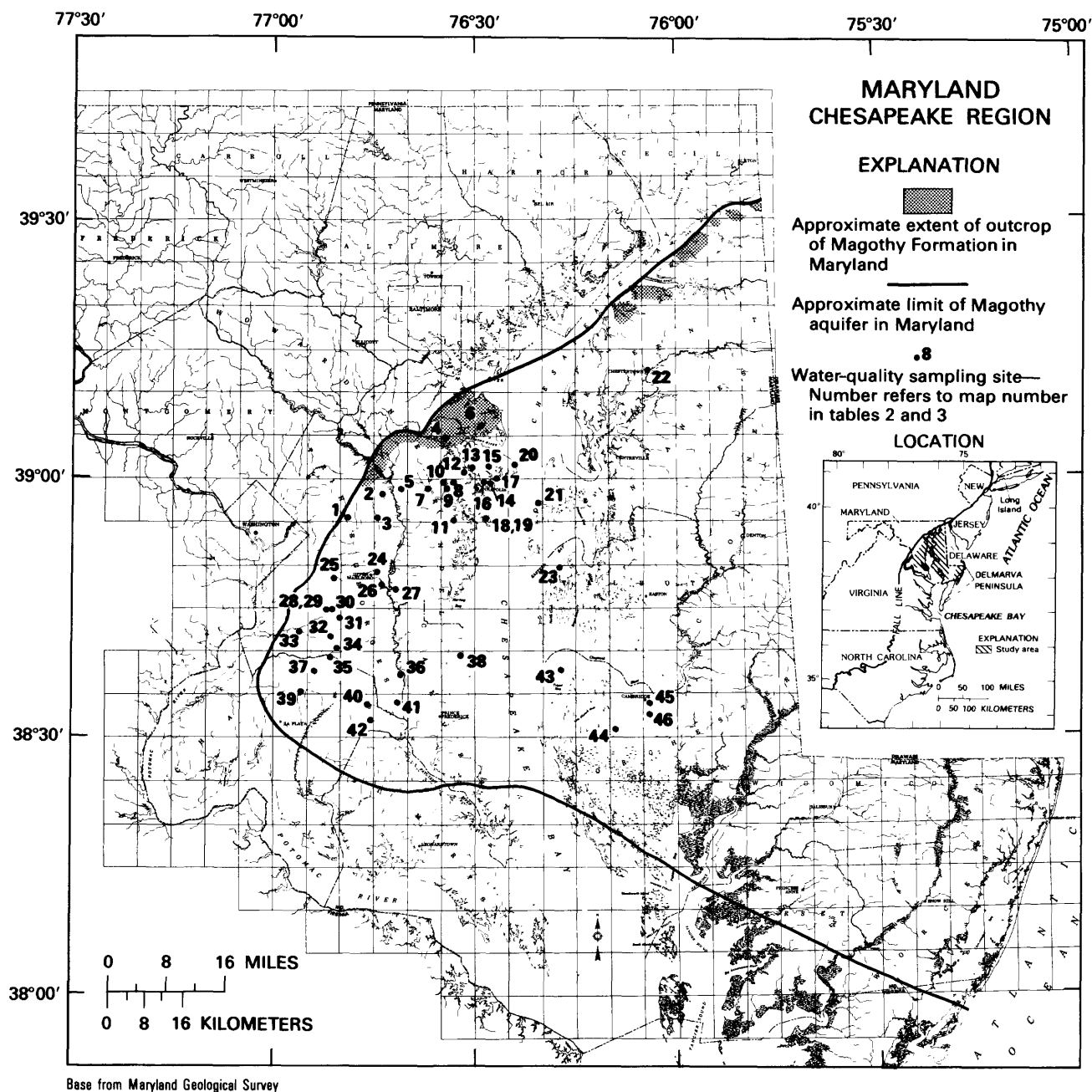
Figure 1. Location of outcrop of Magothy Formation, boundary of Magothy aquifer, and water-quality sampling sites.

The Magothy Formation is generally considered to be Late Cretaceous in age; it is overlain by the Severn Formation of Late Cretaceous age and underlain by the Potomac Group of Early and Late Cretaceous age. The stratigraphy of the coastal plain sediments in the recharge areas of the Magothy aquifer (Regions I and IIA, discussed later in this report) is summarized in table 1. For the purposes of this report, the term "Magothy aquifer"

refers to the Magothy Formation as described by Hansen (1972, p. 46–49).

Acknowledgments

Table 1. Stratigraphy of Cretaceous and Tertiary sediments in recharge areas for the Magothy aquifer (Regions I and IIA)
[Delineation of regions is shown in figure 3]

| System | Series | Group or Formation | | Mineralogy |
		Region I	Region IIA	
Tertiary	Paleocene	Not present where Magothy Formation crops out	Aquia and Brightseat Formations, undifferentiated	Greenish-black to gray sand and silt. Quartz most common mineral; also glauconite. Shell beds and calcite cementation common.
Cretaceous	Upper Cretaceous		Severn and Matawan Formations, undifferentiated	Dark- to medium-gray sand, silt and clay. Quartz most common mineral; also glauconite, sparse lignite and mica.
		Magothy Formation	Magothy Formation	Light-gray and white to dark-gray sand and clay. Quartz most common mineral; some feldspar, mica, pyrite, limonite and lignite.
	Lower Cretaceous	Potomac Group, undifferentiated	Potomac Group, undifferentiated	Light-gray to yellowish-red interbedded silt, sand and clay. Quartz most common mineral.

Chapelle, William Back, Don A. Vroblesky, and William B. Fleck of the U.S. Geological Survey.

MINERALOGY AND MINERAL STABILITY

The Magothy aquifer consists largely of quartz sand and gravel (about 75 to 86 percent), with interbedded clay layers (about 14 to 25 percent). The aquifer ranges in thickness from a featheredge at the western edge of the outcrop to 150 ft (feet) near Annapolis, Md. (Otton, 1955, p. 56–68; Glaser, 1969, fig. 31), and generally becomes finer upwards. The sand-to-clay ratio decreases to the east (fig. 2).

Otton (1955) noted that arkosic sand is common in the Magothy aquifer, and microscopic examination of cores and drill cuttings indicates the presence of plagioclase feldspar, muscovite, and traces of biotite. However, Glaser (1969, table 3) examined four samples from the Magothy outcrop and noted that feldspar was absent. Small amounts of potassium feldspar were identified in a core sample composed primarily of quartz sand from a well at Cambridge, Md. (Trapp and others, 1984, table 13). X-ray analysis of the clay fraction of a subsample from the same zone of the Cambridge well indicates that kaolinite and montmorillonite are the predominant clay types.

Carbonaceous material, lignite, and pyrite (Bennion and Brookhart, 1949, p. 46; Glaser, 1969, p. 43) as well as mica and feldspar (Otton, 1955, p. 294) are associated with the clay. Other iron minerals present in the Magothy aquifer include marcasite, hematite, magnetite, ilmenite, siderite, and ferric oxyhydroxides. Back and Barnes (1965, p. C6) use the term "limonite" to indicate the presence of undifferentiated iron oxides. In addition to these minerals, the Magothy contains trace amounts of epidote, garnet, chloritoid, staurolite, kyanite, sillimanite, tourmaline, rutile, zircon, brookite, anatase, sphene, and monazite (Glaser, 1969; Trapp and others, 1984).

The concentrations of inorganic constituents in ground water are controlled by the type, abundance, and reaction rates of minerals in the aquifer. Nearly all minerals react with ground water to some extent; however, minerals that react slowly have less effect on the chemical composition of ground water than do minerals that react rapidly (Chapelle, 1983, p. 546). Goldich (1938) studied the weathering of igneous and metamorphic rocks and proposed a silicate mineral-stability series associated with rock weathering. He attributed the differences in mineral stability to the changing equilibrium conditions during formation of the minerals (such as changing temperature and pressure in a magma), which have been described by Bowen (1922). Goldich (1938, p. 56) suggests that equilibrium conditions at the time of silicate-mineral formation are significantly different from surface conditions and that this is the reason for mineral weathering and the variability in rates of mineral weathering. For example, plagioclase is less stable under surface conditions than potassium feldspar, which in turn is less stable than crystalline quartz (Goldich, 1938, p. 56).

Garrels (1976, p. 76–78), on the basis of normative mineral calculations, inferred a "'rank list' of minerals and their relative rates of reaction." This list is in general agreement with Goldich's (1938, p. 56) stability series. Conversely, other minerals, such as calcite and pyrite, that are formed at or near the Earth's surface, do not undergo large changes in temperature and pressure. The stability of these minerals is influenced more by changes in pH and concentrations of dissolved gases, such as carbon dioxide (CO_2) and oxygen (O_2). In general, however, calcite (Stumm and Morgan, 1981, p. 544, 545) is more prone to weathering than are feldspar minerals.

The relative abundance of minerals in an aquifer also has an effect on water chemistry. For example,
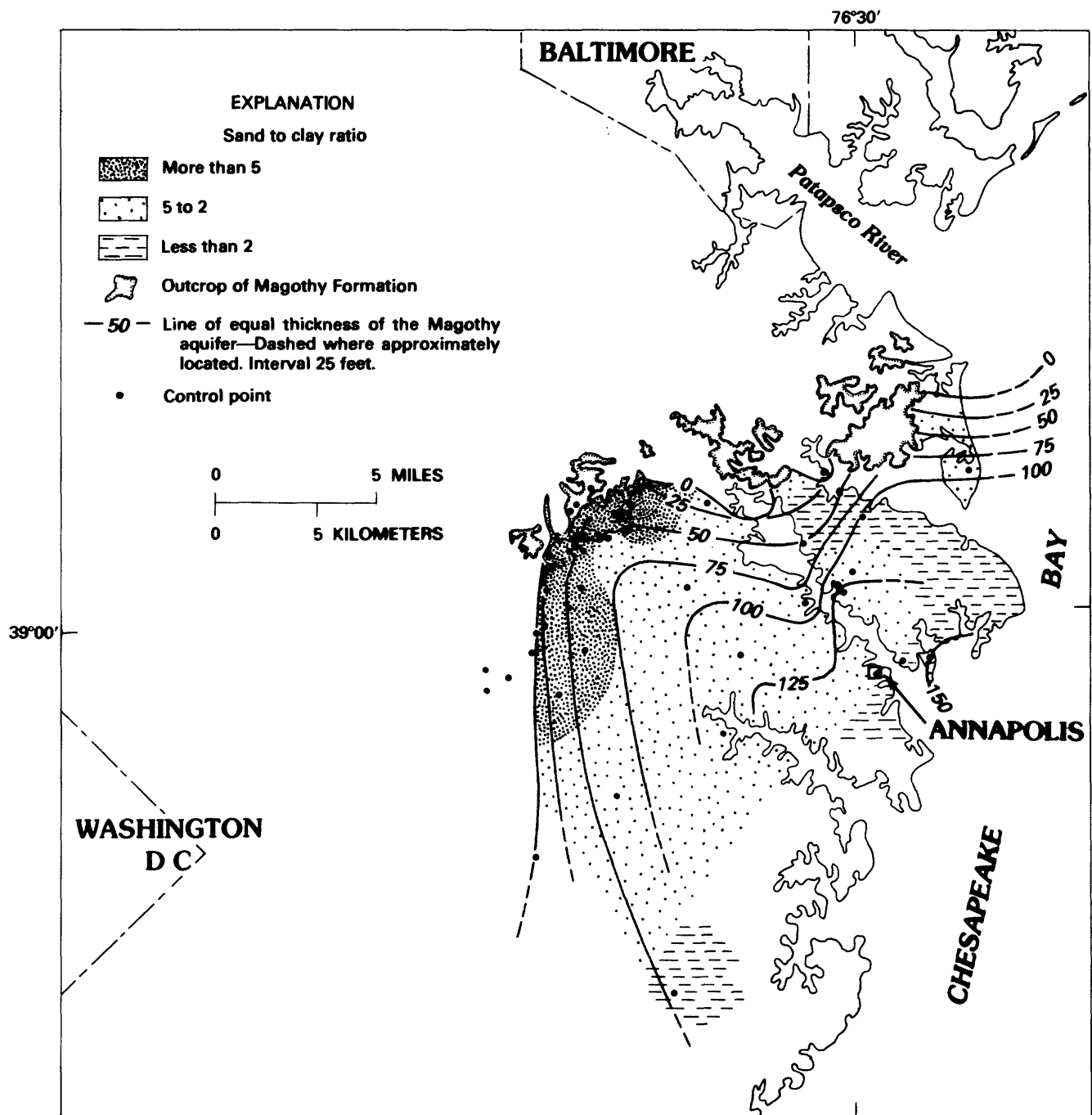
Figure 2. Sand-clay ratio and thickness of the Magothy aquifer in the vicinity of Annapolis, Md. (modified from Glaser, 1969, fig. 31).

Garrels (1976, p. 77) concluded that the rate of alteration of hornblende in a rhyolite is greater than that of plagioclase feldspar (on the basis of normative mineral calculations), even though the calculations indicate that plagioclase makes a larger contribution of ions to the reconstructed water chemistry. These observations and the fact that the predominant mineral in the rhyolite is plagioclase indicate that dissolution of minerals that con-

stitute a large percentage of the parent material (but are less reactive) can contribute to water chemistry. Therefore, in this report it is assumed that Magothy aquifer water chemistry is dominated by the faster reacting and more abundant minerals and that the effects of slow-reacting minerals are negligible.

Quartz is the most abundant mineral in the sand and gravel of the Magothy aquifer. However, dissolved

silica is mostly derived from the incongruent dissolution of faster reacting aluminosilicate minerals (Garrels and MacKenzie, 1967, p. 241) because quartz reacts slowly with water. As a result, quartz is considered nonreactive in this report. Garrels (1967, p. 409; 1976, p. 76–78) notes that the silicate minerals biotite and plagioclase react relatively rapidly with ground water to produce the more stable clay minerals and the following dissolved constituents: sodium (Na^+), magnesium (Mg^{+2}), calcium (Ca^{+2}), bicarbonate (HCO_3^-), and silica (SiO_2). Similarly, microcline adds potassium (K^+) to ground water even though the relative reaction rate is lower than biotite and plagioclase (Goldich, 1938, p. 56; Garrels, 1976, p. 76–78). Other oxide and silicate trace minerals mentioned earlier generally are found in such small quantities in the Magothy aquifer that they are considered insignificant for the purposes of this report.

An important source of CO_2 to ground water is soil gas that reacts with rainwater percolating through the unsaturated zone (Pearson and Friedman, 1970, p. 1780). Additionally, Foster (1950, p. 40) proposed that CO_2 can be generated by slow "dynamochemical" changes (inorganic processes acting on lignitic material because of increased temperature and pressure) in deep aquifers. Chapelle and Knobel (1985, p. 598, 599) suggested that the diagenesis of carbonaceous material, such as lignite, by methanogenic bacteria may be a significant source of CO_2 to ground water. As a result of these observations, the Magothy aquifer is considered to be an open system with respect to CO_2.

The most common form of ferric iron in natural waters is probably the ferric oxyhydroxide species ($FeOOH$), which reacts similarly to ferric hydroxide, $Fe(OH)_3$, and its varying dehydration products. These commonly form relatively stable colloidal suspensions that, with time, can settle and recrystallize to hematite, Fe_2O_3, or other iron minerals. In addition, oxidation of pyrite (FeS_2) can be expected in environments rich in dissolved oxygen. Pyrite and ferric hydroxide are assumed to be the reactive phases with respect to iron in the Magothy aquifer. For a more detailed discussion of iron chemistry, see Hem and Cropper (1959), Barnes and Back (1964), Langmuir (1969), and Chapelle (1984).

GROUND-WATER FLOW

The Magothy Formation is a water-table aquifer where it crops out (fig. 1) and an artesian aquifer where it is buried by confining beds. Flow direction within the aquifer is indicated by the prepumping potentiometric map shown in figure 3, which resulted from a steady-state computer simulation (William B. Fleck and Don A. Vroblesky, U.S. Geological Survey, written commun., 1985). The potentiometric surface is in general agreement with historical water levels published by Darton (1896), Clark and others (1918), and Otton (1955). In areas where the aquifer crops out, the flow patterns are dominated by potentiometric highs and flow is to either the northeast or the southwest, where water discharges into Chesapeake Bay and the Patapsco River. In the area southeast of Washington, D.C., a major potentiometric high is produced by downward leakage from the Aquia aquifer in the Aquia Formation through the silts and clays of the Brightseat, Severn, and Matawan Formations (Hansen, 1972, p. 53). The direction of ground-water flow is toward the southeast, and discharge is upward into the overlying hydrologic units of the Delmarva Peninsula (Trapp and others, 1984, p. 36).

The Magothy aquifer can be divided into geographical regions on the basis of ground-water flow patterns and the source of recharge to the aquifer. The area in which atmospheric water enters the aquifer through the outcrop belt and flows down the hydraulic gradient, discharging into Chesapeake Bay and the Patapsco River, is designated Region I. The area in which water enters the Magothy through downward leakage from the Aquia aquifer and flows southeastward toward the Delmarva Peninsula is Region II, which has been subdivided into Regions IIA, IIB, and IIC. These subdivisions are discussed subsequently in this report. The locations of Region I and subdivisions of Region II are shown in figure 3. The separation of waters in Regions I and II results from the divergence of flow lines in the aquifer system (fig. 3). Hence, only a minimal amount of mixing occurs at the boundary of the two regions.

ION DISTRIBUTION

The evolution of water chemistry in the direction of ground-water flow is shown by graphs of ionic concentrations as a function of distance along a flowpath (figs. 4–7). Distance of each sample location with respect to a flowpath was estimated from the simulated prepumping potentiometric-head map of the Magothy aquifer (fig. 3). The northern limit of the outcrop and areas of potentiometric highs at the aquifer boundary were arbitrarily defined as the starting point for measuring distance.

The concentrations of HCO_3^- as a function of distance along a flowpath in the Magothy aquifer are shown in figure 4. Figure 4 indicates that HCO_3^- concentrations can be divided into two distinct groups, one group ranging from 0 to 88 mg/L (milligrams per liter) and another group ranging from 129 to 376 mg/L. The lower concentrations are found in water from Region I (except for one value from Region IIB), whereas the higher concentrations are found in water from Region II. These differences are largely related to the chemical nature of the two types of recharge water. The higher HCO_3^- values in
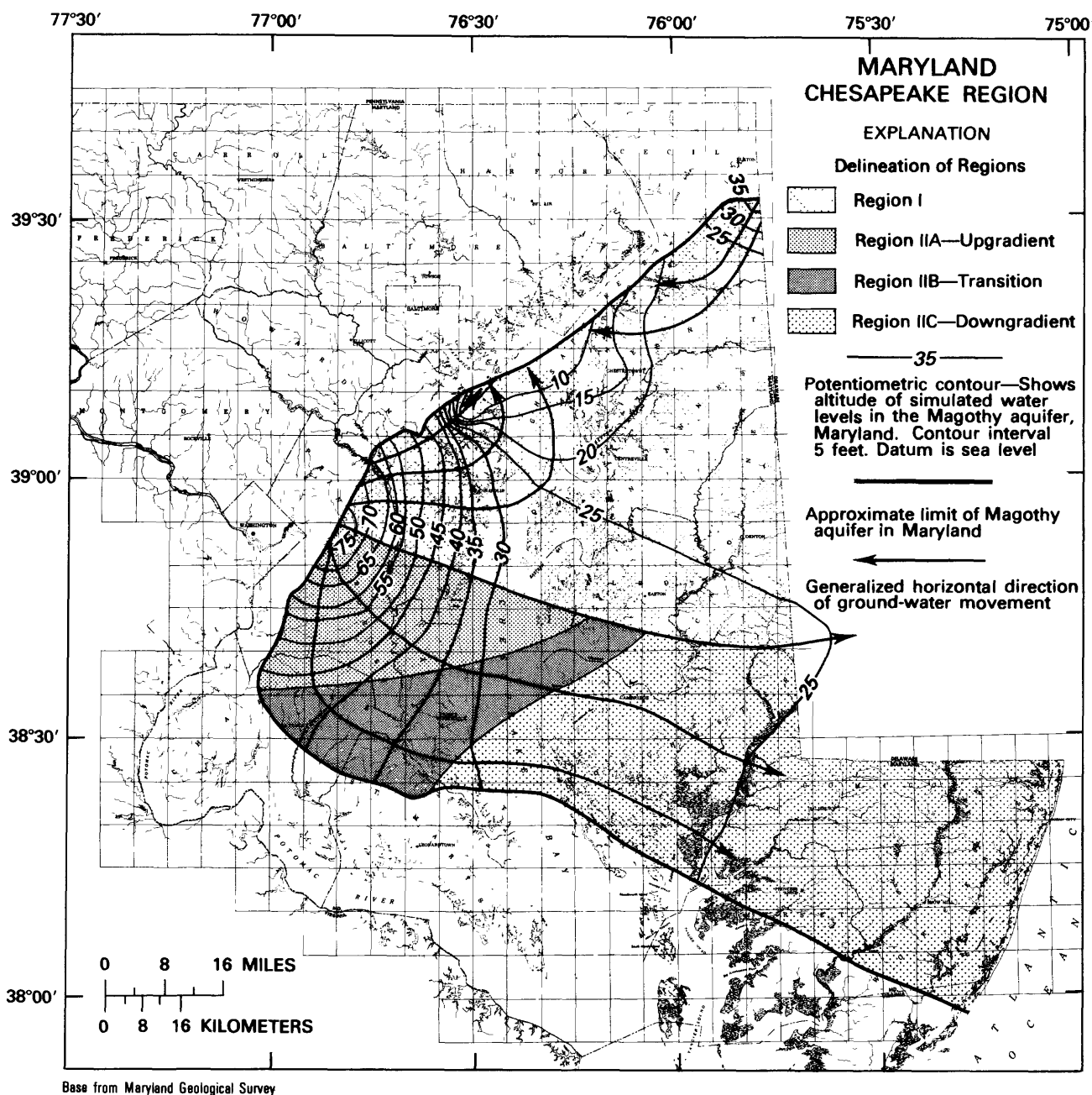
Figure 3. Simulated prepumping potentiometric surface and locations of Regions I, IIA, IIB, and IIC in the Magothy aquifer, Maryland.

Region II result from the control of alkalinity in the Aquia aquifer by dissolution-precipitation reactions involving carbonate material (Chapelle, 1983). This is not the case in Region I of the Magothy aquifer, which is generally free of carbonate material.

Concentrations of Fe_T and sulfate (SO_4^{-2}) for Region I are shown in figure 5 and for Region II in figure 6. Comparison of figures 5 and 6 indicates that ground water in Region I has significantly higher concentrations of Fe_T and SO_4^{-2} than ground water in Region II. Total iron concentrations in Region I range from 0.002 to 0.466 mmol/kg (millimole per kilogram) and in Region II from 0.002 to 0.079 mmol/kg (except for one value of 0.251 mmol/kg). Sulfate values range from 0.104 to 0.593 mmol/kg in Region I compared with 0.025 to 0.239 mmol/kg in Region II. In Region I, both Fe_T and SO_4^{-2} increase with distance along the flowpath; however, iron
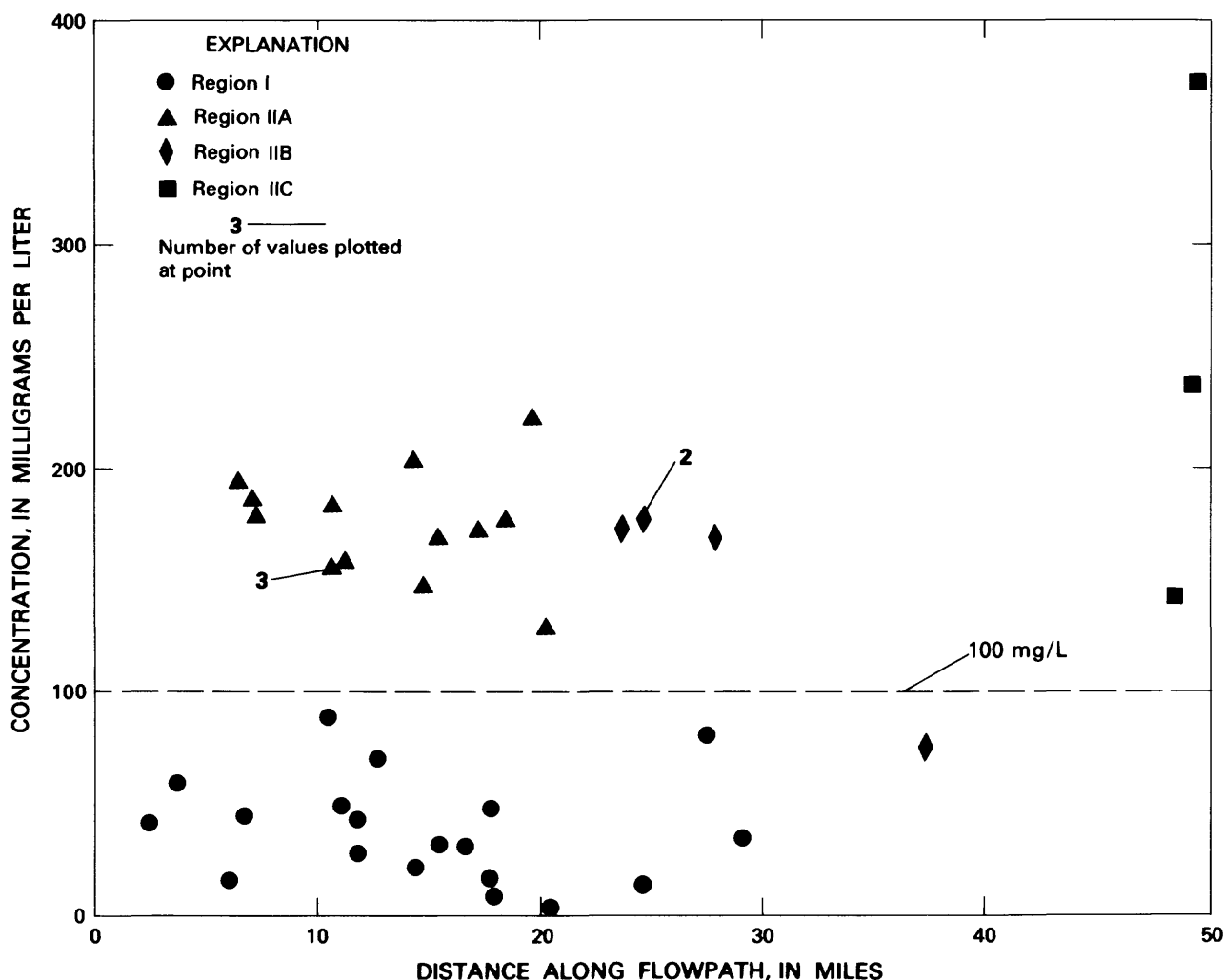
Figure 4. Concentrations of HCO₃⁻ as a function of distance along a flowpath in the Magothy aquifer, Maryland. Regions are delineated in figure 3.

concentrations decrease farther downgradient (beyond 20 mi). No such trends were found in Region II.

In Region I, Ca^{+2} is the dominant cation (table 2); in Region II, however, the dominant cation changes from Ca^{+2} in the upgradient area to Na^+ in the downgradient area (table 3). Values of Ca^{+2} and Na^+ are lower in Region I than in Region II. Ca^{+2} values in Region I range from 0.050 to 0.674 mmol/kg and Na^+ concentrations range from 0.052 to 0.383 mmol/kg; Ca^{+2} and Na^+ concentrations do not increase or decrease with distance along the flowpath. Conversely, figure 7 shows distinctive trends in Ca^{+2} and Na^+ with distance along the flowpath in Region II. Concentrations of Ca^{+2} are highest in the upgradient area (Region IIA; 0.374 to 1.497 mmol/kg) and diminish to 0.022 to 0.130 mmol/kg downgradient (Region IIC). Na^+ concentrations show an opposite trend, with low values in the upgradient area (0.117 to 0.378 mmol/kg, except one value of 1.827 mmol/kg) and higher values (2.523 to 6.046 mmol/kg) in the down-

gradient area. Concentrations of Ca^{+2} and Na^+ in Region IIB (transition area) are intermediate between those of the upgradient and downgradient areas.

Differences in K^+ and Mg^{+2} concentrations in the respective regions are not as distinguishable as differences in concentrations of the previously discussed ions. K^+ concentrations are 0.026 to 0.164 mmol/kg in Region I, 0.031 to 0.256 mmol/kg in the upgradient area of Region II, and 0.087 to 0.136 mmol/kg in the downgradient area of Region II. In Region I, Mg^{+2} concentrations range from 0.041 mmol/kg near the outcrop to 0.329 mmol/kg downgradient. Region II Mg^{+2} concentrations decrease downgradient; values range from 0.617 mmol/kg in the upgradient area to 0.004 mmol/kg in the downgradient area.

Concentrations of Cl^- and SiO_2 are fairly uniform throughout Regions I and II. Cl^- concentrations range from 0.003 to 0.367 mmol/kg; SiO_2 concentrations range from 0.073 to 0.749 mmol/kg.

Figure 5. Concentrations of Fe_T and SO_4^{-2} as a function of distance along a flowpath in Region I, Magothy aquifer, Maryland. Regions are delineated in figure 3.

Ground water in Region I ranges in pH from 3.8 to 7.5 and in Region II from 6.5 to 8.2. No dissolved oxygen was detected in water from well AA-DE 88, located in the confined part of Region I. This is consistent with the trend of decreasing Eh (high Eh values indicate oxygenated water) downgradient from the outcrop in Anne Arundel County (Back and Barnes, 1965, pl. 1). Dissolved oxygen was not measured in the other wells included in tables 2 and 3.

HYDROCHEMICAL FACIES

Hydrochemical facies are useful tools for describing the chemical character of ground water. A hydrochemical-
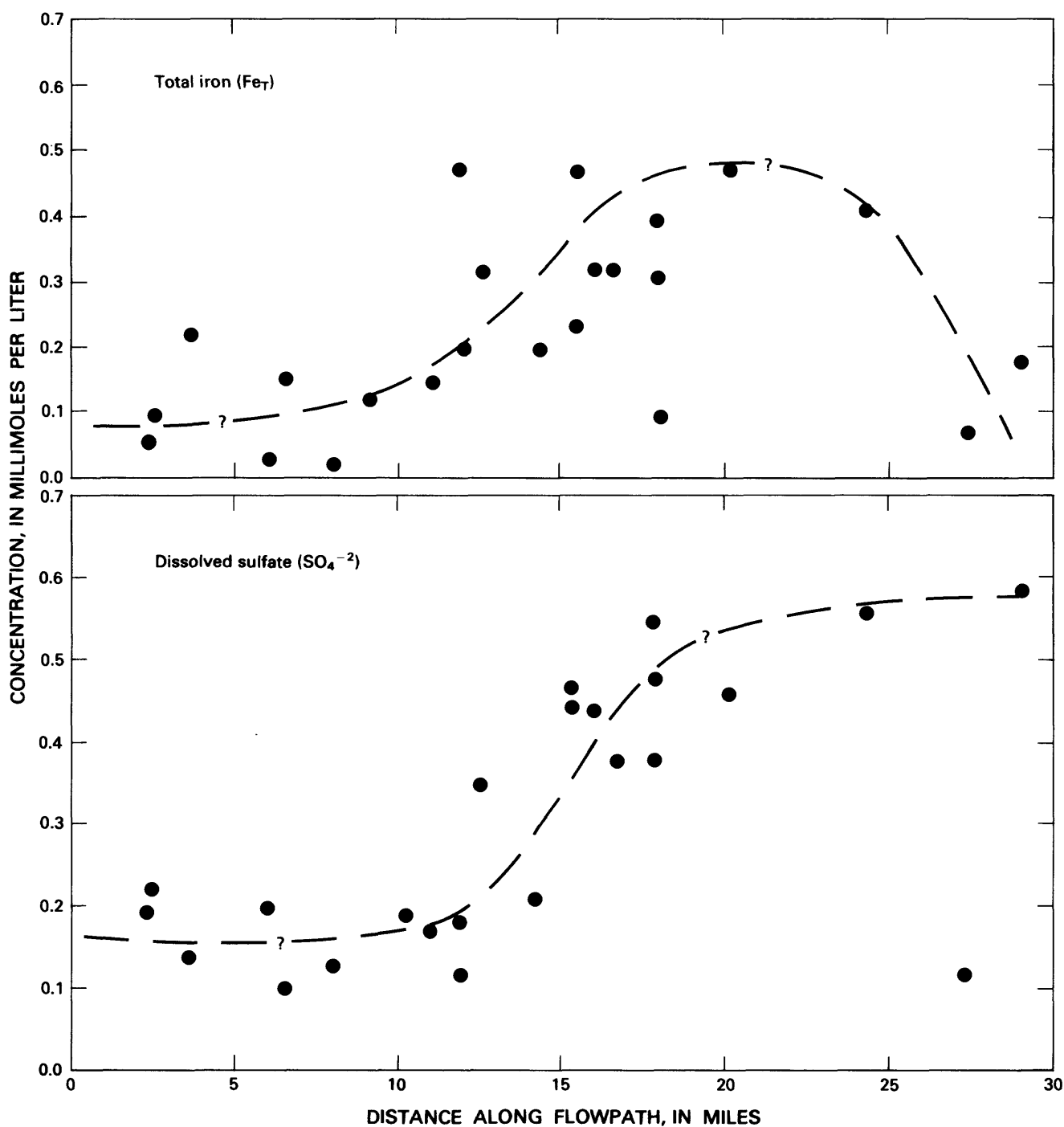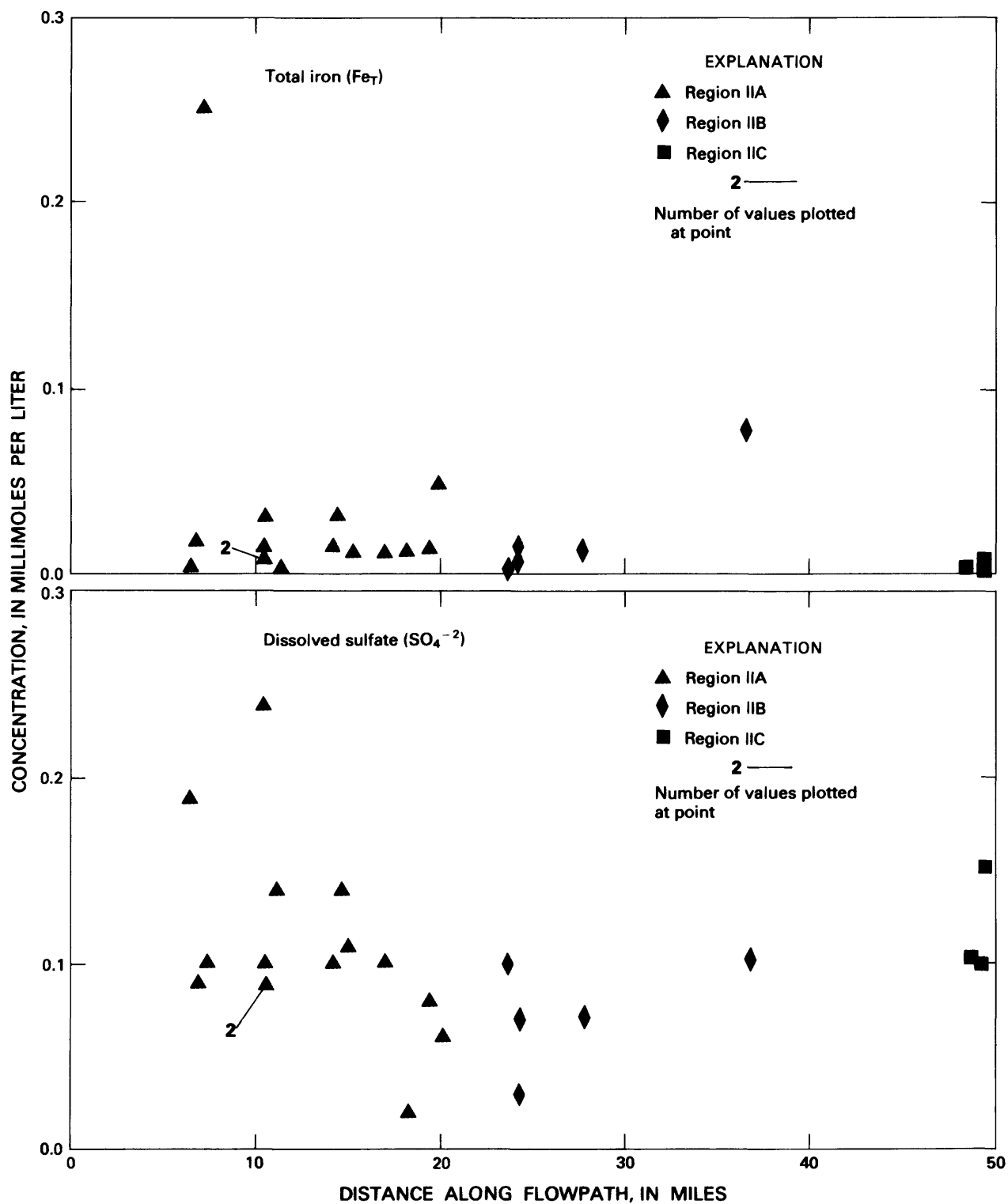
Figure 6. Concentrations of Fe_T and SO_4^{-2} as a function of distance along a flowpath in Region II, Magothy aquifer, Maryland. Regions are delineated in figure 3.
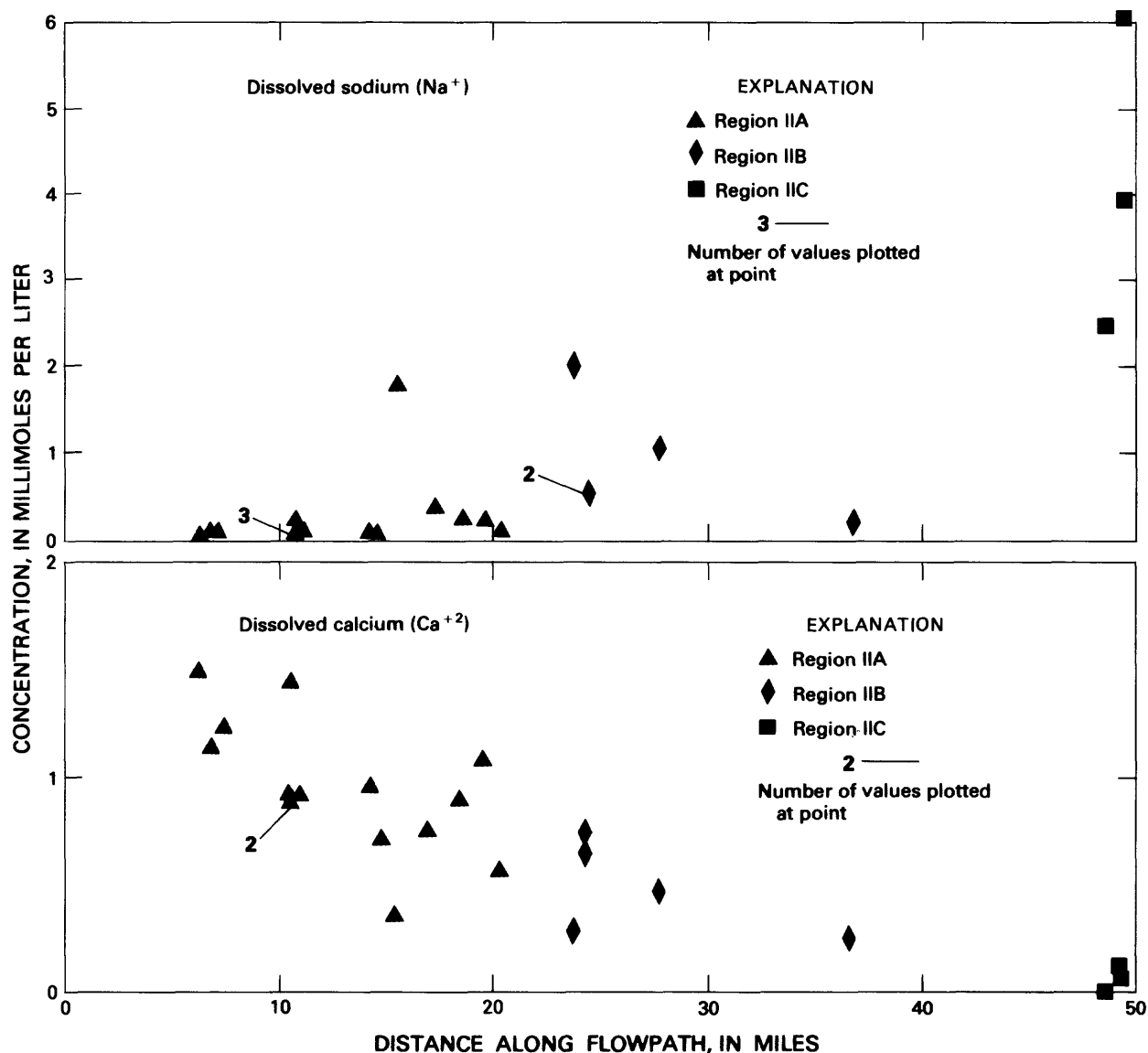
Figure 7. Concentrations of Ca^{+2} and Na^+ as a function of distance along a flowpath in Region II, Magothy aquifer, Maryland. Regions are delineated in figure 3.

facies diagram was originated by Durov (1948) and described by Zaporozec (1972). The advantage of Durov's diagram over conventional hydrochemical-facies diagrams is that it allows the plotting of two characteristics in addition to relative concentrations of common ions. Freeze and Cherry (1979, p. 249–251) give a brief description of the diagram and its uses. Generally, only Ca^{+2}, Mg^{+2}, Na^+, and K^+ are considered when analyzing the hydrochemical facies of cations in ground water. However, data in table 2 indicate that Fe_T is a significant constituent in Region I. As a result, Mg^{+2} is included with Ca^{+2} in figure 8A, and Fe_T is included as a component of the cation hydrochemical facies in Region I. Because Fe_T is not a significant constituent in Region II, the hydro-

chemical facies in this region (fig. 8B) were treated in the traditional manner (Back, 1966, p. A11–A14).

Figures 8A and 8B indicate that the hydrochemical facies in Region I differ from those in Region II. Furthermore, figure 8B shows changes in water character among subregions in Region II. The progressive nature of these changes is more evident in figures 8C, 8D, and 8E. In Region IIA, the water has a calcium bicarbonate character; in Region IIC, it has a sodium bicarbonate character; and in Region IIB, it is transitional between these two water characters. The hydrochemical facies in the Magothy aquifer in Maryland are summarized in table 4. The distinctly different hydrochemical facies in each region and subregion strongly suggests that separate chemical

Table 2. Chemical analyses of water from selected wells in Region I, Magothy aquifer, Maryland
[Two dashes indicate that no value was determined]

Map No.[2]	Well identifier	Molalities of dissolved constituents[1]									pH[3]	Distance[4]
		Ca^{+2}	Mg^{+2}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{-2}	Fe_T	SiO_2		
1	PG-CE 17	0.524	0.082	0.148	0.054	0.656	0.056	0.187	0.006	0.073	7.5	2.4
2	PG-CF 33	.050	.045	.052	.084	--	.042	.219	.095	.233	3.8	2.5
3	PG-CF 2	.424	.082	.135	.026	.951	.071	.135	.227	.749	6.5	3.6
4	AA-CE 83	.229	.090	.383	.059	.262	.169	.198	.003	.110	5.9	6.0
5	AA-DC 7	.349	.082	.091	.064	.738	.054	.104	.152	.516	6.3	6.5
6	AA-BF 48	.050	.041	.130	.028	--	.065	.125	.002	.135	4.4	8.0
7	AA-DD 42	.674	.128	.113	.079	1.442	.054	.187	.118	.433	7.4	10.2
8	AA-DE 88	.275	.099	.074	.049	.780	.051	.167	.147	.217	6.6	11.0
9	AA-DE 3	.247	.173	.100	.067	.721	.056	.115	.466	.266	--	11.9
10	AA-DE 47	.250	.107	.091	.049	.459	.056	.177	.197	.216	--	11.9
11	AA-DE 104	.624	.251	.091	.077	1.147	.062	.354	.322	.200	7.0	12.5
12	AA-CE 46	.195	.144	.091	.069	.344	.056	.208	.197	.216	5.6	14.2
13	AA-CE 69	.172	.185	.078	.051	--	.042	.437	.233	.156	3.9	15.4
14	AA-DF 15	.374	.234	.078	.061	.525	.039	.469	.466	.143	5.8	15.4
15	AA-CF 101	.177	.148	.052	.041	--	.023	.437	.322	.135	5.7	16.0
16	AA-DF 9	.424	.206	.065	.067	.508	.054	.375	.322	.163	5.8	16.6
17	AA-DF 81	.299	.226	.100	.074	.131	.367	.375	.304	.127	7.0	17.8
18	AA-DF 84	.449	.206	.065	.084	.279	.017	.552	.093	.120	7.2	17.8
19	AA-DF 92	.599	.222	.109	.069	.754	.037	.479	.394	.148	6.3	17.8
20	AA-CG 6	.195	.156	.191	.072	.049	.025	.458	.466	.138	4.7	20.1
21	QA-EA 26	.399	.214	.091	.072	.213	.023	.562	.412	.123	6.8	24.3
22	KE-CD 50	.449	.218	.157	.164	1.344	.928	.124	.075	.102	7.3	27.3
23	TA-CB 89	.374	.329	.196	.130	.590	.056	.593	.179	.136	6.3	29.0

[1] Units are millimoles per kilogram water unless otherwise indicated
[2] Location shown in figure 1
[3] Negative base-10 logarithm of hydrogen ion activity in moles per liter.
[4] Miles along a flowpath.

Table 3. Chemical analyses of water from selected wells in Region II, Magothy aquifer, Maryland

Molalities of dissolved constituents[1]

Map No.[2]	Well identifier[3]		Ca[+2]	Mg[+2]	Na^{+}	K^{+}	HCO3[-]	Cl^{-}	SO4[-2]	Fe_T	SiO2	pH[4]	Distance[5]
24	PG-EF	5	1.497	0.276	0.135	0.043	3.147	0.056	0.187	0.006	0.416	7.5	6.5
25	PG-ED	8	1.148	.350	.200	.113	[6]3.037	.056	.086	.012	.266	8.0	7.1
26	PG-EF	3	1.248	.214	.218	.049	2.917	.059	.104	.251	.250	6.9	7.4
27	AA-FC	4	1.447	.259	.144	.066	2.999	.054	.239	.016	.216	7.4	10.7
28	PG-FD	10	0.873	.354	.117	.123	2.508	.051	.099	.005	.266	7.9	10.7
29	PG-FD	11	.848	.366	.152	.123	[6]2.557	.042	.094	.029	.266	8.2	10.7
30	PG-FD	64	.923	.251	.239	.138	2.540	.065	.092	.006	.233	7.9	10.7
31	PG-FD	6	.923	.325	.148	.031	2.590	.042	.135	.004	.216	7.7	11.3
32	PG-FD	32	.973	.617	.213	.141	3.327	.039	.096	.015	.200	7.8	14.2
33	PG-FC	14	.724	.452	.183	.235	2.409	.034	.135	.032	.216	7.7	14.8
34	PG-FD	63	.374	.206	1.827	.182	2.770	.197	.115	.013	.166	7.9	15.4
35	CH-BF	5	.773	.452	.378	.256	2.819	.034	.103	.011	.160	7.6	17.2
36	PG-GF	35	.923	.395	.326	.197	2.917	.031	.025	.013	.153	7.5	18.4
37	CH-BF	15	1.098	.617	.274	.253	3.639	.034	.076	.014	.266	8.0	19.6
38	CA-CC	56	.574	.304	.222	.146	2.114	.031	.056	.047	.161	7.8	20.1
39	CH-BE	17[7]	.274	.123	2.044	.199	2.852	.028	.104	.002	.165	7.4	23.7
40	CH-CG	15[7]	.649	.411	.609	.281	2.934	.014	.075	.007	.150	7.7	24.3
41	PG-HF	41[7]	.748	.452	.609	.238	2.934	.031	.034	.014	.145	6.5	24.3
42	CH-CG	18[7]	.474	.321	1.174	.281	2.770	.003	.066	.013	.143	7.4	27.8
43	DO-BB	12[7]	.240	.239	.309	.245	1.246	.042	.104	.079	.166	7.0	36.7
44	DO-CD	17[8]	.022	.004	2.523	.087	2.377	.056	.096	.002	.216	7.9	48.6
45	DO-CE	3[8]	.080	.099	6.046	.136	[6]6.168	.192	.146	.004	.300	8.2	49.2
46	DO-CE	81[8]	.130	.012	4.046	.100	[6]3.934	.260	.102	.002	.183	8.2	49.2

[1] Units are millimoles per kilogram water unless otherwise indicated.
[2] Location shown in figure 1.
[3] Well located in Region IIA (upgradient area) unless otherwise indicated.
[4] Negative base-10 logarithm of hydrogen ion activity in moles per liter.
[5] Miles along a flowpath.
[6] Bicarbonate value in Woll (1978) was corrected to include alkalinity reported as carbonate (see Knobel, 1985, p. 20).
[7] Well located in Region IIB (transition area).
[8] Well located in Region IIC (downgradient area).

Figure 8A. Hydrochemical facies of ground water from Region I, Magothy aquifer, Maryland.

Figure 8B. Hydrochemical facies of ground water from Region II, Magothy aquifer, Maryland.
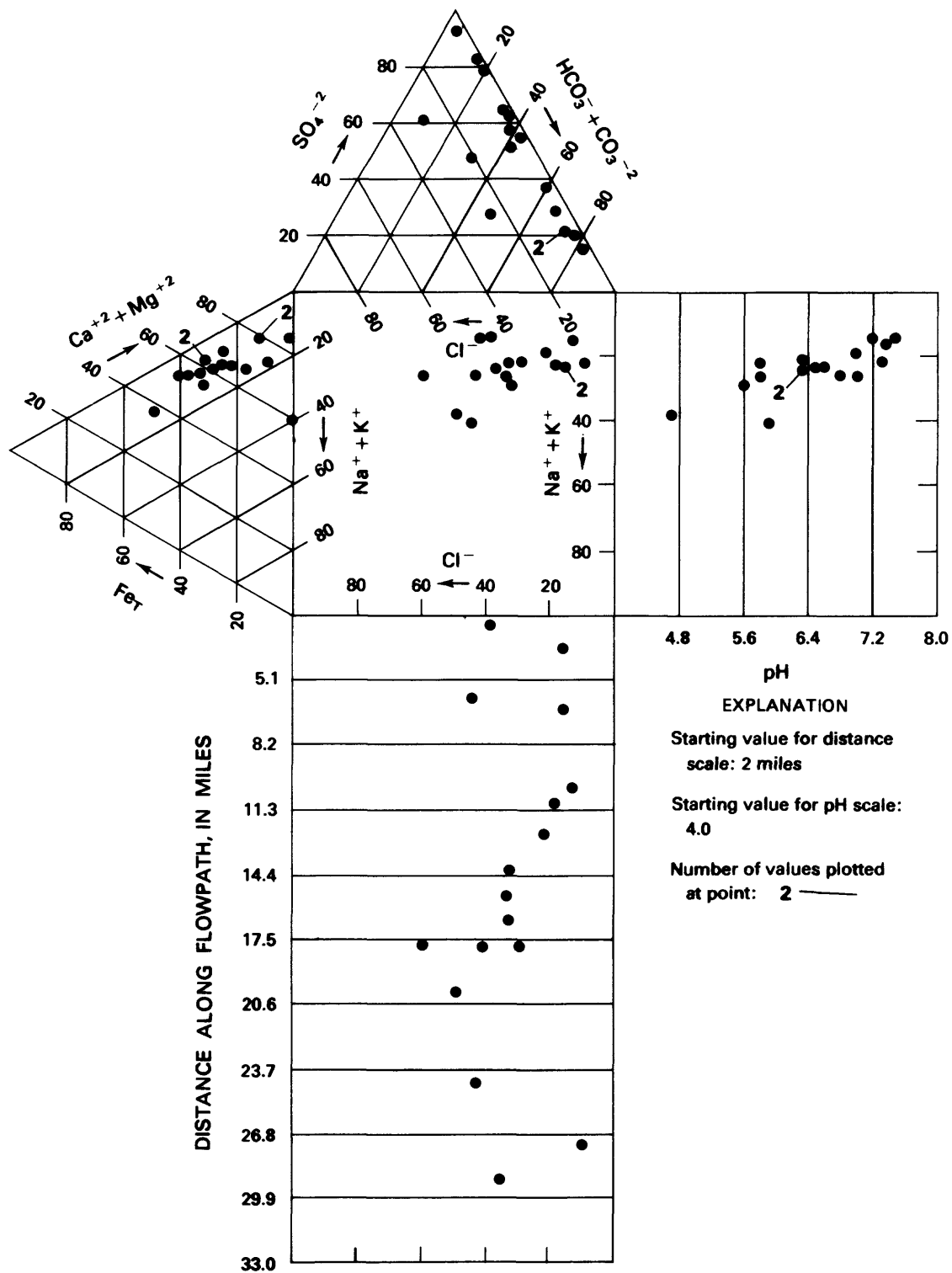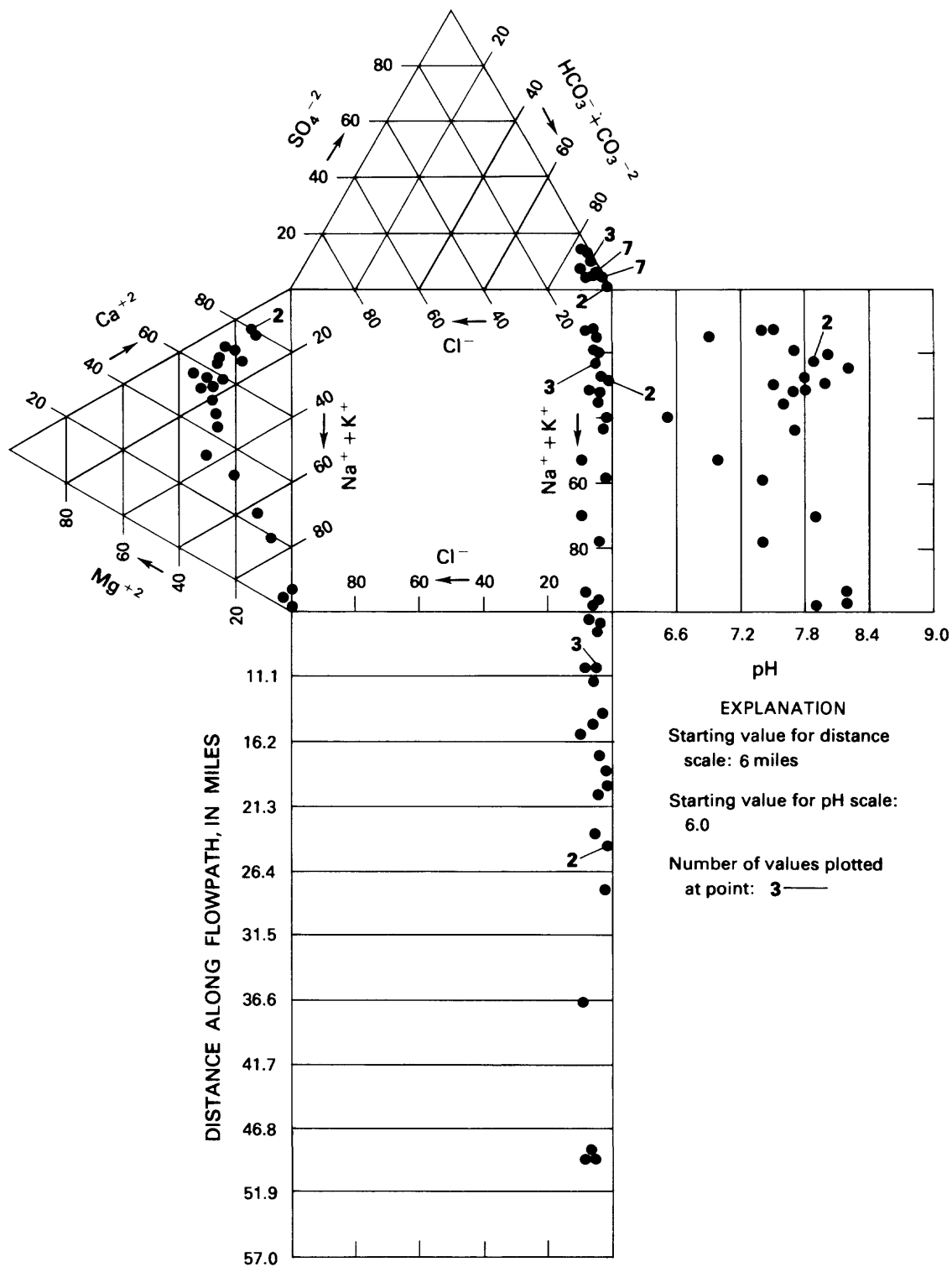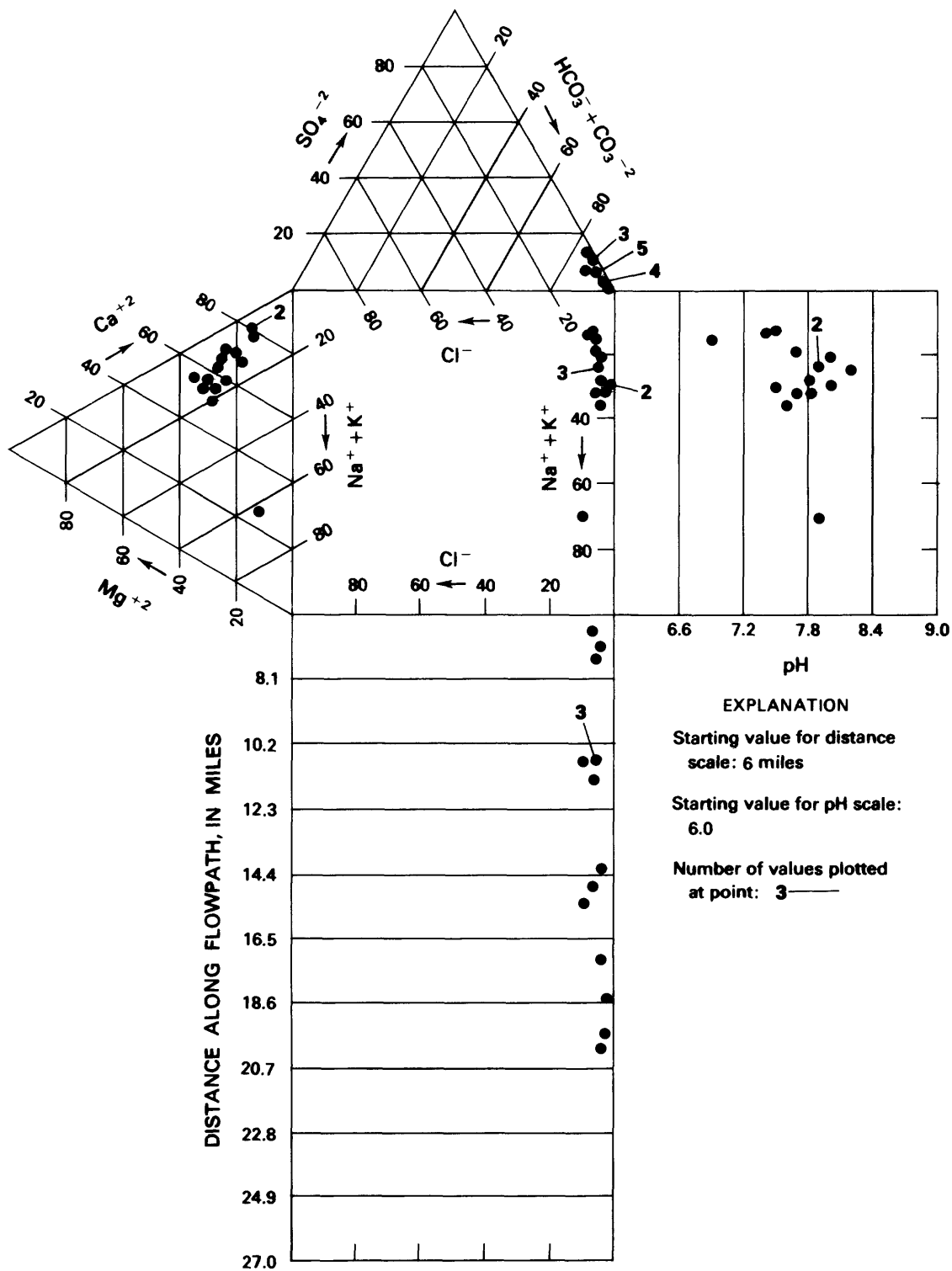
Figure 8C. Hydrochemical facies of ground water from Region IIA, Magothy aquifer, Maryland.

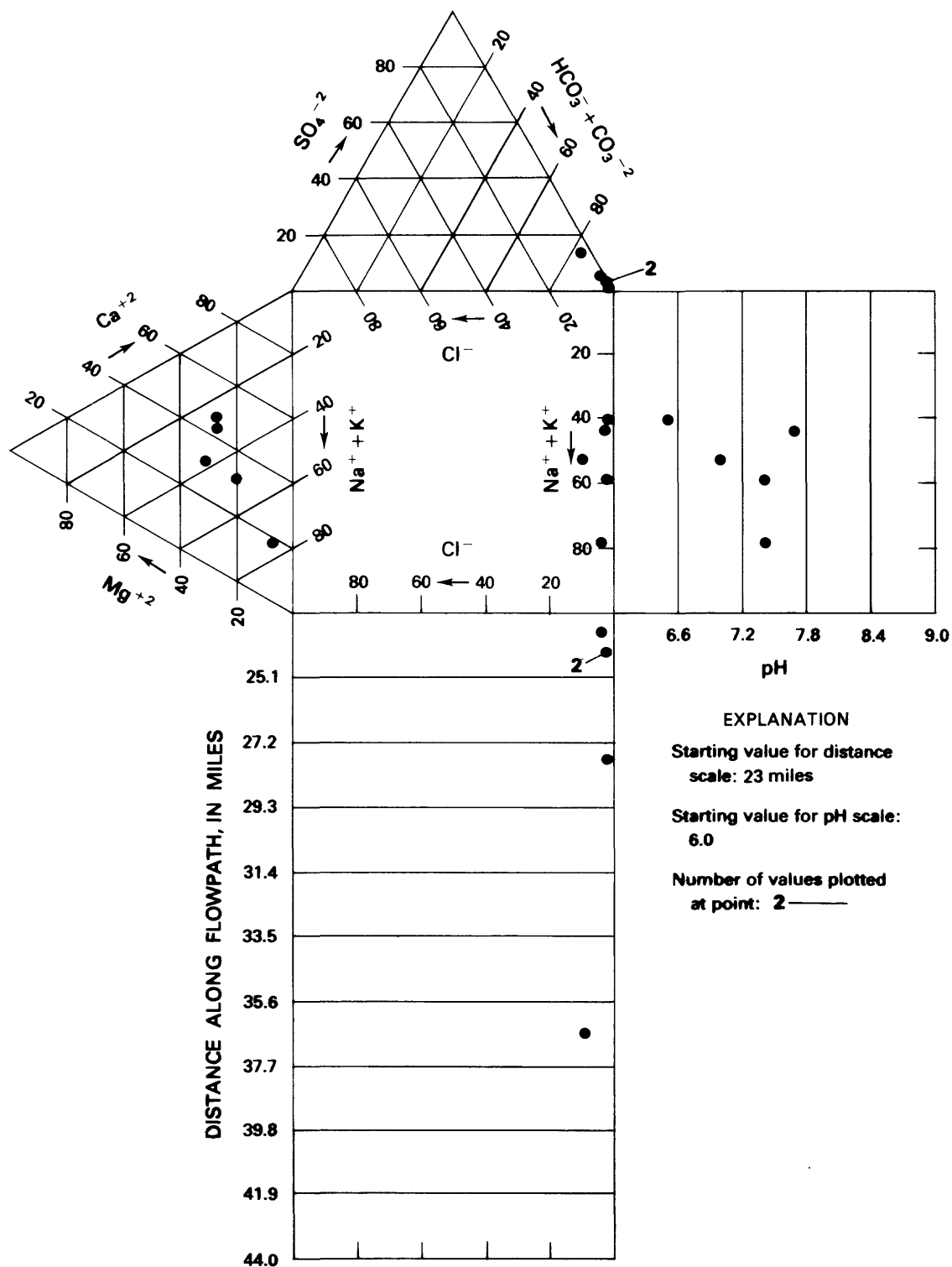Figure 8D. Hydrochemical facies of ground water from Region IIB, Magothy aquifer, Maryland.
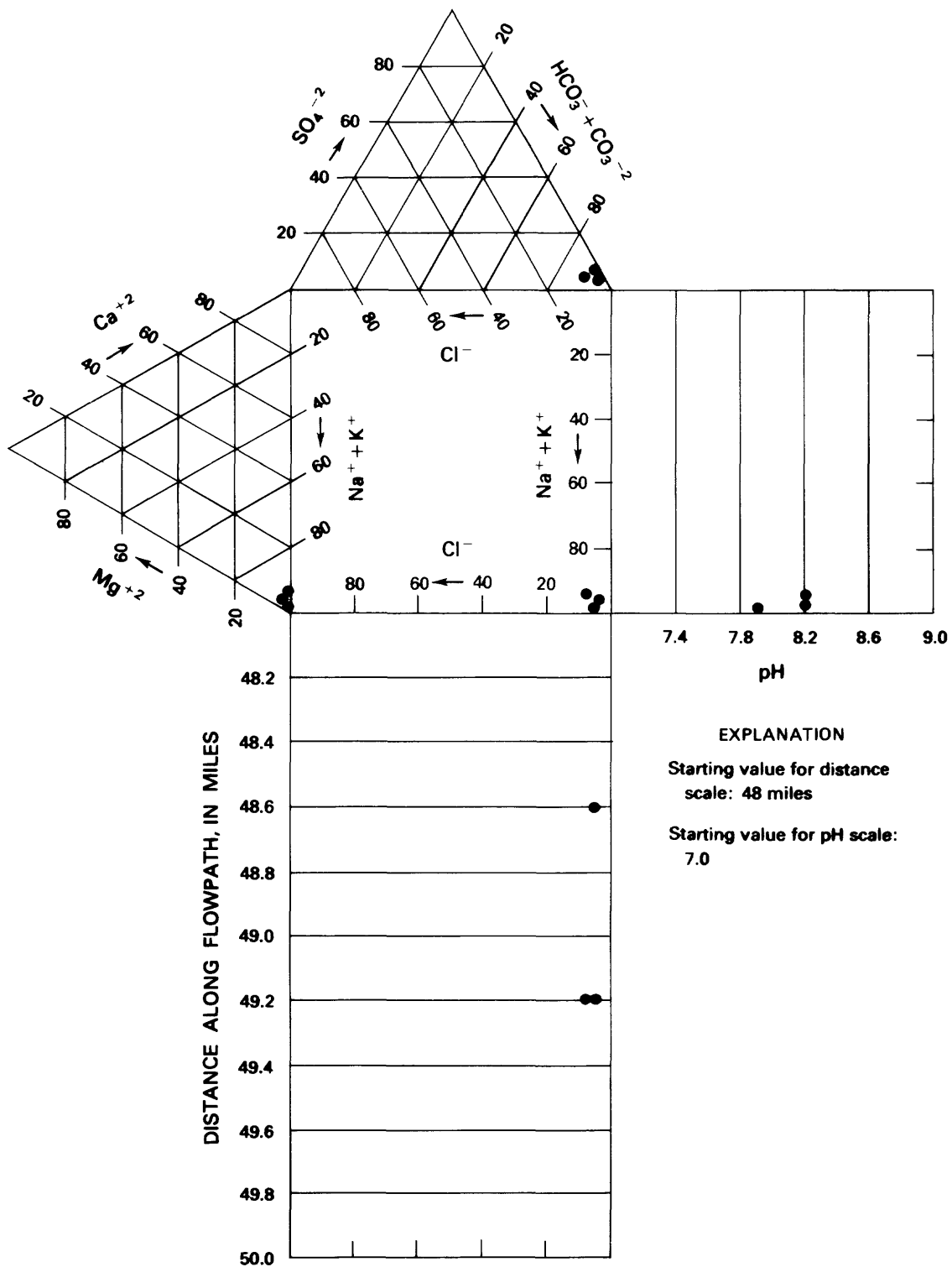
Figure 8E. Hydrochemical facies of ground water from Region IIC, Magothy aquifer, Maryland.

Table 4. Summary of hydrochemical facies by region
[Delineation of regions is shown in figure 3]

Type of facies	Region 1	Region IIA upgradient	Region IIB transition	Region IIC downgradient
Cation	Ca^{+2} and Fe_T	Ca^{+2}	Ca^{+2} and Na^+	Na^+
Anion	HCO_3^- and SO_4^{-2}	HCO_3^-	HCO_3^-	HCO_3^-

processes control water chemistry in the Magothy aquifer.

CHEMICAL EVOLUTION OF GROUND WATER FROM THE MAGOTHY AQUIFER

As noted earlier, two distinct types of recharge occur in the Magothy aquifer and different hydrochemical facies are present in the regions associated with these types of recharge. In addition, ground water in the two regions undergoes a minimal amount of mixing because of the directions of ground-water flow. Hence, the chemical processes that control the distribution of the ions in the aquifer and their relation to the aquifer mineralogy and recharge are discussed separately for Regions I and II.

Region I

In the area where the Magothy aquifer crops out, most of the recharge is from atmospheric precipitation. Rainfall in coastal areas commonly contains small amounts of Na^+, Cl^-, and SO_4^{-2}. Rainfall generally is saturated with respect to atmospheric CO_2 (partial pressure$=10^{-3.5}$ atmosphere; atm) and oxygen (partial pressure$=10^{-0.68}$ atm). As the infiltrating water passes through the soil zone, it accumulates additional CO_2. The dissolved gases increase the capacity of the ground water (H_2O) to dissolve minerals. CO_2 reacts with H_2O and the silicate minerals to produce dissolved ions and a residual solid phase.

Kaolinite is commonly assumed to be the stable weathering product in reactions involving aluminosilicate minerals (Faust and Aly, 1981, tables IX–XI). To test this assumption, it is necessary to evaluate the stability relations for silicate minerals. One convenient method for evaluating the microcline-muscovite-gibbsite-kaolinite system is to plot $\log_{10}$ $[K^+]/[H^+]$ as a function of $\log_{10}$ $[Si(OH)_4]$ (the brackets indicate ion activity). Data for the Magothy aquifer are plotted in figure 9. All analyses plot within the stability field of kaolinite, indicating that kaolinite is a stable weathering product in this system. Two samples (fig. 10) indicate that calcium montmorillonite also may be a stable weathering product in Region I.

The dissolved ions produced by silicate weathering depend on the original chemical composition of the minerals. Feldspar minerals have been observed in the Magothy aquifer by several investigators. Trapp and others (1984, compare their fig. 2 and table 13) noted the presence of potassium feldspar in the downgradient part of the Magothy aquifer. Glaser (1969) noted that this mineral was not present in four samples of the Magothy Formation collected from the area where it crops out. This suggests that potassium feldspar has been weathered almost completely in the outcrop by CO_2- and O_2-charged atmospheric precipitation. Farther downgradient, however, potassium feldspar has not been completely removed, and the chemical weathering process continues. The chemical weathering of potassium feldspar can be represented by the following equation:
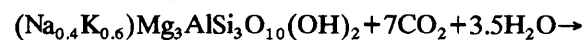
Potassium feldspar
$$2KAlSi_3O_8 + 2CO_2 + 3H_2O \rightarrow \tag{1}$$

Kaolinite
$$Al_2Si_2O_5(OH)_4 + 2K^+ + 2HCO_3^- + 4SiO_2.$$
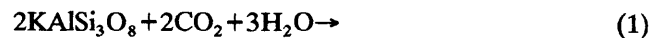
In a similar manner, minerals such as plagioclase and biotite can react to release Ca^{+2}, Mg^{+2}, K^+, and Na^+ to solution as follows:

Biotite
$$(Na_{0.4}K_{0.6})Mg_3AlSi_3O_{10}(OH)_2 + 7CO_2 + 3.5H_2O \rightarrow$$

Kaolinite
$$0.5Al_2Si_2O_5(OH)_4 + 3Mg^{+2} + 0.6K^+ \tag{2}$$
$$+ 0.4Na^+ + 7HCO_3^- + 2SiO_2$$

and

Plagioclase ($Ab_{10}An_{90}$)
$$(Na_{0.1}Ca_{0.9})Al_{1.9}Si_{2.1}O_8 + 1.9CO_2 + 2.85H_2O \rightarrow$$
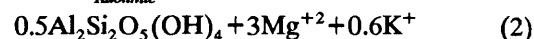
Kaolinite
$$0.95Al_2Si_2O_5(OH)_4 + 0.1Na^+ + 0.9Ca^{+2} \tag{3}$$
$$+ 1.9HCO_3^- + 0.2SiO_2.$$
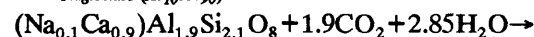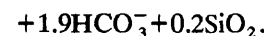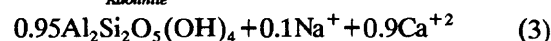
The solubilities of silicate minerals such as potassium feldspar, plagioclase, and biotite are sufficiently large to account for the low concentrations of Ca^{+2}, Mg^{+2}, Na^+,
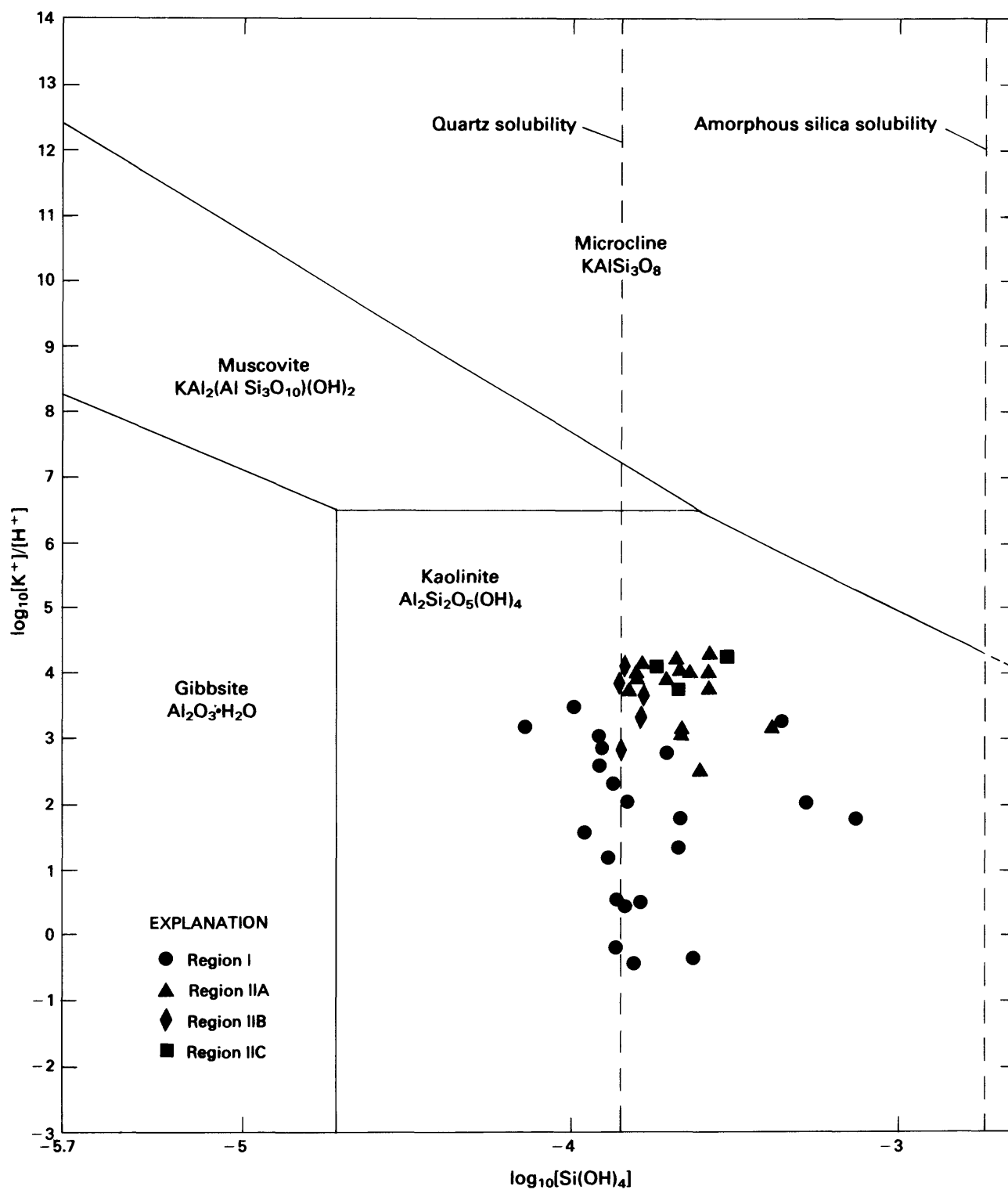
Figure 9. Stability relations for gibbsite, kaolinite, muscovite, and microcline with compositions of waters from the Magothy aquifer, Maryland, superposed. (After Freeze and Cherry, 1979, p. 272.) Regions are delineated in figure 3. Brackets indicate thermodynamic activity of indicated species.

K^+, and silica found in ground water from Region I of the Magothy aquifer in Maryland.

Glaser (1969, p. 60, 61) noted that iron minerals are common in the Magothy aquifer. One of the minerals, iron oxide, is present as simple staining or as a well-indurated cementing agent, commonly crossing bedding planes. Glaser interpreted this crosscutting relation as evidence that iron oxide minerals have a postdepositiona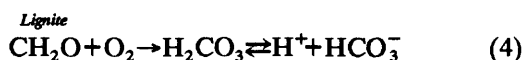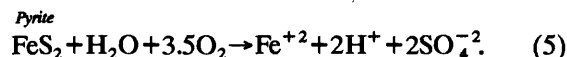l origin— that is, the minerals have resulted from the chemical action of ground water. Chapelle (1984, p. 46) introduced the concept of microchemical environments to explain the distribution of similar iron-cementation patterns in the Patuxent aquifer in the Patuxent Formation of the Potomac Group near Baltimore, Md. This process probably applies to the Magothy aquifer in Region I because similar conditions are present there. In fine-grained silt and clay layers containing lignite and pyrite, rapid oxidation of these materials consumes dissolved oxygen.

These oxidation processes can be represented by the following equations:

$$\overset{\textit{Lignite}}{CH_2O + O_2 \rightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-} \tag{4}$$

and

$$\overset{\textit{Pyrite}}{FeS_2 + H_2O + 3.5O_2 \rightarrow Fe^{+2} + 2H^+ + 2SO_4^{-2}.} \tag{5}$$

As dissolved oxygen is consumed, these environments become reducing, particularly as distance along the flowpath increases. A reducing environment is consistent with the observation that dissolved oxygen has not been detected in ground water from the confined parts of the Magothy aquifer in Region I. Ground water in reducing environments such as this can contain significant amounts of total iron. The processes represented by equations 4 and 5 are the likely cause of the increases in Fe_T and SO_4^{-2} concentrations between about 12 and 18 mi along the flowpath, shown in figure 5.

Flow velocities in ground-water systems tend to be higher in coarse-grained sediments than in fine-grained sediments, resulting in more efficient transport of dissolved oxygen. In addition, the coarse-grained sediments of the Magothy aquifer are less likely to have oxidizable material than are adjacent fine-grained sediments (Glaser, 1969, p. 42, 43). Hence, the coarse-grained sediments are more likely to contain dissolved oxygen. As water from reducing environments mixes with water from oxidizing environments, the dissolved ferrous ion becomes unstable and is oxidized to produce solid ferric hydroxide,

$$2Fe^{+2} + 5H_2O + 0.5O_2 \rightarrow 2Fe(OH)_3 + 4H^+, \tag{6}$$
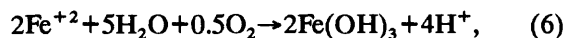
particularly in or near the outcrop. Equation 6 is consistent with Glaser's (1969) observation that secondary iron cementation patterns are common at or near the contacts of coarse- and fine-grained sediment interfaces, and sometimes cut across bedding planes.

The hydrogen ions released by the oxidation reactions (eqs. 4 through 6) are consumed by the silicate hydrolysis reactions (eqs. 1 through 3) discussed earlier in this paper. Sulfate produced by the oxidation of pyrite (eq. 5) remains in solution as sulfate or is reduced to sulfide, depending on local conditions.

Region II

In the area where the Magothy aquifer is recharged by downward leakage from the Aquia aquifer, the ground water has an overall chemical composition similar to that of the Aquia aquifer. Because the dissolved gases (normally associated with atmospherically recharged ground water) reacted with minerals in the Aquia aquifer, the water recharging the Magothy aquifer through downward leakage is relatively nonreactive. Hence, the process that controls the water chemistry in Region II is primarily the physicochemical cation-exchange reaction:

$$(1-X)Ca^{+2} + XMg^{+2} + Na_2 \cdot Ex \rightleftharpoons \tag{7}$$

$$2Na^+ + (Ca_{1-x}Mg_x) \cdot Ex,$$
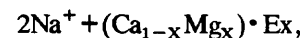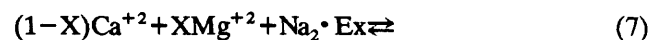
where Ex indicates an exchanging substrate.

The cation-exchange process has been described in detail by Chapelle and Knobel (1983). They concluded, on the basis of analyses of paired samples of ground water and glauconite in the Aquia aquifer, Maryland, that the exchangeable cation composition of glauconite changes systematically in the direction of ground-water flow in a manner similar to changes in the concentrations of cations in the ground water. These data suggest that cation-exchange reactions simultaneously alter water and glauconite composition along flowpaths.

In fresh-ground-water systems, the order of selectivity for cations on exchange sites is $Ca^{+2} > Mg^{+2} > K^+ > Na^+$. Because the exchange reaction is rapid, any Ca^{+2} in solution would replace Na^+ on the exchange sites according to equation 7. This process would continue until Na^+ is no longer available and Ca^{+2} is the dominant ion both in the solution and on the exchange sites.

The same principles governing ion exchange discussed by Chapelle and Knobel (1983) apply to Region II of the Magothy aquifer, except that the exchanging medium is not glauconite. The most probable exchanging medium in the Magothy aquifer is montmorillonite. Trapp and others (1984, table 19, p. 43) noted that the mean cation-exchange capacity (CEC) of triplicate samples from a core in the Magothy aquifer at Cambridge, Md., is 14.3 milliequivalents (meq) per 100 grams (g).

The clay minerals in this sample are predominately kaolinite and montmorillonite. Because kaolinite typically has a low exchange capacity and because the analytical values represent an average CEC for the bulk sample, it is reasonable to assume that CEC values of montmorillonite are actually higher than the value reported above. Hence, the CEC of montmorillonite in the Magothy aquifer is probably comparable to values reported for glauconite in the Aquia aquifer (about 20 meq/100 g) (Chapelle and Knobel, 1983, table 1, p. 348).

Ground water in the upgradient part of Region II is a calcium bicarbonate water. As water moves down the hydraulic gradient in Region II, it takes on a sodium bicarbonate character according to equation 7. With the exception of magnesium (which is chemically similar to calcium), the concentrations of other constituents in ground water remain relatively constant throughout Region II; however, small amounts of silicate hydrolysis undoubtedly occur according to equations 1 through 3.

Figure 9 indicates that water from the Magothy aquifer associated with microcline is in chemical equilibrium with kaolinite. $\log_{10}[Ca^{+2}]/[H^{+}]^{2}$ is plotted as a function of $\log_{10}[Si(OH)_4]$ in figure 10, and $\log_{10}[Na^{+}]/[H^{+}]$ is plotted as a function of $\log_{10}[Si(OH)_4]$ in figure 11. Figure 10 indicates that water associated with anorthite is in equilibrium with kaolinite, calcium montmorillonite, or both minerals. Similarly, figure 11 indicates that water associated with albite is in equilibrium with kaolinite, sodium montmorillonite, or both minerals. Water that is in equilibrium with sodium montmorillonite (fig. 11) comes from Region IIC, whereas water that is in equilibrium with calcium montmorillonite is from Region I or Region IIA. The following conclusions can be drawn from these data:

1. The formation of montmorillonite in the Magothy aquifer is consistent with theoretical considerations involving stability relations (figs. 10 and 11), and montmorillonite has also been observed in the field (Trapp and others, 1984, table 3).
2. The stability of calcium montmorillonite in Region IIA and the presence of ground water having a calcium bicarbonate character suggests that cation-exchange sites of the sediments are occupied by calcium. Conversely, the stability of sodium montmorillonite in Region IIC and the presence of sodium bicarbonate ground water suggests that enough exchange sites are occupied by sodium so that ion exchange continues to be an active process in this part of the aquifer.

The precise chemical composition of plagioclase and its abundance in the Magothy aquifer are not known. Further, the stability relations plotted in figures 10 and 11 assume pure end member compositions for albite and anorthite. The actual plagioclase composition probably

lies somewhere between these two and, hence, the phase boundaries involving plagioclase in figures 10 and 11 should be considered approximate. It should also be noted that, in preparing diagrams such as figures 9 through 11, it is necessary to assume that aluminum is conserved in the solid phase. Because small concentrations of dissolved aluminum (Al^{+3}) are found in ground water (Hem, 1985, p. 75, 76), conclusions based on water equilibrium and mineral stability with respect to these diagrams should be considered tentative.

Chapelle and Knobel (1985) suggest that concentrations of sodium plotted as a function of bicarbonate should fall on a straight line having a slope of two, if dissolution of carbonate shell material and ion exchange occur in an environment that is closed with respect to CO_2:

$$(Ca_{1-x}Mg_x)CO_3 + H_2O + Na_2 \cdot Ex \rightarrow \qquad (8)$$
$$2Na^+ + HCO_3^- + OH^- + (Ca_{1-x}Mg_x) \cdot Ex.$$
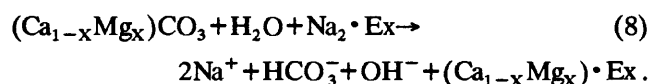
Conversely, if the system is open with respect to CO_2, the same chemical processes would generate sodium and bicarbonate concentrations that would plot on a straight line having a slope of one:

$$(Ca_{1-x}Mg_x)CO_3 + H_2O + CO_2 + Na_2 \cdot Ex \rightarrow \qquad (9)$$
$$2Na^+ + 2HCO_3^- + (Ca_{1-x}Mg_x) \cdot Ex.$$
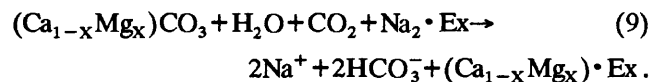
Concentrations of Na^+ and HCO_3^- from ground water obtained in Region IIC are plotted in figure 12. Also shown in figure 12 are lines representing the predicted trends of Na^+ as a function of HCO_3^- for equations 8 and 9.

The plot of Na^+ concentrations as a function of HCO_3^- concentrations for Region IIC is close to that predicted by equation 9. This implies that the processes of ion exchange, coupled with carbonate dissolution in an open system with respect to CO_2, can explain the presence of a sodium bicarbonate water in Region IIC. Although the water chemistry implies that dissolution of shell material occurs in the southeastern part of the Magothy aquifer in Maryland, the existence of shell material is not widely recognized in this aquifer. Indeed, the only references to shell material known to the authors are by Trapp and others (1984, table 3, p. 19, and table 14, p. 32), Otton (1955, table 34, p. 289), and Rasmussen and others (1957, table 38, p. 332). These workers noted trace amounts only, and, as a result, carbonate dissolution in Region IIC of the Magothy aquifer cannot be confirmed.

The scarcity of carbonate shell material in the Magothy aquifer suggests that the increase in HCO_3^- concentrations in Region IIC is caused by other processes. Combining equations 3 (incongruent dissolution of plagioclase) and 7 (ion exchange) yields

Figure 10. Stability relations for gibbsite, kaolinite, calcium montmorillonite, and anorthite with compositions of waters from the Magothy aquifer, Maryland, superposed. (After Freeze and Cherry, 1979, p. 272.) Regions are delineated in figure 3. Brackets indicate thermodynamic activity of indicated species.

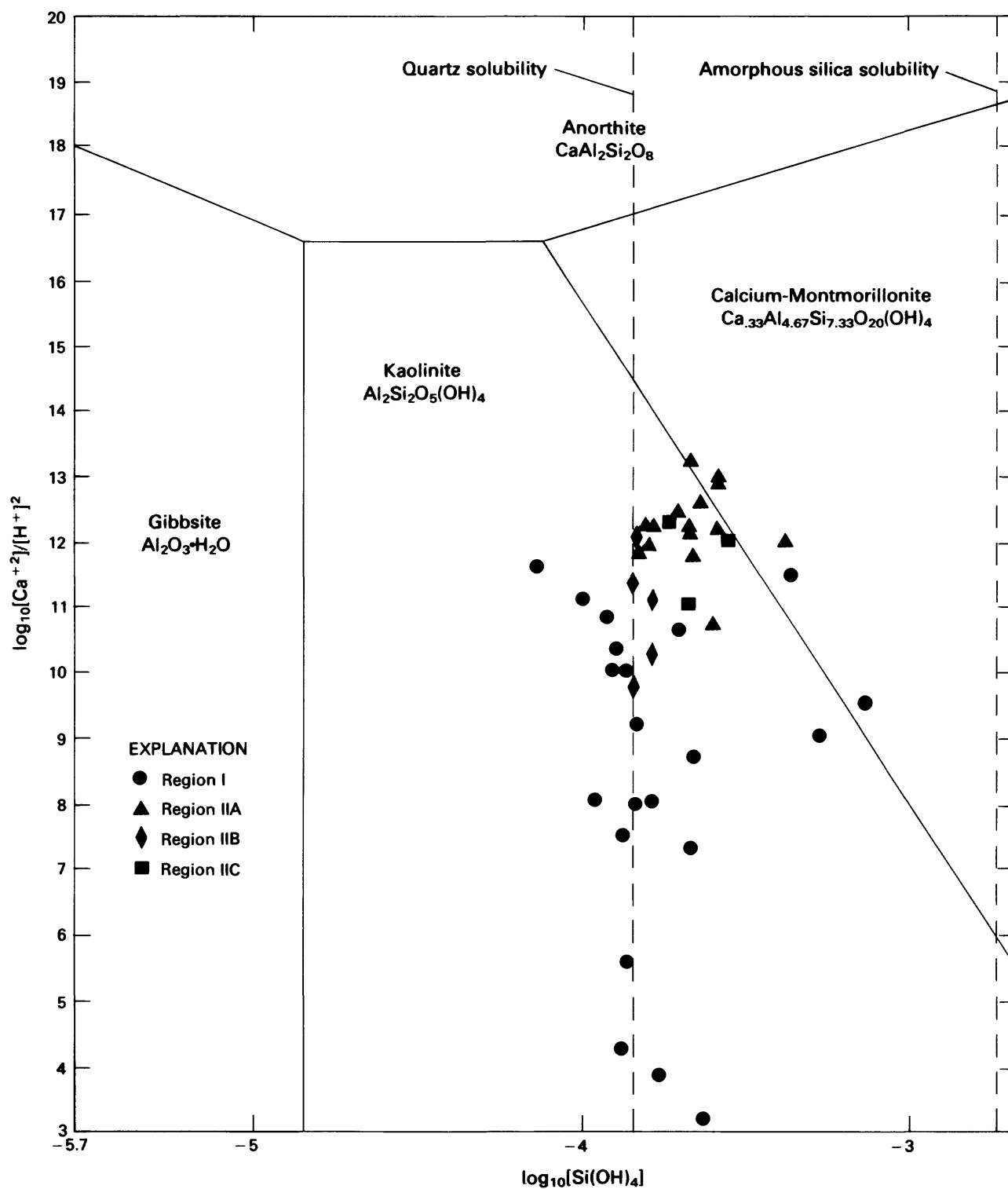**Figure 11.** Stability relations for gibbsite, kaolinite, sodium montmorillonite, and albite with compositions of waters from the Magothy aquifer, Maryland, superposed. (After Freeze and Cherry, 1979, p. 272.) Regions are delineated in figure 3. Brackets indicate thermodynamic activity of indicated species.
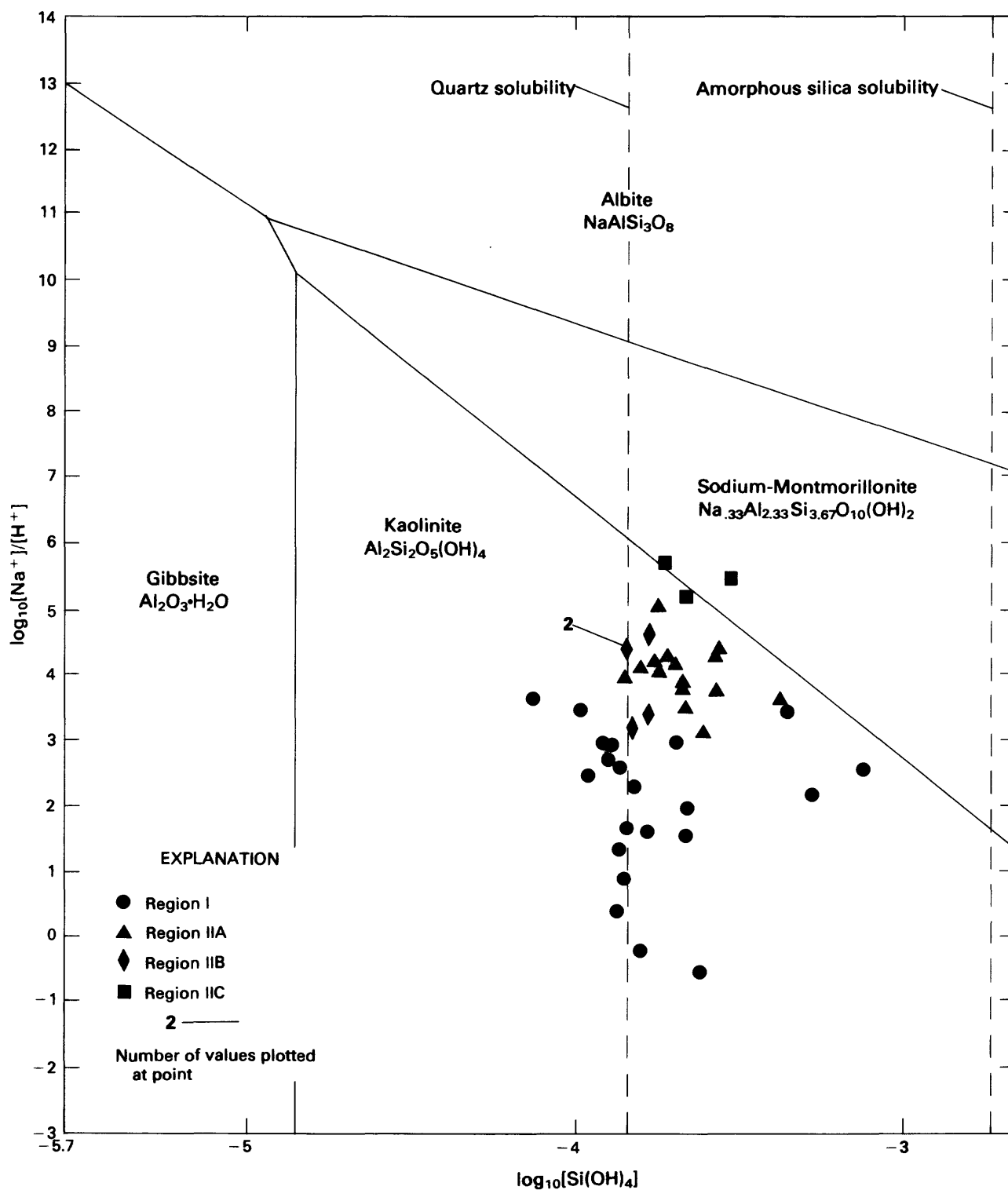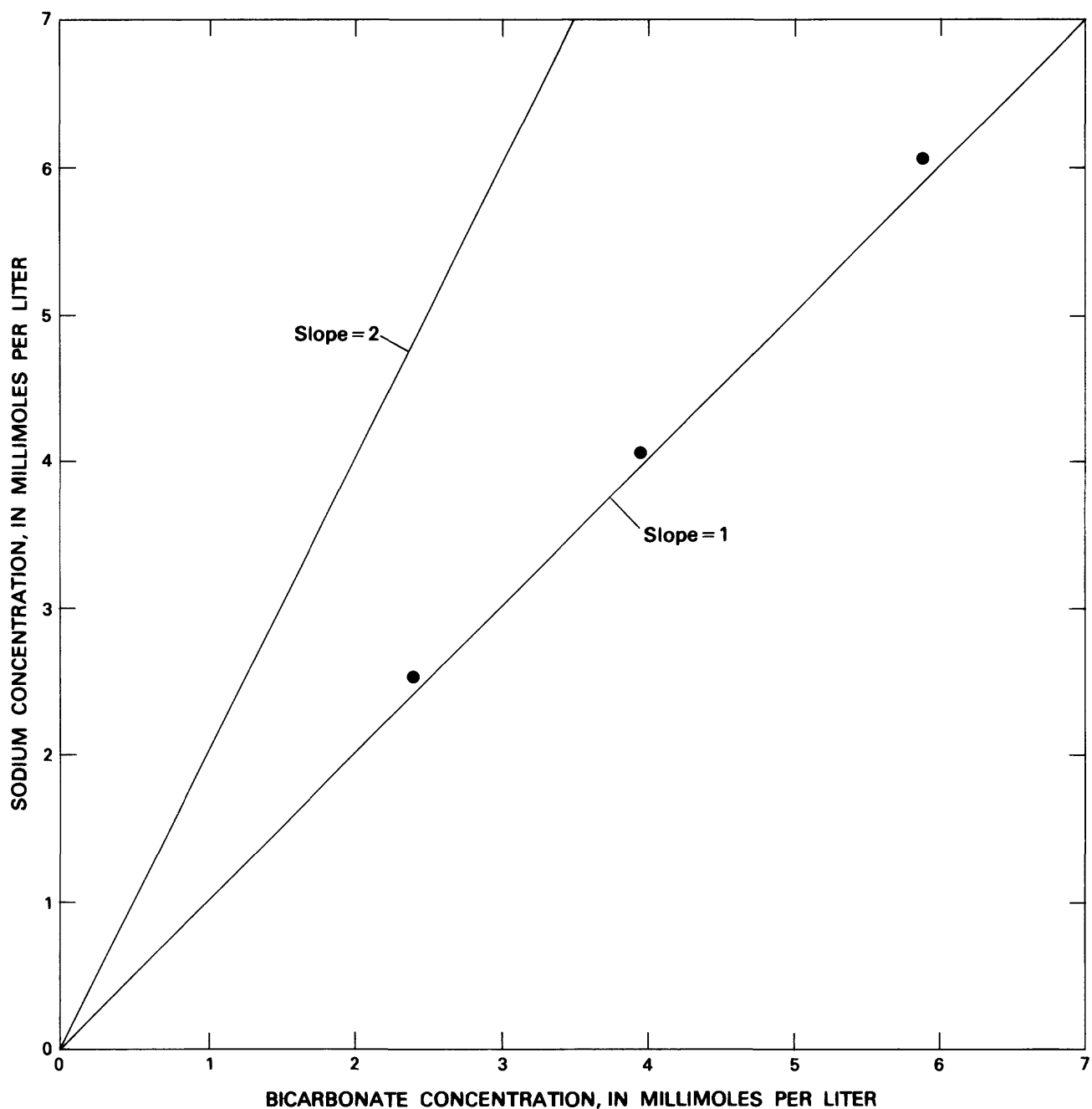
Figure 12. Sodium concentration as a function of bicarbonate concentration for water analyses from Region IIC, Magothy aquifer, Maryland. Regions are delineated in figure 3.

Plagioclase (Ab₁₀An₉₀)

$$(Na_{0.1}Ca_{0.9})Al_{1.9}Si_{2.1}O_8+1.9CO_2+2.85H_2O+$$

Kaolinite

$$0.9Na_2 \cdot Ex \rightarrow 0.95Al_2Si_2O_5(OH)_4+1.9Na^+ \quad (10)$$

$$+1.9HCO_3^-+0.2SiO_2+0.9Ca \cdot Ex.$$
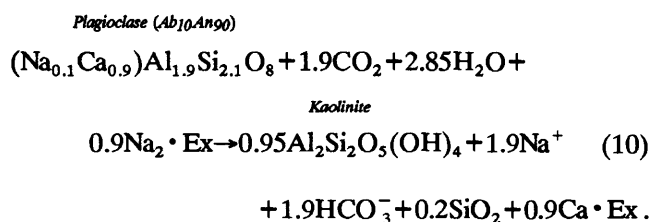
The stoichiometry of equation 10 is consistent with the Na^+ and HCO_3^- data from Region IIC that are plotted in figure 12. Similar equations could be derived by combining the incongruent dissolution of potassium feldspar (eq. 1) or biotite (eq. 2) with the cation-exchange reaction (eq. 7). All these equations would predict Na^+ and HCO_3^- concentrations that plot on a line having a slope of one.

An additional cation-exchange reaction that may occur in Region IIC of the Magothy aquifer involves the hydrogen ion (H^+):

$$H^+ + Na \cdot Ex \rightarrow Na^+ + H \cdot Ex. \qquad (11)$$
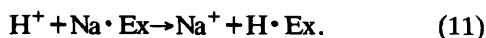
If a source of H^+ is available, such as the reaction of CO_2 and H_2O (Hem, 1985, p. 62), then reaction 11 could occur. The combination of these processes can be represented as follows:

$$CO_2 + H_2O + Na \cdot Ex \rightarrow Na^+ + HCO_3^- + H \cdot Ex. \qquad (12)$$

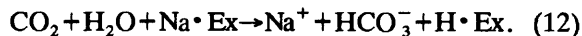This chemical model also accounts for the 1:1 ratio of Na^+ to HCO_3^- plotted in figure 12. Equation 12 would not add other dissolved constituents to the ground water.

Equations 9, 10, and 12 demonstrate that either incongruent dissolution of aluminosilicate minerals, dissolution of CO_2, or congruent dissolution of shell material when combined with ion exchange can account for the observed water chemistry. Because of the general lack of shell material in the Magothy aquifer, it is likely that either dissolution of aluminosilicate minerals in the presence of CO_2 or dissolution of CO_2 coupled with ion exchange accounts for the increased bicarbonate (fig. 4) and sodium (fig. 7) concentrations in Region IIC.

Another possible source of Na^+ and HCO_3^- ions in the Magothy aquifer is the mixture of Magothy water with sodium bicarbonate water from deeper aquifers. However, this process does not explain the depletion of the calcium ion in solution.

The increased concentrations of HCO_3^- in Region IIC indicate that there must be a source of CO_2. Equations 9, 10, and 12 also require a source of CO_2. Because the Magothy aquifer is confined by several hundred feet of overlying sediments in Region IIC, it is unlikely that atmospheric CO_2 diffuses into the aquifer in that area. This implies that CO_2 is being generated within the Magothy aquifer. Chapelle (U.S. Geological Survey, written commun., 1985) proposed that microbial activity is a source of CO_2 in coastal-plain sediments and cited as part of his evidence the presence of bacteria in four cores from the Magothy aquifer in Region IIB. The cores were collected at depths ranging from 450 to 485 ft below the land surface, which is 192 ft above NGVD of 1929. Sulfate-reduction and methanogenic activity were identified. An additional type of microbial activity (possibly fermentation) also was detected.

Chapelle and Knobel (1985) suggested that the metabolic processes of fermentive and methanogenic bacteria produced CO_2 in the Aquia aquifer, Maryland. Microbial processes such as these are complex, but the overall stoichiometries can be represented simply (Klass, 1984). Chapelle and Knobel (1985, eqs. 10 through 14) summarized the CO_2-producing fermentative and

methanogenic processes that occur in the Aquia aquifer. The presence of methanogenic bacteria in the Magothy aquifer implies that these processes generate CO_2 in this aquifer also.

Sulfate-reducing bacteria also can produce CO_2 as a result of their metabolism. This process can be represented as

$$2CH_2O + H^+ + SO_4^{-2} \rightarrow 2CO_2 + 2H_2O + HS^-. \qquad (13)$$

CO_2 is produced as the bacteria oxidize carbon. The CO_2 produced by these processes can then enter into reactions involving aluminosilicate minerals (such as eq. 10), H^+-Na^+ exchange (eq. 12), or shell material (eq. 9).

SUMMARY AND CONCLUSIONS

The mineralogy of the Magothy aquifer of Maryland is generally homogeneous and consists of quartz sand and gravel (75 to 86 percent) with interbedded clay - layers (14 to 25 percent). The aquifer also contains minor amounts of lignite and trace quantities of feldspar, mica, and iron minerals.

The Magothy receives recharge from two sources. In the outcrop (located in Region I), recharge is derived from precipitation and the aquifer is under water-table conditions. Flowpaths are relatively short (less than 30 mi) and discharge is to Chesapeake Bay and its tributaries. Southeast of Washington, D.C., the aquifer is confined. In this area (Region IIA), a major potentiometric high is caused by downward leakage from the Aquia aquifer through the silts and clays of the Brightseat, Severn, and Matawan Formations. In Region II, the aquifer functions as an artesian aquifer. Flowpaths are toward the southeast and are relatively long (up to 50 mi). Discharge is through upward leakage into overlying units.

The distribution of ions in Region I differs from that in Region II, as reflected by distinctly different hydrochemical facies in these regions. Calcium and iron are the dominant cations, and bicarbonate and sulfate are the dominant anions in Region I. Region IIA has a calcium bicarbonate water, Region IIC has a sodium bicarbonate water, and Region IIB has a transitional character.

The differences in the distribution of ions and the associated differences in the hydrochemical facies in the regions of the Magothy aquifer depend partly on the source of recharge to the aquifer; the differences are maintained by patterns of ground-water flow. These differences also depend on different chemical processes that prevail in Regions I and II. In Region I, silicate hydrolysis of microcline, plagioclase, and biotite, oxidation of pyrite, lignite, and ferrous ion, and reduction of sulfate are the likely chemical processes that control the geochemistry of the ground water. In Region II, the replacement of

sodium on exchange sites by ions in solution is the dominant process. Microbially produced CO_2 that reacts with aluminosilicate minerals (or, possibly, trace amounts of carbonate shell material) accounts for the increased HCO_3^- levels in Region IIC.

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METRIC CONVERSION FACTORS

For those readers who prefer to use metric (International System) units rather than inch-pound units used in this report, the conversion factors are listed below:

Multiply inch-pound unit	By	To obtain metric unit
atmosphere, standard (atm)	101.3	kilopascal (kPa)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)

National Geodetic Vertical Datum of 1929 (NGVD of 1929): A geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called *"Mean Sea Level."*