

Geochemical investigation of salt-water intrusion into a coastal carbonate aquifer: Mallorca, Spain

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ABSTRACT

Geochemical processes occurring within the mixing zone on Mallorca, Spain, were investigated in relation to the diagenesis of carbonate minerals and to the development of porosity and permeability within the Pleistocene limestone aquifer. Rock core and ground-water samples were obtained from the fresh-water zone, the mixing zone, and the top of the sea-water zone at two sites near the coast. Ground-water withdrawals in the vicinity of one study site depressed the water table to below sea level, resulting in sea-water encroachment and a thin mixing zone. Laboratory tests conducted on the rock core indicated that porosity and hydraulic conductivity were not enhanced within the transitory location of the present-day mixing zone. Vuggy zones in the core correspond to the approximate location of the water table. Because the ground water was supersaturated with respect to the carbonate minerals, dissolution of the limestone aquifer is not predicted for the present-day mixing zone. Results of mass-balance and source-rock calculations indicated an excess of calcium and stron-

tium in the mixing-zone waters in relation to what was expected from conservative mixing. These elevated concentrations are hypothesized to result from limestone dissolution in the vadose zone.

INTRODUCTION

As sea water intrudes into coastal aquifers, it mixes with the discharging fresh water in a zone of mixed ground-water composition (Cooper, 1959). In limestones, this mixing zone has been hypothesized to be an area of enhanced calcite dissolution (Back and others, 1979; Smart and others, 1988), aragonite dissolution (Plummer and others, 1976b; Stoessell and others, 1989) or neomorphism (Back and others, 1986), and dolomitization (Hanshaw and others, 1971; Magaritz and others, 1980; Ward and Halley, 1985; Randazzo and Bloom, 1985). These diagenetic processes can aid in the redistribution or enhancement of porosity and permeability (Hanshaw and Back, 1979). Mixing-zone processes are important because many marine carbonate units that are now exposed, either by tectonic uplift or as a result of marine regression, have been subjected to the effects

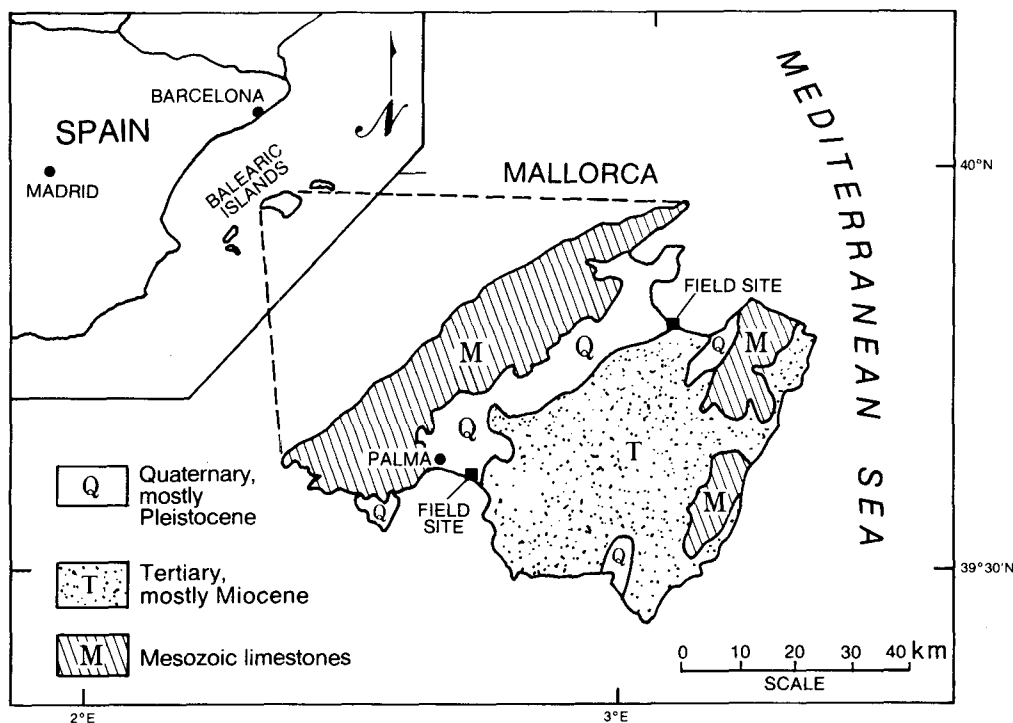


Figure 1. Geologic map of Mallorca (Sanford, 1987) with field site locations. Camp de Tir is the southern site; Serra Nova is the northern site.

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of the mixing zone at least once; further, fluctuations in sea level can cause these carbonate rocks to experience the geochemical influences of the mixing zone several times (Hanshaw and Back, 1980).

Diagenesis in a chemically reactive environment derived from the mixing of natural waters was first discussed by Runnells (1969). The chemical reactivity of the coastal mixing zone stems from the marked undersaturation with respect to carbonate minerals that develops from mixing a carbonate-saturated fresh water with near-surface sea water in a system closed with respect to CO_2 . Wigley and Plummer (1976) attributed the undersaturation to nonlinear effects arising from mixing two waters with different ionic strengths, partial pressures of CO_2 , temperatures, or ion activities of Ca^{2+} and CO_3^{2-} . Prediction of significant calcite dissolution in the mixing zone can be quantified based on geochemical mass-transfer calculations (Herman, 1986). Porosity development in a limestone aquifer has been assessed in computer simulations by coupling a geochemical-reaction model with a solute-transport model (Sanford and Konikow, 1989a). Petrologic evidence of the effects of mixing-zone diagenesis has been obtained in Florida (Randazzo and Bloom, 1985), in the Bahamas (Smart and others, 1988), in Mexico (Ward and Halley, 1985), and in Pacific atolls (Anthony, 1987). Geomorphic expression of large-scale dissolution of coastal limestone is evidenced in the caves, coves, and caletas of the Yucatan Peninsula (Back and others, 1984).

Yet, the exact nature and extent of geochemical reactions in the mixing zone vary among these different settings, suggesting that the processes influencing the geochemical nature of mixing zones are more complex than has been originally hypothesized. Factors that influence the development of present-day mixing zones might include hydrologic conditions, geologic setting, local vegetation, and climate. Elucidation of these factors requires interdisciplinary and quantitative examination of suitable coastal environments.

Of these factors, we found that the hydrogeologic environment was the critical control in determining the effectiveness of geochemical reactions in a modern mixing zone on the island of Mallorca. In our study, we quantified the chemical mass-transfer reactions that give rise to observed ground-water compositions. In addition, the geochemistry of the ground water was related to bedrock petrology, to hydrogeologic setting, and to development of permeability and porosity within the present-day mixing zone.

MALLORCA

Mallorca is an island in the Mediterranean Sea ~180 km south of Barcelona (Fig. 1). Because there are only modest supplies of surface water on the island, ground water is extensively pumped to support domestic, industrial, and irrigation needs (J. A. Fayas, 1985, personal commun.). Average annual precipitation is 600 mm (Centelles, 1973). As is characteristic of most islands, a lens of fresh ground water floats on underlying saline water. As the fresh ground water flows toward the sea, it mixes with the intruding sea water to produce a zone of mixed composition.

The oldest bedrock on the island is Jurassic and Lower Cretaceous dolomitic limestone (Fig. 1). Three mountainous systems, the axes of which run northeast to southwest, are a result of tectonism during the late Oligocene and early Miocene (Butzer, 1962). Shallow-marine limestones deposited during the middle and late Miocene underlie a large part of the island. These Miocene limestones compose the cliffs along the southern coast and contain most of the caves on the island. Large lowland plains underlain by Miocene and Pleistocene limestones occur between the axial highlands and are thought to be epicontinental platforms eroded by an overlying shallow sea (Butzer, 1962). Two sites on Pleistocene bedrock, Camp de Tir (CT) in the south and Serra Nova (SN) in the

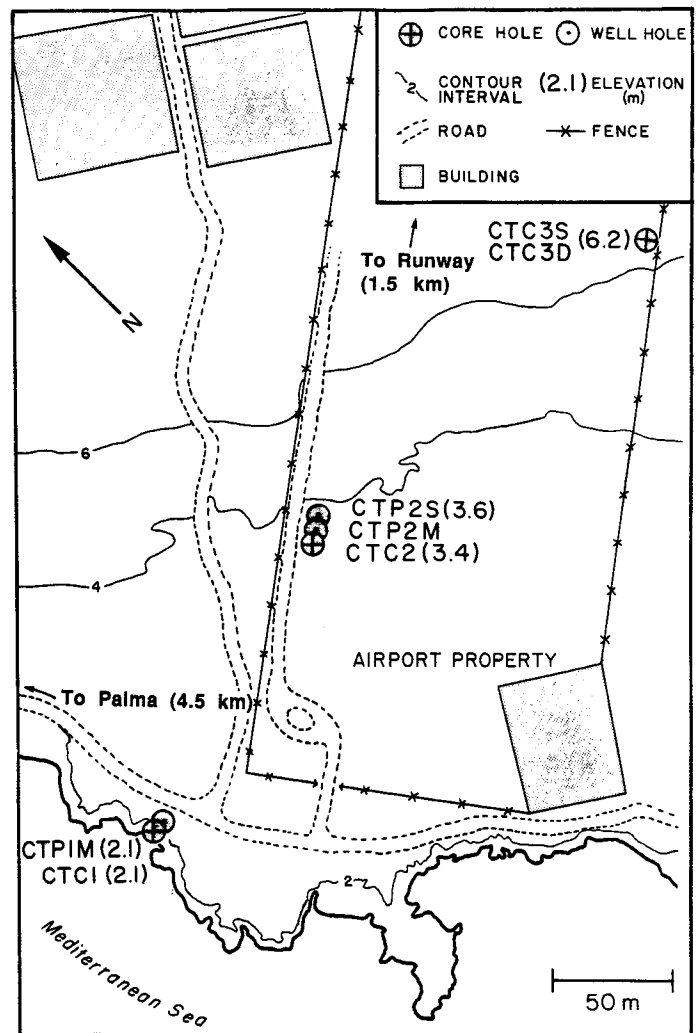


Figure 2. Site map of Camp de Tir, showing well hole and core hole locations.

north, were chosen as field sites for studying the hydrogeochemistry of the mixing zone.

The Camp de Tir site is near the Son San Juan Airport. The Pleistocene bedrock crops out throughout the site, and two cave notches occur at sea level. The bedrock is eolian and beach calcarenite (Sabaris, 1962) that appears to be highly porous with no evidence of large-scale fractures. The site is devoid of soil cover near the coastline. Approximately 100 m inland, a thin calcareous sand cover supports some grasses and scrub bushes. At the Serra Nova site, the Pleistocene bedrock crops out adjacent to the shoreline, but farther inland, the bedrock is covered by a thin layer of calcareous sand that thickens landward toward a dune complex. Grasses and bushes vegetate the sand-covered areas, and small trees grow on the dunes.

METHODS

Field Methods

Drilling and installation of ground-water samplers were accomplished in March 1986 (Price, 1988). At Camp de Tir, 3 core holes (CTC1,

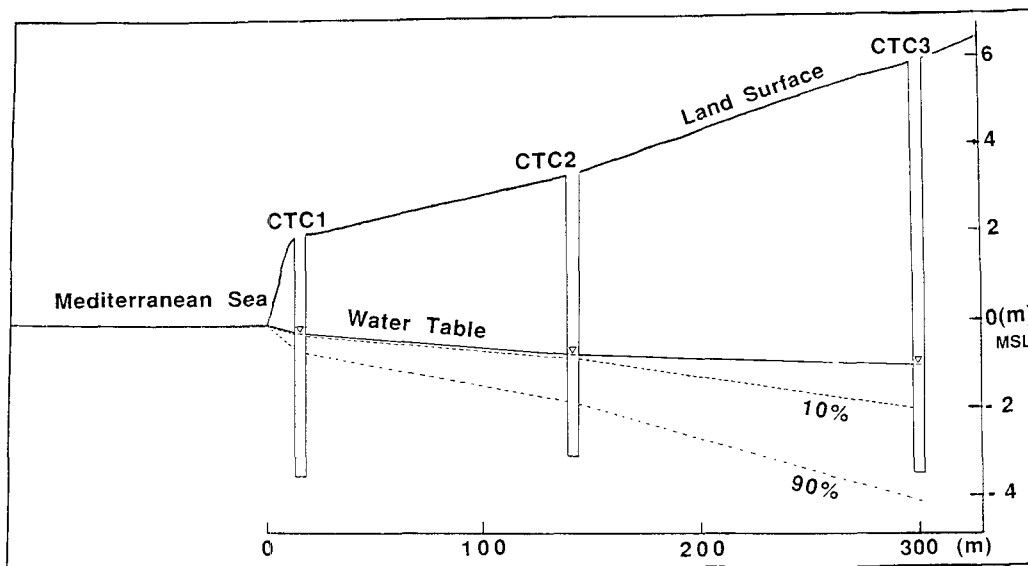


Figure 3. Hydrologic cross section of Camp de Tir. The dashed lines represent ground-water salinities comparable to 10% and 90% sea water in a mixture and delineate the approximate location of the mixing zone.

CTC2, and CTC3) were drilled in a 300-m-long transect perpendicular to the coastline (Fig. 2). Three well holes were drilled to shallower depths: well CTP1M adjacent to CTC1, and wells CTP2S and CTP2M adjacent to CTC2. At Serra Nova, core holes SNC1 and SNC2 were drilled approximately 25 and 110 m from the coastline, respectively. All core holes and well holes were advanced using rotary drilling methods. Drilling fluid was fresh water at Camp de Tir and sea water at Serra Nova.

Ground-water observation wells were installed in core holes CTC1 and CTC2 and well holes CTP1M, CTP2S, and CTP2M. The wells were constructed of 4.4-cm-inner-diameter PVC, with the bottom 20 cm perforated for ground-water collection. A coarse-grained, dolomitic limestone gravel pack was set around the PVC pipe to at least 15 cm above the perforated section. A bentonite slurry at least 40 cm thick was poured on top of the gravel. Well points were placed at various depths in core holes CTC3, SNC1, and SNC2. Well points (31 cm long with 2.5 cm outer diameter) were made of perforated PVC covered with a plastic screen mesh. A hard plastic tygon tube was attached to the top of the well point by a stainless steel Swagelok fitting and extended to the ground surface. Each well point was surrounded by a dolomitic limestone gravel pack. A bentonite seal was placed between two consecutive well points and above the top well point. Depths to screened intervals are given in the section "Geochemical Analysis" of this paper.

Ground-water samples were collected in March and July 1986. Ground water was pumped using a peristaltic pump for approximately 30 min while temperature, conductivity, and salinity were monitored until constant, using a thermometer, a YSI Model 33 conductivity meter, and a refractometer. Ground-water samples were filtered through a 0.45- μ m filter, and acidified and unacidified samples were collected for analysis of cations and anions, respectively. The pH was measured using an Orion Ross combination electrode and an Orion Model 231 pH meter using both pH 4.00 and 7.00 buffers. Alkalinities were performed in duplicate by titrating a continuously stirred 10-mL sample of ground water with 0.02 N HCl using a 2.0-mL Gilmont microburet. Titration end points were taken to be the inflection points in the cumulative acid added versus pH curve. Bicarbonate was assumed to be the only species contributing to alkalinity.

In addition to the ground-water samples, a sample of Mediterranean sea water was collected near each study site. A fresh ground-water sample was collected in July from a private well in Esglaïeta, located ~8 km north of Palma and in the Pleistocene bedrock.

The elevations of the core and well holes at the Camp de Tir site were determined relative to sea level. A clinometer was used with a stadia rod to determine elevation differences, and a tape measure was used to determine horizontal distances. Bearing was measured using a Brunton compass. The elevations and water-level measurements were used to obtain hydraulic gradients.

Rock Properties

Twenty-seven 5-cm-long cylindrical sections of the rock core were selected from depths representing a range in ground-water salinities and

TABLE 1. SUMMARY OF ROCK CORE DATA

| Sample | Depth below water table (m) | Depth below surface (m) | Salinity* (ppt) | Percent sea water | n^{\dagger} | K^{\dagger} (cm s^{-1}) |
|--------|-----------------------------|-------------------------|-----------------|-------------------|---------------|--------------------------------------|
| CT1A | 0.2 | 2.5 | 21.8 | 57 | 0.38 | 0.05 |
| CT1B | 0.7 | 3.0 | 35.4 | 93 | 0.39 | 0.04 |
| CT1C | 1.7 | 4.0 | 36.5 | 96 | 0.42 | 0.02 |
| CT2A | -0.3 | 3.7 | — | — | 0.37 | 0.06 |
| CT2B | 0.5 | 4.5 | 31.8 | 84 | 0.32 | 0.10 |
| CT2C | 1.1 | 5.1 | 37.5 | 99 | 0.40 | 0.17 |
| CT2D | 1.5 | 5.5 | 38.0 | 100 | 0.38 | 0.29 |
| CT2E | 1.8 | 5.8 | 38.0 | 100 | 0.46 | 0.13 |
| CT2F | 2.4 | 6.4 | 28.0 | 74 | 0.03 | 0.12 |
| CT3A | -2.3 | 4.5 | — | — | 0.40 | 0.10 |
| CT3B | -0.3 | 6.5 | — | — | 0.33 | 0.05 |
| CT3C | 0 | 6.8 | 1.2 | 3 | 0.34 | 0.05 |
| CT3D | 0.4 | 7.2 | 3.1 | 8 | 0.42 | 0.08 |
| CT3E | 0.6 | 7.4 | 3.3 | 9 | 0.36 | 0.04 |
| CT3F | 1.1 | 7.9 | 3.8 | 10 | 0.38 | 0.05 |
| CT3G | 1.9 | 8.7 | 5.0 | 13 | 0.30 | 0.03 |
| CT3H | 2.5 | 9.3 | 5.1 | 13 | 0.32 | 0.05 |
| SN1A | 0 | 2.6 | — | — | 0.27 | 0.13 |
| SN1B | 0.4 | 3.0 | 7.3 | 19 | 0.26 | 0.02 |
| SN1C | 1.8 | 4.4 | 8.6 | 23 | 0.45 | 0.13 |
| SN1D | 3 | 5.6 | 8.7 | 23 | 0.32 | 0.06 |
| SN2A | -1.8 | 2.9 | — | — | 0.28 | 0.15 |
| SN2B | -0.9 | 3.8 | — | — | 0.09 | — |
| SN2C | 0 | 4.6 | 8.7 | 23 | 0.33 | 0.04 |
| SN2D | 3.3 | 8.0 | 8.7 | 23 | 0.57 | 0.11 |
| SN2E | 5.3 | 10.0 | 23.2 | 61 | 0.27 | — |
| SN2F | 6.6 | 11.3 | 29.1 | 77 | 0.31 | 0.07 |

*Salinity values correspond to ground-water composition at the depth from which the rock core was collected.
 n^{\dagger} , laboratory-determined porosity; K^{\dagger} , laboratory-determined hydraulic conductivity.

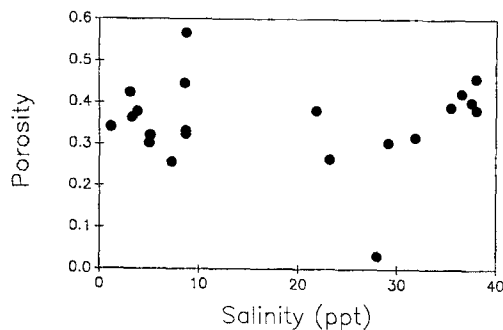


Figure 4. Laboratory-determined porosity values of Mallorcan limestone versus in situ ground-water salinity.

were prepared by rinsing in dilute nitric acid to remove fines created by sawing the cores (Price, 1988). Porosity (n) was determined from the ratio of pore volume (V_{pore}) to bulk volume (V_{bulk}). The bulk volume was computed from the dimensions of the cylindrical core (Lama and Vutukuri, 1978). The pore volume was computed from the difference in the water-saturated and dry masses of the core sample.

The hydraulic conductivity (K) of each rock core was determined by a standard falling-head test (Price, 1988). Rock cores were sealed with silicon rubber into polycarbonate tubing, saturated with deionized water in a vacuum desiccator, and then placed on a stand in a pan that allowed water to flow unobstructed from the bottom of the core into the pan.

Petrographic analysis of the rock core was conducted in the Department of Geology and Geophysics, University of New Orleans, by William C. Ward and Allan Weidmer. The petrographic description of the rock core was compared to the chemical analysis of the ground-water samples in order to identify the geochemical reactions that characterized the mixing-zone ground water.

Chemical Characterization of Water Samples

The chemical composition of the water samples was determined by standard methods in the laboratories of the Water Resources Division, U.S. Geological Survey, Reston, Virginia. The saturation state of the water samples with respect to the major carbonate minerals and the partial pressure of carbon dioxide were determined by use of the equilibrium-speciation model WATEQF (Plummer and others, 1976a). Chemical concentrations and field pH, temperature, and alkalinity were input to the model WATEQF through use of the program WATIN (Moses and Herman, 1986).

The geochemical reaction-path model PHREEQE (Parkhurst and others, 1980) was used to simulate conservative mixing of local, fresh ground water (that is, the sample collected at Esglaieta) with Mediterranean seawater (that is, the average of the compositions of the two seawater samples collected in March and the sample collected in July). The mixing was modeled for a system closed with respect to CO_2 . The assumption of closed-system conditions is valid, because such conditions commonly dominate below the water table. The charge imbalance of the initial solutions was maintained in the mixing calculations, and the temperature of the mixed solutions varied linearly from the end-member solutions. For each mixture, PHREEQE was used to calculate its chemical composition, saturation states with respect to the carbonate minerals, and partial pressure of CO_2 .

Several analytical techniques were used to decipher the geochemical processes that govern the chemical composition of the mixing-zone ground

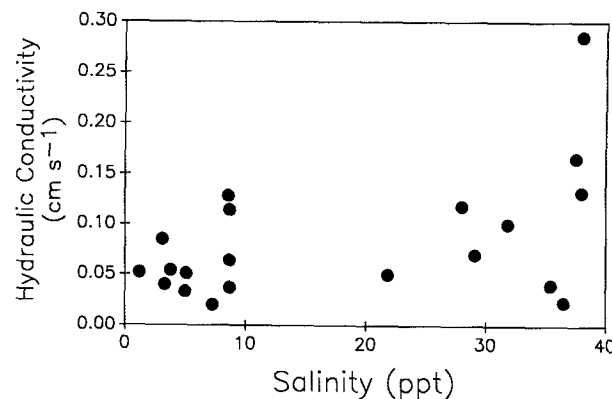


Figure 5. Laboratory-determined hydraulic conductivity of Mallorcan limestone versus in situ ground-water salinity.

water. The basis for each technique was to compare some aspect of the observed ground-water composition in the mixing zone to a value of that same chemical parameter that would result from conservative mixing of sea water and fresh water. Deviations in the observed chemistry from the mixing-generated values provide evidence of nonconservative processes such as carbonate mineral dissolution, precipitation, alteration, and CO_2 ingassing or outgassing occurring in the actual mixing zone.

A mass-balance calculation (Plummer and Back, 1980) was applied to bromide, assuming it to be conservative in the mixing process, to define the fraction of each end-member water in a mixture. The mixing fraction for bromide was applied to all other constituents in the end-member waters in order to estimate their total concentrations in the mixed water, if they too were conserved during mixing. The mixing calculations resulted in the sea-water-dilution line. The observed concentrations of the chemical constituents plotted either above or below the line, indicating enhancement or depletion, respectively. An enhancement of a constituent suggests a contribution to the ground water from mineral dissolution, whereas a depletion suggests mineral precipitation or outgassing.

The amount of a mineral phase required to dissolve or precipitate per mass of H_2O in order to account for the observed water compositions relative to the mixing-generated values was determined by mass-transfer calculations (Plummer, 1977; Plummer and Back, 1980). The calculations are based on the difference in total concentrations between the observed ground-water compositions and the predicted mixture compositions. A positive mass transfer indicates that dissolution of a mineral or ingassing has occurred into the ground water beyond what is expected by conservative mixing. A negative mass transfer indicates that precipitation of a mineral or outgassing has occurred.

Aragonite, calcite, and CO_2 gas were chosen as sources or sinks for Sr^{2+} , Ca^{2+} , and total inorganic carbon (C_T). Although the strontium content of biogenic aragonite varies widely, a molar $\text{Sr}^{2+}/\text{Ca}^{2+}$ of 0.01 is commonly reported (Kinsman, 1969); therefore, this value was used in mass-balance calculations. Mass-balance reactions used to quantify the mass of each mineral or gas transferred into or out of the ground water relative to the sea-water-dilution lines were

$$\text{aragonite} = \Delta \text{Sr}^{2+} + 100 (\Delta \text{Sr}^{2+}) \quad (1a)$$

$$\text{calcite} = \Delta \text{Ca}^{2+} - \Delta \text{aragonite} \quad (1b)$$

$$\text{CO}_2 = \Delta \text{C}_T - (\Delta \text{calcite} + \Delta \text{aragonite}) \quad (1c)$$

The source-rock contributions of calcium and strontium to the observed ground-water composition were determined by subtracting the sea-

TABLE 2. CHEMICAL COMPOSITION OF WATER SAMPLES

| Sample | Date | Screened interval (m) | Temp. (°C) | Cond. (mS cm ⁻¹) | Salinity (ppt) | pH | HCO ₃ ⁻ | Cl ⁻ | F ⁻ | Br ⁻ | NO ₃ ⁻ | SO ₄ ²⁻ | Na ⁺ | K ⁺ | Ca ²⁺ | Mg ²⁺ | Sr ²⁺ | SiO ₂ | Fe(tot) | Mn(tot) |
|--------|------|-----------------------|------------|------------------------------|----------------|------|-------------------------------|-----------------|----------------|-----------------|------------------------------|-------------------------------|-----------------|----------------|------------------|------------------|------------------|------------------|---------|---------|
| CTP1M | 3-22 | 2.25-2.45 | 14.5 | 39.5 | 24.5 | 7.82 | 135.1 | 20500 | 1.9 | 62.0 | — | 2800 | 11600 | 461 | 438 | 1340 | 4.0 | 1.7 | 0.00 | 0.11 |
| | | | 7-30 | 25.2 | 41.1 | 24.5 | 7.56 | 139.6 | 207000 | 2.2 | 76.0 | — | 2910 | 11800 | 491 | 442 | 1370 | 3.9 | 1.4 | 0.03 |
| CTC1 | 3-22 | 4.65-4.85 | 14.4 | 44.5 | 38.0 | 7.62 | 137.3 | 21000 | 2.2 | 70.0 | — | 2770 | 12000 | 486 | 446 | 1390 | 4.1 | 0.4 | 0.00 | 0.11 |
| | | | 7-28 | 26.0 | 47.0 | 28.2 | 7.56 | 135.6 | 21200 | 2.3 | 67.0 | — | 2950 | 12000 | 488 | 435 | 1380 | 3.8 | 1.3 | 0.03 |
| CTP2S | 7-30 | 3.65-3.85 | 19.8 | 10.1 | 6.2 | 7.55 | 272.7 | 4740 | 0.9 | 18.0 | 22 | 612 | 2660 | 122 | 189 | 318 | 2.5 | 3.5 | 0.00 | 0.01 |
| CTP2M | 3-22 | 4.05-4.25 | 18.2 | 12.6 | 9.0 | 7.63 | 217.8 | 5170 | 0.8 | 16.0 | 25 | 632 | 2820 | 124 | 216 | 320 | 2.6 | 4.9 | 0.00 | 0.03 |
| | | | 7-30 | 19.4 | 17.9 | 11.1 | 7.32 | 202.6 | 7950 | 1.2 | 28.0 | — | 1070 | 4410 | 193 | 250 | 550 | 4.5 | 2.5 | 0.07 |
| CTC2 | 3-22 | 4.65-4.85 | 18.6 | 24.0 | 16.0 | 7.59 | 193.2 | 9300 | 1.3 | 29.0 | 20 | 1330 | 5180 | 228 | 255 | 582 | 3.4 | 2.9 | 0.00 | 0.06 |
| | | | 7-30 | 19.7 | 37.8 | 25.2 | 7.46 | 146.4 | 20400 | 2.0 | 71.0 | — | 2790 | 11600 | 482 | 428 | 1340 | 3.8 | 1.9 | 0.01 |
| CTC3S | 3-23 | 7.15-7.46 | 18.1 | 6.60 | 5.0 | 7.42 | 327.3 | 2210 | 0.2 | 15.0 | 32 | 407 | 1220 | 40 | 196 | 180 | 1.9 | 13.0 | 0.00 | 0.01 |
| | | | 7-29 | 22.4 | 7.80 | 4.4 | 7.46 | 349.0 | 2740 | 0.4 | 7.9 | — | 459 | 1450 | 67 | 192 | 225 | 2.0 | 9.0 | 0.03 |
| CTC3D | 3-23 | 8.90-9.30 | 18.1 | 8.28 | 5.0 | 7.27 | 343.3 | 2820 | 0.4 | 11.0 | 21 | 421 | 1530 | 62 | 205 | 232 | 2.4 | 9.8 | 0.00 | 0.01 |
| | | | 7-29 | 20.5 | 7.60 | 4.8 | 7.32 | 349.7 | 2820 | 0.3 | 9.3 | 21 | 475 | 1530 | 65 | 199 | 230 | 2.1 | 9.2 | 0.00 |
| SNC1 | 3-24 | 5.00-5.30 | 18.7 | 12.4 | 8.0 | 7.42 | 300.8 | 4360 | 0.4 | 18.0 | 19 | 657 | 2420 | 86 | 253 | 282 | 2.3 | 8.1 | 0.00 | 0.02 |
| | | | 7-31 | 19.4 | 10.4 | 6.8 | 7.27 | 292.3 | 4580 | 0.4 | 18.0 | 15 | 674 | 2540 | 91 | 260 | 295 | 2.5 | 8.3 | 0.00 |
| SNC2S | 3-25 | 7.50-7.80 | 17.8 | 12.2 | 8.0 | 7.38 | 292.9 | 4680 | 0.5 | 20.0 | 25 | 682 | 2540 | 91 | 268 | 305 | 2.5 | 8.8 | 0.00 | 0.01 |
| | | | 7-31 | 19.0 | 14.0 | 8.1 | 7.42 | 284.3 | 5430 | 0.4 | 23.0 | 19 | 800 | 3060 | 111 | 282 | 355 | 2.7 | 8.5 | 0.03 |
| SNC2D | 3-25 | 11.65-11.96 | 17.8 | 42.0 | 32.0 | 7.73 | 153.8 | 19100 | 1.8 | 63.0 | — | 2660 | 10800 | 438 | 428 | 1240 | 4.1 | 3.9 | 0.00 | 0.09 |
| | | | 7-31 | 19.7 | 34.0 | 22.5 | 7.36 | 178.5 | 18600 | 1.6 | 65.0 | — | 2610 | 10500 | 428 | 424 | 1200 | 4.1 | 6.6 | 0.01 |
| Eslg. | 8-1 | | 19.0 | 7.70 | 0.9 | 7.25 | 334.1 | 58 | 0.0 | 1.9 | 4.7 | 99 | 31 | 2.9 | 119 | 25 | 0.9 | 6.6 | 0.03 | 0.00 |
| CT sea | 3-22 | | 14.4 | 43.6 | 38.0 | 8.29 | 159.9 | 20900 | 2.1 | 70.0 | — | 2910 | 12000 | 491 | 431 | 1350 | 3.9 | 1.0 | — | 0.12 |
| | | | 7-30 | 26.6 | 45.4 | 37.7 | 8.10 | 155.3 | 21000 | 2.2 | 80.0 | — | 2980 | 11700 | 520 | 440 | 1390 | 3.7 | 0.0 | 0.00 |
| SN sea | 3-24 | | 17.4 | 37.0 | 37.0 | 8.33 | 172.7 | 19400 | 2.0 | 66.0 | — | 2710 | 11000 | 458 | 431 | 1270 | 4.1 | 1.4 | 0.00 | 0.09 |

Note: all samples were collected in 1986; all concentrations are reported in mg L⁻¹.

water composition from the mixed-water composition (Plummer and others, 1976b). By using the bromide concentration in the ground water and the molar ratios of Ca²⁺/Br⁻ (12.018) and Sr²⁺/Br⁻ (0.049) in Mediterranean sea water, the sea-water contribution of Ca²⁺ and Sr²⁺ to the mixture was calculated. The sea-water composition was subtracted from the total composition in the mixture to obtain the source-rock contribution. In this calculation, it is assumed that all sources of Ca²⁺ and Sr²⁺ other than rock sources, such as recharging rainfall, either are negligible or have molar ratios similar to that of sea water. It is also assumed in the calculation that the only source of bromide in the ground water is sea water.

RESULTS

Hydrologic Parameters

The hydraulic gradient at Camp de Tir from the coast to well CTC3 was 0.003 in March 1986, indicating that ground-water flow was directed landward (Fig. 3). The location of the mixing zone was determined from the salinity profiles measured in the core holes in March 1986 before piezometers were installed. Mixing zones are commonly characterized by waters varying in salinity from 10% to 90% seawater. With a sea-water salinity of 38 ppt, the mixing zone on Mallorca is represented by salinities from 3.8 to 34.2 ppt (Fig. 3). The thickness of the mixing zone at Camp de Tir increased landward and ranged from 0.35 m in well CTC1 to greater than 2.8 m in well CTC3.

Rock Properties

The porosity values range from 0.03 to 0.57, with a mean value of 0.34 (Table 1). Hydraulic conductivity values range from 0.02 to 0.29 cm s⁻¹, with a mean value of 0.09 cm s⁻¹. Porosity and hydraulic conductivity of the rock core segments were evaluated as a function of their corresponding in situ water salinities (Figs. 4 and 5). Both parameters appear to be independent of salinity.

On the basis of petrographic analysis, the bedrock originally contained 16% to 73% high-Mg calcite, 0% to 63% aragonite, 11% to 63% calcitic mollusks and lithoclasts, and 0% to 11% dolomite lithoclasts (Weidmer, 1990). Currently, aragonite is found in the vadose zone, but not in the phreatic zone. Below the water table, the mollusks that were

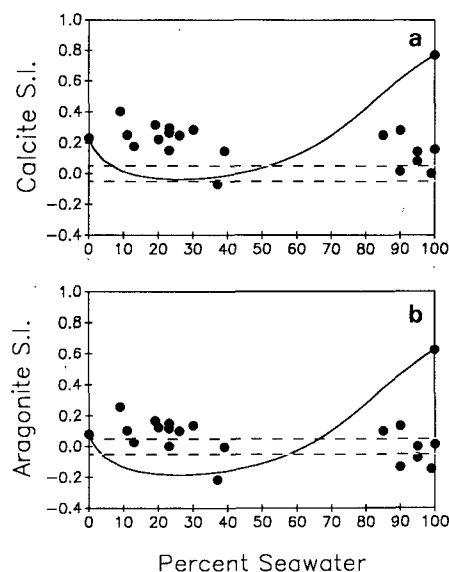


Figure 6. Calcite (a) and aragonite (b) saturation index versus ground-water composition expressed as percent sea water in a mixture. The solid curvilinear line is the saturation state calculated by PHREEQE when simulating the mixing of fresh ground water collected at Esglaieta with an average Mediterranean sea-water composition under closed-system conditions. The saturation states for the ground waters collected in both March and July 1986 are plotted as points.

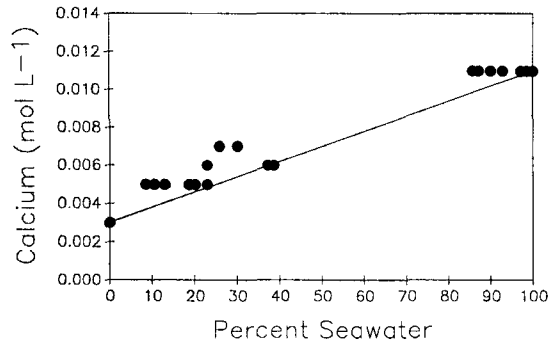


Figure 7. Calcium concentrations of the Mallorcan ground waters (points) are enhanced with respect to the calcium seawater-dilution line.

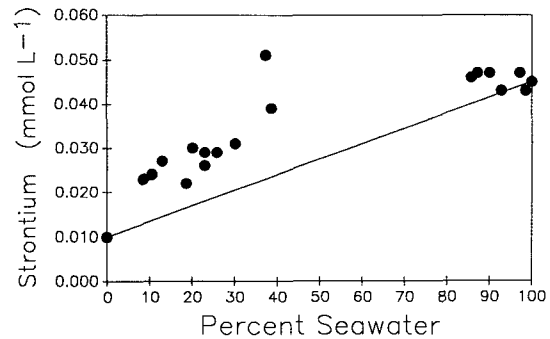


Figure 8. Strontium concentrations of the Mallorcan ground waters (points) are enhanced with respect to the strontium seawater-dilution line.

once aragonite are mostly molds, but some have been neomorphosed to calcite. Calcite cement occurs in both the vadose and phreatic zones. All of the dolomite present appears to be lithoclasts originally deposited in the sediments.

Geochemical Analysis

The results of the chemical analyses of the water samples upon which the geochemical interpretations are based are presented in Table 2. The fresh ground water from Eselaieta was supersaturated with respect to calcite and aragonite ($SI_c = +0.225$, $SI_a = +0.077$; Table 3). The average Mediterranean sea water was supersaturated with respect to all three carbonate minerals ($SI_c = +0.770$, $SI_a = +0.623$, $SI_d = +2.314$). Theoretical calculations of adding Mediterranean sea water to fresh Mallorcan ground water predict that the saturation index with respect to calcite would decrease, reach a minimum value of -0.038 in a mixture of 26% seawater, and then increase (Fig. 6a). Due to uncertainties in the analytical and thermodynamic data, SI_c and SI_a values are accurate to ± 0.05 . Given this range of accuracy, the minimum SI_c value of -0.038 occurring at 26% sea

water cannot be differentiated from equilibrium. The saturation-index curve for aragonite is offset from the calcite curve by -0.148 (Fig. 6b), and the SI_a values for the mixture are negative from 4% to 58% seawater.

The majority of the ground-water samples from the mixing zone were supersaturated with respect to both calcite and aragonite (Table 3). All of the water samples were supersaturated with respect to dolomite. The saturation indices of the water samples do not differ noticeably between March and July; therefore, all the data are combined in Figure 6. The observed saturation states of the ground-water samples, in contrast to those for the calculated mixtures, do not vary with percent sea-water composition.

Mass-Balance Calculations. Calcium and strontium were enriched relative to the sea-water-dilution line in nearly every ground-water sample (Figs. 7 and 8). A Wilcoxon signed-rank test (Lapin, 1983) showed that the differences between the observed water chemistry and the seawater-dilution line were statistically significant at the 5% significance level ($P < 0.0005$). Total inorganic carbon (C_T) was depleted in most of the ground waters relative to conservative mixing (Fig. 9), and the depletion was significant ($P < 0.0005$). Magnesium concentrations in the ground waters plotted near the sea-water-dilution line and were not significantly different ($P > 0.10$) from the predicted values for conservative mixing. The concentrations of sulfate, sodium, and potassium in the ground waters were also statistically similar to their sea-water-dilution values, indicating that these constituents behave conservatively during mixing.

Mass-Transfer Calculations. A positive mass transfer of aragonite, indicating mineral dissolution, was calculated for all but one of the ground-water samples (Table 4). The average mass transfer of aragonite was $+0.869 \text{ mmol kg}^{-1} \text{ H}_2\text{O}$. This result suggests that a large quantity of aragonite must have dissolved into the ground waters to account for the enhanced concentrations of strontium. The calculated mass-transfer values of calcite varied from -2.498 to $+0.723 \text{ mmol kg}^{-1} \text{ H}_2\text{O}$. Seven out of 19 ground-water samples had negative values. The amount of calcite precipitated from these ground waters was large enough to produce an average mass transfer of $-0.027 \text{ mmol calcite kg}^{-1} \text{ H}_2\text{O}$. This result suggests that the amount of aragonite that dissolved into the ground water was large enough to drive precipitation of calcite.

The large mass of aragonite predicted to dissolve and, thus, force calcite precipitation seems unreasonable. The estimate of 0.01 for the $\text{Sr}^{2+}/\text{Ca}^{2+}$ ratio in the aragonite may be inaccurate. Additional mass-transfer calculations were performed without considering aragonite (Table 4). These calculations resulted in positive mass-transfer values for calcite in all but two of the ground-water samples, and the amount of calcite theoretically precipitated from those two samples was at least an order of magnitude smaller than the amount dissolved into the others. Outgassing of CO_2

TABLE 3. SATURATION INDICES OF CALCITE, ARAGONITE, AND DOLOMITE, AND LOG P_{CO_2} OF GROUND WATERS

| Sample | Date | log P_{CO_2} | pH | SI_c | SI_a | SI_d |
|--------|------|-----------------------|------|--------|--------|--------|
| CTP1M | 3-22 | -3.00 | 7.82 | 0.25 | 0.10 | 1.26 |
| | 7-30 | -2.70 | 7.56 | 0.16 | 0.01 | 1.22 |
| CTC1 | 3-22 | -2.80 | 7.62 | 0.08 | -0.07 | 0.92 |
| | 7-28 | -2.70 | 7.56 | 0.14 | 0.00 | 1.21 |
| CTP2S | 7-30 | -2.28 | 7.55 | 0.27 | 0.12 | 1.07 |
| CTP2M | 3-22 | -2.47 | 7.63 | 0.27 | 0.12 | 1.01 |
| | 7-30 | 2.22 | 7.32 | -0.07 | -0.22 | 0.52 |
| CTC2 | 3-22 | -2.52 | 7.59 | 0.15 | -0.00 | 0.96 |
| | 7-30 | -2.59 | 7.46 | 0.00 | -0.15 | 0.85 |
| CTC3S | 3-23 | -2.05 | 7.42 | 0.32 | 0.17 | 0.87 |
| | 7-29 | -2.04 | 7.46 | 0.40 | 0.26 | 1.22 |
| CTC3D | 3-23 | -1.88 | 7.24 | 0.18 | 0.03 | 0.69 |
| | 7-29 | -1.91 | 7.32 | 0.25 | 0.10 | 0.88 |
| SNC1 | 3-24 | -2.11 | 7.42 | 0.30 | 0.15 | 0.94 |
| | 7-31 | -1.97 | 7.27 | 0.15 | 0.00 | 0.66 |
| SNC2S | 3-25 | -2.09 | 7.38 | 0.25 | 0.10 | 0.84 |
| | 7-31 | -2.15 | 7.42 | 0.28 | 0.14 | 0.97 |
| SNC2D | 3-25 | -2.84 | 7.73 | 0.28 | 0.13 | 1.35 |
| | 7-31 | -2.38 | 7.36 | 0.02 | -0.13 | 0.83 |
| Esig. | 8-1 | -1.79 | 7.25 | 0.23 | 0.08 | 0.05 |
| CT sea | 3-22 | -3.48 | 8.29 | 0.73 | 0.58 | 2.23 |
| | 7-30 | -3.23 | 8.10 | 0.70 | 0.55 | 2.46 |
| SN sea | 3-24 | -3.47 | 8.33 | 0.84 | 0.69 | 2.32 |

TABLE 4. MASS TRANSFERS (IN $\text{mmol kg}^{-1} \text{H}_2\text{O}$) OF ARAGONITE, CALCITE, AND CO_2 GAS FOR THE CONDITIONS OF ARAGONITE CONSIDERED IN THE CALCULATIONS AND NOT CONSIDERED

| Sample | Date | Considering aragonite | | | Without aragonite | |
|---------|------|-----------------------|---------|---------------|-------------------|---------------|
| | | Aragonite | Calcite | CO_2 | Calcite | CO_2 |
| CTP1M | 3-22 | 0.596 | 0.628 | -1.961 | 1.224 | -1.961 |
| | 7-30 | 0.000 | 0.228 | -0.335 | 0.228 | -0.335 |
| CTC1 | 3-22 | 0.333 | 0.229 | -0.778 | 0.563 | -0.778 |
| | 7-28 | 0.131 | 0.470 | -1.052 | 0.601 | -1.052 |
| CTP2S | 7-30 | 1.050 | -1.106 | -0.573 | -0.055 | -0.573 |
| CTP2M | 3-22 | 1.263 | -0.409 | -2.556 | 0.853 | -2.556 |
| | 7-30 | 2.868 | -2.498 | -1.573 | 0.370 | -1.573 |
| CTC2 | 3-22 | 1.535 | -1.197 | -1.766 | 0.339 | -1.766 |
| | 7-30 | -0.081 | 0.038 | 0.046 | -0.043 | 0.046 |
| CTC3S | 3-23 | 0.495 | -0.062 | -0.149 | 0.433 | -0.149 |
| | 7-29 | 0.949 | 0.166 | -0.897 | 1.116 | -0.897 |
| CTC3D | 3-23 | 1.273 | -0.146 | -0.629 | 1.127 | -0.629 |
| | 7-29 | 1.000 | 0.134 | -0.667 | 1.134 | -0.667 |
| SNC1 | 3-24 | 0.818 | 0.723 | -1.600 | 1.542 | -1.600 |
| | 7-31 | 1.050 | 0.666 | -1.803 | 1.716 | -1.803 |
| SNC2S | 3-25 | 0.677 | 0.220 | -0.945 | 0.897 | -0.945 |
| | 7-31 | 0.576 | -0.014 | -0.668 | 0.562 | -0.668 |
| SNC2D | 3-25 | 0.939 | 0.742 | -2.006 | 1.681 | -2.006 |
| | 7-31 | 1.040 | 0.677 | -1.106 | 1.717 | -1.106 |
| Average | | 0.869 | -0.027 | -1.106 | 0.842 | -1.106 |

from all but one of the ground-water samples was calculated. The mass transfers of CO_2 were equal in both calculations.

Source-Rock Contribution. The average source-rock contributions of calcium and strontium to the ground waters were 2.18 mmol L^{-1} and 0.02 mmol L^{-1} , respectively (Table 5). These results combined with the results of the mass-balance and mass-transfer calculations demonstrated that strontium and calcium concentrations were enhanced in the ground water relative to conservative mixing and that the excess strontium and calcium were derived from dissolution of the limestone.

DISCUSSION

Flow Conditions

The present ground-water flow regime at Camp de Tir is not what one expects for a coastal aquifer under natural conditions (see Hubbert, 1940; Glover, 1959; Cooper, 1959). Fresh water no longer discharges from the aquifer to the coast. Instead, the water table occurs below sea level, and the ground water flows landward (Fig. 3). A 1979 potentiometric map (Servicio Hidraulic de Baleares, 1979) depicted a cone of depression in the vicinity of the Camp de Tir site. As a result of lower fresh-water head caused by ground-water withdrawals, sea water inevitably intruded farther into the aquifer, thus displacing the mixing zone higher and landward in the aquifer.

The mixing-zone thickness varied from 0.3 m to greater than 2.8 m at Camp de Tir (Fig. 3), which is thin compared to other reported mixing-zone thicknesses. Although there are differences among these studies in terms of distance from coastline and inclusive salinity range for the mixing zone, other authors have reported significantly thicker mixing zones: 6 m in aquifers on Cape Cod, Massachusetts (Reilly and others, 1987); 9 m in blue holes of Andros Island, Bahamas (Smart and others, 1988); 3 to 9 m in Bermuda (Vacher, 1978); and 13 to 25 m in Miami, Florida (Kohout, 1960). Two mechanisms that influence the thickness of the mixing zone are the flux of fresh water to the sea and the rise and fall of the local sea level as a result of tides (Cooper, 1959). The Mediterranean Sea experiences modest tides on the order of 0.6 m in response to barometric pressure changes. On Mallorca, the local ground-water withdrawals pre-

vent the flow of fresh water from the aquifer to the sea at Camp de Tir. The minor tidal effects and the absence of ground-water discharge results in a thin mixing zone at Camp de Tir.

Porosity and Hydraulic Conductivity

An enhancement in porosity or hydraulic conductivity is not observed in the rock core in contact with the transitory present-day mixing-zone ground water (Figs. 4 and 5). In addition, supersaturation of the ground water with respect to the carbonate minerals indicates that dissolution of the aquifer is not expected within the present mixing zone (Table 3). There was, however, a noticeable increase in the vugginess of the rock core collected from beneath the present-day water table as compared to the vadose zone.

Sanford and Konikow (1989b) used a coupled reaction-transport model to calculate the porosity increase resulting from calcite dissolution to equilibrium in the Camp de Tir aquifer. They assumed that before a cone of depression had developed near Camp de Tir, ground water flowed to the coast at a specific discharge of $6.4 \times 10^{-3} \text{ cm s}^{-1}$ and that the mixing zone was 3 m thick near the discharge area. If an initial aquifer porosity of 30% was assumed, predicted porosity values between 31% and 45% resulted, depending upon location in the aquifer. The simulation results further showed that a moving interface, due to change in sea level, would cause the dissolution of calcite in the mixing zone to spread over such a large area that little significant increase in porosity would be realized in any one position.

Quaternary glacially induced sea-level changes have had an effect on the position of the mixing zone since the Pleistocene calcarenites were deposited on Mallorca (Ginés and others, 1981a, 1981b). Present sea level, however, has been relatively stable for the past 2,000 to 3,000 yr, as compared to a fast-rising sea level 3,000 to 15,000 yr ago (Butzer and Cuerda, 1962; Pomar and Cuerda, 1979). Due to the cone of depression in the ground-water table, the present position of the mixing zone at Camp de Tir is not indicative of a long-term position. Thus, a measurable enhancement in porosity and permeability in the mixing zone relative to the rest of the aquifer would be difficult to discern.

Geochemical Interpretation

Most of the ground-water samples collected on Mallorca are in equilibrium or supersaturated with respect to aragonite, calcite, and dolomite (Table 3). Therefore, carbonate mineral precipitation, not dissolution, is expected from the mixing-zone ground waters. Calcite-supersaturated wa-

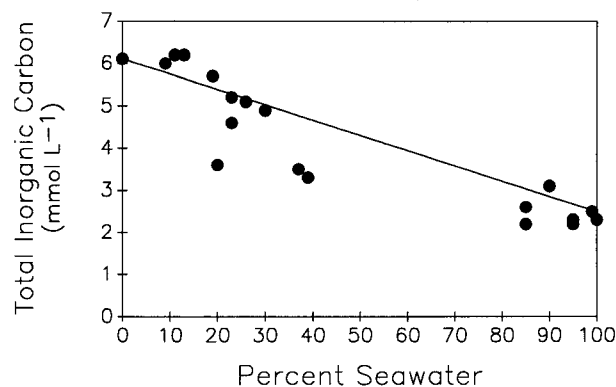


Figure 9. Total inorganic carbon (C_T) concentrations of the Mallorcan ground waters (points) are depleted with respect to the C_T sea-water-dilution line.

ters are common in caves and at springs where carbon dioxide outgassing is significant (Jacobson and Langmuir, 1970; Butler, 1982). Back and Hanshaw (1970) concluded that the dissolution of aragonite and high-Mg calcite, minerals with a higher solubility than calcite, resulted in calcite-supersaturated ground water in central Florida. Few studies have reported ground water supersaturated with respect to aragonite. Anthony and others (1989) reported mixing-zone waters on Laura Atoll, Marshall Islands, to have aragonite saturation indices as high as +0.73, but they did not provide an explanation for the highly supersaturated water.

Factors controlling the saturation states of ground water with respect to the carbonate minerals include changes in temperature, processes of cation exchange, fluxes of CO_2 , effects of mixing, and dissolution or precipitation of other carbonate minerals. Although changes in temperature affect the solubility of calcite (Thraillkill, 1968), in non-geothermal waters the effect of mixing two solutions of different temperature is relatively minor compared to the effect of mixing two solutions with different P_{CO_2} or ionic strength values (Wigley and Plummer, 1976). The seasonal temperature differences measured between the March and July sampling events were small (Table 2), and the relationship of temperature to the saturation index of calcite for the water samples (Table 3) was not consistent. Temperature effects are not considered a significant factor influencing the saturation states of the ground water on Mallorca.

When sea water intrudes into a coastal aquifer containing clay minerals, sodium ions in the sea water typically replace the calcium ions on exchange sites, causing a depletion of sodium with a corresponding enhancement of calcium in the ground water (Sayles and Mangelsdorf, 1977). Such ion-exchange reactions are thought to be responsible for ground water in the mixing zone in Coos Bay, Oregon, being supersaturated with respect to calcite and dolomite (Magaritz and Luzier, 1985). The ground water on Mallorca was significantly enhanced in calcium relative to conservative mixing of two end-member solutions (Fig. 7). Sodium concentrations, however, were similar to those predicted by seawater-fresh-water mixing (Price, 1988), and therefore, ion-exchange reactions are believed not to be influencing the saturation states of the mixing-zone ground water on Mallorca.

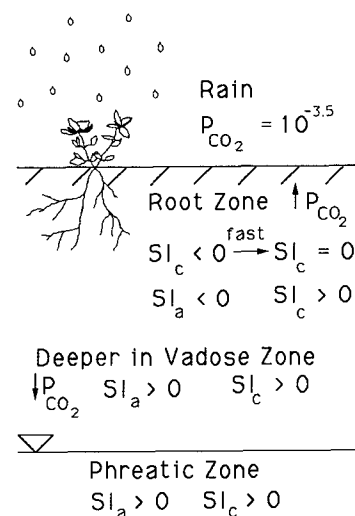
Carbon Dioxide Fluxes. The calculated P_{CO_2} values for all of the ground-water samples are above the atmospheric level of $10^{-3.5}$ atm

TABLE 5. SOURCE-ROCK CONTRIBUTIONS OF CALCIUM, MAGNESIUM, AND STRONTIUM

| Sample | Date | Ca | Mg | Sr |
|---------|------|-------|-------|------|
| CTP1M | 3-22 | 1.60 | 7.77 | 0.01 |
| | 7-30 | -0.40 | -1.68 | 0.00 |
| CTC1 | 3-22 | 0.60 | 3.72 | 0.01 |
| | 7-28 | 0.78 | 5.60 | 0.01 |
| CTP2S | 7-30 | 2.01 | -0.67 | 0.02 |
| CTP2M | 3-22 | 2.98 | 0.94 | 0.02 |
| | 7-30 | 2.03 | 1.24 | 0.04 |
| CTC2 | 3-22 | 2.00 | 1.79 | 0.02 |
| | 7-30 | 0.00 | 0.90 | 0.00 |
| CTC3S | 3-23 | 2.63 | -4.05 | 0.01 |
| | 7-29 | 3.60 | 3.22 | 0.02 |
| CTC3D | 3-23 | 3.46 | 1.14 | 0.02 |
| | 7-29 | 3.57 | 2.36 | 0.02 |
| SNC1 | 3-24 | 3.61 | -2.15 | 0.02 |
| | 7-31 | 3.78 | -1.61 | 0.02 |
| SNC2S | 3-25 | 3.68 | -2.73 | 0.02 |
| | 7-31 | 3.58 | -2.96 | 0.02 |
| SNC2D | 3-25 | 1.20 | 2.90 | 0.01 |
| | 7-31 | 0.80 | -0.28 | 0.01 |
| Average | | 2.18 | 0.81 | 0.02 |

Note: all results are expressed in mmol L^{-1} .

Figure 10. Schematic diagram of the geochemical reactions in the vadose zone influencing the chemical character of the mixing-zone ground water.



(Table 3). This result suggests that the ground water was charged with CO_2 following isolation from the Earth's atmosphere. Ground water can become charged with CO_2 by contact with soil gas during infiltration through the unsaturated zone or by gas production below the water table by chemical or biochemical reactions. The field sites on Mallorca have discontinuous soil cover, but grasses and scrub bushes grow at both sites. The roots of these plants are a source of CO_2 for infiltrating rainwater.

Figure 9 indicates an overall depletion of inorganic carbon in the ground-water samples relative to conservative mixing, and suggests an overall outgassing of CO_2 from the ground water. In addition, mass-transfer calculations, which consider dissolution of aragonite and calcite, indicate outgassing of CO_2 from the ground water (Table 4).

Outgassing of CO_2 is a probable cause for the supersaturated waters collected on Mallorca. Water in equilibrium with calcite will become supersaturated upon loss of dissolved CO_2 . Because outgassing would normally occur more rapidly than precipitation of calcite, the water can remain supersaturated with respect to calcite. Significant outgassing of CO_2 was unlikely from the time of sampling to the time of pH measurement, because the pH was measured within 15 min of sampling, and a considerable drift in the pH, an indication of CO_2 outgassing from the sample, was not observed.

Plummer and others (1976b) found that ground waters on Bermuda with $\log P_{\text{CO}_2}$ values between -2.0 and -3.0 were supersaturated with respect to aragonite and calcite. Bermudian limestones are Pleistocene in age and contain varying percentages of aragonite and low- and high-magnesium calcite. Plummer and others (1976b) determined that outgassing of CO_2 was responsible for the supersaturation with respect to calcite and aragonite. Outgassing was thought to occur from the ground water to the atmosphere through the permeable vadose zone in areas of incomplete soil cover such as hill tops or rocky areas near the shoreline.

Both study sites on Mallorca have discontinuous soil cover, and the water table is located only 2.2 to 6.6 m below the ground surface; therefore, a loss of CO_2 to the atmosphere through the permeable vadose zone is possible from the ground water located near the water table, either vadose-zone water or the phreatic lens. Carbon dioxide can be lost from infiltrating water as it passes the root zone to an area in the vadose zone with a lower P_{CO_2} , thereby losing CO_2 to the vadose-zone atmosphere (Reardon and others, 1980). This mechanism may be favored by a water table significantly below the root zone and by low infiltration rates, as found at our study sites.

The hydrologic configuration of the mixing zone observed on Mallorca is such that the ground water is mainly a mixture of local rainwater

which infiltrates through the vadose zone with the underlying Mediterranean sea water within the aquifer. Whether from vadose-zone water or from the phreatic lens, the chemical evidence is that CO_2 outgassing occurs, and this outgassing of CO_2 is the likely cause of the supersaturation with respect to the carbonate minerals. Further sampling from the vadose zone would be necessary to better define the mechanism of CO_2 loss.

Common-Ion Effect. As rainwater infiltrates through the vadose zone, it dissolves calcite and aragonite to equilibrium. Reardon and others (1980) concluded that calcite saturation is attained over a short time and distance in a calcareous sandy soil. The solubility of aragonite is higher for a given P_{CO_2} than calcite; therefore, calcite equilibrium is reached in the infiltrating rainwater before aragonite equilibrium. As aragonite continues to dissolve, the water may become supersaturated with respect to calcite.

Strontium concentrations are elevated relative to sea-water dilution in the Mallorcan ground water (Fig. 8). Strontium fits readily into the orthorhombic structure of aragonite but not into the rhombohedral structure of calcite; therefore, elevated strontium concentrations may indicate incongruent dissolution of aragonite with precipitation of low-magnesium calcite (Hanshaw and Back, 1985). Source-rock and mass-transfer calculations considering aragonite and calcite suggest dissolution of aragonite with precipitation of calcite (Tables 5 and 4). Petrographic analysis reveals that aragonite is readily available for dissolution in the vadose zone of the Pleistocene rock of Mallorca (Weidmer, 1990). The presence of crystalline calcite cement in both the vadose and phreatic zones of the Pleistocene bedrock suggests that calcite has precipitated from the ground water.

Dolomitization. All of the ground-water samples are supersaturated with respect to dolomite; therefore, dolomite formation is possible. A depletion of magnesium in the ground water would suggest formation of dolomite. It is thought that dolomitization is not occurring in this study area, because the magnesium concentrations in the ground-water samples are consistent with conservative fresh-water-sea-water mixing. Dolomite lithoclasts occur in the Pleistocene bedrock, but they are assumed to be a part of the original sediment (Weidmer, 1990).

The Active Vadose Zone

Our common concept of a coastal mixing zone, discharging fresh water mixing with intruding sea water at the downgradient boundary of the dynamic fresh-water flow system, is not realized at the study site at Camp de Tir. The pumping wells and the resulting cone of depression just inland of Camp de Tir prevent most of the fresh water from discharging to the sea. The mixing zone at Camp de Tir, therefore, is a function of mixing localized recharge, that is, rainwater which has percolated down through the vadose zone, with the underlying sea water. The composition of the small amount of fresh water entering the present-day mixing zone may be influenced by processes within the vadose zone.

We hypothesize that geochemical reactions in the vadose zone lead to the observed ground-water composition within the mixing zone of Mallorca. Rainwater enters the vadose zone and becomes charged with CO_2 near the surficial root zone (Fig. 10). This rainwater is initially undersaturated with respect to calcite and aragonite, and it proceeds to dissolve these minerals. Deeper within the vadose zone, the infiltrating water may reach equilibrium with respect to calcite, but still be undersaturated with respect to aragonite. Further dissolution of aragonite results in supersaturation with respect to calcite. As the water infiltrates to depths beneath the root zone, CO_2 outgasses, resulting in a supersaturation with respect to both minerals. Calcite precipitates, but not to a great enough extent for the water to reach equilibrium. With this theoretical model, we attempt to describe the observed water composition within the present-day mixing zone on Mallorca; however, we realize that sampling within the vadose zone is necessary to test this hypothesis.

CONCLUSIONS

The chemical composition of the mixing zone on Mallorca is not entirely described by conservative mixing of Mallorcan fresh water and Mediterranean sea water under closed-system conditions. Instead, the chemical composition of the ground water near the coast of Mallorca is strongly influenced by the local hydrologic setting. Nearby ground-water withdrawal results in a cone of depression and a hydraulic gradient that slopes inland at the Camp de Tir study site. The absence of fresh water discharging to the coast has resulted in a thin and geologically transitory mixing zone most probably formed by mixing of infiltrating rainwater with the underlying sea water.

Chemical compositions of the mixing-zone ground water suggest that dissolution of the limestone has occurred. Strontium and calcium concentrations were enriched in the ground water relative to sea-water dilution. Positive calcium and strontium source-rock contributions and aragonite and calcite mass transfers indicate that ground water has dissolved aragonite and calcite. Pleistocene bedrock on Mallorca contains aragonite in the vadose zone. Calcite cement occurs in both the vadose and the phreatic zones. A depletion in total inorganic carbon relative to conservative mixing of fresh water and sea water suggests that CO_2 outgassed from the ground water.

Porosity and hydraulic conductivity were not enhanced within the present position of the mixing zone. Most of the ground waters were at equilibrium or supersaturated with respect to the carbonate minerals; therefore, dissolution of the limestone aquifer was not expected within the present-day mixing zone.

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