33. INTERSTITIAL WATER CHEMISTRY IN THE WESTERN MEDITERRANEAN:
RESULTS FROM LEG 161

Stefano M. Bernasconi

ABSTRACT

The inorganic geochemistry of the interstitial waters recovered at all sites during Ocean Drilling Program Leg 161 is influenced by the presence of saline brines at depth. In general, this is reflected by a systematic downcore increase in salinity and chlorinity, commonly coupled with increases in the concentrations of Na, Ca, Mg, Sr, and Li. At Sites 974 (Tyrrhenian Sea) and 975 (Menorca Rise), where Messinian gypsum deposits are present at depth, sulfate is present throughout the cored intervals down to 200 and 306 meters below sea floor (mbsf), respectively. In contrast, sulfate is completely depleted by bacterial sulfate reduction at depths below 15–50 mbsf in the Alboran Basin. Despite the absence of Messinian evaporites, the highest salinities and chlorinities were observed at Sites 976 and 979 in the Alboran Basin. The increase in salinity at these sites can be related to the presence of a Messinian paleofluid trapped at depth or migrating laterally within the sedimentary sequence. Strontium, magnesium, and calcium concentrations, although also influenced by the presence of the brines at depth, are primarily controlled by carbonate recrystallization.

INTRODUCTION

The study of changes in the chemical composition of interstitial waters provides a powerful tool for characterizing bacterially mediated processes of organic matter degradation, diagenetic reactions, and processes of fluid diffusion and advection in marine sediments. Depth profiles of sulfate, ammonia, and alkalinity, unless evaporites are present at depth, are typically determined by the bacterial processes of decomposition of organic matter. Changes in Ca, Mg, alkalinity, and Sr can be used to characterize processes of carbonate precipitation and recrystallization. In addition, the concentration profiles of conservative solutes such as chloride, which are not involved in diagenetic reactions, can give valuable information about fluid sources. The oxygen isotope geochemistry of the interstitial waters in marine sediments is influenced by multiple factors, such as the original isotopic composition of the connate waters, isotopic exchange during diagenesis, and/or fluid flow. However, the combination of isotope geochemistry with major- and trace-element data provides important constraints on the origin of interstitial fluids. This paper presents the results of Ocean Drilling Program (ODP) Leg 161 shipboard analyses and postcruise oxygen isotope measurements. These collective data have been employed to constrain the origin and evolution of the pore fluids. The main goal of this study was to characterize the origin of the saline brines observed in the Alboran Basin. The origin of highly saline brines found throughout the Mediterranean in interstitial waters and in the eastern Mediterranean in deep hypersaline basins has long been a matter of debate (see Vengosh and Starinsky, 1993, and Vengosh et al., 1994, for recent reviews). In many instances, the increase in salinity with depth has been explained by dissolution of Messinian salts. However, as pointed out by Vengosh et al. (1994), the chemistry of most Mediterranean interstitial waters is not compatible with simple dissolution of salts. The results of this study support the interpretations of Vengosh et al. (1994), which suggested that most of the saline interstitial waters in the western Mediterranean are not produced by evaporite dissolution, but represent relics of ancient evaporated seawater.

METHODS

Interstitial water samples were obtained immediately after core recovery using the standard ODP titanium/stainless-steel squeezer (Manheim and Sayles, 1974) and Teflon disks. The interstitial waters were analyzed for salinity, alkalinity, chloride, sulfate, lithium, potassium, sodium, calcium, magnesium, strontium, ammonium, silica, and phosphate according to the methods described by Gieskes et al.

Figure 1. Map of the western Mediterranean showing the location of the sites drilled during Leg 161.
At Site 976 in the Western Alboran Basin, Pleistocene sediments (0–365 mbsf) are composed of hemipelagic nanofossil clays with an average carbonate content of 30% and background TOC content of 0.5%. A total of 28 organic carbon-rich layers with TOC contents varying between 0.8% and 1.85% occur intermittently in the Pleistocene sediments. Some of the organic carbon-rich layers reach a thickness of up to 3 m. Pliocene (365–570 mbsf) sediments consist predominantly of sands and silty clays, with average carbonate content of 33% and TOC contents of 0.26%. These layers overlie Miocene/Pliocene nanofossil clays. The base of the sedimentary sequence drilled at Hole 976B is composed of a 4.2-m-thick unit of poorly sorted sands and pebbly sands of Serravallian–Tortonian age that unconformably overlie high-grade metamorphic schists and gneisses. Sedimentation rates range from 33 m/m.y. for the late Miocene to 185–340 m/m.y. for the Pliocene–Pleistocene.

The sediments drilled at Site 977 in the Eastern Alboran Basin are predominantly Pliocene and Pleistocene hemipelagically derived clays, with an average TOC content of 0.55%, intercalated with 52 organic carbon-rich layers containing up to 2.1% TOC. Sedimentation rates at Site 977 vary between 96 and 154 m/m.y. Poor core recovery (<1%) was obtained between 532 and 598.5 mbsf because of the occurrence of poorly cemented, porous sandy gravel that consists predominantly of volcanic clasts. The gravel may represent an erosive interval corresponding to the top of the Messinian or lowermost Pliocene. No Messinian evaporites were recovered at this site.

At Site 978 in the Eastern Alboran Basin, the sediments consist of hemipelagically derived clays of Pliocene–Pleistocene age, to 620 mbsf. Sedimentation rates range from 111 to 127 m/m.y. Average TOC content is 0.3%, with organic-rich layers containing up to 1.25% TOC. This unit is underlain by a 10-m-thick (620–630.65 mbsf) gravel-bearing interval of late Miocene age, which in turn is underlain by a sequence of sandy and silty clays of Messinian age. No Messinian evaporites were recovered at Site 978. At this site, interstitial water data are available only below 225 mbsf, where coring began.

At Site 979 in the Southern Alboran Basin consist of a very homogeneous sequence of Pliocene–Pleistocene, open-marine nanofossil clays with minor siliciclastic detrital layers. Carbonate contents reach 69%, and the average background TOC content is 0.7%. A total of 68 organic carbon-rich layers with TOC of up to 2.02% were recovered at this site. Sedimentation rates vary between 176 and 196 m/m.y. Drilling was terminated above the Miocene/Pliocene boundary.

RESULTS AND DISCUSSION

The results of shipboard chemical analyses are presented in Figures 2A–2J, and the oxygen isotope compositions of the interstitial water samples are given in Figures 3A–3F. As in the discussion of sediment properties, the results from Sites 974 and 975 (Tyrrhenian Sea and Menorca Rise) and Sites 976–979 (Alboran Basin) are considered separately. In the Tyrrhenian Sea and Menorca Rise, interstitial water samples were obtained from Holes 974B, 975B, and 975C. Interstitial water samples from the Alboran Basin sediments were analyzed from Holes 976B, 976C, 976D, 977A, 978A, and 979A. In this paper, we present only the results from the hole with the most complete sample set at each site. Concentration profiles for the replicate holes show an excellent agreement with those of the holes presented in this paper (Comas, Zahn, Klaus, et al., 1996) and are, therefore, not discussed further.

At all sites, organic carbon-rich layers (sapropels) are intercalated with the pelagic to hemipelagic sediments. The thickness and distribution of these layers vary within the sedimentary column and between the different sites (Murat, Chap. 41, this volume). However, no obvious influence of the presence of sapropels was observed for the solutes (e.g., sulfate, ammonia, alkalinity) that are influenced by microbiologically mediated processes of organic matter degradation. The main reason may be that the sampling resolution (9–30 m) of the interstitial waters is very low compared to the thickness of the organic carbon-rich layers (10 cm to a maximum of 3 m at the Alboran Sea sites). In addition, although the organic carbon content of these layers
is high compared to the background sediments, their total thickness represents only a few percent of the total sediment thickness.

**Sites 974 and 975**

Sites 974 and 975 are characterized by relatively low sedimentation rates and by interstitial water chemistries that are directly influenced by the presence of the underlying Messinian gypsum deposits. Sulfate concentrations decrease slightly in the top portion of the sediment column as a consequence of bacterial sulfate reduction, but then increase again toward the bottom of the holes (Fig. 2F). Sulfur isotope compositions (Böttcher et al., Chap. 32, this volume) indicate that the increase in sulfate concentrations can be attributed to dissolution of gypsum at depth. Other general features of these two sites are moderate downcore increases in salinity, chlorinity, and in the concentration of calcium, strontium, and lithium. The higher concentrations of calcium, strontium, and lithium are necessary to better constrain these interpretations.

The oxygen isotope composition of the interstitial waters decreases monotonously with depth from +1.3‰ to –1.5‰ in Hole 974B and from +1.5‰ to –0.5‰ in Hole 975B (Figs. 3A, 3B). This style of decrease in δ18O with depth is a commonly observed feature in marine sediment sequences (Lawrence, 1989) and results from low-temperature mineral alteration. The clays, carbonates, and zeolite minerals that form during diagenesis preferentially incorporate the heavy isotope, 18O, leading to a decrease in δ18O in the residual interstitial pore fluids.

Diagenetic dolomite formation is indicated by the decrease in magnesium concentrations in the lowermost interval of Hole 975B (Fig. 2D). This is in agreement with the observed increased abundance of dolomite towards the base of the cored interval (Shipboard Scientific Party, 1996). The occurrence of maximum strontium concentrations from 190.85 to 249.25 mbsf in Hole 975B may be attributed to carbonate recrystallization and suggests that evaporites are not the sole source of strontium at this site. The decrease in strontium below 249.25 mbsf suggests that Sr may be consumed at depth by precipitation of celestite, which was reported at 303 mbsf (Shipboard Scientific Party, 1996). The occurrence of maximum strontium concentrations from 190.85 to 249.25 mbsf in Hole 975B may be attributed to carbonate recrystallization and suggests that evaporites are not the sole source of strontium at this site. The decrease in strontium below 249.25 mbsf suggests that Sr may be consumed at depth by precipitation of celestite, which was reported at 303 mbsf (Shipboard Scientific Party, 1996). More accurate mineralogical studies are necessary to better constrain these interpretations.

At Site 974, the sodium concentration profile shows an increase to concentrations of 538 mM between 11 and 49 mbsf, then a decrease to 490 mM, and finally an approximately linear increase towards the bottom of the hole. Na leaching from the abundant ash layers present at this site could be a source of the Na in the top 50 m of the section. The linear increase observed below this depth and the correlation with the Cl increase suggest an additional deep source of...
Na. Because no halite deposits are known from this site, and dissolution of gypsum will not supply chloride to the interstitial waters, an additional explanation is required to explain the downcore increase in chlorinity (Fig. 2A). The Na/Cl ratio at the bottom of the hole is 0.86, corresponding to the seawater ratio. The increase in Cl and Na concentrations could, therefore, result from the presence of evaporated seawater in the gypsum deposits. An additional contribution of chloride, and possibly other elements, from a source located well below the Messinian gypsum deposits at these two sites cannot be ruled out. In previous interstitial water studies of Site 652 in the Tyrrenian Sea (Shipboard Scientific Party, 1987), which is located very close to Site 974, higher concentrations of Cl (up to 1428 mM) were found below the top of the evaporites, the maximum depth reached by Leg 161 drilling. At the Menorca Rise (Site 372) and in the South Balearic Basin (Site 371), Deep Sea Drilling Project Leg 42 (McDuff et al., 1978), brines with much higher concentrations of chloride (up to 4 mol/l at Site 371) and marine Na/Cl ratios were found. A puzzling feature of the Site 372 data is that the maximum chloride concentrations were found 580 m below the Messinian evaporite deposits in marls of Serravallian age. These data indicate that a high salinity brine is present well below the evaporite deposits. Vengosh et al. (1994) interpreted the high salinity brines with marine Na/Cl ratio (which rules out halite dissolution) as residues of an early Miocene evaporative event. Lower Miocene evaporites are reported from Mallorca and Barcelona, but are restricted to intramontane basins and have a limited lateral extension (Esteban, 1996). Based on these facts, and on the absence of lithologic evidence for an early Miocene evaporative event at Site 372, we suggest that these salinity peaks could also be caused by Messinian brines seeping to deeper sediment layers in the basin or that large-scale circulation of fluids may transport the salts within the sedimentary sequence over long distances.

Sites 976–979

The interstitial water samples from the Alboran Sea sites show large downhole increases in evaporite-related elements (Figs. 2A–2H), although no evaporites are reported in the area. Chloride concentrations at Sites 976 and 979 reach values of up to 1278 mM and 1654 mM, respectively. Other elements showing a downcore increase include Na, Ca, Sr and Li. In contrast, potassium consistently decreases with depth (Fig. 2E), whereas Mg concentrations decrease in the top part of the drilled interval and then either become constant (Hole 977A), increase toward the bottom of the core (Holes 976B and 978A), or show maximum concentrations at ~300 mbsf (Hole 979A). Sulfate concentrations rapidly decrease to zero in the top 30–50 m of all of the cores in the Alboran Sea because of bacterial sulfate reduction (Fig. 2F). As a result of the relatively high sedimentation and sulfate reduction rates (Böttcher et al., Chap. 32, this volume), consumption of sulfate is more rapid than the diffusional replenishment from the water column. At Sites 977 and 978, an increase in sulfate concentration is observed in the lowermost sample at the base of the core (Holes 976B and 978A), or show maximum concentrations at ~300 mbsf (Hole 979A). Sulfate concentrations rapidly decrease to zero in the top 30–50 m of all of the cores in the Alboran Sea because of bacterial sulfate reduction (Fig. 2F). As a result of the relatively high sedimentation and sulfate reduction rates (Böttcher et al., Chap. 32, this volume), consumption of sulfate is more rapid than the diffusional replenishment from the water column. At Sites 977 and 978, an increase in sulfate concentration is observed in the lowermost sample at the base of the core (Hole 977A), increase toward the bottom of the core (Holes 976B and 978A), or show maximum concentrations at ~300 mbsf (Hole 979A). Sulfate concentrations rapidly decrease to zero in the top 30–50 m of all of the cores in the Alboran Sea because of bacterial sulfate reduction (Fig. 2F). As a result of the relatively high sedimentation and sulfate reduction rates (Böttcher et al., Chap. 32, this volume), consumption of sulfate is more rapid than the diffusional replenishment from the water column. At Sites 977 and 978, an increase in sulfate concentration is observed in the lowermost sample at the base of the core (Hole 977A), increase toward the bottom of the core (Holes 976B and 978A), or show maximum concentrations at ~300 mbsf (Hole 979A).
sites (Figs. 2I, 2J). This is a consequence of the high rates of bacterial sulfate reduction and methanogenesis, which are fueled by the relatively high background concentrations of organic matter in these rapidly accumulating sediments. The sulfur and carbon isotope geochemistry is discussed in more detail by Böttcher et al. (Chap. 32, this volume).

On the basis of oxygen isotope geochemistry of the interstitial water samples, two distinct trends can be distinguished in the Alboran Sea sites (Figs. 3C–3F). In Hole 977A (Fig. 3D), δ¹⁸O values decrease steadily with depth down to 280 mbsf, below which the values become constant at ~0.6‰. In Hole 978A (Fig. 3E), where only samples below 200 m are available, the δ¹⁸O values decrease slightly down to 300 m and then remain relatively constant to the bottom of the hole.

At Sites 976 and 979 (Figs. 3C, 3F), the oxygen isotope compositions of the interstitial waters decrease until depths of 350 and 200 m, respectively, then increase again toward the bottom of the holes. The isotopic compositions of the interstitial water samples at the bottom of the hole at Site 976 reach a δ¹⁸O value of 1.8‰, 0.4‰ higher than in Hole 978A (Fig. 3E), where only samples below 200 m are available, the δ¹⁸O values decrease slightly down to 300 m and then remain relatively constant to the bottom of the hole.

Progressive evaporation of seawater produces characteristic trends in major-element concentrations in the residual brine resulting from the progressive precipitation of different mineral assemblages (McCaffrey et al., 1987). For example, precipitation of halite results in a decrease in the Na/Cl ratio of the residual brine because halite removes Na and Cl in a molar ratio of 1:1, compared with a Na/Cl ratio of 0.86 in seawater. Upon evaporation, the slope of Na vs. Cl is linear, with a constant slope of 0.86 up to ~11 × seawater concentration. The slope then abruptly changes with the onset of halite precipitation (Fig. 4A). Consequently, a brine that has precipitated halite will have a lower Na/Cl ratio than seawater, as is observed at most sites in the Alboran Basin. In contrast, if the brine is formed by dissolution of halite, it will have a Na/Cl ratio closer to 1. In general, brines with Na/Cl ratios >0.86 and a predominance of Na over Ca, Mg, and K are good indications that halite is the main source of chloride. However,
higher concentrations of dissolved Ca, Mg, and K relative to Na suggest that the brine is derived from dissolution of late-stage evaporite minerals, such as bischofite (MgCl$_2$·6H$_2$O), tachyhydrite (CaMg$_2$Cl$_6$·12H$_2$O), and carnallite (KMgCl$_3$·6H$_2$O) (Manheim et al., 1974).

In Figures 4A–4D, the Cl vs. Na concentrations from the four Alboran Basin sites are compared with the evolution path of the concentration of Cl and Na during progressive evaporation of seawater (with associated halite precipitation), as derived from the experimental study of McCaffrey et al. (1987). With the exception of Site 977, the excellent linear correlation between Na and Cl indicates that Na behaves conservatively. Regression lines of the data from Sites 976 and 979, those sites that also show an increase in δ$^{18}$O of the interstitial water at depth and the highest salinities, cross the seawater-evaporation curve at evaporation factors between 20 and 25 for Site 976 and factors between 11 and 20 for Site 979. This feature, combined with the fact that the slopes of the regression lines are lower than the seawater ratio, indicate that halite dissolution cannot be responsible for the observed increase in Cl. More likely, the increase in salinity may be attributed to the presence of a brine formed by 11–25 × evaporated seawater (i.e., with a Na/Cl ratio modified by halite precipitation). If halite dissolution were the source of the Cl, an increase toward a Na/Cl ratio of 1 would be expected.

Bromide concentrations provide additional constraints on the origin of brines. Bromide is generally a conservative tracer in pore waters, as its concentration is only slightly modified by postdepositional diagenetic reactions, with the exceptions of organic matter decomposition (Martin et al., 1993, and references therein) and in situ dissolution of late-stage Mg and K evaporite minerals (Hanor, 1994). Brines formed by subaerial evaporation of seawater should have high Br/Cl ratios because Br is preferentially partitioned into the fluid phase and its concentration increases linearly up to seawater concentration factors of 90 (McCaffrey et al., 1987). This results from the facts that bromide does not form any solid precipitate and the Br distribution coefficient between brine and halite is very small. As a consequence of this behavior, upon evaporation, the Br/Cl ratio of evaporating seawater will remain constant up to the point of halite precipitation and then increase dramatically because of the removal of Cl through halite precipitation. In summary, brines formed by halite dissolution will tend to have low Br/Cl ratios, whereas high Br/Cl ratios are generally indicative of salinity derived from subaerially evaporated seawater (Hanor, 1994). An alternative mechanism to produce brines with high Br/Cl ratios is the dissolution of late-stage evaporites at higher temperature (Hanor, 1994). Br is generally enriched in late-stage K and Mg phases, and incongruent dissolution of evaporites can lead to high Br/Cl ratios. However, these types of brines should also be associated with large increases in Mg and K. At all sites drilled, the K and Mg concentrations and the Mg/Cl and K/Cl ratios decrease with increasing chloride concentration, thus indicating that dissolution of late-stage evaporites is an unlikely cause of the high Br/Cl ratios observed at Site 976.

In Figure 5, the Br-Cl evolution of evaporating seawater, determined experimentally by McCaffrey et al. (1987), is compared with the halogen concentrations at Site 976. It is important to note the data...
The composition of the deep brine is assumed to be between 4‰ and 6‰ SMOW, corresponding to that of 12–20 times evaporated seawater (Craig and Gordon, 1965; Lloyd, 1966), mixing calculations indicate that the highest salinities may represent a mixture of 10%–15% brine with Mediterranean seawater having a δ18O value of +1.4‰. These estimates are only approximate because the oxygen isotope composition of the interstitial waters is not conservative, as indicated by the shape of the δ18O depth profiles. In addition, the oxygen isotope composition of the paleobrines may also have been altered by diagenetic processes. These estimates, however, are in the same range as those calculated with Na and Cl concentrations. The observed concentrations of Cl and Na for the deepest sample at Hole 976B could represent a mixture of modern Mediterranean seawater with 12%–13% of 20 times evaporated seawater.

If the salinity was derived by dissolution of evaporites in modern seawater, the increase in salinity would not be coupled with an increase in δ18O of the waters because the dissolution of salts does not alter the oxygen isotope composition of the water. Moreover, for Site 976, the δ18O value of the water sample at the maximum depth is higher than the oxygen isotope composition of modern Mediterranean bottom waters.

At Sites 977 and 978, a downcore increase in evaporite-related elements is observed (Fig. 2). However, the oxygen isotope composition of the interstitial waters does not show a corresponding increase. At Site 977, the Cl concentrations increase only to 778 mM, implying a very small brine component. The combination of a decrease in oxygen isotope composition resulting from diagenesis and the small contribution of water with heavy isotope composition may explain the lack of a clear increase in δ18O. At Site 978, the concentration of chloride reaches 1364 mM, but the Na vs. Cl regression (Fig. 4C) indicates that this brine can be considered as formed by seawater evaporated below the onset of halite precipitation. At these Cl concentrations, an increase in oxygen isotope composition would be expected. In contrast, the oxygen isotope ratios remain constant at δ18O values of 0.2‰. The lack of δ18O increase and the Na/Cl relationship (Fig. 4) could indicate a less extreme evaporative isotopic enrichment of the original brine that is masked by the diagenetic alteration of the oxygen isotope composition of the interstitial waters. However, the Na/Cl slope slightly higher than that produced by seawater evaporation may also indicate a contribution of halite dissolution. Salt deposits are not known to be present in the Alboran Sea; however, based on seismic data, Mauffret et al. (1992) proposed the presence of salt deposits ~50 km to the west of Sites 977 and 978 (Fig. 6). The dissolution of these salt deposits, coupled with large-scale fluid circulation, would provide a viable source for the elevated salinities observed at these two sites.

![Figure 5. Bromide plus iodide vs. chloride concentrations at Hole 976B compared to the Br vs. Cl concentrations in seawater during progressive evaporation (data from McCaffrey et al., 1987). The inset plot is an enlargement of the data from Hole 976B.](image)

![Figure 6. Map of the Alboran Basin showing the distribution of salts (broken lines = thick deposits, black = thin salt layers) inferred from seismic profiles (from Mauffret et al., 1992). The closest salt layers are ~50 km from Sites 977 and 978.](image)
Diagenesis

The mixing calculations discussed above provide explanations for the Na and Cl profiles, which can be considered to be approximately conservative elements. The profiles for other elements, such as Sr, Ca, Mg, K, and Li, are more difficult to model because they are involved in diagenetic reactions and their concentrations are controlled by multiple factors such as carbonate dissolution and precipitation. This is also clearly demonstrated by the nonlinearity of the profiles in Figure 2 and indicates that these elements are consumed or produced by diagenetic reactions at various depths in the sedimentary column.

The potassium concentration profiles at all sites show decreasing trends with depth, which is opposite to the chloride trends. If the increase in salinity was caused mainly by leaching of late-stage evaporites (e.g., carnallite), a positive correlation would be expected, as potassium is enriched in residual brines and precipitates at the late-stage of evaporite formation (McCaffrey et al., 1987). Potassium concentrations in interstitial waters are also more prone to diagenetic alteration resulting from clay and zeolite formation.

The high lithium concentrations found at the sites in the Alboran Sea cannot be explained solely by the presence of a residual brine corresponding to 10–20 times that of evaporated seawater because the measured concentrations cannot be accounted for with this evaporative enrichment alone. Lithium is not incorporated into any evaporite mineral except at extreme concentrations and, therefore, becomes successively enriched in the residual brines by up to concentration factors of 117 (Zherebtsova and Volkova, 1966). Only at very high concentrations does lithium coprecipitate with late-stage evaporite minerals. The lithium concentrations measured at the Alboran sites (up to 1.2 mM) are very high and comparable to those reported by Martin et al. (1991) in interstitial waters of the Peru Margin. These authors concluded that the origin of the high lithium concentrations must be related to low- to high-temperature reactions with continental basement and/or continentally derived clay minerals. Hydrothermal activity in the Alboran Basin basement, which may be related to Messinian and younger volcanism (Bellon et al., 1983; Hernandez et al., 1987), may have produced Li enrichments in deep fluids that are diffusing upwards. The presence of hydrothermal activity in the Alboran Basin was inferred from the presence of local thermal anomalies (Polyak et al., 1996). Direct evidence of a phase of increased temperatures and heat flow in the Pliocene was observed at Site 977. An abrupt increase in the thermal maturity of organic matter indicates that the sediments below 200 mbsf reached temperatures in the range 125°–150°C (Shipboard Scientific Party, 1996). More detailed studies, particularly of hydrogen and Sr isotopes in the pore fluids, may help detect the presence of a hydrothermal component.

Within the halite facies, an unmodified marine brine has lower Ca/Cl and Sr/Cl and higher Mg/Cl ratios than seawater. If these elements behaved conservatively and the evolution of their depth profiles were controlled simply by mixing of the two end-member brines, a progressive depth increase in Mg/Cl and decrease in Ca/Cl and Sr/Cl ratios would be observed. The depth evolutions of these ratios for all holes are plotted in Figure 7. The profiles indicate that the concentrations of these elements are more strongly influenced by carbonate diagenesis than by the simple mixing of two end-member fluids. At all sites, the Mg/Cl ratio decreases steeply at the top of the core with a more gradual decrease at depth. At Sites 976, 977, and 979, the decrease in Mg/Cl ratio at the top of each core is coupled

![Graphs](image-url)
with an increase in the Mg/Ca ratio and a rapid increase in the Sr/Ca ratios (Fig. 8). The decrease in Mg/Cl ratio could indicate active dolomitization in the zone of sulfate reduction. However, the concomitant increase in Mg/Cl ratio and Sr/Ca ratios coupled with a decrease in Ca/Cl ratios indicate that calcite precipitation is also occurring. The steep decreases in Sr/Ca ratios with depth at Sites 975, 977, and 978, which are coupled with increases in Ca concentrations, may be caused by calcite dissolution, a contribution of Ca to the deep brine from gypsum dissolution or to the precipitation of celestite, which was observed at Site 975 (Shipboard Scientific Party, 1996).

CONCLUSIONS

The interstitial waters at all sites drilled in the western Mediterranean consistently show increasing salinities and chlorinities with depth, which indicates the ubiquitous presence of a deep-seated saline brine. Sites 974 and 975 are characterized by a moderate salinity increase and by high sulfate concentrations at depth. These features can be attributed to the presence of evaporated seawater at depth, coupled with the dissolution of the underlying gypsum deposits. Changes in the concentrations of sodium, chloride, and bromide and the oxygen isotope compositions of the interstitial waters at Sites 976 and 979 reflect the presence of a paleobrine (~15–20 x evaporated seawater), possibly of Messinian age. At Sites 977 and 978, a contribution of salts derived from the dissolution of evaporite dissolution may also have influenced the observed interstitial water geochemistry.

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Figure 8. Mg/Ca and Sr/Ca vs. depth for Sites 974–979. Note the different depth scales for Sites 974 and 975.