Paleoenvironment of the Messinian Mediterranean "Lago Mare" from Strontium and Magnesium in Ostracode Shells

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Ostracodes from Deep Sea Drilling Project (DSDP) site 376 (Florence Rise, Levantine Basin) in the eastern Mediterranean have been studied to elucidate the environments of the "Lago Mare" during the Messinian (Late Miocene). Additional ostracode samples from the Lago Mare from DSDP site 372 (East Menorca Rise, Balearic Basin) in the western Mediterranean, and from outcrops in the Sorbas Basin in southeastern Spain, the Polemi Basin in Cyprus, and from the Sitia-Lithinais Basin in Crete, were also studied.

All samples contained valves of the euryhaline ostracode genus Cyprideis *for which the distribution coefficient* K_D *for Sr and Mg is known from analyses of modern specimens grown in the laboratory and from modern field collections. Because the Sr/Ca of ostracode shells is controlled by the Sr/Ca of the host water, and because the Mg/Ca of the shells is controlled both by the Mg/Ca of the water and by water temperature, Ca, Sr, and Mg analyses of individual fossil* Cyprideis *shells from the Lago Mare indicate the environment in which they lived.*

Throughout the sequence at DSDP site 376, the water was fresh or close to fresh, except for layers just above the uppermost gypsum layers, at the base of the sequence where water with some marine affinity is recognized. Above these layers, the "continental" aspect of the Lago Mare water is indisputable. Chemical analyses of single ostracode shells from site 376 and the other sites mentioned above indicate that at no time during the life of the Cyprideis *ostracodes was the Lago Mare connected to the ocean. Furthermore, there is no indication that the individual basins of the Mediterranean studied here were in direct connection to one another.*

INTRODUCTION

The paleoenvironmental history of the Mediterranean Sea during the Late Miocene has been the focus of numerous scientific investigations (Initial Reports of the Deep Sea Drilling Project Leg 13 [Ryan, Hsü et al., 1973], and Leg 42A [Hsü, Montadert et al., 1978c]; Drooger, 1973) with their interpretation originally attracting controversy (for a review see Rouchy, 1980). The latter especially was related to the understanding of the mode of deposition of evaporites within the various basins of the Mediterranean, and of the conditions which prevailed directly afterwards. It is the recovery of specimens of the ostracode *Cyprideis* from some of the Mediterranean DSDP cores which suggested a brackish to hypersaline environment during the life of the ostracodes (Ryan et al., 1973). This discovery led Hsü et al. (1977, p. 401; 1978b, p. 1072) to use the term "Lago Mare" (lake-sea), coined by Ruggieri (1967), to characterize the Mediterranean during the latest Messinian for an oligohaline environment postdating the deposition of evaporites, and predating Pliocene marine sedimentation. Benson (1973, 1978) studied the composition of the ostracode fauna obtained through the DSDP coring program for a variety of sites (129, 372, 375, 376) in the Mediterranean (Fig. 1), and concluded that when *Cyprideis* was present "shallow (?) lac mer conditions were almost universal." In the same Initial Report of the DSDP Project reference is made (Hsü et al., 1978a, 1978b; Cita et al., 1978) to the presence of the euryhaline foraminifer *Ammonia beccarii* in association with *Cyprideis*. Paleoenvironmental conditions related to these two micro-organisms were never well defined, because both *Cyprideis* and *A. beccarii* can tolerate a broad range of water conditions and salinities. Both organisms are characteristically euryhaline: *Cyprideis* is found today in salinities up to 100‰ (De Deckker, 1981) and *A. beccarii* up to 67‰ (Bradshaw, 1957).

From stable-isotope evidence Pierre and Fontes (1978) and McKenzie and Ricchiuto (1978) postulated that for site 376 (Fig. 1), the Lago Mare carbonate sediments formed under waters of continental origin (McKenzie and Ricchiuto, 1978, p. 655) or marine waters diluted by an influx of continental water (Pierre and Fontes, 1978, p. 641). Further, Pierre and Fontes (1978) concluded: "The concept of a unique basin (in the Mediterranean) which existed during the Messinian must be abandoned in favour of a system of minor basins which were partially and intermittently connected allowing sporadic influences of surficial, underground and Atlantic waters." Based on the interpretation of mineralogical assemblages for site 376, on the other hand, Mélières et al. (1978) postulated that a "fresh (or nearly fresh) water body" must have prevailed during the upper Messinian overlying the evaporites. These authors further concluded (on p. 378) that after deposition of the Messinian evaporites in shallow water, "infilling of the area by fresh to brackish waters" occurred, followed by "extensive transportation of terrigenous material by turbidity currents, possibly triggered by changes in the water level." They also stated that "in the last part of this episode discrete influxes of marine waters inducing magnesium-rich

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mineral paragenesis near-shore probably occurred."

On the basis of the work pioneered by Chivas et al. (1985, 1986a, 1986b) and De Deckker et al. (in prep.) establishing a correlation between the Mg and Sr contents of ostracode shells with conditions of the aquatic environment (salinity, temperature, and some ionic ratios), we aim in the present work, by carrying out trace-element analyses on selected *Cyprideis* ostracode shells, to solve the questions of salinity and water composition in the Lago Mare. DSDP core material and samples from three outcrops in Crete, Cyprus, and southeastern Spain have been analyzed for this purpose. We also consider whether the waters in the various basins in the Mediterranean were of the same composition, thereby implying their possible connection.

OSTRACODES AND TRACE-ELEMENT STUDIES

There are several advantages in using ostracodes to reconstruct past environments. Ostracodes are ubiquitous microcrustaceans that can live in nearly every type of aquatic environment, ranging from marine to fresh, and even in hypersaline waters. These organisms build calcitic shells consisting of two valves encasing a prawn-like soft body, and before adulthood shed their valves up to nine times, each time forming new valves. These valves consist of low-Mg calcite, and the material used to build them (10 to 100 μg per valve for this study) is taken directly from the host water at the time of shell formation (no material is stored prior to molting [Turpen and Angell, 1971]).

From laboratory cultures and field collections of ostracodes, Chivas et al. (1983, 1985, 1986a, b), established the relationships between Sr and Mg uptake in the low-Mg calcite shells of ostracodes, and conditions of the aquatic environment. Some of the significant results are summarized here: the Sr/Ca ratio of the ostracode shell is directly related to the Sr/Ca of the water at the time of shell formation, and it is apparently unaffected by water temperature. The shell Mg/Ca on the other hand is controlled by water temperature and the Mg/Ca of the water, both at the time of shell formation. The molar distribution coefficient K_D, for Sr and Mg between shell and water, varies among ostracode genera. For *Cyprideis*, the ostracode of interest here, the K_D has been determined (Chivas et al. 1986b):

$$K_D[\mathrm{Sr}]\ \textit{Cyprideis} = \frac{(\mathrm{Sr/Ca})_{\mathrm{shell}}}{(\mathrm{Sr/Ca})_{\mathrm{water}}} = 0.475 \pm 0.057;$$

$$K_D[\mathrm{Mg}]\ \textit{Cyprideis}\ \text{at}\ 25°\mathrm{C} = \frac{(\mathrm{Mg/Ca})_{\mathrm{shell}}}{(\mathrm{Mg/Ca})_{\mathrm{water}}} = 0.00458 \pm 0.00072$$

Further, De Deckker et al. (1988) illustrated with their study of Mg and Sr in fossil *Cyprideis* specimens from the Gulf of Carpentaria in northern Australia, which during the Late Quaternary became disconnected from the sea and filled with water of continental origin, that it is possible to reconstruct the conditions of the aquatic environment from the ostracode shell chemistry. Thus: 1) oceanic water chemistry can be recognized through the Sr/Ca and Mg/Ca of the shells; 2) water of marine origin, either diluted or partly evaporated (but for the latter below gypsum-saturation levels), or in contact with ocean water (e.g., as in an estuary) would retain a Sr/Ca ratio fairly similar to that of sea water; 3) the former presence of freshwater conditions can be established with a good degree of confidence if the Mg/Ca of the water calculated from Mg/Ca of the shell is in the vicinity of 1.0; 4) if for within an assemblage all Sr/Ca values are very similar, salinity and conditions for authigenic carbonate precipitation, have not varied; and 5) if, for within an assemblage, all Mg/Ca values are also similar, water temperature should also have remained unchanged.

Examination of ostracode assemblages can also be very informative. For example, in order to differentiate between a reworked assemblage and an intact one, a number of features can be examined; the presence of juvenile ostracode valves belonging to all molt (growth) stages together with adult ones within one sample indicate that it has undergone little or no reworking by current activity, turbidity flows or bioturbation. Since ostracode valves are quite fragile, any mechanical effect on the sample would break or abrade the shells. Similarly, signs of dissolution would indicate a change of pH of either the interstitial or host water after death of the organisms. For futher details on the use of ostracodes for paleoenvironmental reconstruction, refer to the review by De Deckker (1988).

STUDY SITES IN THE LAGO MARE

Site 376—Florence Rise, Levantine Basin, Eastern Mediterranean

Lithology and Stratigraphy

Hsü et al. (1978a) provide a complete description of the core. A summary of the parts of the core studied here is presented below and in Figure 2. In core 16, termination of the evaporite phase is indicated by a change from coarsely crystalline gypsum near the base to a marlstone with gypsiferous sandstone and siltstone. Above this, cores 15 to 12 consist of marlstone. In core 11, there is a change to dolomitic marl, which continues to near the base of core 6 where the Messinian/Pliocene boundary occurs. That boundary is characterized by a slumped (deformed) Miocene marl; the contact with overlying sediments is sharp and undeformed.

Fossil Biota

Two types of samples yielding *Cyprideis* ostracodes have been recovered from site 376. There are those that characteristically contain an *in situ* living population; juvenile and adult specimens are found together within the one sample, and material shows little abrasion or effect of reworking/transportation. The main concentration of these samples occurs in core 9, section 3, samples M 24-31. The other group of ostracodes represents an allochthonous fauna, as none of the characteristics of the previous group is found; "artificial" reworking of ostracodes in samples recovered in core catchers (samples labelled CC) results from coring procedures. Other ostracode samples, bearing all the characteristics of reworking, also commonly contain (and in some samples, in large quantities) specimens of marine, planktonic foraminifers. The latter are commonly abraded and fragmented, and are of much older ages; for example, samples recovered from core 6, section 4: levels 100-131 (samples M 14-20).

Site 372-East Menorca Rise, Balearic Basin, Western Mediterranean

Although several (eight) samples were examined, fragments only of *Cyprideis* were found in one sample: core 4, 2: level 90-92 (sample M 9). Reworked foraminifers are present in this sample, which consists of marl, and is thought to occur at the Miocene/Pliocene boundary. For more details on this site, refer to Hsü et al. (1978c), and for its location see Figure 1.

Onshore Sites-Southeastern Spain, Cyprus, and Crete

These samples, supplied as washed and picked *Cyprideis* only, were given to us by D. van Harten, Vrije Universiteit van Amsterdam. They originate from the following localities:

1. DK-75059 from the Messinian of southeastern Spain from the "White Layer" of the Sorbas Basin. Specimens consist of *Cyprideis agrigentina*, and originate from the lowermost white limestone band in the Zorreras Member described by Roep and Beets (1977:33). Roep and van Harten (1979:1039) refer to this band in their section labelled Sorbas Centre III.
2. GG-CY-6 from the Messinian of Cyprus from the "Coupe de Stroumbi, Polemi Basin"; specimens also consist of *C. agrigentina*. For more detail on this section, refer to the summary paper by Orszag-Sperber et al. (1980).
3. PJ-83 K 118 from the Middle Tortonian of Crete. Specimens belong to *C.* aff. *sarmatica*. Peters (1985:162, Fig. 73) refers to this sample which originates from the Sikia-Ethia area in the Sitia-Lithinais Basin.

METHODS

Sediment samples obtained from the DSDP core library were treated in 10% H_2O_2 for several weeks before being washed with distilled water over a 90 μm sieve, and then oven dried at 40°C. Individual ostracodes were picked under a binocular microscope. Care was taken to select only extremely clean ostracode valves. For some samples, parts of valves had to be broken off and discarded to remove minute sediment particles, especially inside the inner lamella of the ostracodes, which would otherwise lead to erroneous results. Analyses of single ostracode valves, placed in 5 ml of 2% HCl in 25-ml scintillation vials, were carried out using a very high-resolution Inductively-Coupled Argon-Plasma Emission Spectrometer (ICAPES) (Shelley and Taylor, 1981) with limits of detection of Ca^{2+} 0.02 ppb, Mg^{2+} 0.04 ppb, and Sr^{2+} 0.03 ppb in solution.

RESULTS: Sr AND Mg ANALYSES OF OSTRACODE SHELLS

Site 376

For the lower half of the profile (cores 15-11, Fig. 2), evidence of mixed assemblages of ostracodes is obvious for most of the studied levels, simply through an examination of the Sr/Ca values for individual ostracode shells at each level. The scatter of Sr/Ca values for most samples (except M-39) is commonly broad. Of interest too is that none of the ostracode Sr/Ca ratios is within the range 0.00339-0.00374, which represents the calculated values for *Cyprideis* grown in Messinian seawater.[1]

All but one of the Sr/Ca ratios in samples M-40 and M-39 indicate that the host water had Sr/Ca ratios greater than that of seawater of Messinian age, inferring that the water in which the ostracodes lived originated from evaporated sea water. Gypsum precipitation (as occurred early in the sequence) would have caused an enrichment of the Sr/Ca of the residual water. There is a general progressive diminution of the Sr/Ca values higher in the sequence that indicates an increase in the degree of continentality of the water in the Lago Mare. Nevertheless, the waters in which the ostracodes lived must have been close to fresh as the Mg/Ca values of the ostracodes, even allowing for likely temperature-induced variations in Mg/Ca, indicate Mg/Ca values of the host water close to 1.0. This is a typical feature of fresh/dilute water. This interpretation is confirmed from sample M-33 in which a few valves of typically freshwater ostracodes (*Metacypris, Candonopsis*) were recovered. Two other genera, *Ilyocypris* and *Herpetocypris*, which have species known to tolerate slightly saline waters today, are also recorded in this sample.

The upper portion of the profile is distinguished by a marked change in ostracode Sr/Ca and Mg/Ca values. The autochthonous ostracode populations recovered in core 9 display a rather narrow spread of Sr/Ca values within individual layers. This feature is also maintained in the upper part of the sequence. In addition, a further departure from seawater Sr/Ca values is indicated in this core and no return to oceanic affinity can be seen in this core and core 6. The consistent Sr/Ca values higher up the sequence show that no drastic changes in carbonate precipitation or salinity occurred. There is a broad spread of Mg/Ca values from individual layers in core 9. From this we conclude that water-temperature variations occurred, implying a shallow, but permanent[2], waterbody. The generally low Mg/Ca values for the waters in core 9 still imply near-freshwater conditions.

In the uppermost portion of the sequence, for core 6, section 4, evidence of reworking of the ostracode fauna is

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[1] *Estimation of the Sr/Ca value of sea water during the Messinian* (for convenience here, the Messinian is given an age of 5 Ma). From the work of Graham et al. (1982), which documents changes in the Sr/Ca ratios of planktonic foraminifers during the Cenozoic, it is possible to roughly estimate the Sr/Ca of sea water at particular times. By using the distribution coefficient for Sr of foraminifers (K_D Sr = 0.16, Graham et al., 1982), and the recorded values of Sr/Ca of foraminifers in Graham et al. (1982) at 5 Ma which ranged between 0.00114 and 0.00126 (mean value: 0.00117), the range of Sr/Ca of sea water must have been 0.00713-0.00788, with a mean of 0.00732. This set of values is quite different from the modern seawater Sr/Ca value of 0.0086 ± 0.004 reported by Kinsman (1969).

Calculating the Sr/Ca value *Cyprideis* shells (K_D Sr = 0.475) should have if grown in Messinian sea water, the range of values should be: 0.00339-0.00374, with a mean value of 0.00348. No range of errors is given because of the rough approach to this calculation.

[2] *Cyprideis* requires permanent water to reproduce because its eggs, unlike those of most other lacustrine ostracodes, cannot withstand desiccation.

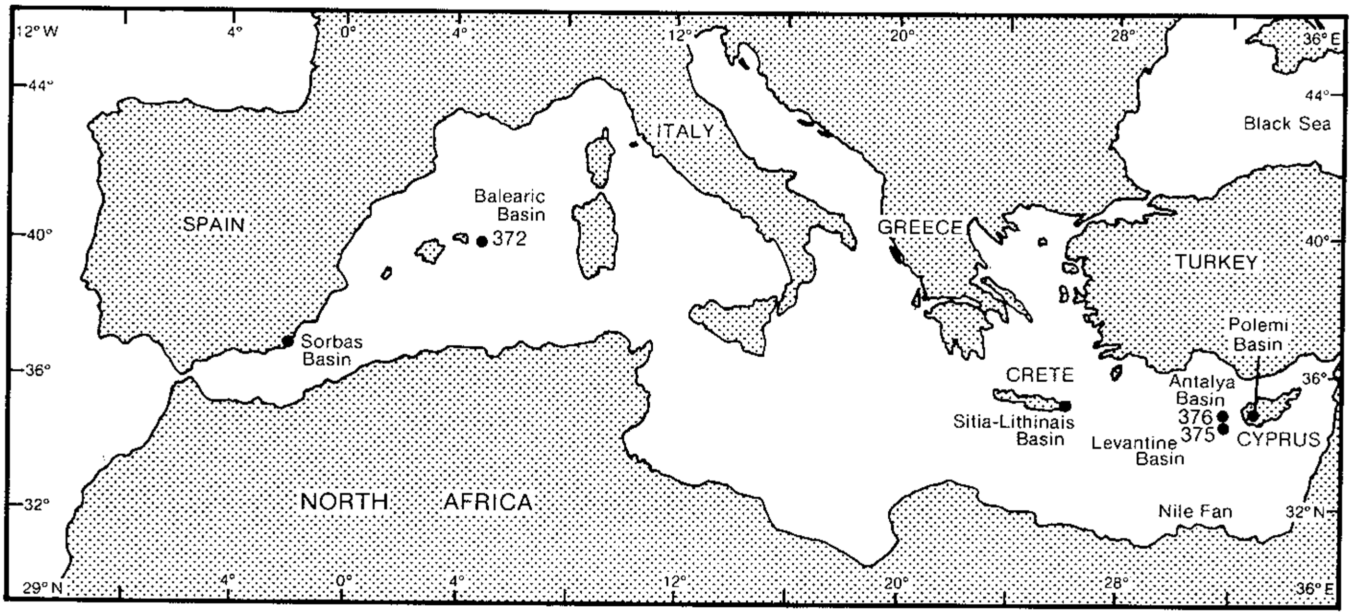

FIGURE 1—Location of the DSDP coring sites and onshore basins mentioned in the text and from which *Cyprideis* ostracodes have been obtained for trace-element analyses.

based on the broader spread (compared to samples in core 9) of individual Mg/Ca and Sr/Ca values for the various levels. Nevertheless, these ostracods must have originated from a non-marine, near-freshwater environment as indicated by the trace elements analyzed, which show no affinity to seawater composition.

Site 372

The fragments of ostracode valves recovered in core 4, section 2, level 90-92, have Mg/Ca values in the vicinity of those of freshwater *Cyprideis*, with apparently little temperature variation (implying a major body of water), although only three analyses cannot suffice to substantiate this argument. The Sr/Ca values tend to indicate close affinity with Messinian sea water, but this does not mean sea water *per se;* it more likely indicates water of oceanic origin (for more details refer to discussion of samples M-40 and M-39) but which could have been diluted considerably.

Onshore Sites-Southeastern Spain, Cyprus, and Crete

A variety of environmental conditions can be inferred for these three samples. Ostracodes in sample GG-CY-6 from the Messinian of Cyprus must have been growing in fresh water because their Mg/Ca values indicate Mg/Ca ratios for the water slightly less than 1.0. Temperature variations were also minimal because all Mg/Ca values are tightly clustered. However, the Sr/Ca values display a larger spread. This feature can only be explained if the Sr concentration of the water varied during the life of the ostracodes. A possible cause for this change might have been the relative loss of oceanic Sr during biogenic or authigenic aragonite precipitation.

The ostracodes from the Spanish sample (DK-75059), also of Messinian age, indicate a similar phenomenon to the sample from Cyprus, although the spread of values for Sr/Ca and Mg/Ca is even larger. This feature cannot be adequately explained although Roep and van Harten (1979) have postulated numerous transgressions and regressions for the Sorbas Centre III Section. In any case, there is no indication from either sample studied here that the host water was marine.

The Middle Tortonian sample from Crete (PJ-83K 118) has Sr/Ca values showing an affinity to sea water (the data in Graham et al. [1982] indicate that the Sr/Ca value of sea water was even lower before 5 m.y.), but this water must have been diluted as shown by the Mg/Ca values. The broad range of the latter values indicates temperature variations, hence probably a shallow waterbody. This interpretation appears consistent with that of Peters (1985), who collected the ostracodes within lignitic clays in association with charophyte algae which live in shallow, non-marine waters. It is interesting to note, however, that conditions during Middle Tortonian times in Crete were already quite similar to those which occurred during the Messinian.

CONCLUSIONS

The detailed study of the non-marine ostracode fauna combined with the Sr and Mg analyses of selected ostracode shells from site 376 on the Florence Rise in the Levantine Basin demonstrates unequivocally that no marine incursion occurred in this part of the Lago Mare after the last deposition of gypsum beds and prior to the Pliocene marine transgression. During the deposition of marlstones in the lower part of the profile, ostracode faunas indicate

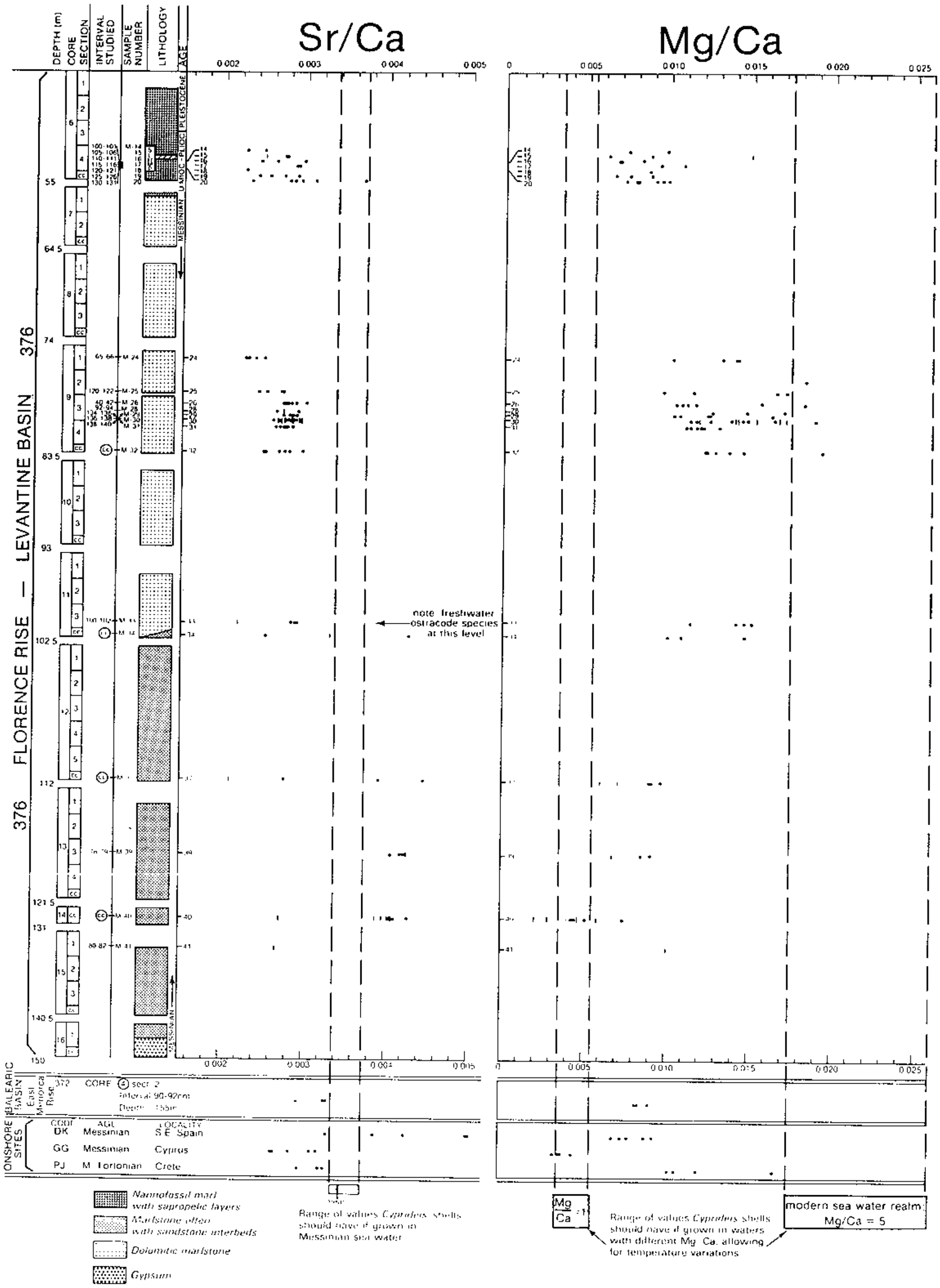

FIGURE 2—Values of Sr/Ca and Mg/Ca (molar ratios) obtained from analyses of individual *Cyprideis* shells (• = adult valves, | = juvenile valves) for stratigraphic horizons from DSDP sites 376 and 372 and for onshore sites from Spain, Cyprus, and Crete. The lithological logs for the DSDP sites are schematized and are interpreted from those presented in Hsü et al. (1978c). The sample numbering for the DSDP material (M-14 to M-41) is our nomenclature; CC refers to a core-catcher sample. For an explanation of the calculation of the Messinian seawater Sr/Ca refer to Footnote 1.

near-freshwater conditions but the waters had some seawater origin as shown by Sr/Ca values (as for example diluted relict seawater would be). Higher in the sequence, more "continentality" is inferred for this fresh to near-freshwater body from Sr/Ca analyses, but shallow-water conditions must have prevailed as inferred from the spread of Mg/Ca values, which nevertheless remain within the freshwater range.

Comparison of the trace-element analyses carried out on shells from one level taken at coring site 372, and those from the three onshore sites (in south-eastern Spain, Crete, and Cyprus), with those of site 376, show differences in Sr/Ca and Mg/Ca values for the waters in which the ostracodes lived. There is no indication that the Lago Mare was ever transgressed by sea water when these ostracodes were forming their shells. In addition, there is no evidence that any of the basins studied here were in direct connection with one another. (The Tortonian sample from Crete obviously has to be ignored in this respect because of its different age from the others.) Non-marine conditions seem to have prevailed all over the Lago Mare, which consisted of a series of disconnected shallow basins receiving waters of continental origin. The ostracode data presented here provide confirmation of the interpretation of the stable-isotope data carried out on bulk carbonate samples for similar DSDP sites by Pierre and Fontes (1978) and McKenzie and Ricchiuto (1978). The advantage of using ostracode material is that by using conventional paleontological techniques it is possible to ascertain whether the specimens used for trace-element analyses are reworked (trace-element analyses of authigenic precipitates can also clarify this, but it is almost impossible to discern whether precipitates are authigenic). With a knowledge of ecological requirements of individual ostracode species, it is also possible to provide additional paleoenvironmental information unobtainable from mineralogical investigations. Finally, by examining Sr/Ca and Mg/Ca values of individual ostracode valves from the same level it is possible to obtain valuable information on water conditions like temperature and salinity fluctuations, origin of the water, etc. Because ostracodes can live in marine, brackish, fresh- and hypersaline waters, and thus occupy most niches along a typical marine/non-marine transition, their study can provide valuable information, perhaps unobtainable otherwise from other oganisms or minerals.

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Causality in biology is a far cry from causality in classical mechanics.

—Ernst Mayr