

## VARIATION IN $\delta^{13}\text{C}$ AND $\delta^{18}\text{O}$ IN LATE JURASSIC CARBONATES, SUBMEDITERRANEAN PROVINCE, EUROPE

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**Abstract:** Carbon and oxygen stable isotopic relationships have been investigated in brachiopod shell and bulk carbonate rock samples from late Jurassic strata of Spain, southern Germany, and southern Poland. The results show, first, an increase in  $\delta^{13}\text{C}$  by approximately 1‰ up to +3‰ in the Upper Oxfordian and, then, a decline back to the original values in the Kimmeridgian. There is tremendous geographic and temporal variation in  $\delta^{18}\text{O}$ . These data suggest a substantial, though presumably local or at most regional, transient influx of nutrient- and carbon dioxide-rich waters onto the shelf.

**Key words:** carbon isotopes, oxygen isotopes, carbonates, Upper Jurassic, Central Europe

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### INTRODUCTION

A recent publication (Hoffman *et al.*, 1992) suggests that substantial lateral variation may have occurred in oxygen and carbon isotopic compositions of the carbonate system in late Jurassic ocean, in particular between the Submediterranean and Boreal Provinces.

In the present study, we have undertaken to look into the potential geographic variation in the oceanic  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  within the Submediterranean Province, northern shelf of the Tethys in Europe. To this end, we have analysed samples taken from Callovian through Kimmeridgian sections in southern Poland, southern Germany, and Spain. Our results may thus bear also on the temporal variation in the isotopic composition of the carbonate system in late Jurassic ocean, which in fact has thus far been rather poorly known. They

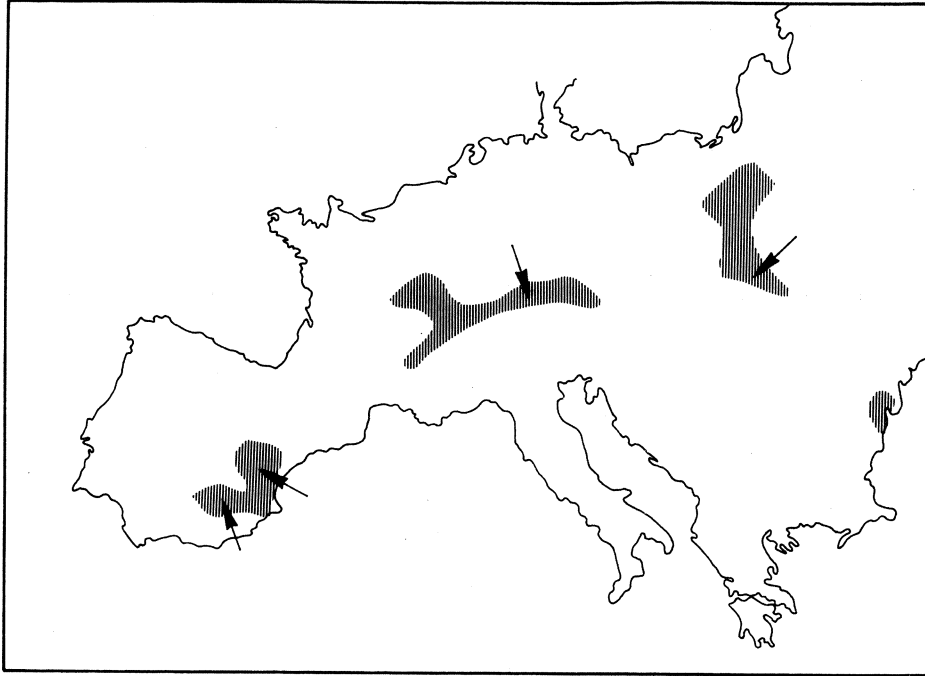


Fig. 1 Documented distribution of the late Jurassic sponge megafacies at the northern shelf of Tethys, Europe (after Trammer, 1982), with sampling areas indicated by arrows

may consequently contribute to elucidation of the paleoceanographic characteristics of the investigated area and time interval.

### MATERIALS AND METHODS

The samples we have analysed come mostly from a large complex of lithofacies located in a specific paleogeographic position, on the northern shelf of the Tethys, and termed the sponge megafacies (see Trammer, 1982; Gaillard, 1983; Kutek *et al.*, 1984; Matyja & Pisera, 1992; Pisera, 1991) but also from some related shallow-water carbonate deposits. The samples have been taken in a number of geological sections in southern Poland, southern Germany, and Spain (Fig. 1), which are correlated by means of ammonite biostratigraphy (Trammer, 1982; Gaillard, 1983). For comparative purposes, we have analysed a few samples from France and we also considered the samples from Poland which had been previously discussed by Hoffman *et al.* (1992).

The sample material represents largely rhynchonellid and terebratulid brachiopod shells, the two groups of fossils being approximately randomly distributed among various sections and stratigraphic intervals. Modern brachio-

pods do not fractionate carbon and oxygen they use for shell production (Lowenstam, 1961). This has also been recently confirmed for fossil brachiopods (Bates & Brand, 1991). The carbon and oxygen isotopic composition of low-magnesium calcite of the brachiopod shell is, moreover highly resistant to post-mortem diagenetic alternations (Veizer & Fritz, 1976; Al-Aasm & Veizer, 1982, Bates & Brand, 1991). Brachiopod shell calcite provides therefore ideal materials for stable carbon and oxygen isotopic analyses in geology. For comparative purposes, we have also analysed bulk rock samples of limestones representative of the sponge megafacies.

The sample material (3 - 6 mg  $\text{CaCO}_3$ ) was treated with 100%  $\text{H}_3\text{PO}_4$  and the resulting carbon dioxide was analyzed by mass spectrometry on Finnigan MAT 251 at the Technical University in Munich. The results are expressed in  $\delta$  notation relative to the PDB standard, using the NBS-18 reference sample. The standard error of measurements approximates 0.02 ‰.

## RESULTS

The results of carbon and oxygen isotope analyses are plotted in Fig. 2. For the sake of simplicity, the results obtained previously by Hoffman *et al.* (1992) on Polish samples are here presented in the form of a generalized curve rather than individual datapoints. This is also the case with the samples from France.

The carbon isotope data quite clearly show a temporal trend, at first increasing up to  $\delta^{13}\text{C}$  values of approximately +3‰ in the Bimammatum Zone (Upper Oxfordian), then falling down by 1.0 - 1.5‰ in the Kimmeridgian. This trend is in fact consistent with the one recorded previously by Hoffman *et al.* (1992). Its apparent difference from the preliminary curve presented by Gruszczynski *et al.* (1990) stems from the fact that the latter presentation was only intended to show, for comparative purposes, the level of  $\delta^{13}\text{C}$  in the Oxfordian of Poland but not to analyse details of the carbon isotope curve.

The brachiopod shell data consistently fall within a distinct band of variation, the range of variation approximating 1 ‰. Interestingly, a considerable majority of our bulk rock data also fall within the same band of variation, thus demonstrating that insofar as carbon isotopic composition is concerned, bulk rock samples may provide quite reliable results.

In contrast, the oxygen isotope data show a tremendous amount of variation, both geographic and temporal. Generally, the samples from Poland, Germany and France seem to have, on the average, a bit higher  $\delta^{18}\text{O}$  values than those from Spain, but there is too much intraregional variation to take this impression as firm evidence. Actually, even the sharp shift in  $\delta^{18}\text{O}$  observed previously in the Upper Oxfordian of Poland by Hoffman *et al.* (1992) becomes invisible in the cloud of datapoints. This variation would make any attempts at paleotemperature estimation unreliable.

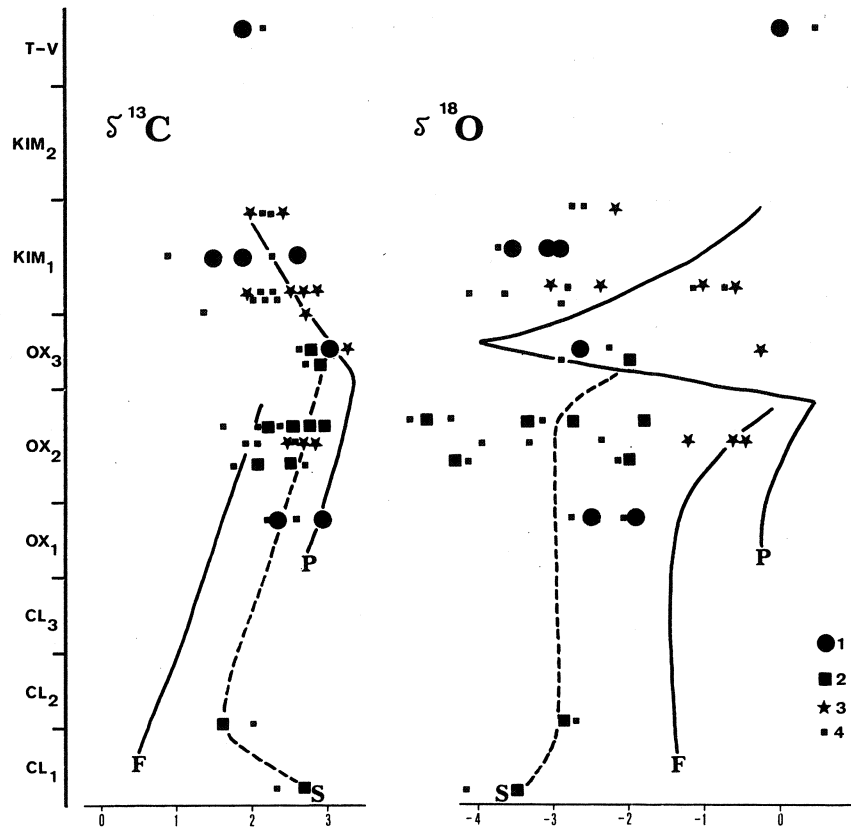


Fig. 2  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  data as measured in brachiopod shell and bulk carbonate rock samples in late Jurassic strata. Submediterranean Province. 1 – brachiopod samples from southern Poland; 2 – brachiopod samples from Spain; 3 – brachiopod samples from southern Germany; 4 – bulk rock samples. Solid lines marked *F* designate the average for brachiopod samples from France, provided kindly by Dr. B. A. Matyja; solid lines marked *P* designate the average for brachiopod samples from Poland, analysed previously by Hoffman *et al.* (1992); dashed lines marked *S* designate the average for brachiopod samples from Spain, considered in this study. *CL* – Callovian, *OXF* – Oxfordian, *KIM* – Kimmeridgian, *T-V* – Tithonian and Volgian

Bulk rock data have, on the average, lower  $\delta^{18}\text{O}$  values than those measured in brachiopod shell materials. This is in fact what can be expected, given that bulk rock samples are more vulnerable to diagenetic alterations (Hudson, 1977). A couple of samples have their oxygen isotopic composition drastically decreased relative to the remainder of samples, in spite of the fact that their  $\delta^{13}\text{C}$  values are quite typical of the sample set. This confirms the reliability of carbon isotope data as compared to that of oxygen isotope data.

It is also worth noting that the range of geographic variation in  $\delta^{13}\text{C}$  observed in late Jurassic samples from the Submediterranean Province corresponds in fact quite closely to the range of short-term fluctuations recorded in a very wide variety of Cenozoic sections of open-oceanic sediments (see e.g.

Shackleton & Pisias, 1985; Keigwin, 1987). The commonness of this phenomenon in these different time intervals and oceanographic settings might suggest that such small-scale fluctuations in carbon isotopic composition of the oceanic carbonate system are inherently linked to the very nature of the Earth's exosystem.

## DISCUSSION

The amount of both intra- and interregional variation observed in our oxygen isotope data – even with the analysis restricted solely to the measurements on brachiopod shell materials – is striking, particularly when compared to the consistency of carbon isotope data on the same samples. In fact, this variation is so large that it practically rules out a sound interpretation of the oxygen isotope results. (One might perhaps claim that the generally lower  $\delta^{18}\text{O}$  values in Spanish samples reflect higher seawater temperatures in their depositional environment than in either Poland or Germany, but this is about as much as can presently be postulated on the basis of the available data on the Submediterranean Province.) This pessimistic assessment appears indeed inevitable because oxygen isotopic composition of the oceanic carbonate system depends not only on temperature and global ice volume but also on some other environmental factors (Hoffman *et al.*, 1991, 1992), and the interplay of all these agents cannot possibly be disentangled without strong independent evidence. Consequently, we have to conclude that it is carbon isotope data which are more likely to offer some potential as a starting point to paleoenvironmental and paleoceanographic interpretation of the geological records of isotopic composition of the oceanic carbonate system. This corollary agrees well with the presumptions underlying the oceanographic model of overfed/hungry ocean (Małkowski *et al.*, 1989; Hoffman *et al.*, 1990, 1991).

Assuming this oceanographical model, the generally high  $\delta^{13}\text{C}$  values observed in this study (cf. also Holser, 1984) suggest that, on the global scale, the late Jurassic was a time of predominantly stagnant and stratified ocean (cf. Gruszczynski *et al.*, 1990; Hoffman *et al.*, 1992). Then, the inflexion recorded in the carbon isotope curve in the Upper Oxfordian of the Submediterranean Province is to be regarded as reflecting a substantial, though presumably local or regional, influx of nutrient- and carbon dioxide-rich waters from the lower oceanic box onto the shelf. This influx (or local mixing of different water masses) seems to have persisted at least well into the Kimmeridgian.

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## Streszczenie

 **$\delta^{13}\text{C}$  AND  $\delta^{18}\text{O}$  W PÓŹNOJURAJSKICH WAPIENIACH  
PROWINCJI SUBMEDITERRAŃSKIEJ (EUROPA)****Andrzej Pisera, Muharrem Satir, Michał Gruszczyński,  
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Stosunki izotopowe węgla i tlenu zbadano w skorupach brachiopodów i w próbkach skalnych pobranych w późnojurajskich wapieni z Hiszpanii, południowych Niemiec i południowej Polski (Fig. 1). Dodatkowo uwzględniono też kilka próbek brachiopodów z Francji. Wyniki (Fig. 2) wskazują, że krzywa izotopowa węgla wzrastała w ciągu dolnego i środkowego oksfordu, aż do poziomu  $\delta^{13}\text{C}$  około +3‰, a następnie spadła w górnym oksfordzie i kimerydzie o mniej więcej 1‰. Stosunki izotopowe tlenu wykazują w badanym materiale ogromne zróżnicowanie, zarówno pionowe, jak i oboczne. Dane te sugerują, że w rozważanym okresie na szelf dostawały się, lokalnie lub co najwyżej regionalnie, przejściowo wody z głębszych stref oceanu, bogate w substancje odżywcze i dwutlenek węgla.

