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Sr-Isotope Stratigraphy: Assigning Time in the Campanian, Pliensbachian, Toarcian, and Valanginian

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ABSTRACT

The trend of marine \(^{87}\text{Sr}/^{86}\text{Sr}\) against stratigraphic level through sections, whether linear or not, can identify hiatuses and changing rates of sedimentation through those sections and so be a valuable constraint on attempts to assign numerical ages to sediments on the basis of astrochronology or U/Pb dating of zircons. Here we illustrate that value for the Campanian, Pliensbachian, Toarcian, and Valanginian ages by comparing \(^{87}\text{Sr}/^{86}\text{Sr}\) profiles for different localities and comparing those to the \(^{87}\text{Sr}/^{86}\text{Sr}\) profile through time. The analysis reveals possible problems both with current time scales and with some astrochronological calibrations. Our analysis is neither comprehensive nor final; rather, with a few examples, we show how Sr-isotope stratigraphy can be used to moderate other methods of assigning numerical ages to sediments.

Introduction

The seminal hypothesis of Wickman [1948], that \(^{87}\text{Sr}/^{86}\text{Sr}\) of Sr dissolved in the ocean should increase linearly with time, was falsified by the pioneering work of Peterman et al. [1970], Dasch and Biscaye [1971], Veizer and Compston [1970], and Burke et al. [1982], who showed that the \(^{87}\text{Sr}/^{86}\text{Sr}\) of marine Sr rose and fell repeatedly during the Phanerozoic. Since then, that variation in \(^{87}\text{Sr}/^{86}\text{Sr}\) through time has become well documented, especially for the period 0–40 Ma (fig. 1). For this interval, the \(^{87}\text{Sr}/^{86}\text{Sr}\) calibration (fig. 1) shows many linear segments separated by intervals, mostly around 1 Ma, during which the rate of change in \(^{87}\text{Sr}/^{86}\text{Sr}\) with time itself changed.

The trend through time shown in figure 1 and the longer-term trend of marine \(^{87}\text{Sr}/^{86}\text{Sr}\) through Phanerozoic time are patched together from numerous profiles of \(^{87}\text{Sr}/^{86}\text{Sr}\) against stratigraphic level through sedimentary sections that are assumed to be largely complete and to which numerical dates have been assigned. It is profiles of \(^{87}\text{Sr}/^{86}\text{Sr}\) against stratigraphic level, rather than against time, that are most revealing. The shape of such a profile can reveal the presence of hiatuses, faults, and changes in sedimentation rate. The interplay of sedimentation rate and the rate of change in \(^{87}\text{Sr}/^{86}\text{Sr}\) with time are shown in figure 2.

Comparisons between sections of Sr-isotope profiles against stratigraphic level can be revealing as to whether the reference curve is linear (fig. 2). Nevertheless, such trends are most easily interpreted by comparison with the linear parts of the reference curve (fig. 1) because the human eye perceives departures from linearity more easily than it does departures from curvature. Fortunately, through some geological intervals, \(^{87}\text{Sr}/^{86}\text{Sr}\) changed linearly with time (fig. 1) or the change was so close to being linear that it makes no practical differences to an assumption of linearity. The earliest exploitation of linearity was that of Miller et al. [1988], who used it to calculate the duration of hiatuses in deep-sea sediments.

Here we use linear or nearly linear parts of the reference curve to examine aspects of time scales given in the geological time scale of Gradstein et al. [2012, hereafter, GTS12] and in other publications and assign durations to biozones of several stages. In addition, as both GTS12 and the other time scales we cite make use of cyclostratigraphy for numerical
calibration, we show how profiling $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level through a sedimentary section can constrain and inform that process.

**Rock and Time**

To begin, we emphasize the old adage that rock does not equal time (Ager 1973). While all geologists know this, departures from the principle are not unknown—for example, use of the phrase “a rapid rise in $^{87}\text{Sr}/^{86}\text{Sr}$” with implications of time, when what was observed was a rise in $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level greater than that recorded in either underlying or overlying strata [i.e., condensation; fig. 2]. To emphasize the well-known difference between rock and time, we differentiate them as follows: by the term $dR/dt$ we mean the rate at which $^{87}\text{Sr}/^{86}\text{Sr}$ changed with time. By the term $dR/dl$, we mean the rate at which $^{87}\text{Sr}/^{86}\text{Sr}$ changes with stratigraphic level upward through a sedimentary section.

Where $^{87}\text{Sr}/^{86}\text{Sr}$ profiles against stratigraphic level is linear through a section [i.e., $dR/dl$ is constant], then it follows that $dR/dt$ was constant through that interval [i.e., that $^{87}\text{Sr}/^{86}\text{Sr}$ increased linearly though time during that interval]. In such sections, the relative thicknesses of the events recorded in the section (e.g., ammonite zones, isotopic excursions) therefore reflect their relative durations. By “constant” is meant at a rate sufficiently steady for hiatuses not to be detectable by departures of $^{87}\text{Sr}/^{86}\text{Sr}$ from a linear trend. With the present analytical uncertainty of no better than ±0.000003, the time thus represented has a lower limit of no less than 50 k.yr. for periods of time when marine $^{87}\text{Sr}/^{86}\text{Sr}$ was changing rapidly with time ($\approx 0.000060$ per Ma; Oligocene, earliest Triassic) and is greater for periods where $^{87}\text{Sr}/^{86}\text{Sr}$ was changing less rapidly with time. The uncertainty on whatever calibration curve is used will increase the duration of the period below which a hiatus might be identified.

**Figure 1.** Evolution of marine $^{87}\text{Sr}/^{86}\text{Sr}$ through time ($dR/dt$) for the past 25 m.yr., modified from the locally weighted scatterplot smoothing (LOWESS) fit of McArthur et al. (2012) in the geological time scale of Gradstein et al. (2012; GTS12). The profile comprises linear sections A–D, connected by intervals of changing $dR/dt$. Least squares linear regression coefficients for each segment are shown, together with the maximum deviation from the regression line (the residuals) of the LOWESS line. The deviations are all less than typical analytical uncertainty of singlet analysis of $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.000015. This time period is used to illustrate linearity because the temporal calibration is unequivocal. All dates are normalized to standard values of 0.710248 for NIST987, which equals 0.709175 for EN-1. A color version of this figure is available online.
Figure 2. Comparison of trends of marine $^{87}\text{Sr}/^{86}\text{Sr}$ through time ($dR/dt$) with trends of marine $^{87}\text{Sr}/^{86}\text{Sr}$ with stratigraphic level ($dR/dl$). A color version of this figure is available online.
Comparisons to Cyclostratigraphy

Cyclostratigraphic analysis has contributed much to calibrating the geological time scale when it has been applied to pelagic and hemipelagic carbonate-rich sediments in which sedimentation for long periods may have been continuous and sedimentation rate reasonably constant or closely tied to repetitive orbital cycles (Weedon 2003; Kuiper et al. 2008). When applied to clastic sediments deposited on shallow continental shelves in shallow epeiric seas, where sedimentation is anything but continuous and sedimentation rate highly variable (Ager 1973), cyclostratigraphy appears to be less successful (Bailey and Smith 2008a, 2008b; Vaughan et al. 2011, 2014; Ruebsam et al. 2015).

Cyclostratigraphic analysis requires that the expression of cyclic forcings is captured in sediments that either accumulate at a constant rate or accumulate at a rate that varies with rigorous repetitiveness through being tied tightly to cyclic forcings for long periods of time. A change in sedimentation rate will change the frequency with which a cycle is expressed in the sediment where stratigraphic level is used as a reference frame. Such changes in sedimentation rate can be detected by adoptions of the cyclostratigraphic method (Huang et al. 1993), but unless detected, multiple peaks at differing wavelengths will present for the same cycle. In view of this, the finding in Toarcian sediments of the Paris Basin of “a rich series of sub-Milankovitch to Milankovitch frequencies [precession, obliquity and eccentricity]” by Boulila et al. (2014) might suggest that the series has been enhanced by multiple changes in sedimentation rate (cf. Ruebsam et al. 2015), thereby giving opportunity to misassign detected frequencies to incorrect orbital cycles. Furthermore, it seems odd that most cyclostratigraphic analysis in deep time involves an initial detrending step that removes variation in the signal that itself might be cyclic in origin. Such a step needs to be rigorously justified but seldom is.

Durations derived via cyclostratigraphy are accurate only where a complete set of cyclostratigraphic expressions are present. Sedimentary hiatuses may not be identified by cyclostratigraphic analysis (e.g., Myers and Sageman 2004) because even multiple gaps in a section may only degrade the power of any periodicity seen rather than remove it entirely (e.g., Bailey and Smith 2008a, 2008b). Unless means exist to recognize hiatuses and estimate the time they represent, durations obtained by cyclostratigraphy will be underestimates.

Finally, cyclostratigraphic data are often “sampled” or “resampled” to obtain even distance values for analysis. This process involves interpolation between real data points and yields “virtual” data points, seldom explicitly identified as such, that are more evenly spaced than the raw data. The use in cyclostratigraphy of such a term should not be taken to imply that new, real samples were collected. In addition, cyclostratigraphers often employ the term “tune” as a synonym for “assign by guesswork.” Taken together, such terminology may project, to some, an image of unwarranted rigor. While undoubtedly powerful, cyclostratigraphic analysis can, like any method, be misapplied by, for example, not fully accounting for confidence limits in a rigorous way (Vaughan et al. 2011, 2014). Finally, in deep time, the method relies not only on tuning but also on the assumption that all orbital parameters in deep time were the same as today’s, a matter still in debate for all but the approximately 405 ka cycle.

Application

Campanian. In figure 3a we plot the record of marine $^87$Sr/$^{86}$Sr through time for the Campanian of the US Western Interior (US WI). Numerical ages and the ammonite zonation are from GTS12, and zonal values of $^87$Sr/$^{86}$Sr are from McArthur et al. (1994), with additional data from the analysis of a new sample given in table 1. The trend is calibrated by numerous dates for bentonites (Obradovich 1993; Cobban et al. 2006). The trend is reasonably linear in its upper half, from the Baculites scotti Zone upward, but is nonlinear in its lower half, which shows two strong points of inflection between the zones of Scaphites hippocrepis III and Baculites obtusus.

The record of marine $^87$Sr/$^{86}$Sr against stratigraphic level through the Chalk of northwestern Germany is plotted in figure 3b; the data are from McArthur et al. (1993), updated with new $^87$Sr/$^{86}$Sr values for 34 belemnites, a revised stratigraphy from Voigt and Schönfeld (2010), and the base of the Maastrichtian now placed at the base of the Belemnella obtusa Zone (Gradstein et al. 2012) rather than at the base of the Belemnella lanceolata Zone, a traditional earlier placement. The profile of $^87$Sr/$^{86}$Sr against level fits well to two linear segments, one below the level of 167 m above datum (the top of the Patagiosites stobaei ammonite zone) and the other above it. As $dR/dt$ was constant in each segment, it follows that $dR/dt$ must have been constant in each (fig. 2). The simplest interpretation of the change in slope is that sedimentation rate changed at that point, although a change in $dR/dt$ might equally well explain the change in slope.

The shape of the trend of $^87$Sr/$^{86}$Sr through the early and middle Campanian of the US WI differs
markedly from the bilinear trend of $^{87}\text{Sr}/^{86}\text{Sr}$ shown by the Chalk of Germany. The discrepancy may have three explanations: critical dates for the US WI may be wrong, critical bentonite samples from the US WI may have been miscorrelated, and the $^{87}\text{Sr}/^{86}\text{Sr}$ data for the US WI are wrong in part. We examine these possibilities below.

First, for the numerical calibration of the Campanian, much hinges on the accuracy of the date for the $B. \text{obtusus}$ Zone, as it is the middle date of only three of 11 contiguous zones from the $B. \text{hippoceppis II}$ Zone to the $B. \text{scotti}$ Zone. Are these dates incorrect? In the following discussion, dates are given relative to Fish Canyon Tuff of 28.201 Ma and the decay constants of Min et al. (2000). Numerical dates for the $B. \text{obtusus}$ Zone (appendix 2 of GTS12; largely from Obradovich 1993 and Cobban et al. 2006) are 80.62 ± 0.40 Ma (95% confidence interval) for the Ardmore Bentonite of the Red Bird section of Wyoming [Hicks et al. 1999] and 81.3 ± 0.55 Ma for the Big Bentonite (taken to be the Ardmore Bentonite) of the Elk Basin [Hicks et al. 1995]. These localities are 500 km apart. The two dates were obtained by similar methods, and repeat analysis by Sageman et al. (2014) of four older bentonites dated by similar methods gave results indistinguishable from the original dates. For example, a date of 81.84 ± 0.22 Ma was obtained by Sageman et al. (2014) for a bentonite low in the zone of $\text{Scaphites hippocrepis II}$, while the date of a bentonite in this zone of 81.87 ± 0.25 Ma (re-calculated) is reported in GTS12 (after Cobban et al. 2006 and Obradovich et al. 1993). The agreement attests to the robustness of the Ar/Ar dates for the US WI given in GTS12. Error in dating therefore seems unlikely.

Second, there is a possibility that the bentonites dated by Hicks et al. [1995, 1999] from the $B. \text{obtusus}$
Table 1. Results of $^{87}\text{Sr}/^{86}\text{Sr}$ analysis of samples of molluscan shell material from the US Western Interior analyzed for this study as a check on the data of McArthur et al. [1994]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zone</th>
<th>Unit</th>
<th>Locality</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D4261</td>
<td>B. asperiformis</td>
<td>Cody Shale</td>
<td>Johnson County, Wyoming</td>
<td>.707572 ± 8</td>
</tr>
<tr>
<td>D4255</td>
<td>B. sp. (weakly ribbed)</td>
<td>Cody Shale</td>
<td>Johnson County, Wyoming</td>
<td>.707572 ± 9</td>
</tr>
<tr>
<td>AMNH 102643</td>
<td>B. smooth (early)</td>
<td>Pierre Shale</td>
<td>Butte County, South Dakota</td>
<td>.707517 ± 11</td>
</tr>
<tr>
<td>AMNH 51754</td>
<td>B. smooth (early)</td>
<td>Pierre Shale</td>
<td>Butte County, South Dakota</td>
<td>.707518 ± 9</td>
</tr>
<tr>
<td>AMNH 102654 [a]</td>
<td>B. smooth (early)</td>
<td>Pierre Shale</td>
<td>Butte County, South Dakota</td>
<td>.707516 ± 7</td>
</tr>
<tr>
<td>AMNH 102654 [b]</td>
<td>B. smooth (early)</td>
<td>Pierre Shale</td>
<td>Butte County, South Dakota</td>
<td>.707518 ± 10</td>
</tr>
</tbody>
</table>

Isotope standards:
- EN-1
- SRM 987
- SRM 987

Note. All of the samples are from the name-bearing species of Baculites within each zone except for D4261, which is a Hoploscaphites species from the B. asperiformis Zone. D = USGS Mesozoic locality; AMNH = American Museum of Natural History.

Zone were not collected from that zone. As those authors pointed out, the Ardmore Bentonite Bed actually consists of an interval of shale with multiple bentonite beds. However, this interval has been very well documented at the informal type section of the Pierre Shale at Red Bird, Wyoming (Gill and Cobban 1966), where it occurs near the bottom on the Sharon Springs Member at the base of the B. obtusus Zone. Thus, it is unlikely that Hicks et al. [1995] sampled the wrong bentonite.

Third, the values of $^{87}\text{Sr}/^{86}\text{Sr}$ are incorrect for the interval Baculites sp.光滑 to Baculites gregoryensis. For this to be the case, it would be necessary for 12 values of $^{87}\text{Sr}/^{86}\text{Sr}$ derived from 11 separate ammonites spread through five zones all to be incorrect in a systematic manner such that the errors in the $^{87}\text{Sr}/^{86}\text{Sr}$ values first increase upsection and then decrease upsection.

To test the $^{87}\text{Sr}/^{86}\text{Sr}$ data, we have analyzed five new specimens of ammonites, the data are shown in table 1. They confirm the validity of the $^{87}\text{Sr}/^{86}\text{Sr}$ data of McArthur et al. [1994]. There is also a good agreement between the $^{87}\text{Sr}/^{86}\text{Sr}$ value used here of 0.707674 ± 10 [2 SE, n = 5] for the Baculites compressus Zone [from McArthur et al. 1994] and that obtained independently on different specimens by Cochran et al. [2010] for the same zone of 0.707684 ± 13 [mean and range of their two best-preserved samples]. The agreement is similar for two specimens from the Didymoceras cheyennense Zone reported by Landman et al. [2012], which, at 0.707692 and 0.707701, are some 0.000030 higher [twice analytical uncertainty] than those inferred from the trendline of McArthur et al. [1994] and shown in figure 3. Furthermore, the values of $^{87}\text{Sr}/^{86}\text{Sr}$ for the base of the Maastrichtian and the base of the Campanian agree well (fig. 3) for the present definitions of these boundaries, considering the uncertainties inherent in both the analytical uncertainty of the $^{87}\text{Sr}/^{86}\text{Sr}$ analysis and the biostratigraphic correlation (unquantifiable).

There is a possibility that nonmarine influences affected the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the US WI, either through dilution by freshwater runoff (McArthur et al. 1994; Cochran et al. 2003) or through the action of methane seeps (Landman et al. 2012). We discount the former for reasons given at length in McArthur et al. [1994], not least of which is that those authors analyzed mostly ammonites, which are mostly stenohaline. We discount the latter because biogenic calcite in specimens affected by exhalations from methane seeps typically have very depleted values of $\delta^13\text{C}$ and may also show depleted values of $\delta^18\text{O}$ (Landman et al. 2012); the data of McArthur et al. [1994] excluded samples with anomalous stable-isotopic compositions. Furthermore, methane seeps identified to date are found in strata of middle late Campanian to Early Maastrichtian age; our major anomaly in $^{87}\text{Sr}/^{86}\text{Sr}$ is in the late Early through middle Campanian.

A need for adjustment to the scaling for the Campanian in GTS12 is highlighted by Walaszczyk et al. [2008], who correlated the northern European zones of P. stobaei and (overlying) Gaterites vulgaris to the US WI zones of B. obtusus and the (overlying) Baculites maclearni, respectively (fig. 3). The lower biostratigraphic correlation agrees well with the Sr-isotope correlation, considering the uncertainties inherent in both methods. The $^{87}\text{Sr}/^{86}\text{Sr}$ correlation of the European G. vulgaris Zone, however, includes zones from the B. maclearni up to the B. scotti Zone because of the low slope of the plateau region of the middle Campanian of the US WI. This amounts to a potential error in correlation of up to 5 m.yr. and emphasizes the perplexity of the paradox noted here. Much, but not all, of the plateau in $^{87}\text{Sr}/^{86}\text{Sr}$ is in the
middle Campanian of the US WI can be removed by adjusting zonal durations for the middle Campanian—for example, decreasing the durations of zones in the upper part of the middle Campanian and increasing those in the lower part—but the plateau cannot be entirely removed by this process without reducing some zonal durations almost to zero, which seems unreasonable.

A need for adjustment to the scaling for Campanian in GTS12 is also highlighted by Voight et al. (2010), who used cyclostratigraphy to assign a date of 77.5 ± 0.4 Ma to the boundary between the early and late Campanian in northern Germany (Lägerdorf-Kronsborn, fig. 3). The rigor of this date has not been assessed here, but we note that it agrees well with the correlation of Walaszczyk et al. (2008), highlights the discrepancy between Germany and the US WI, and requires [as does the 87/86Sr] the presently compressed durations of the zones S. hippocrepis II to B. (weakly ribbed) to be greatly expanded and the durations of the overlying zones up to the B. scotti Zone to be greatly compressed.

Differential rates of sedimentation in different zones or groups of zones might influence scaling of time between those zones. The base of the Sharon Springs Member probably represents a condensed interval that formed at the beginning of the Claggett transgression (Gill and Cobban 1966). It consists of organic-rich shale with abundant fish teeth and scales. In contrast, the stratigraphic interval above the B. obtusus Zone and extending to the B. scotti Zone is much more expanded. Hicks et al. (1999, their table 4) estimated that the sedimentation rate in this part of the section was 45% greater than that in the lower part of the section. This difference in sedimentation rate can explain only a small part of the 87/86Sr paradox.

The application of linear 87/86Sr has therefore revealed a problem affecting the scaling of zonal duration zonation for the US WI, the Sr-isotope stratigraphy of the US WI, the numerical age of bentonites from the B. obtusus Zone, the interpretation of the rates of sedimentation through the section, or an unfortunate combination of one or more of these factors. To establish the relative contributions of these factors, dating of new middle Campanian tuffs are required. Also required are further analysis for 87/86Sr of specimens from localities known to be free of methane seeps and located away from the well-known shorelines of the time (Gill and Cobban 1973; Wright 1987; Lillegraven and Ostresh 1990; Slattery et al. 2013). Bellemnite calcite would be the best sampling medium, as the low-magnesium calcite of the bellemnite rostrum resists diagenetic alteration better than does ammonite aragonite and is easier than ammonite aragonite to assess for alteration.

**Pliensbachian.** Sr-isotope stratigraphy. The ammonite zonation of the lower Jurassic of northwestern Europe is summarized in Page (2003). For the Pliensbachian of Yorkshire, United Kingdom, ammonite zonal boundaries have been defined to decimeter accuracy in the well-exposed coastal sections of Yorkshire by Howarth (1955) and Phelps (1985), summarized in Hesselbo and Jenkyns (1995). The record of 87/86Sr against stratigraphic level through the Pliensbachian of Yorkshire is shown in fig. 4a. The 87/86Sr of the ammonite zonal boundaries are defined well. The trend of 87/86Sr against stratigraphic level shows some sinuosity, which might result from variations in sedimentation rate, dR/dt, or both. The plateau in 87/86Sr through the Davoei Zone was ascribed by McArthur et al. (2000) to an increase in sedimentation rate through this interval. The steep decline in 87/86Sr in the upper gibbosus Subzone is known to arise from the presence of a hiatus at this level in coastal exposures, a hiatus that cuts out an increasing thickness of Pliensbachian strata with increasing distance inland (Howard 1985).

To compare the Yorkshire profile to those from elsewhere, we take the 87/86Sr values of the zonal boundaries in Yorkshire (fig. 4a) and place them into other sections. Figure 4b shows the profile of 87/86Sr with stratigraphic level in a composite section through the Pliensbachian of the Basque-Cantabrian Basin (BCB) of northern Spain (Rosales et al. 2003). Through the BCB profile, dR/dt is constant except in the Jamesoni Zone. It follows that, Jamesoni Zone apart, dR/dt was also constant through the section in Spain, and so, Jamesoni Zone apart, the zonal thickness reflects zonal duration. The linearity of the 87/86Sr profile through most of the BCB section proves that the sinuosity of the Yorkshire profile was caused by variations in sedimentation rate.

The profile of 87/86Sr against time and ammonite nomenclation as given in GTS12 is shown in figure 4c. The profile approximates to linear. That time scale applied a linear Sr trend from McArthur et al. (2000) for scaling the A. margaritatus and P. spinatum Zones and then an equal-subzone scale for the lower 10 subzones of the early Pliensbachian (J. Ogg, pers. comm., March 2016). Application of a rigorously linear 87/86Sr model gives the zonal durations in figure 5, which differ a little from those given in GTS12.

Figure 4d shows the profile of 87/86Sr against stratigraphic level in the Llanbedr [Mochras Farm] borehole, United Kingdom (Woodland 1971). For
Figure 4. Stratigraphy is from Ivimey-Cook [1971]; ammonite zonation and boundaries were redetermined for this work by K. Page and are largely confirmed: the base of the Jamesoni Zone is placed here 8.5 m lower than in Ivimey-Cook [1971].a, Profiles of $^{87}$Sr/$^{86}$Sr against stratigraphic level for Pliensbachian sections in the United Kingdom (Yorkshire). Data for Yorkshire are from McArthur et al. [2000]; data for the Jamesoni Zone are from Jones et al. [1994] and Hesselbo et al. [2000]. b, Profiles of $^{87}$Sr/$^{86}$Sr against stratigraphic level for Pliensbachian sections in Spain. Stratigraphy is from Rosales et al. [2003]. c, Profiles of $^{87}$Sr/$^{86}$Sr through Pliensbachian time to the geological time scale of Gradstein et al. [2012; GTS12]. d, Profiles of $^{87}$Sr/$^{86}$Sr against stratigraphic level for the Pliensbachian core from Mochras, Wales. Stratigraphy is from Ivimey-Cook [1971], updated by Page [2013], with ammonite zonation redetermined for this work by K. Page using ammonites from a curated core held at the British Geological Survey, Keyworth, United Kingdom. Apart from the position of the base of the Jamesoni Zone, which is placed here 8.5 m lower than in Ivimey-Cook [1971], other differences in level are too small to show on the diagram. To illustrate departures of trends from linear, dotted straight lines are drawn arbitrarily through $^{87}$Sr/$^{86}$Sr values for the base of the Toarcian and the base of the Ibex Zone. A color version of this figure is available online.
figure 4, zonal boundaries were redetermined by examination of several hundred ammonites from the curated core. The extant zonal boundaries were largely confirmed and any differences in level are too small to show on our figures. The Mochras profile approximates a linear trend but shows two weak inflections, one at the base of the Ibex Zone and the other at the base of the subnodosus Subzone. Nevertheless, the weak inflection in the base of the Ibex Zone gives a trend through the Jamesoni Zone that is much lower in dR/dl (and so putative dR/dt) than that seen in the profile for Spain or GTS12. The Mochras profile therefore shows that the sedimentation rate for the Jamesoni Zone in Spain was lower than it was for that zone at Mochras and also that the duration of the zone in GTS12 may be underestimated.

Cyclostratigraphy. In the Mochras profile, dR/dl varies from 10.9 per 10 m of section in the Jamesoni Zone through 6.3 per 10 m in the middle Pliensbachian to 11.5 per 10 m in the upper Pliensbachian. The sedimentation rate thus varied through the period of deposition by a factor of about two. Attempts to use cyclostratigraphy to estimate event durations or the duration of the Pliensbachian stage and its component zones would need to accommodate such changes in the rate of sedimentation.

Toarcian. Sr-isotope stratigraphy. For the Toarcian of Yorkshire, ammonite zonal boundaries have been defined to decimeter accuracy in the well-exposed coastal sections by Howarth (1962, 1973, 1992), and the sequence was used to establish the high-resolution biohorizonal scheme of Page (2004). The record of 87Sr/86Sr against stratigraphic level through those composited sections is shown in figure 6a, updated from McArthur et al. (2000) with additional 87Sr/86Sr data for the Dumortiera levesquei Zone of the uppermost Toarcian and some redeterminations of 87Sr/86Sr in other zones. The profile comprises four linear segments with different dR/dl. The parts are as follows, with rates of change of 87Sr/86Sr with stratigraphic level in units of 10⁻⁶ per 10 m of section:

- 9.0 above 69 m; the section’s top lacks the aalenensis Subzone and part of the moorei Subzone.
- 6.0 between 22 and 69 m; 0.3 m above base falciferum Subzone to mid-fibulatum Subzone.
- 93 between 14 and 22 m; exaratum Subzone plus 0.3 m of falciferum Subzone.
- 14 between 0 and 14 m; Tenuicostatum Zone.

The differing dR/dl occur because the four parts of the profile accumulated at different rates [McArthur et al. 2000; this work]. The upper two parts represent samples collected either side of a strike-slip fault that has juxtaposed strata for which sedimentation rates differed in Toarcian time. Downsection, dR/dl is particularly high through the exaratum Subzone because the unit is condensed [McArthur et al. 2000; Jenkyns et al. 2002; McArthur and Wignall 2007; Trabucho-Alexandre 2014].

It is illustrative to compare the profile of 87Sr/86Sr against stratigraphic level (i.e., through rock) for the Yorkshire Toarcian to profiles through time and through Toarcian sediments elsewhere. The 87Sr/86Sr values of the zonal boundaries in Yorkshire (fig. 6a) are therefore inserted into GTS12, the [incomplete] Amellago section of Morocco (Bodin

![Figure 5](https://example.com/figure5.png)
Figure 6. Profiles of $^{87}$Sr/$^{86}$Sr against stratigraphic level for Toarcian sections in Yorkshire, United Kingdom (a); against time for Gradstein et al. (2012; b), against stratigraphic level for the Mochras borehole, Wales, United Kingdom (c); and for the section at Amellago, Morocco (Bodin et al. 2010; d). Data for $^{87}$Sr/$^{86}$Sr are from McArthur et al. (2000), with additional analysis for the Levesqui Zone and some reanalysis of samples from lower levels. To illustrate departures of trends from linearity, dotted straight lines are drawn through $^{87}$Sr/$^{86}$Sr values for the base of the Toarcian (0.707073) and the base of the Aalenian (0.707290). Sz. = subzone. A color version of this figure is available online.
et al. 2010), and the biostratigraphic record for the Mochras Farm borehole of the United Kingdom (Wales).

Figure 6b shows the profile of $^{87}\text{Sr}/^{86}\text{Sr}$ through time according to the time scale of GTS12. A distinct step in $^{87}\text{Sr}/^{86}\text{Sr}$ is seen in the exaratum Subzone in comparison to the smoother profiles in the Mochras borehole and the Amellago section. The comparison suggests that GTS12 has underestimated the duration of the exaratum Subzone: the stepped temporal profile retains some of the extreme condensation in that subzone shown to occur by McArthur et al. (2000; further discussed in McArthur and Wignall 2007).

In the Mochras borehole, zonal boundaries appear mostly to be resolved with the accuracy of a few meters [Ivimey-Cook 1971; this work]: the profile of $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level through the borehole (fig. 6c) lacks the severe distortion seen in the H. exaratum Subzone of the Yorkshire profile and so is not condensed as it is in Yorkshire. The Mochras profile approximates to two near-linear segments, one above the base of the fibulatum Subzone and the other below it. Values of $dR/dl$ per 10 m of strata are around 14 for the lower part and 6 for the upper part (fibulatum Subzone and upward). A similar shape to the profile is seen in the Amellago section of Bodin et al. (2010) for Morocco (fig. 6d), where the upper part of the profile has a lower $dR/dl$ per 10 m of strata than the lower part (2.0 vs. 8.4).

The profiles of $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level for Mochras and Amellago approach linearity much more closely than does the profile for Yorkshire and express little of the condensation shown by the Yorkshire sections. Change in $dR/dl$ in Amellago, Mochras, and Yorkshire occurs in the Bifrons Zone, but in Yorkshire it occurs in the upper part while in Amellago and Mochras it occurs in the lower part, confirming that it is caused by a change in the sedimentation rate rather than a change in $dR/dt$.

The profiles suggest that a linear $^{87}\text{Sr}/^{86}\text{Sr}$ model for assigning time in the Toarcian is appropriate, in line with the models shown in figure 2. The results of applying a linear model to apportion time is shown in figure 7, which is updated from table 2 of McArthur et al. [2000]. Using the linear model, the rise in $^{87}\text{Sr}/^{86}\text{Sr}$ through the exaratum Subzone (figs. 6a, 7) is 28% of the rise in $^{87}\text{Sr}/^{86}\text{Sr}$ through the entire Toarcian, so the duration of the exaratum Subzone must be 28% of the time allotted to the Toarcian age, thus 2.4 m.yr. using GTS12 dates for age boundaries. Similarly, the rise through the Falciferum Zone (subzones falciferum over exaratum) is 44% of the total rise through the Toarcian,
so 44% of Toarcian time and thus 3.8 m.yr. using that time scale.

An alternative near-linear “Mochras model” can be derived to apportion time in the Toarcian on the basis of the fact that the profile of \( dR/dt \) is similar in both Mochras and Amellago (fig. 6). This model requires that the sedimentation rate in both localities was constant during deposition of Toarcian sediments and that the similarity of profiles of \( dR/dt \) arises because \( dR/dt \) was 30% lower in the late Toarcian than in the early Toarcian. This model is falsified by the Yorkshire profile and is further suspect because a “probable fault” is recorded in the middle of the \( \text{exaratum} \) Subzone in the Mochras borehole; if real, it may have repeated, or cut out, some of the \( \text{exaratum} \) Subzone. Both possibilities would alter the interpretation of the profile. Nevertheless, the model has a limited use in that it can provide limiting values on the durations of biozones, and these are also shown in figure. The \( \text{Falciferum} \) Zone had a duration of 24% of the total duration of the Toarcian, or 2.1 m.yr., while the \( \text{exaratum} \) Subzone lasted 1.1 m.yr. The main value of this model is to show that even on a suspect nonlinear model, the duration of the \( \text{exaratum} \) Subzone exceeds estimates derived from cyclostratigraphy, which are discussed below.

**Cyclostratigraphy.** A negative isotope excursion in the \( \delta^{13}C \) of organic carbon (CIE\textsubscript{om}) occurs in the \( \text{exaratum} \) Subzone of the lower Toarcian sediments of northwestern Europe [Küspert et al. 1982 and many since] and elsewhere. It is assumed by many that the excursion is the expression of a synchronous event and is of uniform duration everywhere. That duration has been estimated by cyclostratigraphy to range from 120 k.yr. (Clémence 2006) through 260 k.yr. [Ikeda and Hori 2014], ~300–500 k.yr. [Boullia et al. 2014], 500 k.yr. [Sabatino et al. 2009], 620 k.yr. [Huang and Hesselbo 2014], 790 k.yr. [\textit{elegantulum} Subzone of Ruebsam et al. 2014], and 930 k.yr. [Suan et al. 2008]. Either the event is not synchronous and so not of equal duration everywhere, as implied recently by Neumeister et al. [2014], or some or all of these estimates of duration are incorrect.

In the lower Toarcian sediments of Yorkshire, the CIE\textsubscript{om} is marginally longer in duration than the coincident \( \text{H. exaratum} \) Subzone [i.e., the \textit{elegantulum} Subzone of the Mediterranean province; Page 2003]. The duration of the \( \text{H. exaratum} \) Subzone is shown here to be around 2.4 m.yr., with a less likely minimum duration of 1.1 m.yr. derived from the Mochras model. The estimate of 1.1 m.yr. is 56% longer [i.e., 480 k.yr. longer] than the duration of 620 k.yr. arrived at for the sections in Yorkshire by Huang and Hesselbo (2014) using cyclostratigraphy. That cyclostratigraphic analysis claimed to reveal six C-isotope cycles in six separate European sections, one of which contains condensation and hiatuses ([fig. 8], is a matter of record elsewhere [McArthur et al. 2000; McArthur and Wignall 2007; Trebucho-Alexandre 2014]. Clearly, if the cycles identified are real, they are not a complete set. Others attempting cyclostratigraphic analysis of the \( \text{H. exaratum} \) Subzone in Yorkshire found no cyclicity at all in its upper part [Kemp et al. 2011].

**Valanginian.** Sr-isotope stratigraphy. For the Valanginian sediments of the Vocontian basin of southeastern France, accounts of the lithostratigraphy and biostratigraphy have been given by Busnardo [1979], Busnard and Thieuloy [1979], Cotillon et al. [1980], Reboulet et al. [1992], Bulot et al. [1993], and many since. Zonal boundaries, and so the bases of the

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**Figure 8.** Schematized hiatuses and condensation in the \( \text{H. exaratum} \) Subzone of Yorkshire, United Kingdom, figured in Jenkyns et al. (2002).
Figure 9. Profiles of $^{87}$Sr/$^{86}$Sr for Valanginian sections in southeastern France against stratigraphic level (a) and time (b) from Gradstein et al. (2012); against time from Gréselle and Pettit (2010; c), against time from Martinez et al. (2013; d), and against stratigraphic level from Möller et al. (2015; e). Data for $^{87}$Sr/$^{86}$Sr are from McArthur et al. (2007). To illustrate departures of trends from linearity, dotted straight lines are drawn through $^{87}$Sr/$^{86}$Sr values from McArthur et al. (2007) for the base of the Valanginian (0.707294) and the base of the Hauterivian (0.707383); in e, these two values are shown as larger filled black circles. A color version of this figure is available online.
Valanginian and Hauterivian stages, can be positioned with decimeter accuracy. We take the $^{87}\text{Sr}/^{86}\text{Sr}$ values of these zonal boundaries as determined in the Vocontian Basin of southeastern France by McArthur et al. (2007) and use them to compare age models for the interval that are given in GTS12, Gréselle and Pettit (2010), Martinez et al. (2013), and Möller et al. (2015). The comparisons are shown in figure 9.

A high $dR/dt$ in the lowermost $T$. pertransiens Zone (fig. 9a) confirms condensation of the strata in the basal Valanginian, as noted by others (for a discussion, see sect. 8.4.2 of McArthur et al. 2007). The rest of the profile is fitted well by two linear regressions, with $dR/dt$ being steeper in the lower Valanginian than in the upper Valanginian. The profile of $^{87}\text{Sr}/^{86}\text{Sr}$ against numerical age, with ages from GTS12, is shown in figure 9b. The numerical ages are based largely on the cyclostratigraphy of Huang et al. (1993). Using that apportionment of time, the $^{87}\text{Sr}/^{86}\text{Sr}$ profile approximates a straight line. The apportioning of time through the Valanginian by Gréselle and Pettit (2010; fig. 9c), which is based on sequence stratigraphic recognition of cyclicity in the sediments, closely approximates the apportioning of time given in GTS12, and so the profile of $dR/dt$ is similar to that for GTS12 (fig. 9b). In contrast, the allocation of time based on the cyclostratigraphy of Martinez et al. (2013; fig. 9d) lengthens the late Valanginian at the expense of the early Valanginian. This process generates a distinctly nonlinear profile for $dR/dt$. Huang et al. (1993) stated that, for their studied sections at Angles and Vergons in the Vocontian Basin, the sedimentation rate in the upper Valanginian was around 50% higher than that in the lower Valanginian. That interpretation is not accepted in Martinez et al. (2013), but it fits the profile of $^{87}\text{Sr}/^{86}\text{Sr}$, which has lower $dR/dt$ in the upper Valanginian than in the lower Valanginian (fig. 9a).

The data of Möller et al. (2015) for East Greenland, although sparse, appear to fit a linear trend and suggest that a linear model for apportionment of Valanginian time might be appropriate. It further suggests that the apportionment of time in GTS12 is reasonably accurate. In Möller et al. (2015), values of $^{87}\text{Sr}/^{86}\text{Sr}$ at stage boundaries are indistinguishable from those for the Vocontian Basin of southeastern France (McArthur et al. 2007); the base of the Hauterivian is $0.707383 \pm 0.000005$, while a value of $0.707380 \pm 0.000003$ pertains to the base of the Hauterivian at Speeton, United Kingdom (McArthur et al. 2004). The base of the Valanginian [base of the $T$. pertransiens Zone] has an $^{87}\text{Sr}/^{86}\text{Sr}$ value of $0.707294 \pm 0.000005$ in southeastern France (McArthur et al. 2007). This value is unchanged if the first occurrence of Calpionellites darderi is used to define the base of the Valanginian [Bulot et al. 1996], as this level is close to the first occurrence of $T$. pertransiens; for example, at Montbrun-les-Bains, these levels are $<3$ cm apart (McArthur et al. 2007).

Cyclostratigraphy. The Valanginian sediments of Vocontian Basin, southeastern France, are good candidates for cyclostratigraphic analysis because of their apparently rhythmically interbedded marls and limestones. Nevertheless, estimates of the duration of the Valanginian interval that have been derived from cyclostratigraphy range from 4.7 m.yr. (Gréselle and Pettit 2010) through 5.08 m.yr. (Martinez et al. 2013), 5.9 m.yr. (Huang et al. 1993; but including the Thurmanniceras otopeta ammonite zone, now assigned to the Berriasian), 6.9 m.yr. (Sprovieri et al. 2006), and 7.04 m.yr. (Giraud et al. 1995; also including the $T$. otopeta ammonite zone). Allowing for the changes to boundary definitions, their remains some disagreement about the duration of the age.

The $^{87}\text{Sr}/^{86}\text{Sr}$ profile against stratigraphic level through the Valanginian strata of southeastern France (fig. 8) shows two points of inflection that join three linear segments of the profile, while the profile for East Greenland is linear. The latter profile (fig. 8) constrains to two the number of times sedimentation rate changed in the studied section of the Vocontian Basin of southeastern France; once at the termination of basal Valanginian condensation, and once more at the boundary of the base of the pronoecestatum Subzone. Such change should be incorporated into further attempts at cyclostratigraphic analysis of the Valanginian of southeastern France.

Conclusions

Profiling of $^{87}\text{Sr}/^{86}\text{Sr}$ through sedimentary sections can identify hiatuses, faulting, and changes in sedimentation rate. In sections where the profile of $^{87}\text{Sr}/^{86}\text{Sr}$ changes linearly with stratigraphic level, $^{87}\text{Sr}/^{86}\text{Sr}$ was changing linearly with time. In such sections, sediment thickness is directly proportional to time passed.

Using profiles of $^{87}\text{Sr}/^{86}\text{Sr}$ against time and against stratigraphic level, we have shown the following:

- Condensation, hiatuses, and changes in sedimentation rate can be identified. Such profiling should be used to constrain and guide cyclostratigraphy, as has been done here.
- Cyclostratigraphic estimates of the duration of several ages differ greatly from author to author and would benefit by being moderated by $^{87}\text{Sr}/^{86}\text{Sr}$.
$^{86}$Sr profiling of the sections studied to identify major breaks in sedimentation and changes in sedimentation rate.
• The calibration of the Gradstein et al. (2012) time scale (i.e., GTS12) for the lower Campanian does not agree with an apportionment based on $^{87}$Sr/$^{86}$Sr. This discrepancy can be resolved only by further work.
• The apportioning of Pliensbachian time by the GTS12 mostly agrees with a linear model for the evolution of $^{87}$Sr/$^{86}$Sr through the interval but may underestimate the duration of the Jamesoni Zone, the lowermost ammonite zone of the Pliensbachian.
• The GTS12 for the Toarcian does not agree with the apportionment of time based on $^{87}$Sr/$^{86}$Sr and appears to allot too little time to a period of severe condensation in the H. exaratum Subzone of the interval that is represented by black shales.
• Cyclostratigraphic estimates of the duration of the Toarcian H. exaratum Subzone, the early Toarcian CIE$_{om}$, or any other interval in clastic, near-shore sediments are likely to be estimates of minimum duration only.
• The duration of the early Toarcian negative excursion in the $\delta^{13}$C of marine organic matter, which is closely coincident with the H. exaratum Subzone, is around 2.4 m.yr., some 1.5 m.yr. longer than the longest cyclostratigraphic-based estimate of 930 k.yr., in a range that reaches down to 120 k.yr.
• The best apportionment of time for the Valanginian is GTS12, although a strictly linear profile of $^{87}$Sr/$^{86}$Sr through the Valanginian of East Greenland suggests that minor refinement might be needed.

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Apennines) and Monte Mangart (Julian Alps) sections: palaeoceanographic and stratigraphic implications. Sedimentology 56:1307–1328.


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