Reports

Quantitative Formulation of Reliability in Stratigraphic Correlation

Abstract. *The probability that two stratigraphic events are in a particular order in a section in which they occur in sequence is* p. *Because of finite sampling, statistical techniques are used to calculate the parameters* p' *and* p^l, *which express the uncertainty of our knowledge of* p; $\hat{p}'$ *is the measured value of the maximum likelihood estimator of* p *and* p^l *is the lower end point of the confidence interval on which* p *must lie. The most reliable sequence for stratigraphic correlation is obtained by maximizing the parameter* $\hat{p}'/(1 - p^l)$ *between pairs of events.*

Ten years ago virtually all of the data on the distribution of strata and fossils useful for interpretation of geologic history came from stratigraphic sections exposed or drilled on the continents and consequently representing a small proportion of the earth's surface. Largely as a result of the Deep Sea Drilling Project, knowledge of the distribution of Mesozoic and Cenozoic sediments and their plankton fossils has become global. This vast amount of accumulating data offers much new information about the history of the oceans and development of the planet, but the complexities of distribution introduce significant problems of interpretation. A quantitative formulation of stratigraphic correlation provides a framework for consistent treatment of global data.

Stratigraphy is the study of layered rocks; stratigraphic correlation is the determination of equivalence of age and stratigraphic position. Stratigraphy developed as two fields distinguished by the nature of the data considered: (i) lithostratigraphy, which is concerned with the establishment of continuity and determination of lateral relations of strata, and (ii) biostratigraphy, which is concerned with the use of fossils to establish stratigraphic correlations. From these two observational fields an interpretive field, chronostratigraphy, soon developed; chronostratigraphy is concerned with the determination of the geologic age of rocks. Each of these fields now has a highly developed nomenclature for recognizable units or intervals. Stratigraphic terminology in each of these fields is rigidly defined in formal stratigraphic codes approved by national and international bodies (*1*).

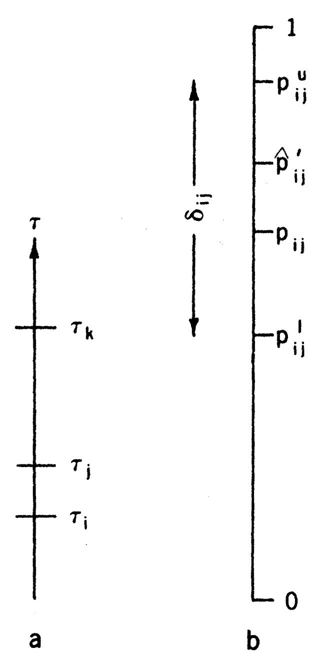

Fig. 1. (a) Stratigraphic events *i*, *j*, and *k* represented as points along a stratigraphic axis, τ. (b) Relations between the probability of a pair of events occurring in a particular order, p_{ij}; the maximum-likelihood estimator, $\hat{p}'_{ij}$; the confidence interval, δ_{ij}; the lower end point of the confidence interval, p^l_{ij}; and the upper end point of the confidence interval, p^u_{ij}.

If, however, the boundaries between units or end points of the intervals rather than the units or intervals themselves are considered, a single system emerges which expresses the relations within and between all areas of stratigraphy in a common language and uses general scientific terminology. Stratigraphic correlation becomes an expression of the relations between end points and is determined directly from observational data.

Stratigraphic correlation using traditional methods has been a simple matter if confined to a small area where the sequence of rock types and fossil occurrence is constant, but it becomes more uncertain as the size of the area and the number of stratigraphic sections considered increases. Ambiguities arise as the relative positions of end points in the sequence shift from one section to the next. The traditional solution to this problem, which forms the basis for almost all formal stratigraphic codes, is the designation of type sections or formal zonations which serve as reference standards. Comparison with a reference standard is a means of extending correlations over a larger area, but uncertainties again arise as the size of the area considered increases to contain stratigraphic sections in which the end points of intervals are in a wholly different order or which have no end points in common with the reference standard. Interest in correlation over long distances has increased greatly in the past decade, and as a consequence a number of possible methods for developing quantitative expressions for stratigraphic correlation have been suggested (*2*).

In this report we present a quantitative technique for constructing and evaluating alternative schemes for stratigraphic correlation, using the ordering of a sequence of end points of stratigraphic intervals. The technique is based on a statistical analysis which assigns to each ordering of interval end points a probability and confidence interval. The generality of the method makes it equally applicable to lithostratigraphic or biostratigraphic data or to any com-

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bination of the two types of information; the schemes for stratigraphic correlation remain objectively defined, but because they are an integrated description of knowledge of stratigraphic sequence, they are analogous to chronostratigraphic interpretation. The technique has the additional feature of being applicable to cases where the number of stratigraphic sections available for study is small and the area under consideration is large.

The starting point for this analysis is the definition of a stratigraphic event as an occurrence of some importance in stratigraphy, such as a change in rock type, or the lowest or highest occurrence of a fossil (*3*). An event can be represented as a point on a stratigraphic axis (that is, a τ-axis). According to this interpretation, stratigraphic data are represented by a series of points on a stratigraphic axis. This is illustrated in Fig. 1a for events i, j, and k satisfying $\tau_i < \tau_j < \tau_k$.

The problem facing the stratigrapher is to properly order and interpret this sequence of events. Our method of accomplishing this is to consider the relationship between all possible pairs of events; that is, for events i and j either $\tau_i < \tau_j$ or $\tau_j < \tau_i$. For this pairwise ordering of events the data are most conveniently represented by an $M \times M$ matrix where M is the total number of events being considered. This matrix is denoted by

$$A = \begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdot & \cdot & \cdot & a_{1M} \\ a_{21} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ a_{M1} & \cdot & \cdot & \cdot & \cdot & \cdot & a_{MM} \end{bmatrix} \quad (1)$$

with the matrix elements given by $a_{ij} = n_{ij}/N_{ij}$, where n_{ij} is the number of stratigraphic sections in which events i and j $(i \neq j)$ satisfy $\tau_i < \tau_j$ (hence n_{ji} is the number of stratigraphic sections in which $\tau_j < \tau_i$) and N_{ij} is the number of stratigraphic sections in which either $\tau_i < \tau_j$ or $\tau_j < \tau_i$ (that is, $N_{ij} = n_{ij} + n_{ji}$). The diagonal matrix elements have no stratigraphic interpretation and may be arbitrarily defined by $a_{ij} = ½$ for $i = j$. Clearly, the matrix elements satisfy the relation $a_{ij} = 1 - a_{ji}$ for all i and j. Hence it is necessary to consider only the matrix elements either above or below the main diagonal. Thus, the number of independent matrix elements is reduced from $M(M-1)$ to $M(M-1)/2$. When a large number of events are being considered, this can amount to a large savings in computer storage and computation time.

In order to interpret the data it is necessary to construct a model so that statistical methods may be applied. The model we consider is based on the hypothesis that the experiment satisfies three conditions: (i) the matrix elements are determined by independent repetitions of the experiment; (ii) the outcome of the experiment is one of two mutually exclusive and exhaustive possibilities, that is, either $\tau_i < \tau_j$ or $\tau_j < \tau_i$; and (iii) the probability p_{ij} of the outcome $\tau_i < \tau_j$ is the same on each repetition, so the probability of the outcome $\tau_j < \tau_i$ is $p_{ji} = 1 - p_{ij}$. Clearly, conditions (i) and (ii) are satisfied in all experimental situations. For condition (iii) to be satisfied requires spatial homogeneity. This condition is well approximated on a regional basis.

This model predicts that the outcomes of repeated trials of the experiment are described by the binomial probability density function

$$f(x) = \frac{N_{ij}!}{x!(N_{ij} - x)!} p_{ij}^{x} (1 - p_{ij})^{N_{ij} - x} \qquad x = 0, 1, 2, \ldots, N_{ij};\ i \neq j \quad (2)$$

where $f(x)$ is the probability that the relation $\tau_i < \tau_j$ for events i and j occurs exactly x times in N_{ij} repetitions of the experiment. The parameter of interest

$N\backslash n$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	.050															
2	.025	.224														
3	.017	.135	.369													
4	.013	.098	.249	.473												
5	.010	.076	.189	.342	.549											
6	.009	.063	.153	.271	.418	.607										
7	.007	.053	.128	.225	.341	.479	.652									
8	.006	.046	.111	.192	.289	.400	.530	.668								
9	.006	.041	.098	.169	.251	.345	.450	.571	.717							
10	.005	.037	.087	.150	.223	.302	.393	.493	.606	.741						
11	.005	033	.079	.135	.199	.271	.349	.436	.530	.635	.762					
12	.004	.031	.072	.123	.181	.245	.316	.390	.473	.562	.661	.779				
13	.004	.028	.066	.113	.165	.224	.287	.355	.426	.505	.590	.683	.794			
14	.004	.026	.061	.104	.153	.206	.263	.325	.391	.458	.534	.614	.703	.807		
15	.003	.024	.057	.096	.142	.191	.243	.300	.359	.422	.487	.560	.637	.721	.819	
16	.003	.023	.053	.090	.132	.179	.227	.278	.333	.391	.451	.514	.583	.656	.736	.829

Table 1. Values of the lower end point of the confidence interval such that $P(p^l_{ij} < p_{ij} < 1) = .95$, given n_{ij}, the number of sections in which the events occur in a particular order, and N_{ij}, the number of sections in which the events occur in any order.

$N\backslash n$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	.950															
2	.949	.776														
3	.848	.848	.631													
4	.739	.805	.739	.527												
5	.647	.734	.734	.647	.451											
6	.573	.666	.694	.666	.573	.393										
7	.513	.606	.646	.646	.606	.513	.348									
8	.464	.554	.600	.615	.600	.554	.464	.312								
9	.424	.509	.558	.580	.580	.558	.509	.424	.283							
10	.389	.470	.520	.548	.555	.548	.520	.470	.389	.259						
11	.360	.437	.485	.516	.530	.530	.516	.485	.437	.360	.238					
12	.335	.408	.455	.488	.504	.510	.504	.488	.455	.408	.335	.221				
13	.313	.382	.429	.461	.479	.489	.489	.479	.461	.429	.382	.313	.206			
14	.293	.360	.405	.437	.456	.469	.473	.469	.456	.437	.405	.360	.293	.193		
15	.276	.339	.384	.416	.435	.450	.457	.457	.450	.435	.416	.384	.339	.276	.181	
16	.261	.322	.363	.396	.417	.431	.441	.444	.441	.431	.417	.396	.363	.322	.261	.171

Table 2. Width of the confidence interval such that $P(p^l_{ij} < p_{ij} < p^u_{ij}) = .90$, given n_{ij}, the number of sections in which the events occur in a particular order, and N_{ij}, the number of sections in which the events occur in any order.

for interpreting stratigraphic data and for use in prediction is p_{ij}. The experimental situation is such that $x = n_{ij}$ and N_{ij} are known and p_{ij} must be inferred. Exact knowledge of p_{ij} is prohibited by the limitation of finite sampling. However, statistical techniques can be applied to estimate p_{ij} and obtain a confidence interval.

To obtain information about p_{ij} we introduce the maximum-likelihood estimator $\hat{p}_{ij} = x/N_{ij}$. The density function of $\hat{p}_{ij}$ is

$$f(\hat{p}_{ij};p_{ij}) = \frac{N_{ij}!}{(N_{ij}\hat{p}_{ij})!(N_{ij} - N_{ij}\hat{p}_{ij})!} p_{ij}^{N_{ij}\hat{p}_{ij}}(1 - p_{ij})^{(N_{ij} - N_{ij}\hat{p}_{ij})} \quad (3)$$

$$\hat{p}_{ij} = 0, 1/N_{ij}, 2/N_{ij}, \ldots, 1; i \neq j$$

The value of the estimator $\hat{p}_{ij}$ obtained from N_{ij} repetitions of the experiments is $\hat{p}'_{ij} = n_{ij}/N_{ij}$. These values of the estimator are recognized to be the matrix elements of Eq. 1. The usual methods for calculating the confidence intervals for the binomial distribution make use of the fact that the distribution function of Eq. 2 can be approximated by the normal distribution for large numbers of repetitions (for large N_{ij}) when the distribution possesses a minimum amount of skewness ($p_{ij} \approx \frac{1}{2}$). However, typically the data available to the stratigrapher do not satisfy this approximation. Thus, we have formulated a technique for calculating confidence intervals that are applicable even when the number of repetitions of the experiment is small and the distribution is highly skewed. To be specific, we have a method for calculating the value of the lower end point p^l_{ij} and the upper end point p^u_{ij} of the confidence interval such that $P(p^l_{ij} \leqslant p_{ij} \leqslant p^u_{ij}) = .90$. The conditions that the p^l_{ij} and p^u_{ij} must satisfy are

$$\sum_{\hat{p}_{ij} = \hat{p}'_{ij}}^{1} f(\hat{p}_{ij};p^l_{ij}) = 0.05 \qquad (4a)$$

$$\sum_{\hat{p}_{ij} = 0}^{\hat{p}'_{ij}} f(\hat{p}_{ij};p^u_{ij}) = 0.05 \qquad (4b)$$

To perform the necessary summations, we make use of the relation

$$\sum_{s=a}^{n} \frac{n!}{s!(n-s)!} p^s(1-p)^{n-s} = Q(F/\nu_1, \nu_2) \qquad (5)$$

where $\nu_1 \approx 2(n - a + 1)$, $\nu_2 = 2a$ and $p = a/[a + (n - a + 1)F]$. The $Q(F\nu_1, \nu_2)$ are related to the incomplete beta functions (*4*).

The results of the statistical analysis describing the ordering of events i and j are conveniently summarized in Fig. 1b. The actual probability of the ordering p_{ij} and its observed estimator p'_{ij} lie within the confidence interval between p^l_{ij} and p^u_{ij}. The width of this interval, $\delta_{ij} = p^u_{ij} - p^l_{ij}$, is represented by the distance between the points p^l_{ij} and p^u_{ij}.

The values of p^l_{ij} calculated from Eq. 4a are collected in Table 1 as a function of N_{ij} and n_{ij} for $N_{ij} = 1, 2, \ldots, 16$. Similarly, values of p^u_{ij} are calculated from Eq. 4b. However, it is more instructive to consider the width of the confidence interval δ_{ij}, which is presented in Table 2 as a function of N_{ij} and n_{ij}. For fixed values of the ratio $\hat{p}'_{ij}$, δ_{ij} is a monotonic decreasing function of N_{ij}, and for large N_{ij} it decreases as $1/N_{ij}^{1/2}$. This slow decrease in the width of the confidence interval with increasing N_{ij} must be weighed by the stratigrapher against the time and money to be invested in measuring, collecting, and studying samples from the stratigraphic sections.

The closer p_{ij} approaches 1 the more certain the relation $\tau_i < \tau_j$ between events i and j becomes. Hence for stratigraphic correlation it is desirable to have a parameter which expresses how closely p_{ij} approaches 1. Two necessary conditions for p_{ij} to approach 1 are: (i) $\hat{p}'_{ij}$ must approach 1 and (ii) $1 - p^l_{ij}$ must approach 0. Thus we can define a single reliability parameter ($R = \hat{p}'/(1 - p^l_{ij})$), which incorporates both of these conditions. The most reliable sequence of events is that set of events which maximizes R between each pair of events. For sequences with the same number of events or stratigraphic levels, the most reliable is that which has the largest geometric average value of R. The largest values of the geometric average of R correspond to sequences with a small number of levels. As the number of levels increases, this reliability parameter tends to decrease. Depending on the application, the stratigrapher must weigh the usefulness of a fine stratigraphic subdivision with a large number of levels against the increased reliability obtained by considering a smaller number of levels.

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Molecular Geometry in an Excited Electronic State and a Preresonance Raman Effect

Abstract. *Observations of Raman spectra of various molecules at different exciting laser wavelengths lead to an empirical rule. If a Raman line becomes stronger when the exciting frequency is brought closer to the frequency of an electronic band, this means that the equilibrium conformation of the molecule is distorted along the normal coordinate for the Raman line in the transition from the ground to the excited electronic state.*

In examining the Raman spectra of various molecules, we have observed that some Raman lines become more intense as the exciting frequency approaches the absorption frequency corresponding to an excited electronic state. Some of the results of such examinations are given in Table 1, where the amount, ξ, of the intensity enhancement caused by changing the exciting laser beam from 5145 Å to 2573 or 3511 Å is given for several Raman lines. The 5145-Å and 3511-Å laser beams were obtained with a Coherent Radiation model 52G argon ion laser, and the 2573-Å beam was obtained with the same laser by converting the fundamental power at 5145 Å in a nonlinear optical crystal, ammonium dihydrogen phosphate.