

Pitfalls of Normalization of Trace Elements in Sediments

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Owing to the composite nature of sediments, comparison of the trace-element (T) concentrations in sedimentary records is often made on the basis of their normalized values in search for variations with time or for correlations among them. Usually, the basic problems in using ratios of T's and a major element such as Al for these purposes are not realized or accounted for. Formerly, Pearson (1897) warned for 'spurious' correlations created by the ratio method, and recently Rollinson (1993) reviewed the problems inherent in this practice. However questionable from a statistical point of view, the ratio method seems attractive. Division of a T concentration by the Al content of a sediment adjusts this concentration for dilution by not only carbonate, but also by free quartz (Q) and eventually by organic matter (OM), only giving unbiased results if the T of interest is absent in these phases. As an alternative, the T concentration can be recalculated on a carbonate-, Q-, and OM-free basis. In essence, both methods relate the T concentration to the clay-mineral fraction of the sediment, but the ratio method advantageously circumvents the analytical problem of Q determination. As an example, consider the trace-element content of a sediment (T_{sed}) consisting of contributions of the sediment components:

$$T_{sed} = a.T_{cl} + b.T_{ca} + c.T_{OM} + d.T_{ox} + e.T_{hy} \quad (1),$$

where a-e are fractions of the total sediment, thus: $a+b+c+d+e=1$; $T_X = mgT/gX$, and X=clay (cl), carbonate (ca), organic matter, (Fe,Mn)-oxyhydroxide (ox), other hydrogenous phases (hy); note: Q is assumed to be devoid of T's.

Applying some massage to this mass balance, the following relation can be derived:

$$\frac{T_{sed}}{Al_{sed}} = (T/Al)_{ss} + b.(T_{ca}/Al_{sed}) + 0.01.T_{orgC}.(orgC/Al_{sed}) + T_{enr}/Al_{sed} \quad (2),$$

where Al_{sed} =Al content of sample (%), $(T/Al)_{ss}$ =trace-element to Al ratio in standard shale (ppm/%), $T_{orgC}=f.TOM$, $f=OM/orgC$ (%/%), T_{enr} =diagenetically enriched T (ppm).

When $T_{ca}=0$ and T_{orgC} has a constant value, a linear relationship is expected in a plot of T_{sed}/Al_{sed} vs $orgC/Al_{sed}$, with a slope equal to T_{orgC} . If so, the intercept with the ordinate is determined by the first and the last term on the r.h.s. of (2). This can be used to estimate the diagenetic enrichment in T of sediments under hitherto favourable conditions. Correlation between different normalized T_{sed} 's requires correlation between the totals of the terms on the r.h.s. of (2) for each of these T's. Beside the problem of spuriousness, this condition is only met when the T's have very similar geochemical behaviour with respect to incorporation in carbonates, OM and hydrogenous phases. More games can be played with these or other ratios, but the usefulness depends strongly on the coefficients of variation of the variables used (see Rollinson, 1993). Several scenarios of theoretical compositions will be considered to demonstrate the (in)applicability of the ratio method. Additionally, some examples of applications to trace-element compositions of natural sediments will be given.

Pearson K, *Proc. R. Soc. London*, **60**, 489-502, (1897).

Rollinson H, *Using geochemical data: Evaluation, Presentation, Interpretation. Longman Scientific & Technical, Harlow, UK*, 352 pp, (1993).