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Discussion on Sm–Nd isotopic age of Precambrian–Cambrian boundary in China

M. J. M. Turnbull & S. Moorbath comment: The paper of Yang *et al.* (1996) describes a novel dating approach, using the Sm–Nd method on phosphatic material, to determine the age of the Precambrian–Cambrian boundary. The dates reported are of a precision which, in light of the relatively small range of $^{147}Sm/^{144}Nd$ ratios (0.09–0.17), is surprising. We have recalculated the published data using the ISOPLOT program of Ludwig (1991) and this is shown below in Table 1. These results cast considerable doubt on the statistical analysis of Yang *et al.* (1996). While this technique may have utility with Precambrian successions it would appear to be of limited use for the high precision dating required for Phanerozoic stratigraphic correlation.

Table 1. Comparison of Sm–Nd regressions

Sample suite	Yang *et al.* (1996)	Recalculated using ISOPLOT[1]
Meishucun section, fossils only	562.8 ± 7.9 Ma 0.51076 ± 0.00001 (MSWD not reported)	563 ± 170 Ma 0.51078 ± 0.00014 MSWD = 4.1
Meishucun section, fossils and collophanite minerals	562.1 ± 5.7 0.51076 ± 0.00001 MSWD = 1.6	575 ± 82 Ma 0.51076 ± 0.00002 MSWD=2.4
All samples	570.3 ± 17.1 0.51077 ± 0.00001 MSWD = 0.45	574 ± 48 Ma 0.51076 ± 0.00004 MSWD = 1.9

[1] Published analytical errors in Yang *et al.* (1996) are assumed to be 2 sigma, although their age error is given at 1 sigma. Our recalculated age errors are given at the more generally quoted 2 sigma level.

Bor-ming Jahn comments: Yang *et al.* (1996) published an interesting article on the age of the Precambrian–Cambrian boundary in China. Based on their newly obtained Sm–Nd isochron ages of 562 ± 6 to 570 ± 17 Ma for phosphatic skeletal fossils and collophanitic minerals collected from three stratigraphically equivalent but widely separated regions, the authors believed that the period of 560–570 Ma is the best age estimate for the Precambrian–Cambrian boundary, instead of the more commonly accepted age of 530–544 Ma (Odin *et al*. 1983; Odin, Gale & Doré, 1985; Bowring *et al.* 1993; Grotzinger *et al.* 1995).

Calibration of ancient evolutionary events requires precise absolute age dating. As the authors also pointed out, the Precambrian–Cambrian boundary marks the most fundamental changes in the biological evolution of the Earth, hence it is highly significant to obtain a precise age determination for this boundary. I generally subscribe to the authors's intention and the logic behind the choice of biophosphates and sedimentary phosphates as potentially suitable materials for Sm–Nd isotopic dating. However, I have found that the article contains a significant flaw in the isochron age calculations and also a place of inconsistency in data reporting (Table 2). Using the York (1969) regression method, or the slightly modified Yorkfit program in the ISOPLOT of Ludwig (1990), a recalculation of the same data reported in table 1 of Yang *et al.* (1996) gave similar ages (560 to 575 Ma) but with much greater errors (2 sigma), ranging from ± 120 Ma, ± 100 Ma and ± 84 Ma for the 4-point, 6-point and 12-point isochrons, respectively. Such large errors are somewhat expected from the visual scatter of data points displayed in figures 3 and 4 of Yang *et al*. (1996), but are in complete disagreement with the published small uncertainties of 562.8 ± 7.9, 562.1 ± 5.7 and 570.3 ± 17.1 Ma. Consequently, the important implications given in this paper collapse and the recommendation by the authors of the Sm–Nd method as an effective approach for precise dating of the Precambrian–Cambrian boundary is not supported. In the following I give some more details about the real problems of this article.

(1) York's line-fitting program (York, 1969) is widely used in the geochronology community. It is also used in the procedures of line-fitting given by Faure (1977). I do not understand why the errors quoted by the authors, who used Faure's model III, are so different (10 to 15 times) from those obtained by ISOPLOT and 'our' York program. The authors did not mention the input errors used in their calculations, but I suppose 0.2 to 0.5 % for $^{147}Sm/^{144}Nd$ and 0.01 % for $^{143}Nd/^{144}Nd$ to be most reasonable when all possible sources of analytical errors including reproducibility are taken into consideration. I also made a calculation using very small input errors (0.1 % and 0.005 % for the two ratios, respectively), which I do not believe to be realistic in routine analyses, in order to produce smaller uncertainties in the calculated ages and initial ratios so that they may be more comparable to the published values. The results of my recalculations are shown in Table 2. It is clear that in no cases such small errors as published (± 8, ± 6 and ± 17 Ma) were obtained. Using the more realistic input errors, the 4-point isochron would yield an age of 560 ± 120 Ma, the 6-point isochron, 570 ± 100 Ma, and the 12-point isochron, 575 ± 86 Ma. Note that the 12-point isochron involves samples from widely separated regions. The large errors simply make the isochron ages unacceptable for the purpose of calibration for this important Precambrian–Cambrian boundary event. We have also to realise that the whole-rock Sm–Nd isochron method is not a very good technique for obtaining precise ages (≤ 1 or 2 %) for Phanerozoic events; this is simply due to the inherently limited range of Sm/Nd ratios in cogenetic rocks. If the Sm/Nd ratios have a very large range, the chance is that the samples may not be related, hence did not possess the same initial isotopic ratios.

(2) In table 1 of Yang *et al.* (1996), there exists a serious error for sample MZ3F. Note that this is the most radiogenic and pivotal point in the isochron calculation. If the concentration data of Sm and Nd are both correct, then the $^{147}Sm/^{144}Nd$ ratio should be 0.2006, instead of 0.1699 as published, and the consequence is severe as it would have a model age (T_{DM} assuming a linear evolution) of about 11 Ga. So I guess that the ratio of 0.1699 is correct, and one of the concentration data could have been misprinted. I then assumed one of them was correct, but the calculated second one was very different and it did not seem to be due only to a misprinting. Anyway, the error and inconsistency remain unexplained. Besides, in the isochron diagrams (figs. 3 and 4), this particular data point does not fall on the abscissa at 0.1699, but more like at 0.1799. We note that both the abscissa and ordonate are scaled with very inconvenient and unusual readings, such as 0.045–0.090–0.135–0.180, and 0.51092–0.51112–0.51132–0.51152, respectively. Sample MZ4F was also wrongly placed at ≈ 0.153 on the abscissa instead of the reported value of 0.1442. These points are of course trivial, but they point out the carelessness of the authors in the manuscript preparation. Perhaps the reviewer(s) and editor should also share the responsibility of the overall problem.

Table 2. Results of recalculation based on the data published by Yang *et al.* (1996)

Location and strata (number of data points)	Input errors (2 sigma, in %) $^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	Isochron age (Ma)	± 2σ	MSWD	$^{143}Nd/^{144}Nd$ init	εNd(T)	Remarks
Meishucun fossils (4)	0.5	0.01	560	121	0.59	0.510776 ± 104	–6.6 ± 2.0	
	0.2	0.01	560	121	0.59	0.510776 ± 104	–6.6 ± 2.0	
	0.1	0.005	560	93	2.36	0.510776 ± 80	–6.6 ± 1.6	
Article values	*	*	**563**	**8**	*	**0.510760 ± 10**	*	* not given
Meishucun fossils + collophanitic samples (6)	0.5	0.01	573	103	0.34	0.510763 ± 80	–6.8 ± 1.6	
	0.2	0.01	573	103	0.34	0.510763 ± 80	–6.8 ± 1.6	
	0.1	0.005	573	59	1.31	0.510763 ± 46	–6.8 ± 0.9	
	0.1	0.004	573	82	2.1	0.510763 ± 64		
Article values	*	*	**562**	**6**	**1.6**	**0.510760 ± 10**	*	* not given
Meishucun + Emei + Wushi (12)	0.5	0.01	575	86	0.25	0.510760 ± 69	–6.9 ± 1.4	
	0.2	0.01	575	86	0.25	0.510760 ± 69	–6.9 ± 1.4	
	0.1	0.005	575	43	0.99	0.510760 ± 35	–6.9 ± 0.7	
Article values	*	*	**570**	**17**	**0.45**	**0.510770 ± 10**	*	* not given

Note:
1. Isotopic ratios of $^{143}Nd/^{144}Nd$ were obtained using the Caltech normalization, assuming $^{146}Nd/^{142}Nd = 0.636151$.
2. Programs of calculation used: Rennes-York and ISOPLOT-Yorkfit (Ludwig, 1990). Both programs yielded identical results. The ages published in this article were calculated using the program of Faure, 1977, Model III.
3. Errors in age and initial $^{143}Nd/^{144}Nd$ ratio reported in this article are not known as 1 or 2 sigma.

(3) Twice in this article the authors claim that because the samples possess a small range of εNd(T) values (which are equivalent to initial $^{143}Nd/^{144}Nd$ ratios) from -6.1 to -7.1, which is close to the analytical errors; therefore, all samples could be considered to have essentially identical initial $^{143}Nd/^{144}Nd$ ratios. This statement is then used to support their idea about a homogeneous Nd isotopic composition in the Precambrian–Cambrian boundary ocean from which the phosphatic fossils were deposited. However, this is entirely a circular argument. It is clear that the εNd(T) values were calculated with correction of radiogenic growth of $^{143}Nd/^{144}Nd$ ratio for the period of their formation age, which, in turn, is obtained with an assumption that all samples had the same initial Nd isotopic ratios. Evidently, all εNd(T) values must be quite similar, if not necessarily identical, if the age used for correction of isotopic growth is the isochron age! Consequently, the existence of a homogeneous initial Nd isotopic composition for the local Precambrian–Cambrian boundary ocean cannot be supported by the circular argument, even it could have been true.

(4) A few $^{87}Sr/^{86}Sr$ ratios are also reported in table 1 of Yang *et al.* (1996). The authors stated that the correction for radiogenic growth is negligible as the Rb/Sr ratios of these samples are very low. Maybe, but the Rb/Sr ratios have only been so guessed, but not measured at all. I happen to have a few Rb–Sr data for phosphates and dolomitic rocks from precisely the same locality at Meishucun, which show that Rb/Sr ratios are not negligible ($^{87}Rb/^{86}Sr = 0.02$ to 0.2). These ratios could contribute to a significant change in $^{87}Sr/^{86}Sr$ ratios by a quantity of 0.00016 to 0.00163.

In conclusion, this article contains a serious error in data presentation and a severe underestimation of age uncertainties by more than 10 times. The data do not provide age(s) sufficiently precise (≤ 10 Ma) to be useful in the purpose of determining the Precambrian–Cambrian boundary. It is the responsibility of the authors to find out the problem of the underestimation. I hope that this will not be reproduced in any international or domestic jounals. The recommendation by the authors of the Sm–Nd method as an effective approach for precise dating of the Precambrian–Cambrian boundary is simply not supported.

Yang Jiedong & Sun Weiguo reply: Our attempt of dating the Precambrian–Cambrian boundary by the Sm–Nd method (Yang *et al.* 1996) has received two comments (this issue), one from Turnbull & Moorbath and the other from Jahn. Both are welcome and some involved problems are explained and discussed in this reply.

We have checked the final manuscript with the original and found a typing mistake and a drafting mistake, as pointed out by Jahn, in our published paper. In table 1 of Yang *et al.* (1996) the Nd concentration of sample MZ3F should be 157.3, instead of the mistyped 134.3; however, as the $^{147}Sm/^{144}Nd$ ratio (0.1699) of sample MZ3F is correct, the mistyped Nd concentration actually did not affect the isochron calculation. In the isochron diagrams (figs 3 and 4, Yang *et al.* 1966), the data points of MZ3F and MZ4F are slightly misplaced. This drafting mistake was caused when the diagrams were redrawn from the original. Nevertheless, it is we authors, rather than anybody else, who should take full responsibility for these mistakes of carelessness.

Our isochron calculation was made by using the program given in Appendix I of Faure's book (1977). This program is suitable for the Rb–Sr method and, with little changes also for the Sm–Nd method. The weighting model that we used is Model III. The errors of $^{143}Nd/^{144}Nd$ ratios determined on mass spectrometer and the age errors in table 1 of Yang *et al.* (1996) are both quoted at 1 sigma. The relative standard deviation in $^{147}Sm/^{144}Nd$ is estimated at ~ 0.1 % on the basis of determination for the standard material, the experimental chemical blank and replicate sample analyses (Yang *et al.* 1996).

Both Turnbull & Moorbath and Jahn suggested using the ISOPLOT program of Ludwig (1990, 1991) in calculation, but they did not explain what was wrong with using Faure's program (1977) in our calculation (Yang *et al.* 1996). Is the ISOPLOT the only program which has been universally accepted? We did not know the ISOPLOT program when our report was prepared, otherwise we would have compared the results obtained by using different programs.

In fact, both Faure's program (prepared by M. S. McSavency) and the ISOPLOT program are based on the regression method of York (1969). However, it is not surprising that different calculations by the same regression method, such as that based on the equation of York (1969), may obtain unconformable ages and

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errors from the same data due to the adoption of different weighting models. In the program introduced by Faure (1977), there are three weighting models for selection:

Model I: all points are weighted equally;

Model II: reciprocals of squares of analytical errors are used for weights;

Model III: reciprocals of squares of residuals are used for weights.

Comparison between the results obtained by using the identical program but different weighting models for the same data (table 1 of Yang *et al*. 1996), as shown below in Table 3, indicates that the error estimates in Model II are greater than those in Model III. Calculation with Model III is based on the results of Model I and Model II. 'The third model usually gives a smaller value of the error estimate. In general, the model rejecting the fewest points should be selected' (Faure, 1977).

Comparison between our results with those in Turnbull & Moorbath and Jahn's comments is not feasible at present, because neither of them has mentioned what kind of weighting models was used in their recalculation. Incidentally, whether the models as used in the Faure treatment differ from the models (of error structure) used within ISOPLOT is not yet known. Without adequate specification, it would be misleading if the results obtained by using different programs and weighting models are put together for comparison. Besides, the selection of some parameters, such as estimation of input errors, correlation coefficients between errors of $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ for each sample, tolerance level and so on, would also have influence on calculation results of various models.

An example is the results presented by Turnbull & Moorbath and by Jahn, who independently recalculated our data from table 1 of Yang *et al*. (1996) by the ISOPLOT program. The ages (560 to 575 Ma) obtained by them are similar to our results, but with much greater errors, ranging from ± 170 Ma to ± 48 Ma (Turnbull & Moorbath's Table 1) or from ± 120 Ma to ± 84 Ma (Jahn's comments). It should be noticed that they used the same ISOPLOT program and calculated the same data but obtained results with remarkable differences. It would be too difficult to tell from them which is more correct or less wrong, but Jahn is responsible for the problem of using inconsistent results in his Table 2 and his comments with unexplained reasons.

A final and critical problem that should have been commented on is whether the Model III treatment in Faure's program appears to be statistically flawed and thus can not be used in isochron calculation. If only the results of Model II treatment in Table 3 can be adopted, we would agree that the results of Model II treatment (Table 3) are not sufficiently precise for correlation and determination of the Precambrian–Cambrian boundary.We look forward to hearing the comments on the problem. The sufficient precision (≤ 10 Ma) presented by Jahn is surely useful in the purpose of calibration for this important Precambrian–Cambrian boundary event. However, it is not an absolute limit acceptable, simply because the different commentators (Turnbull & Moorbath, and Jahn) independently calculated the same data using the same ISOPLOT program but obtained results of remarked differences not only in age errors (much larger than 10 Ma) but also in age values. Except the obvious differences resulted only from purely statistical calculation itself as mentioned above, if considering again the influences on age errors from changes in sampling locations and the uncertainty of correlation between sampling horizons, distinction in kinds and degree of alteration and metaphorphism of determined samples, and even difference in isotopic dating methods, the validity of limit of precision (≤ 10 Ma) is often doubted.

Table 3. Comparison of the results obtained by using different weighting models in Faure's program

Sample	Model II	Model III (Yang *et al*. 1996)
Meishucun section	567.3 ± 39.6 Ma	562.8 ± 7.9 Ma
(four samples)	0.51077 ± 0.00003	0.51076 ± 0.00001
	MSWD = 0.97	MSWD = 1.0
Meishucun section	573.8 ± 28.9 Ma	562.1 ± 5.7 Ma
(six samples)	0.51076 ± 0.00002	0.51076 ± 0.00001
	MSWD = 0.6	MSWD = 1.6
All samples	570.1 ± 20.8 Ma	570.3 ± 17.1 Ma
	0.51077 ± 0.00002	0.51077 ± 0.00001
	MSWD = 0.5	MSWD = 0.5

Age errors are 1 sigma.

It is true that 'We have to realize that the whole-rock Sm–Nd isochron method is not a very good technique...' (Jahn), but this has little to do with our experiment, simply because our approach is not a whole-rock method (Yang *et al*. 1996).

Concerning the Rb/Sr ratios, the pure phosphatic solution that we analysed possesses much lower Rb/Sr ratios than those of the whole-rock phosphorites. Although the Rb/Sr ratios of the samples are not negligible as mentioned by Jahn ($^{87}Rb/^{86}Sr$ = 0.02 to 0.2), after being corrected by the Rb/Sr ratios, the $^{87}Sr/^{86}Sr$ ratios of samples would become much lower, more surely falling within or close to the range of isotopic variation of seawater in the interval of the Precambrian–Cambrian transition as reported by Burke *et al.* (1982).

Precise dating of the Precambrian–Cambrian boundary remains a goal to reach and therefore as many as possible suitable approaches should be tried. Our Sm–Nd method on phosphatic material, as 'a novel dating approach', 'may have utility with Precambrian successions' (Turnbull & Moorbath) and its potential significance in radiometric calibration and correlation of the Precambrian–Cambrian boundary is to be justified in practice. Instead of claiming for precision in our results, we always consider that the techniques and the results of this new isotopic dating approach can be improved and refined in future practice.

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M. J. M. TURNBULL & S. MOORBATH, Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, UK

BOR-MING JAHN, Géosciences Rennes (CNRS), Université de Rennes I, 35042 Rennes Cedex, France

YANG JIEDONG, Center of Modern Analysis, Nanjing University, Nanjing 210008, Jiangsu, People's Republic of China

SUN WEIGUO, Nanjing Institute of Geology and Palaeontology, Academia Sinica, Nanjing 210008, Jiangsu, People's Republic of China

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