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REPLY TO COMMENT
OMAN CHRONOSTRATIGRAPHY

(Reply to comment by Erwan Le Guerroué, Ruben Rieu and Andrea Cozzi on "Geochronologic Constraints on the Chronostratigraphic Framework of the Neoproterozoic Huqf Supergroup, Sultanate of Oman", American Journal of Science, v. 307, p. 1097–1145)

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Le Guerroué and others (this issue) highlight several questions regarding the Neoproterozoic stratigraphy of Oman in response to the publication of Bowring and others (2007). We take this opportunity to respond to each of their points, to reiterate some of the conclusions made in our original paper, stress the importance of understanding all sources of uncertainty in geochronological data, and re-emphasize the distinction between geochronological constraints and predictive models.

correlation of the mirbat group

Le Guerroué and others (this issue) take issue with: (1) an inconsistency of interpretation by Bowring and others (2007); and (2) lack of consideration of an earlier paper by Rieu and others (2007). Firstly, the apparent inconsistency in the Bowring and others (2007) paper is just that, apparent. It stems from an over-interpretation by Le Guerroué and others (this issue) of figure 2 in Bowring and others (2007) which attempts to summarize the *lithostratigraphy* of the Neoproterozoic to early Cambrian rocks in Oman and does not necessarily differentiate different glacial episodes. Secondly, the Ayn Formation and associated rocks were not the main subject of the study presented by Bowring and others (2007) and therefore were not discussed in detail. The paper by Rieu and others (2007) provides an excellent description of the Ayn Formation.

the nature, age and significance of the khufai-shuram boundary

The Shuram Formation contains a record of a globally correlated large-magnitude (16‰) carbonate $\delta^{13}C$ excursion that has been implicated as a signature of a massive reorganization of the carbon cycle during mid to late Ediacaran times (Condon and others, 2005; Fike and others, 2006). Constraining the absolute timing and duration of the anomaly is critical to understanding its cause. The termination of this global $\delta^{13}C$ excursion is generally accepted at ca. 551 Ma (Condon and others, 2005; Bowring and others, 2007); however the timing of its onset, and therefore its duration, is poorly constrained (Condon and others, 2005; Le Guerroué and others, 2006; Bowring and others, 2007). With regards to the age of the base of the Shuram Formation (and age of the base of the $\delta^{13}C$ excursion), Le Guerroué and others (this issue) take issue with Bowring and others (2007) on the following points: (1) the comparison of SHRIMP

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and ID-TIMS U-Pb detrital zircon ages; (2) age assignment for the Khufai-Shuram boundary based upon basin subsidence models versus calculated sediment accumulation rates; and (3) the stratigraphic nature of the Khufai-Shuram boundary.

(1) A major criticism made by Le Guerroué and others (this issue) is that the Bowring and others (2007) paper does not give the SHRIMP U-Pb detrital zircon dates of Le Guerroué and others (2006) equal weight compared to their ID-TIMS U-Pb detrital zircon dates. Bowring and others (2007) presented new, high-precision ID-TIMS dates on a small number (n = 9) of detrital zircons from the Shuram Formation, two of which yielded concordant ^{206}Pb/^{238}U dates of 625 ± 4 Ma and 621 ± 1 Ma (uncertainties are 2σ and include tracer calibration error). Le Guerroué and others (2006) published U-Pb zircon data from the SHRIMP (two samples, 56 zircons analyzed) including a number (ca. 13) of analyses with ^{206}Pb/^{238}U dates in the range of ca. 600 to ca. 630 Ma with uncertainties between 15 to 30 Myr (2σ including 0.43% error in U-Pb normalization) for each analysis. Le Guerroué and others (2006) averaged the youngest analyses resulting in their age estimation of 609 ± 9 Ma (2σ, not including U-Pb normalization error) for detrital zircons and inferentially the maximum age of the Khufai-Shuram boundary. We would like to stress that since these are detrital zircon dates, assuming 'coherent age populations' is not valid and the age (and uncertainty) of each zircon date must be considered in isolation. An effort was made in our original paper to discuss the differences between the two datasets, and we take this opportunity to further elaborate on our position and provide the reasoning behind it.

Figure 1 compares the youngest ID-TIMS detrital analyses from Bowring and others (2007) and the youngest 'population' from Le Guerroué and others (2006). All data points are plotted at the 95 percent confidence level and include both analytical uncertainties and systematic errors relating to tracer calibration (ID-TIMS) and U-Pb normalization (SHRIMP). There is no question that most single spot SHRIMP analyses overlap within uncertainty the youngest ID-TIMS analyses. Furthermore, the lower analytical precision of the SHRIMP U-Pb data makes it impossible to evaluate 'subtle' (that is, at a level similar in magnitude to the analytical precision) open system behavior such as Pb-loss. As discussed in detail in Bowring and others (2007), the technique of thermal annealing and acid leaching (CA-TIMS) has been very effective at removing the effects of Pb-loss; all zircon samples we analyzed from Oman before using this approach show evidence for Pb-loss. Subtle Pb-loss would result in a younger ^{206}Pb/^{238}U date that, because of the relatively high uncertainty of the ^{207}Pb/^{235}U dates (>3%) could still appear to be concordant (Bowring and others, 2006). This has been proposed to explain the subtle difference in U-Pb ID-TIMS (Condon and others, 2005) and U-Pb SHRIMP (Zhang and others, 2005) data from the Doushantuo Formation (Bowring and others, 2006). The higher precision of the ID-TIMS analyses enables assessment of concordance (and therefore accuracy of the U-Pb system) at the 0.2 percent level. Therefore it is possible that the detrital zircon ^{206}Pb/^{238}U dates of ca. 600 Ma measured by Le Guerroué and others (2006) are anomalously young due to 'subtle' Pb-loss, hence our preference for choosing the more robust ID-TIMS date as the maximum age constraint for the Shuram Formation.

(2) To move beyond the maximum age constraint provided by the ca. 621 Ma detrital zircon in the Shuram Formation (Bowring and others, 2007) and the ca. 551 Ma date from the top of the δ^{13}C excursion in the Doushantuo Formation (Condon and others, 2005) it is necessary to develop age models to predict the onset and duration of the Shuram δ^{13}C anomaly. Bowring and others (2007) determined sediment accumulation rates for parts of the Ara and Buah Formations using high-precision geochronology and C isotope stratigraphy from Oman, China, and Namibia. These rates were then extrapolated down-section to provide an age model for the Shuram and Buah Formations indicating a duration of ca. 7 to 15 Myr for accumula-

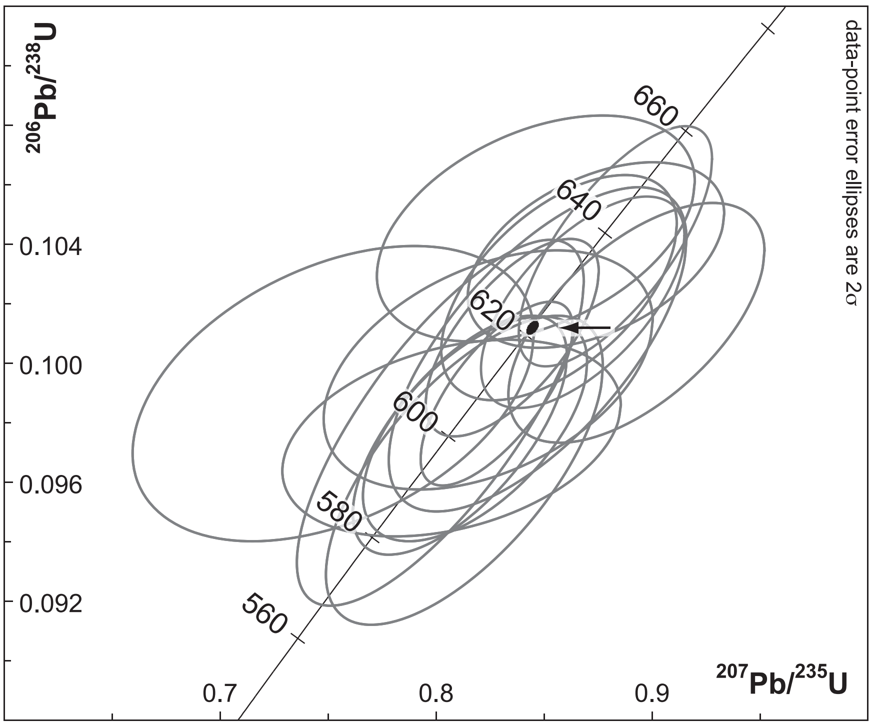

Fig. 1. Conventional U-Pb concordia plot of detrital zircon analyses from the Shuram and Khufai Formations. The youngest concordant ID-TIMS analysis from Bowring and others (2007) is plotted as a filled black ellipse and highlighted by an arrow whereas U-Pb SHRIMP analyses from Le Guerroué and others (2006) are shown as open ellipses. Uncertainty estimates for the ID-TIMS include a 0.1% error in tracer calibration, SHRIMP ellipses include a 0.43% error in U/Pb normalization (Le Guerroué and others, 2006). Analytical uncertainties and systematic errors have been combined in quadrature. Note that nearly all SHRIMP analyses overlap with the ID-TIMS analyses.

tion of the Shuram and Buah Formations and an estimated age of ca. 554 Ma to ca. 562 Ma for the base of the Shuram Formation. Assuming this was a thermally subsiding basin, sediment accumulation rates should be highest at the onset of subsidence and decrease with time, making our ages only maximum estimates. Le Guerroué and others (2006) developed a simple 'time transformation' model using two tie points at 635 Ma (top Fiq Formation) and 542 Ma (A3C stringer within Ara Formation) and assumed post-rift thermal subsidence driven by thermal contraction of the lithosphere. They obtained an older estimate in the range of 615 to 585 Ma for the Khufai-Shuram boundary (Le Guerroué and others, 2006, fig. 4).

Le Guerroué and others (2006, this issue) consider the broad coincidence of the SHRIMP U-Pb dates and model 'ages' for the Khufai-Shuram boundary at ca. 600 Ma to be 'significant'. We do not consider this to be significant given consideration of the geochronological uncertainties (see above; quantification of uncertainties for the thermal subsidence model is less straightforward), especially given the fact that the subsidence model of Le Guerroué and others (2006) is constrained by an assigned 635 Ma age for the base of the Nafun Group and 542 Ma age for the Ediacaran-Cambrian boundary.

Le Guerroué and others (this issue) correctly point out that differential compaction of carbonates and siliciclastics will affect the decompacted thickness of the Miqrat-1 Well section which Bowring and others (2007) used for their sediment accumulation rate calculations and extrapolations. However, these estimates did include chronostratigraphic uncertainties which are high (ca. 40%) due to the relatively close spacing of dated horizons near the top of the section and likely are a more significant source of uncertainty. However, the greatest source of uncertainty in both of these models is in the geodynamic setting assigned for the region during accumulation of the Nafun Group and assumption of stratigraphic coherence. Given the ambiguities over the tectonostratigraphic evolution of the Oman region during the late Neoproterozoic, there is no *a priori* reason to assume a post-rift passive margin subsidence model.

One additional point we would like to make is that the vertical scale for figure 11 (Bowring and others, 2007) is non-linear. We therefore suggest Le Guerroué and others (this issue) were incorrect to make any assumptions about the duration of any inferred discontinuities within the Huqf Supergroup.

(3) Le Guerroué and others (this issue) argue that we have misjudged the evaluation of time along the Khufai-Shuram boundary. The long list of references supplied by them to emphasize their point that an unconformity does not occur along the boundary includes one notable omission—the Ph.D. thesis of G. McCarron (2000). This thesis is mentioned in their introduction but not included in the citation that refers to the lack of evidence for an unconformity. This is unfortunate because this thesis is the most comprehensive work to date on the sedimentology and stratigraphy of the Khufai Formation, as well as its contact with the overlying Shuram Formation. McCarron (2000) interprets a major sequence boundary to coincide with the Khufai-Shuram contact based on recognition of dissolution features in the Khufai Formation, the abrupt first appearance of Shuram siliciclastics on top of Khufai carbonates, and the presence of pebble conglomerates along the contact. This is clearly illustrated in Figure 7.4 of McCarron (2000). Our own observations agree with McCarron's earlier work. In the Oman Mountains the contact is very abrupt, the surface is locally incised, and the facies are strongly juxtaposed across it. In addition, coarse-sand-filled channels are developed in the shale-rich beds within the basal strata of the Shuram Formation. We take these observations as evidence of a possible unconformity.

As described above, we disagree with Le Guerroué and others (2006, this issue) that the transition from Khufai to Shuram is gradational. However, to the extent that this may be the case, the observed "gradational" lithologic trends described by Le Guerroué and others (this issue) in the Huqf outcrops are not inconsistent with many other unconformities described in the Phanerozoic stratigraphic record where biostratigraphic data prove the existence of substantial unconformities despite the presence of subtle lithologic transitions. Indeed, the cornerstone of sequence stratigraphic analysis asserts that lithostratigraphic data alone often fail to locate the position of important unconformities (Christie-Blick and Driscoll, 1995). The Khufai-Shuram transition which Le Guerroué and others (2006, this issue) infer to be conformable shares many similarities to the well-documented middle Ordovician transition in upstate New York from shallow-water, peritidal carbonates of the Beekmantown Group to deepening-upward increasingly siliciclastic carbonates of the Trenton Group (Fischer, 1980; Ross and others, 1982). However, for the Middle Ordovician example, the base of the flooding interval is also coincident with a subaerial exposure surface that only locally produced karst. In most outcrops the unconformity surface is represented by a bedding plane, whereas biostratigraphic data constrain this unconformity to be as great as 10 to 20 million years, depending on the location (Fischer, 1980; Ross and others, 1982). It is a sobering reminder that many prominent unconformities with known substantial duration have only a subtle lithostratigraphic expression. The notion that the stratigraphic record is complete unless proven otherwise is a fallacy. As noted by Sadler (1981), "the convenient assumption that sedimentation has been steady could prove to be as inappropriate as applying the continuum convention to a dripping faucet". Consequently, the gamma ray data referred to by Le Guerroué and others (this issue)—which are only a proxy to lithology—could be highly misleading. The gamma ray data provide little additional insight beyond what direct lithologic observation provides, at least as applied here. In addition, we note that gamma ray data for the Khufai-Shuram contact have been previously presented by McCarron (2000), who argued for the presence of a sequence boundary at the contact (Figure 7.2; McCarron, 2000). Similarly, the record of C-isotope variations across the Khufai-Shuram contact also has been argued by Le Guerroué and others (2006, this issue) to provide evidence for the absence of an unconformity. However, we note that these curves may also not have any bearing on possible unconformities, which can juxtapose similar shapes of different isotopic events as demonstrated by Myrow and Grotzinger (2000).

Finally, since no new wells that penetrate the lower Nafun Group have been drilled in over 20 years, the absence of any new data should restrict such a major re-interpretation of the deep subsurface seismic records as Le Guerroué and others (this issue) have proposed. We prefer to accept the interpretations of earlier workers (Petroleum Development Oman unpublished data) who wrestled with the difficult task of tying the seismic records to well logs. In a major re-evaluation of this work in 2001, one of us (JPG) found no compelling reason to overturn these earlier conclusions regarding the chronostratigraphic significance of the Khufai-Shuram contact (Grotzinger and others, 2002). The interpretations of earlier PDO workers may not be correct, but they should certainly not be rejected in the absence of new data.

To conclude, we still find it hard to accept Le Guerroué and others' (2006, this issue) affirmation that ca. 600 Ma remains the best estimate for the Khufai-Shuram boundary. As outlined above and in Bowring and others (2007), the SHRIMP U-Pb dates of Le Guerroué and others (2006) should be considered with their individual uncertainties (ca. $\pm$ 15 to 30 Myr, 2σ) and the caveat that it is assumed they have not been perturbed by subtle Pb-loss. Given the importance of detrital zircons for constraining the maximum age of the Shuram Formation (and the onset of the Shuram $\delta^{13}C$ excursion) we still consider the youngest U-Pb ID-TIMS detrital zircon date of ca. 621 $\pm$ 1 Ma (Bowring and others, 2007) as the most robust maximum age constraint for the Shuram Formation at present. Downward extrapolation of sediment accumulation rates determined for parts of the Ara and Buah Formations *suggests* an age of $<$570 Ma for the base of the Shuram negative $\delta^{13}C$ excursion. Finally, we would like to reiterate our position that "until more direct temporal constraints become available, use of the carbon isotopic record in the Shuram as a global chemostratographic reference invites caution" (Bowing and others, 2007, page 1126).

References

Bowring, S. A., Schoene, B., Crowley, J. L., Ramezani, J., and Condon, D. J., 2006, High-precision U-Pb zircon geochronology and the stratigraphic record: progress and promise, *in* Olszewski, T. D., editor, Geochronology: Emerging Opportunities: The Paleontological Society Papers, v. 12, p. 25–46.

Bowring, S. A., Grotzinger, J. P., Condon, D. J., Ramezani, J., Newall, M., and Allen, P. A., 2007, Geochronologic constraints of the chronostratigraphic framework of the Neoproterozoic Huqf Supergroup, Sultanate of Oman: American Journal of Science, v. 307, p. 1097–1145, doi:10.2475/10.2007.01.

Christie-Blick, N., and Driscoll, N. W., 1995, Sequence Stratigraphy: Annual Review Of Earth and Planetary Sciences, v. 23, p. 451–478, doi:10.1146/annurev.ea.23.050195.002315.

Condon, D., Zhu, M. Y., Bowring, S., Wang, W., Yang, A. H., and Jin, Y. G., 2005, U-Pb ages from the Neoproterozoic Doushantuo Formation, China: Science, v. 308, p. 95–98, doi:10.1126/science.1107765.

Fike, D. A., Grotzinger, J. P., Pratt, L. M., and Summons, R. E., 2006, Oxidation of the Ediacaran Ocean: Nature, v. 444, p. 744–747, doi:10.1038/nature05345.

Fischer, D. W., 1980, Bedrock geology of the Central Mohawk Valley, New York: New York, Museum Map and Chart, Series 33, 1:48,000 map, 44 p.

Grotzinger, J., Al-Siyabi, A. H., Al-Hashimi, R. A., and Cozzi, A., 2002, New model for tectonic evolution of Neoproterozoic-Cambrian Huqf Supergroup basins, Oman, *in* 5th Middle East Geosciences Conference, Abstracts: Geoarabia, v. 7, p. 241.

Le Guerroué, E., Allen, P. A., Cozzi, A., Etienne, J. L., and Fanning, M., 2006, 50 Myr recovery from the largest negative $\delta^{13}C$ excursion in the Ediacaran ocean: Terra Nova, v. 18, p. 147–153, doi:10.1111/j.1365-3121.2006.00674.x.

McCarron, G., ms, 2000, The sedimentology and chemostratigraphy of the Nafun Group, Huqf Supergroup, Oman: Oxford, University of Oxford, Ph. D. thesis, 175 p.

Myrow, P. M., and Grotzinger, J. P., 2000, Chemostratigraphic proxy records: forward modeling the effects of unconformities, variable sediment accumulation rates, and sampling-interval bias, *in* Grotzinger, J., and James, N., editors, Carbonate Sedimentation and Diagenesis in the Evolving Precambrian World: SEPM Special Publication 67, p. 43–55.

Rieu, R., Allen, P. A., Cozzi, A., Kosler, J., and Bussy, F., 2007, A composite stratigraphy for the Neoproterozoic Huqf Supergroup of Oman; integrating new litho-, chemo- and chronostratigraphic data of the Mirbat area, southern Oman: London, Journal of the Geological Society, v. 164, p. 997–1009, doi:10.1144/0016-76492006-114.

Ross, R. J., Jr., Adler, F. J., Amsden, T. W., Bergström, D., Bergström, S. M., Carter, C., Churkin, M., Cressman, E. A., Derby, J. R., Dutro, J. T. J., Ethington, R. L., Finney, S. C., Fisher, D. W., Fisher, J. H., Harris, A. G., Hintze, L. F., Ketner, K. B., Kolata, D. R., Landing, E., Neuman, R. B., Sweet, W. C., Pojeta, J., Potter, A. W., Rader, E. K., Repetski, J. E., Shaver, R. H., Thompson, T. L., and Webers, G. F., 1982, The Ordovician System in the United States—Correlation chart and explanatory notes: International Union of Geological Sciences Publication, v. 12, 73 p.

Sadler, P. M., 1981, Sediment Accumulation Rates and the Completeness of Stratigraphic Sections: Journal of Geology, v. 89, p. 569–584.

Zhang, S. H., Jiang, G. Q., Zhang, J. M., Song, B., Kennedy, M. J., and Christie-Blick, N., 2005, U-Pb sensitive high-resolution ion microprobe ages from the Doushantuo Formation in south China: Constraints on late Neoproterozoic glaciations: Geology, v. 33, p. 473–476, doi:10.1130/G21418.1