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Reply to Discussion on 'A high-precision U–Pb age constraint on the Rhynie Chert Konservat-Lagerstätte: timescale and other implications'

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We welcome the opportunity to address the points raised by Mark *et al.* in their discussion of the CA–ID–TIMS U–Pb age constraint on the Rhynie Chert Konservat-Lagerstätte presented by Parry *et al.* (2011) and also to make some further observations of our own. We begin by briefly providing some context for the benefit of the wider readership. Two radio-isotopic age constraints on the Rhynie Chert Konservat-Lagerstätte and, by corollary, its parental hydrothermal (hot-spring) system have recently been published. The first of these is a weighted mean $^{40}Ar/^{39}Ar$ plateau age of 403.9 ± 2.1 Ma (2σ) derived from the analysis of two samples of vein-hosted hydrothermal K-feldspar and a single sample of hydrothermally altered andesite (Mark *et al.* 2011). In order to account for systematic uncertainties associated with the $^{40}Ar/^{39}Ar$ geochronometer, Mark *et al.* (2011) recalculated their individual sample ages with reference to the Fish Canyon Tuff sanidine (FCs) age of 28.201 Ma (Kuiper *et al.* 2008), thereby producing a "U–Pb comparable" mean age of 407.1 ± 2.2 Ma (2σ). An alternative "preferred age" for the Rhynie hot-spring activity (407.6 ± 2.2 Ma [2σ]) has now been produced from the 'raw' data using the optimization model of Renne *et al.* (2010, 2011) (this discussion). The $^{40}Ar/^{39}Ar$ system calibrations on which these various ages are based are summarized in Table 1. The second radio-isotopic age constraint in question is a weighted mean $^{206}Pb/^{238}U$ zircon age of 411.5 ± 1.3 Ma (2σ, including decay constant- and tracer calibration-related uncertainties; MSWD = 0.12, n = 4) yielded by the Milton of Noth Andesite, a moderately altered basaltic andesite lava flow (cum near-surface sill?) that lies along the northwestern margin of the Rhynie Outlier (Parry *et al.* 2011). U–Pb titanite data corroborate the zircon data, and *c.* 411.5 Ma is interpreted as the crystallization/eruption age of the Milton of Noth Andesite. Lavas and tuffs of andesitic composition occur elsewhere within the northern half of the Rhynie Outlier (Rice & Ashcroft 2004) and a holistic view of the available evidence would suggest that these volcanic rocks represent the surficial expression of the thermal drive for the Rhynie hot-spring system. Parry *et al.* (2011) therefore concluded that that the U–Pb zircon age yielded by the Milton of Noth Andesite dates the Rhynie hydrothermal activity *within error* [our italics].

The recurring theme of Mark *et al.*'s discussion is the uncertainty over the stratigraphic position of the Milton of Noth Andesite and their doubts concerning the proposed link between the volcanic rocks of the Rhynie Outlier and the hot-spring activity. It is true that the *exact* stratigraphic position of the Milton of Noth Andesite is uncertain (as stated by Parry *et al.* 2011). The poorly exposed Rhynie Outlier (basin) is internally complex, a consequence of its probable transtensional origins (Rice & Ashcroft 2004) and possible subsequent tectonic modification during the Acadian Event (see Mendum & Noble (2010) for a discussion of the evidence for Acadian tectonic activity in northern Scotland). There is little doubt, however, that andesitic lavas occur near to the base of the succession in the northern half of the outlier (Tillybrachty Sandstone Formation; Rice & Ashcroft 2004). From a stratigraphical perspective, this is as distant as the Milton of Noth Andesite could lie from the Rhynie cherts (i.e. *c.* 700 m below; Rice & Ashcroft 2004). Parry *et al.* (2011) conservatively estimated that the period of time corresponding to this stratigraphic interval equates to *c.* 1.4 Ma, whereas Mark *et al.* (2011) suggested a figure of *c.* 700 ka (the difference arising from contrasting assumed depositional rates). These estimates are either comparable to or, in the case of the latter, significantly less than the total uncertainty associated with the U–Pb age constraint on the Milton of Noth Andesite (1.3 Ma), which (in part) led Parry *et al.* (2011) to make their statement that the "...U–Pb age yielded by the Milton of Noth Andesite does in fact date the Rhynie cherts, and hence hot-spring activity at Rhynie, *within error*" [our italics]. Three further lines of evidence support this stance. Firstly, the entire volcano-sedimentary succession of the northern half of the Rhynie Outlier seemingly belongs to a single biostratigraphic interval (of early, but not earliest, Pragian to (?)earliest Emsian age), and a latest Pragian to (?)earliest Emsian age may be indicated by the presence of *Dictyotriletes subgranifer* amongst the recovered spore assemblages. Secondly, the Milton of Noth Andesite has a peperitic 'contact' with sediments resembling those of the Dryden Flags Formation (the host of the Rhynie cherts) and which pass laterally (effectively up-succession) over a few tens of metres – and with no proven break – into strata of undoubted Dryden Flags Formation parentage (Rice & Ashcroft 2004). Thirdly, there is neither physical nor geochronological evidence (Parry 2004, unpubl. data; Parry *et al.* 2011) for any other Devonian igneous activity of similar age to or younger than the Rhynie Outlier volcanism in the local area. On the basis of the collective evidence, which points to both a spatial and temporal association, we still consider it perfectly reasonable to infer a genetic link between the Rhynie Outlier volcanism and the hot-spring system. We see no need to appeal to a separate episode of "granitic" igneous activity, especially one that has no surface expression, to explain the hydrothermal activity.

In the course of their discussion, Mark *et al.* partially reinterpret the U–Pb dataset of Parry *et al.* (2011) in an attempt to 'reconcile' the U–Pb and $^{40}Ar/^{39}Ar$ age constraints on Rhynie. The suggestions of Mark *et al.* are, in our opinion, implausible – there is no compelling evidence of 'hydrothermally induced Pb-loss' affecting the zircons upon which our U–Pb age hinges. First and foremost, a lower concordia-intercept age of $409.9^{+7.4}_{-7.3}$ Ma is of no value whatsoever in terms of statistically distinguishing between an age of 407.6 ± 2.2 Ma and one of 411.5 ± 1.3 Ma. Furthermore, it is unclear why only those zircons apparently carrying a Proterozoic inherited component would be affected by the proposed hydrothermal Pb-loss. We reaffirm our original interpretation of the zircon data and suggest that the most likely explanation for the plotting position of our zircon fraction 1 lies in the fact that its six constituent grains were air-abraded only (cf. our other CA–TIMS zircon analyses). We would argue that the analysis of fraction 1 has been displaced from a mixing line (the lower concordia-intercept of which is *c.* 411.5 Ma) by the effects of Pb-loss whose origin is most probably 'recent' based on the plotting position of this analysis (to the right of the main data cluster) and the trajectory of the discordia defined by those zircons carrying a *c.* 1600 Ma inherited component. Pb-loss from *c.* 411.5 Ma or new hydrothermal growth at *c.* 407.6 Ma would be more likely to produce an essentially concordant analysis plotting between 411.5 Ma and 407.6 Ma. Whatever the true cause of the discordance of fraction 1, its effects were evidently not fully eliminated by the air abrasion treatment it received. This is in stark contrast to our CA–TIMS analyses, and therefore consistent with the general observation by the U–Pb community that the effects of Pb-loss are effectively and reproducibly eliminated by chemical abrasion, particularly when measured against the air abrasion technique. With regard to the Parry *et al.* (2011) titanite data, Mark *et al.* imply that there exist both magmatic and hydrothermal (or fully 'hydrothermally reset') titanite grains within the Milton of Noth Andesite. There is insufficient evidence to support this *ad hoc* assertion and it would be extremely unlikely that from amongst an optically similar population of titanite grain fragments one fraction (#4) comprising 15 fragments of the former was simultaneously picked along with a second fraction (#5) comprising 26 fragments of the latter. We also note that the relatively large uncertainties associated with the $^{207}Pb/^{235}U$ of the titanite analyses make it impossible to discriminate between Pb-loss and any hydrothermal effects. A *c.* 407.6–411.5 Ma discordia (running sub-parallel to concordia) created by 'hydrothermal resetting' or new titanite growth, integrated Pb-loss over time, or (most probably) 'zero-age' Pb-loss induced by acid washing of the air-abraded titanites prior to their dissolution are all possibilities with these data.

Central to this discussion is whether there is a geochronologically resolvable difference in age between the Milton of Noth Andesite and the Rhynie hot-spring activity (taking into consideration all sources of internal and external analytical uncertainty). Whilst we believe that we have successfully dated the Milton of Noth Andesite (a point not disputed by Mark *et al.*), the 'direct' age constraint on the hydrothermal activity proposed by Mark *et al.* (2011) derives from $^{40}Ar/^{39}Ar$ geochronology – a relative dating technique reliant, amongst other things, upon a sound knowledge of the age (strictly, the $^{40}Ar/^{40}K$ ratio) of the mineral standards employed as neutron fluence monitors and propagation of related uncertainty components. There is at present no community-wide consensus on the ages of the various mineral standards used. In the case of FCs, for example, its assumed age remains a matter of debate, with recent estimates ranging from 27.89 to 28.294 Ma (e.g. Kuiper *et al.* 2008; Channell *et al.* 2010; Renne *et al.* 2010, 2011; Rivera *et al.* 2011; Westerhold *et al.* 2012). Compounding this currently unaccounted for dispersion in the age of FCs is the widely known inter-laboratory bias issue affecting the $^{40}Ar/^{39}Ar$ community (e.g. Villa 2011). These matters are under active investigation, but pending their satisfactory resolution U–Pb data such as those presented by Parry *et al.* (2011) can be considered accurate and robust on the basis of: a sound knowledge of the ^{238}U and ^{235}U decay constants; the confirmation of closed system behaviour provided by the dual U–Pb decay system; effective Pb-loss elimination by means of chemical abrasion; accurate, precise and metrologically traceable calibration of the mixed-isotope solutions employed for spiking purposes and; the results of inter-laboratory comparison exercises that illustrate agreement at the 0.1 % level or better (e.g. Sláma *et al.* 2008). Whilst we acknowledge that the analytical work performed by Mark *et al.* (2011) is state-of-the-art, owing to the unresolved calibration issues surrounding the $^{40}Ar/^{39}Ar$ geochronometer, there remains the possibility of residual U–Pb—

$^{40}Ar/^{39}Ar$ bias. This hinders direct comparisons with the U–Pb data of Parry *et al.* (2011), irrespective of any geological uncertainties.

If and when the U–Pb and $^{40}Ar/^{39}Ar$ geochronometers can be successfully ‘synchronized’ then it will become appropriate to realistically assess and compare age constraints on differing geological materials such as those found within the Rhynie Outlier. Until such time, there is no value in simply fitting $^{40}Ar/^{39}Ar$ ages to particular time scale segments (with no uncertainty assigned to the stage or period boundary ages included) as a justification of their reliability. The geological time scale is under constant revision as new biostratigraphical, geochronological and astronomical tuning data become available. For example, the Silurian stage boundary ages in the new Geologic Time Scale (GTS) 2012 (Gradstein *et al.* 2012) have been upwardly revised by *c.* 1 % compared with those of the GTS 2004 (Gradstein *et al.* 2004). The GTS 2004 is (and was) not the ‘definitive’ time scale, and we draw attention to the fact that the ID–TIMS data underpinning the Lower Devonian section of interest were generated prior to the advent of chemical abrasion and the existence of the EARTHTIME tracer solutions (see also Kaufmann 2006). The new GTS 2012 – reliant, in the case of the Lower Devonian, on the same ID–TIMS data – represents the next of what will likely be many stages of an evolutionary process; it is the data that constrain the geological time scale not vice versa.

In conclusion, Parry *et al.* (2011) and Mark *et al.* (2011) present new geochronological data that not only have relevance to the age of the Rhynie Chert Konservat-Lagerstätte, but have implications for the Devonian time scale. Both of these studies, however, are dependent upon a number of assumptions or inferences, which are explicitly stated in the original papers. Nonetheless, for the reasons that we have highlighted, we consider the $^{206}Pb/^{238}U$ zircon age of 411.5 ± 1.3 Ma yielded by the Milton of Noth Andesite to be a robust temporal constraint on the Rhynie hot-spring system and the *polygonalis-emsiensis* Spore Assemblage Biozone. We are of the belief that efforts should be directed towards clarifying and eliminating the systematic uncertainties associated with the $^{40}Ar/^{39}Ar$ geochronometer, further refining the U–Pb geochronometer, and accurately and precisely constraining the Devonian stage boundary ages. Then, and only then, will we be in a position to potentially resolve the dichotomy of opinion created by the existing radio-isotopic age constraints on the Rhynie Chert.

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Table captions:

Table 1. Summary of $^{40}Ar/^{39}Ar$ age constraints on the Rhynie Chert Konservat-Lagerstätte provided by Mark *et al.* (2011).

Table 1. *Summary of $^{40}Ar/^{39}Ar$ age constraints on the Rhynie Chert Konservat-Lagerstätte provided by Mark et al. (2011)*

$^{40}Ar/^{39}Ar$ ages and relevant details*	$^{40}Ar/^{39}Ar$ system calibration†	
	Calibration standard‡	Associated total ^{40}K decay constant
403.9 ± 2.1 Ma		
Weighted mean plateau age based upon three samples	TCs (27.92 ± 0.08 Ma; Duffield & Dalrymple 1990) FCs (28.02 ± 0.56 Ma; Renne *et al.* 1998)	$5.543 \pm 0.020 \times 10^{-10}$ a^{-1} (Steiger & Jäger 1977) $5.543 \pm 0.020 \times 10^{-10}$ a^{-1} (Steiger & Jäger 1977)
407.1 ± 2.2 Ma		
Recalculated weighted mean plateau age	FCs (28.201 ± 0.046 Ma; Kuiper *et al.* 2008)	$5.464 \pm 0.214 \times 10^{-10}$ a^{-1} (Min *et al.* 2000)
407.6 ± 2.2 Ma		
Recalculated weighted mean plateau age	Optimization model of Renne *et al.* (2010, 2011) (Yields FCs = 28.294 ± 0.072 Ma)	Optimization model of Renne *et al.* (2010, 2011) (Yields $5.5305 \pm 0.0150 \times 10^{-10}$ a^{-1})

* Quoted uncertainties are at the 2σ level and are those given by Mark *et al.* (2011).

† Quoted uncertainties on standard ages and decay constant values are at the 2σ level.

‡ TCs, Taylor Creek Rhyolite sanidine; FCs, Fish Canyon Tuff sanidine.