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Status of the impact crater age database 1 2 3 F. Jourdan<sup>a\*</sup>, P.R. Renne<sup>b,c</sup>, W.U. Reimold<sup>d</sup> 4 5 6 7 <sup>a</sup>Western Australian Argon Isotope Facility, Department of Applied Geology, Curtin 8 university of Technology, GPO Box U1987, Perth, WA 6845; Australia. 9 <sup>b</sup>Berkeley Geochronology Center; 2455 Ridge Rd., Berkeley, CA94709, USA <sup>c</sup>Department of Earth and Planetary Science, University of California, Berkeley, CA94720, 10 11 USA <sup>d</sup>Museum f. Natural History (Mineralogy), Humbold University Berlin, Invalidenstrasse 43, 12 13 10115 Berlin, Germany 14 15 \*f.jourdan@curtin.edu.au 16 **Abstract** 17 18 19 The Earth impact crater database (http://www.unb.ca/passc/ImpactDatabase/) lists a total of 20 174 impact structures (early 2008). Most ages compiled in the database are based on dates 21 recommended in the most recent published papers about a given structure. Precise and 22 accurate age constraints are crucial for (1) correlating causes and effects on the bio- and 23 geosphere of catastrophic processes, (2) better constraining the impactor flux through 24 geological time and evaluation of potential impact periodicity, (3) calibrating the absolute 25 chronostratigraphic time scale, (4) calibrating the age of within-crater continental sedimentary deposits (e.g., for regional paleo-climatic analysis), and (5) correlating impact events and distal impact ejecta occurrences.

Of these 174 listed impact structures only a few have precisely constrained ages (mostly

Of these 174 listed impact structures only a few have precisely constrained ages (mostly using radio-isotopic techniques, e.g. U/Pb and <sup>40</sup>Ar/<sup>39</sup>Ar), with only 25 ages having a stated precision better than  $\pm$  2%, and a mere 16 ages with a precision better than  $\pm$  1%. Yet, even the accuracy of some of these ages can be challenged and probably improved based on more detailed interpretations and statistically more rigorous data analysis. geochronologists are often circumspect and advise caution in accepting calculated ages, these ages tend to propagate into the literature without further critical evaluation, are considered "robust", and become widely accepted ages. A review of the age data for the 25 short-listed structures suggests that 11 ages are accurate, 12 are at best ambiguous and should not be reported with any uncertainty, and 2 are not well characterized at all. We report detailed examples of misleading ages and/or age uncertainties (e.g., poor stratigraphic constraints, data over-interpretations, ambiguity due to inconsistent results), and highlight the robustness of the 11 well-defined ages. Based on observations and modeling, suggestions are made on how to obtain better ages by carrying out adequate sample preparation. We also indicate how to interpret ages for non-geochronologists. This brief review should be interpreted as a call for immediate, drastic qualitative and quantitative improvements of the impact crater age database.

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Keywords: impact, crater, absolute chronology, isotopic dating, <sup>40</sup>Ar/<sup>39</sup>Ar, U/Pb, age database

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### Introduction

One hundred and seventy four confirmed impact structures are currently recognized on Earth (Earth Impact Database, early 2008; (http://www.unb.ca/passc/ImpactDatabase/). Several tens of these impact structures are big enough to have been formed by events of magnitudes that might have triggered catastrophic climatic and tectonic disturbances. Such effects have been linked to severe and rapid mass extinction, with the most famous one being the Chicxulub impact associated with the K/T boundary (e.g., Alvarez et al., 1980; Hildebrand et al., 1991; Swisher et al., 1991), although the connection between the Chicxulub event and the K/T mass extinction has been debated (e.g. Keller, 2005; Arenillas et al., 2006, Schulte et al., 2006). Impact events have also been related to processes such as formation of large igneous provinces, at least during the early earth and moon bombardment (e.g., Elkins-Tanton and Hager, 2005; Ingle and Coffin, 2004), genesis of major ore deposits (e.g., Sudbury and Vredefort structures; Grieve, 2005; Reimold et al., 2005) and disruption of local civilization and environmental degradation (Chapman and Morrison, 1994). Time is a more crucial parameter when one tries to compare a given impact event with one of the effects mentioned above. Impact structures provide first-order chronological information from their stratigraphic constraints. Stratigraphic (relative) dating is a powerful tool to obtain the age of an extinction event, in particular due to the continuous improvement of the absolute age precision of the chronostratigraphic timescale (e.g., Gradstein et al., 2004). However, this method is far less satisfying for deciphering the age of an impact structure, mainly because most of the preserved structures are emplaced in continental and uppermost crustal environments. Thus, impact structures are difficult to correlate with stratigraphy (e.g., the Gardnos structure, Norway, has limited stratigraphic constraints between ca. 500 and 650 Ma - French et al., 1997). Clearly, this approach is not sufficient when one aims at pinpointing the exact timing of an impact event and far better precision is required.

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Much better precision can be obtained by isotopic dating (see review by Deutsch and Schärer; 1994). The different isotopic systems ("clocks") used for dating impact structures are K/Ar, Rb/Sr, fission track dating, cosmogenic exposure, <sup>40</sup>Ar/<sup>39</sup>Ar and U/Pb systematics. The increasing number of dates obtained by absolute dating have been widely used, for instance for tentative temporal correlation of impact (or perceived impact) with mass extinction (e.g. Swisher et al., 1991; Becker et al., 2004), to estimate the impactor flux through time (e.g. Deutsch and Schärer, 1994; Moon et al., 2001), to calibrate the absolute stratigraphic time scale (by dating tektite deposits in sediment layers; e.g. Deutsch and Schärer, 1994), to indirectly calibrate the age of within-crater continental sedimentary deposits (Partridge, 1999) to investigate possible links between specific impact sites and distal ejecta occurrences (e.g., Deutsch and Koeberl, 2006, on North American Tektites and the Chesapeake Bay impact event), and even to propose a periodicity in the impactor flux (e.g., Alvarez and Muller, 1984). In this study, we address the status of the impact crater age database (i.e., using the age data available in the published record), evaluate the relative precisions of these recommended ages, and question the validity of some ages claimed to be known with an excellent precision. As a result, we show that the database contains a substantial amount of poorly constrained ages and a very small percentage of robust (i.e. statistically valid and geologically meaningful: cf. discussion hereafter) ages.

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# How many craters have been dated so far?

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In this study, we use the impact database (<a href="http://www.unb.ca/passc/ImpactDatabase/">http://www.unb.ca/passc/ImpactDatabase/</a>) as a starting point to investigate the number of impact structures dated by radioisotopic methods.

In most cases, the dates reported in the database are the most recent ones available from the literature, and references are provided in the database.

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Figure 1 provides a statistical breakdown of the impact structure ages obtained so far. For this exercise, we assume that each age associated with an error value results from isotopic investigation, whereas ages that are associated with a sign such as "~, <, >" are considered as not constrained, or that the results are not satisfactory enough to be considered as "age". We note that this assumption is not exactly true for some craters, as for instance the age of the Bosumtwi crater is reported as 1.07 Ma without any error margin, whereas a weighted mean of fission track and  $^{40}$ Ar/ $^{39}$ Ar ages with standard error propagation gives an age of  $1.08 \pm 0.04$ Ma. In such a case, we consider the ages and our calculated associated errors as the best estimates of the age of the structure. As a result, about half (n=86) of the impact structures listed have not been successfully dated. The other half has dates of highly variable precision; 30 structures (10% of the total) have ages known with a precision lower than  $\pm$  10%; 19 structures (11% of the total) have precisions between  $\pm 10\%$  and  $\pm 5\%$ ; 14 structures (7% of the total) have precisions between  $\pm 5\%$  and  $\pm 2\%$ . Only 25 impact structures (14% of the total) have relatively well constrained ages with precisions better than  $\pm 2\%$ ; this includes 16 structures with precisions better than  $\pm 1\%$ . In most cases, a poor precision on an isotopic age is due to scatter of the data that is due, in turn, to some perturbation of geological origin (e.g., alteration or metamorphism; cf. discussion below). As a consequence, when the precision given with an age is relatively poor (i.e.,  $>\pm2\%$ ), the age calculated may not be accurate, even within uncertainties calculated from analytical data statistics. As we discuss later on, the error can be expanded by statistical treatment to account for small geological disturbance, but this technique should be used only with data sets that meet the minimum statistical requirement (discussed below in "statistical constrains). Sometimes an estimate with a low precision is the best that one can obtain on a rock whatever the sample preparation quality, but care should be

taken to not over-interpret the results. If high-precision and accurate chronology are required,

then only 25 impact structures of the total 174 impact structures listed, having ages

126 constrained with a precision better than  $\pm 2\%$ , meet this condition.

Although we are going to focus our discussion on these 25 dates, it should be kept in mind that the precision associated with an age depends on the age itself. Indeed, a precision of  $\pm 10\%$  at 200 Ma gives a very imprecise date ranging from 180 to 220 Ma, clearly unsuitable for rigorous correlation with events such as mass extinctions. A precision of  $\pm 10\%$  on 50 ka gives a much more restricted age range between 45 and 55 ka. For instance, the Lonar crater is reported with an age of  $52 \pm 8$  ka [ $\pm 15\%$ ] determined by fission track dating (Sengupta et al., 1997), and Barringer (Meteor) Crater has a thermoluminescence age of  $49 \pm 3$  ka [ $\pm 6.1\%$ ] (Sutton, 1985). In addition, small historical craters are known with a precision of just a few thousand years (e.g., the Henbury craters, the age of which was determined by fission track dating to  $4.2 \pm 1.9$  ka [ $\pm 45\%$ ]; in Haines et al., 2005).

Ironically, good precision (and accuracy) is required for this young timescale, too. For example, the sediment fill of the Tswaing crater, South Africa, has been studied in detail to investigate the recent paleoclimatic record (Partridge, 1999; Partridge et al., 1993; Kristen et al., 2007). High precision on the age of this crater is crucial to calibrate the climate evolution curve recorded in the sedimentary sequence. Currently the best age estimate of this crater is only  $220 \pm 104$  ka [ $\pm 45\%$ ] (Storzer et al., 1999), and a more recent  $^{40}$ Ar/ $^{39}$ Ar investigation has failed to obtain a reliable age (Jourdan et al., 2007a).

In fact, 41 impact structures are known with a precision better than  $\pm 1$  Ma. This mainly includes 28 young craters with ages younger than 5 Ma. The other 13 ages are randomly distributed between 5 and 215 Ma (<a href="http://www.unb.ca/passc/ImpactDatabase/">http://www.unb.ca/passc/ImpactDatabase/</a>) and mostly comprise  $^{40}$ Ar/ $^{39}$ Ar and U/Pb ages included in the  $\pm$  2% ages subset (Table 1).

As a first observation, obtaining a date or improving an existing isotopic age would be highly desirable for ~86% of the craters because the precision of these ages is worse than ± 2%. However, we must keep in mind that a huge proportion of the known impact structures do not have accessible melt rock occurrences (impact melt rock/breccia, fresh melt fragments in suevite deposits, impact melt injections into the crater floor, pseudotachylite [= friction melt] and other "pseudotachylitic breccia" formed in the crater basement), which therefore prevents high-quality isotopic dating (for a proposed impactite classification, refer to Stöffler and Grieve, 2007; regarding pseudotachylite/pseudotachylitic breccia problematics, refer to Reimold and Gibson, 2005).

## **Dating tools**

The various methods that can be used to date impact structures are discussed in detail by Deutsch and Schärer (1994), and are only summarized here. The easiest way to characterize the age of an impact structure or deposit is to estimate the ages of the underlying (impacted) and overlying (post-impact) stratigraphic units through biostratigraphy (e.g. see discussion in Schmieder and Buchner, 2008). If appropriate conditions are met, the precision obtained can be rather good but only to the extent that immediately pre-impact sediments are preserved, that sedimentation and biotic activity resumed rapidly after impact, and that the timescale itself is well-calibrated. Six ages out of our sub-selection of 25 structures with age precision better than  $\pm$  2% are based on stratigraphic constraints. The validity of such good precision is addressed in Table 1, where the listed ages are compared with new constraints based on updated geological timetable (Gradstein et al., 2004) information. We note that there are some problems with this timescale at the 1% level (Mundil et al., 2008), as with all timescales.

One of the most treacherous pitfalls in the interpretation of geochronological data is the conflation of precision (the degree of reproducibility) and accuracy (the degree of veracity). An age can be reported with an excellent precision but may be meaningless, i.e., highly reproducible but wrong (e.g. offset by several hundred million years). The common sources of inaccuracy are variable, depending on which technique is used, as discussed below. Dating methods such as fission track (e.g., Storzer et al., 1999), thermoluminescence (Sutton, 1985), cosmogenic exposure (Phillips et al., 1991), and paleomagnetic measurements (Pesonen et al., 2004) have been used, but both the precision and accuracy obtained by these methods tend to be somewhat poor (e.g., review by Deutsch and Schärer, 1994). The K/Ar and Rb/Sr isotopic techniques have been extensively used to obtain impact ages; however, their flaw resides in the fact that there are no internal reliability criteria to assess the validity of the results. In our subset of 25 allegedly "precisely" dated structures, only one has a reported age based on one of these techniques (the Shoemaker [also known as Teague Ring] crater dated by whole rock Rb/Sr at  $1630 \pm 5$  Ma; Bunting et al., 1980). One way to address the accuracy of a date obtained by one of these techniques would be to analyze many replicate samples from a given crater, but even in this case systematic bias could exist (e.g., mineral alteration and metamorphic overprint). For this reason, the most reliable isotopic chronometers to date impact products are the <sup>40</sup>Ar/<sup>39</sup>Ar and U/Pb methods because of the possibility to test the validity of an age by careful consideration of the age spectrum and the Concordia plot, respectively. The datable products formed during or shortly after the impact include distal ejecta such as tektites and microkrystites, and products of melting formed insitu (impact glass, impact melt rock, pseudotachylitic breccia, and isotopically reset or neoformed minerals (see review by Deutsch and Schärer, 1994). In the case of large impact events, volumetrically important, coherent impact melt sheets (e.g., Sudbury Igneous Complex, Manicouagan impact melt sheet) or offshoots (Offset Dykes at Sudbury; Vredefort

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Granophyre), and even massive occurrences of pseudotachylitic breccias (e.g., Vredefort pseudotachylitic breccia, so-called Sudbury Breccia) can form and allow zircon and/or baddeleyite crystallization. The latter phases can be dated using the U/Pb method and give high precision ages (e.g., Kamo et al., 1996). However, these cases are rare, and only four impact structures have been successfully dated by U/Pb: Vredefort (2023  $\pm$  4 Ma, Kamo et al., 1996; Gibbson et al., 1997); Manicouagan (214.56  $\pm$  0.05 Ma; Ramezani et al., 2005); Sudbury (1850  $\pm$  1 Ma (Krogh et al., 1984; Ostermann et al., 1994), recently confirmed by two more recent  $^{207}$ Pb/ $^{206}$ Pb age determinations with ages at 1849.5  $\pm$  0.2 Ma and 1849.1  $\pm$  0.2 Ma (Davies, 2008) ) and Morokweng (145.2  $\pm$  0.8 Ma; Hart et al., 1997; Koeberl et al., 1997).

Most of the impact products referred to above contain a substantial amount of  $K_2O$  as this is a major constituent of many target rocks. Therefore, the  $^{40}Ar/^{39}Ar$  technique appears to be the most suitable technique for investigating impact crater ages where U-rich minerals are absent. In our 25-structure subset, 20 structures had their ages investigated by  $^{40}Ar/^{39}Ar$ , and with 15 of these, having ages that are based exclusively  $^{40}Ar/^{39}Ar$  results.

# Geological, geochronological and statistical constraints on age data

Whilst the <sup>40</sup>Ar/<sup>39</sup>Ar and U/Pb chronometers are the most appropriate and reliable techniques to precisely determine the age of an impact event, these techniques are far from devoid of problems. For instance, both techniques are sensitive to overprinted history (redistribution of argon components, argon loss, U and Pb mobility – due to alteration and/or metamorphism) and the presence of inherited components (e.g., inherited <sup>40</sup>Ar\*, inherited zircon grains, from target rocks). For these reasons, a systematic study of several replicate samples is desirable in order to test the reproducibility of age data obtained. Similarly, the use

of individual grains instead of multi-grain fractions prevents mixing of different components, such as grains with various <sup>40</sup>Ar/<sup>36</sup>Ar trapped reservoirs, spoiled grains, or inherited grains (e.g. discussion by Mundil et al., 2001). High spatial-resolution <sup>40</sup>Ar/<sup>39</sup>Ar UV-laser spots and U/Pb SHRIMP dating are commonly used to measure the age of a grain at the micrometer scale. In some cases, this approach gives tremendous advantage, in particular when it comes to avoid altered portions or inherited clasts (Kelley, 2002). However, the lack of precision inherent to these techniques, combined with a diminution of information in the case of <sup>40</sup>Ar/<sup>39</sup>Ar (no step-heating age spectrum can be determined) imply that these techniques should be used only when all investigations using conventional approaches (<sup>40</sup>Ar/<sup>39</sup>Ar step-heating and U/Pb TIMS) have failed.

A rapid overview of the potential problems specific to each technique when dating impact products is given hereafter.

 $^{40}Ar/^{39}Ar$  dating

The most common problems encountered during dating of impact products include (1) alteration/superimposed metamorphic-tectonic history yielding <sup>40</sup>Ar\* loss or recrystallized minerals (e.g., Verati and Féraud, 2003; Fuentes et al., 2005); (2) presence of relic <sup>40</sup>Ar\* not degassed during the impact event (inherited <sup>40</sup>Ar\*; e.g., Kelley, 2002; Jourdan et al., 2007a), (3) <sup>39</sup>Ar and <sup>37</sup>Ar recoil redistribution and loss occurring during the irradiation process (e.g., Onstott et al., 1995; Jourdan et al., 2007b). Most of these problems can be readily identified when plotting the results in an apparent age spectrum diagram. Excess/inherited <sup>40</sup>Ar\* often yields a characteristic saddle-shaped age spectrum, whereas alteration and recoil tend to give (although not systematically) tilde shaped (i.e. "~") irregular spectra.

Issue (1) can be partially overcome by careful sample selection followed by substantial chemical leaching, especially with hydrofluoric acid (or eventually nitric acid) (e.g., McDougall & Harrison, 1999; Baksi, 2007a & 2007b). This approach is efficient only when grains show superficial alteration or alteration occurring within cracks, but is not effective with severely altered grains (e.g. Jourdan et al., 2008b). The state of alteration can be estimated using  $^{37}Ar_{Ca}/^{39}Ar_{K}$  and  $^{38}Ar_{Cl}/^{39}Ar_{K}$  ratios relative to composition data as obtained for example by electron microprobe, as described for instance by Verati & Féraud (2003). When inherited <sup>40</sup>Ar\* is absent from the system, then alteration can be detected using <sup>36</sup>Ar/<sup>39</sup>Ar<sub>K</sub> as an alteration index (Baksi, 2007a, 2007b) or when data are plotted using the isochron representation as alteration often leads to <sup>40</sup>Ar/<sup>36</sup>Ar ratio lower than the atmospheric value. Issue (2) has been extensively discussed by Jourdan et al. (2007a and 2008a). If the inherited <sup>40</sup>Ar\* and the <sup>40</sup>Ar\* produced after the impact are homogeneously mixed, then the inverse isochron technique can yield a valid age by taking into account the inherited <sup>40</sup>Ar\* component into the age calculation (e.g., Roddick, 1978; Heizler and Harrison, 1988; Sharp and Renne, 2005). The use of single grains is crucial to avoid mixing grains with different inherited <sup>40</sup>Ar\* reservoirs. However, the isochron should comprise a significant number of steps, and the spread between the radiogenic and trapped reservoir components on the mixing curve should be significant and should not represent a cluster of points. The spread along the

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$$S = 1 - \frac{\sqrt{\left(\frac{39}{40} A r_{i}\right)^{2} + \left(\frac{36}{40} A r_{i}\right)^{2}} - \sqrt{\left(\frac{39}{40} A r_{\max} - \frac{39}{40} A r_{\min}\right)^{2} + \left(\frac{36}{40} A r_{\max} - \frac{36}{40} A r_{\min}\right)^{2}}}{\sqrt{\left(\frac{39}{40} A r_{i}\right)^{2} + \left(\frac{36}{40} A r_{i}\right)^{2}}}$$
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isochron can be verified using the following simple formula:

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where:

S is the spreading factor ranging from 0% (no spread) to 100% (anchor point located at the two intercepts); i stands for intercept values; max and min are the highest and lowest ratios obtained on a sample during step heating experiments. This formula is valid only if the temperature steps are more or less regularly distributed between the minimum and maximum values and becomes meaningless if, for some reasons, a sample population has one imprecise step containing tiny amounts of gas near the 40Ar/36Ar intercept, and all the other step data are clustered near the <sup>40</sup>Ar/<sup>39</sup>Ar axis. Accordingly, points that deviate by more than 3σ from the <sup>39</sup>Ar/<sup>40</sup>Ar and <sup>36</sup>Ar/<sup>40</sup>Ar weighted means can be excluded from S-value calculation if they do not contain significant amounts of gas. Calculation of the S-value is particularly suitable when the data are reported with a scale focused on the data range (the latter being useful to see the scatter of the data) and prevent assessing the full spread along the isochron. For example, sample 58075-10 from the Tswaing impact glass (Jourdan et al., 2007a) yielded a S-value of 29% clearly showing that the "isochron" obtained, (despite the satisfying statistical test results; MSWD = 1.4; P = 0.08) cannot be considered as a true isochron, and thus, the date should not be regarded as valid. This is further evidenced by the discrepancy between the calculated isochron date of  $9.1 \pm 1.3$  Ma compared to the true age of the crater of  $\sim 0.2$  Ma (compare Fig. 2a). In contrast, the isochron (Fig. 2b) from the Strangways impact structure (from Spray et al., 1999) shows an S-value of ~95%, demonstrating a relatively complete spread between the trapped and radiogenic reservoirs. Although the S cut-off value between an isochron and a pseudo-isochron is difficult to estimate, we feel that data giving a S-value below ~40% should be viewed with caution; in these cases other evidence to possibly confirm the age under discussion would be desirable. If the use of the isochron is not required (i.e., <sup>40</sup>Ar/<sup>36</sup>Ar with atmospheric value) then the gas used in the calculation should be distributed over at least three consecutive *significant* (not one large and two tiny) steps and represent more than 50% of the total <sup>39</sup>Ar gas released (e.g., McDougall & Harrison, 1999).

Issue (3) can be problematic especially in the case of the isochron calculation as the redistribution of <sup>39</sup>Ar and <sup>37</sup>Ar can yield erroneous <sup>40</sup>Ar/<sup>36</sup>Ar ratios and, thus, bias the age calculation. This latter problem is mainly observed with cryptocrystalline rocks, when mineral size is less than ~50 μm and if the K-bearing mineral is highly inequant (e.g., Paine et al., 2006; Jourdan et al., 2007b). Obviously, all the problems mentioned previously are not mutually exclusive and rather tend to occur together for a given sample. Again, appropriate sample preparation can strongly help to minimize these problems.

#### U/Pb dating

The two main problems in the case of impact zircon dating is (1) that the zircon grains can have undergone substantial post-impact Pb loss and (2) that zircons available were not formed during the impact but rather inherited from the target rock. Issue (1) has been recently almost entirely eliminated by the chemical abrasion (CA)-TIMS leaching technique (Mattison, 2005). This approach consists in annealing the defects created by radiation damage and subsequent leaching of the grains with HF to remove zircon domains (or their alteration products) that have lost lead. This technique is now routinely used by many laboratories and gives robust and unprecedented precise U/Pb (TIMS) results (e.g., Mundil et al. 2004, Shoene & Bowring, 2007). As mentioned previously, issue (2) can be addressed simply by analysing single grains to avoid mixing grains of different provenance and age (e.g., Mundil et al., 2001). Great care needs to be taken with pre-analysis mineral characterization (optical microscopy, cathodo-luminescence, SEM analysis) to provide a petrographic basis for result interpretation. It may

be considered trivial, but is of utmost importance to always remember that, as in all dating exercises, thorough understanding of geological-stratigraphic contexts must be gained *prior to* sampling for impact chronology. An additional category of U/Pb zircon dating of impacts was exemplified by Krogh et al. (1993), who analyzed shocked zircons from Cretaceous-Tertiary boundary deposits and defined an imprecise concordia intercept age of  $65.5 \pm 3.0$  Ma, coincident with the K/T boundary although at low confidence. It is unclear what mechanism explains the data- whether shock-induced Pb-loss or growth of new zircon-but further work aimed at clarifying the mechanism would probably be useful.

Recent high-precision ages have been obtained on Sudbury zircons by the <sup>207</sup>Pb/<sup>206</sup>Pb technique (Davies, 2008), in excellent agreement with previous U/Pb measurements (Krogh et al., 1984; Ostermann et al., 1994). Further test on the <sup>207</sup>Pb/<sup>206</sup>Pb technique will allow establishing if this method can be use confidently to date impact structures. However, we note that contrary to the CA-TIMS U/Pb method, the <sup>207</sup>Pb/<sup>206</sup>Pb technique does not provide any internal check such as a Concordia plot.

#### Statistical constraints

It may be hard to assess objectively the validity of an isotopic age based solely on age plots (i.e.,  $^{40}$ Ar/ $^{39}$ Ar age spectrum and isochron, U/Pb Concordia diagram), especially as this can be strongly influenced by the scale used to plot the data. This task may therefore be difficult for the non-geochronologist interested in the relevance of a given age. In this case, an objective statistical test is necessary to evaluate properly the validity of a date and the error assigned to it. The mean squared weight deviates (MSWD) is generally used as the main statistical parameter to estimate the goodness of fit of a data range (York, 1969). The MSWD calculation is based on a reduced  $\gamma^2$  calculation (1 degree of freedom for an age spectrum and

2 degrees of freedom for bivariate (e.g., isochron and Concordia) plots; e.g., York, 1969; Baksi, 1994). The ideal MSWD of a given dataset is 1, which means that the scatter of data is exactly consistent with measurement errors. A value <1 indicates that correlated errors are present or that errors on individual data have been overestimated, or that excessive (and likely unwarranted) data-culling has occurred. A value >1 indicates some scatter due to either the underestimated uncertainty individual measurements or geological or analytical perturbations. To decide which phenomenon is mainly responsible for the scatter, the MSWD value should be used in conjunction with the number of measurements in a  $\chi^2$  table to assess the meaning of the MSWD value (e.g. Baksi, 2007a & 2007b). The obtained value is then expressed in terms of probability (P) and assesses whether the data are concordant at the 95% confidence level provided that P >0.05 (Mahon, 1996; Baksi, 2007a & 2007b). In other words, the P value verifies that the scatter can be explained by the uncertainties of the measurements alone. In many ways, P is more useful than the MSWD value alone because it is independent of the number of data. For example, a MSWD of 3 for a set of 10 samples yields a probability of 0.01, whereas a MSWD of 3 for 20 samples yields a much lower P value of 0.00001. Even worse, a MSWD of 3 for 100 data points gives a P of  $10^{-21}$  (Mahon, 1996). When the scatter is large with P values between 0.15 and 0.05, and there is a possibility that individual data errors have been underestimated, the classical age error calculation may be expanded by student's t times the square root of the MSWD (e.g., Jourdan et al., 2007a and references therein), which is equivalent to augmenting the average measurement error so as to make it consistent with the scatter, and may provide a more realistic error propagation. This approach must be used with caution, however, as it can mask the effects of real scatter and provide a false sense of security about invalid ages. When P is <0.05, then the geological perturbations are too important and an age cannot be obtained confidently both in terms of precision and accuracy. Nevertheless, the result can be used as a minimum or maximum value provided that the cause

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of the geological perturbation can be identified (e.g., minimum age given by a sample affected by alteration).

Most of the time, the P value is not provided and only the MSWD is reported leaving the non-geochronologist unable to confidently assess the validity of an age. This is acceptable when the MSWD is very close to 1, but more problematic when it is substantially higher (e.g. >1.5). This can lead to the false impression that the age of an impact structure is well constrained, although it may not be the case (cf. discussion after). It should also be noted that MSWD values << 1, often naively believed to indicate high-precision, are symptomatic of problems as discussed above and can produce probabilities near 1.

We strongly advise that the P value is reported along with the MSWD with any given age, so that readers can estimate by themselves the geological significance of the data.

### Systematic constraints

<sup>40</sup>Ar/<sup>39</sup>Ar and U/Pb ages are dependent on standard and spike quality (e.g., homogeneity) and calibration. Tests of homogeneity and calibration are available for a handful of standards (e.g., Renne et al., 1998; Dazé et al., 2001; Spell and McDougall, 2003; Nomade et al., 2005; Jourdan et al., 2006; Jourdan and Renne, 2007). Many standards are unfortunately still internal laboratory standards, for which quality and age are not fully assessed.

A bias in the age calibration of a standard would imply that an age that appears statistically valid and precise might be off the mark by up to a few percent. This problem can be easily corrected upon a recalibration of the age using the correct age of the standard (Renne et al., 1998). More problematic is the use of heterogeneous standards that might bias the age obtained for an impact event with no possibility of further correction. For these reasons, the use of standards that are not recognized internationally should be avoided. Hereinafter, we use

the more recent calibrations of the international standards to recalculate ages of some samples.

Recent studies based on a comparison between <sup>40</sup>Ar/<sup>39</sup>Ar and U/Pb ages suggest that the <sup>40</sup>K decay constant is slightly inaccurate, thereby systematically biasing the  $^{40}$ Ar/ $^{39}$ Ar age by  $\sim$  -0.6 % for Proterozoic ages to ~ -1.2 % for Cenozoic ages; e.g., Min et al., 2001; Kwon et al., 2002; Mundil et al., 2006; Kuiper et al., 2008). Therefore, future studies will most certainly need to recalculate ages produced by the 40Ar/39Ar technique using a new set of decay constants. This step will be essential to compare, for instance, the age of a stratigraphic limit obtained by U/Pb chronology with the age of an impact structure obtained by <sup>40</sup>Ar/<sup>39</sup>Ar dating. For example, the age of the Chicxulub impact glasses (65.55  $\pm$  0.05 Ma; Table 1 and discussion hereafter) recalculated with the decay constants and standard calibration proposed by Mundil et al. (2006) yields an age of  $66.21 \pm 0.05$  Ma. We note that reconciliation of the results of Jourdan and Renne (2007) for the <sup>40</sup>Ar\*/<sup>40</sup>K  $((1.6407 \pm 0.0047) \times 10^{-3})$  of the FCs standard with the astronomically-calibrated age (28.201)  $\pm$  0.046 Ma) of this standard requires a change in the total decay constant of  $^{40}$ K and/or the electron capture/β<sup>-</sup> branching ratio. As no consensus has been reached yet on these values, we will use in the following discussion the decay constant of Steiger and Jäger (1977), and do not consider the bias induced by the possible 40K decay constant offset. 40Ar/39Ar ages can be readily recalculated to accepted standard ages and decay constants provided that sufficient

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### **Investigation of selected cases**

data are published to facilitate the recalculation.

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Out of the 174 listed impact structures only a few have ages constrained precisely enough, with 25 ages having a precision better than  $\pm$  2%, including 16 ages with a precision better

than  $\pm$  1% (Table 4). Yet, even amongst this very limited dataset, the accuracy of some of these ages has been recently challenged/improved based on more reliable and statistically representative results. For instance, Reimold et al. (2005) demonstrated that the apparent age of the Siljan crater (Sweden; diameter  $\approx$  65-75 km) is 377  $\pm$  2 Ma instead of the long-accepted age of 358  $\pm$  5 Ma (Bottomley et al., 1978). The last example is not an isolated case as ages previously reported (and accepted) have been significantly revised for Haughton (Sherlock et al., 2005), Jänisjärvi (Jourdan et al., 2008a) and Roter Kamm (Hetch et al., 2008).

In the following discussion, we comment on carefully selected case examples of impact structure age data. We show that some ages that were previously claimed to be well constrained (i.e., with a published uncertainty  $< \pm 2\%$ ) should be substantially revised, well beyond the uncertainty reported with the initial ages. The complete characteristics and proposed age review of the 25 structure suite are given in Table 1.

*Gardnos – poor stratigraphic constraints.* 

The Gardnos impact structure (French et al., 1997) is a 5-km-diameter impact structure located in Norway. The structure age has been reported to be  $500 \pm 10$  Ma [ $\pm 2\%$ ]. Stratigraphic constraints bracket the age of the structure to somewhere between 500 and 650 Ma (French et al., 1997). Despite  $^{40}$ Ar/ $^{39}$ Ar dating attempts, no reliable age data could be obtained due to strong alteration of the samples as *clearly* stated by Grier et al. (1999). Based on these observations, the age of  $500 \pm 10$  Ma has no physical basis whatsoever, and it is not clear to us where this age came from. The Gardnos impact age should be cited as 500-650 Ma until successful (if possible!) radioisotope dating will have been achieved.

Gosses Bluff – age spectrum over-interpretation.

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The Gosses Bluff impact structure (Milton et al., 1996) in Australia has a diameter of ~22 km. It has a  $^{40}$ Ar/ $^{39}$ Ar age reported as  $142.5 \pm 0.8$  Ma (1 $\sigma$ ; Milton & Sutter, 1987). These authors also refer to earlier fission track dating on zircon that yielded a  $130 \pm 6$  Ma date (Milton et al., 1972) and give a 133  $\pm$  3 Ma K-Ar date. We express the  $^{40}$ Ar/ $^{39}$ Ar age at  $2\sigma$ (i.e. 95 % confidence level) as  $142.5 \pm 1.6$  Ma [ $\pm 1.1$ %] for comparison with the error limits of other listed impact structures. This age is based on a single <sup>40</sup>Ar/<sup>39</sup>Ar analysis of a sample described as a "clast of pumiceous suevite". Petrographic detail includes the cryptic statement that "although the bulk of the suevite must be sanidine, clean sanidine was never found...". The presence of potentially K-bearing zeolite (such as clinoptilolite) is also mentioned. The age spectrum shows a progressive age increase until it reaches an age at 142.5 Ma over the last ~30% of the <sup>39</sup>Ar degassing spectrum (almost entirely distributed over one major step). The age spectrum shows Ar loss characteristics and does not form a statistically valid plateau. This age should be considered a minimum age as a significant proportion of <sup>40</sup>Ar\* loss might also have affected the high-temperature steps. In addition, the Ar\* loss problem precludes the data from being plotted on an isochron diagram to identify potentially present inherited <sup>40</sup>Ar\*. Aside from the unreliability of this age, only one step-heating experiment has been run on this sample. Isotopic analysis of impact products can show a certain number of "unexplained" outliers which can lead to spurious "ages" if they are not identified (see some examples in Jourdan et al., 2008a). In light of the complexity of this step heating result and the obviously less than pristine state of the material analyzed, we recommend that several additional samples from Gosses Bluff be run to check for sample consistency. Until then the only available 40Ar/39Ar constraint should be listed at ~143 Ma, or perhaps >143 Ma if we can confidently accept that inherited Ar is absent from this sample.

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The Shoemaker (formerly Teague Ring) structure (Pirajno et al., 2003) is located in Australia. This impact structure has a diameter of ~ 30 km (e.g., Pirajno and Glikson, 1998). U/Pb SHRIMP dating of detrital zircon embedded in a sedimentary layer in the target rocks vielded a maximum deposition age of  $2027 \pm 23$  Ma (Nelson, 1997) and thus provides a maximum age for the impact. The age of the impact has been investigated more directly using the Rb/Sr chronometer applied to variably altered samples of quartz-syenite from the central uplift (Bunting et al., 1980) and is listed in the database as  $1630 \pm 5$  Ma [ $\pm 0.3\%$ ]. These authors proposed that the results reflected either a prime magmatic event (i.e., Teague was interpreted as a volcanic crater at this time) or a regional metamorphic event (Solomon and Groves, 1994). The Rb/Sr chronometer is particularly sensitive to alteration (particularly of biotite, which often controls isochrones due to its high Rb/Sr), which can produce statistically valid but geologically misleading isochrons. Dates obtained on four similar (seemingly more altered) samples yielded dates as low as ~1260 Ma (Bunting et al., 1980). The older age at ~1630 Ma may provide a minimum (i.e., least altered) age for the dated material, a granite from the central uplift that, according to Haines (2005), pre-dates the impact event. It is, thus, very unlikely that this date represents the impact age. It certainly does not deserve an uncertainty of  $\pm$  5 Ma. As reviewed by Haines (2005), there is even discussion that the impact may have occurred as late as "during the Late Neoproterozoic" (op. cit.). In light of the unreliable analysis and the lack of information on what has been dated, the age for the Shoemaker impact event can only be vaguely listed as Proterozoic.

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*Manson – Ambiguous dates due to multi-phase age discrepancies.* 

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Izett et al. (1993) obtained an age of  $73.8 \pm 0.3$  Ma [ $\pm 0.4\%$ ] using  $^{40}$ Ar/ $^{39}$ Ar spot fusion on a sanidine crystal from the matrix of a melt breccia of the Manson crater (USA, d =35 km; Koeberl & Anderson, 1996). This age is substantially older that the previous  $^{40}$ Ar/ $^{39}$ Ar age results inferred from partially degassed microcline and suevite matrix giving a mean age of  $65.4 \pm 0.3$  Ma [ $\pm 0.5\%$ ] (Kunk et al., 1989; Kunk et al., 1993), which was interpreted to indicate a Cretaceous/Tertiary age. Although Izett et al. (1993) briefly discussed possible explanations to discard the 65 Ma age, it is not clear to us whether the apparently younger samples underwent alteration or rather that the older age obtained on sanidine has not been reset and possibly forms a false isochron. The spread of the sanidine isochron is quite small with a S-value of ~17% (cf. discussion above). The S-value becomes 7% if two steps with very little gas are excluded from this calculation (these steps were excluded from the age calculation by Izett et al., 1993). In our opinion, the possible implication for the K/T boundary mass extinction event and multiple impacts at this time warrants further geochronological investigation of the Manson impact structure.

Araguainha – ambiguous <sup>40</sup>Ar/<sup>39</sup>Ar age spectra.

The Araguainha impact structure (e.g., Lana et al., 2007 and references therein) has a diameter of 40 km and is located in Mato Grosso State of Brazil. The age of this impact structure is particularly important as it seemingly occurred close to the Permo-Triassic boundary suggesting a possible causal relationship to this mass extinction event. This impact structure has a  $^{40}$ Ar/ $^{39}$ Ar age reported at 244.4 ± 3.5 Ma [± 1.3%] based on the weighted mean of 2 "plateau" ages obtained on 2 multi-grain fractions derived from melt rocks, with grain sizes of 0.3-0.5 mm and 0.5-1.0 mm (Hammerschmidt & Von Engelhardt, 1995). Biotite grains have also tentatively been dated but failed to display reset ages.

Age recalculation shows that the coarser fraction (compare Fig. 3a) yielded a mini-plateau age at 246  $\pm$  4 Ma [ $\pm$  1.7%] over 62% of the total <sup>39</sup>Ar released, with a MSWD of 1.09 and P of 0.35. The smaller fraction failed to yield a plateau and only displayed a flat portion over 30% of the spectrum, which cannot be considered as providing a valid age. Although the mini-plateau age is statistically valid, one can see that the age spectrum defines a strong tildeshaped pattern indicating alteration and/or <sup>39</sup>Ar and <sup>37</sup>Ar recoil. As discussed above, such cases are known to give sometimes statistically valid mini-plateau ages, although they can be offset from the "real" age by anything between a few % to several tens of % (e.g. Jourdan et al., 2003; Nomade et al., 2005). It is not clear which of these phenomena is responsible for the tilde-shaped pattern of this Araguainha sample. Recent SHRIMP U/Pb experiments on zircon grains yielded a lower intercept that suggests a maximum age of  $253 \pm 4$  Ma (Lana et al., 2007b) but this work is still at preliminary stage and would need to be confirmed by further measurements (E. Thover, pers. com.). Interestingly, this new age is now indistinguishable from the age of the Permo-Triassic boundary. Although the impact age appears likely to be close to the age determined by Hammerschmidt & Von Engelhardt (1995) and Lana et al. (2007b), several high-resolution single-grain <sup>40</sup>Ar/<sup>39</sup>Ar and U/Pb experiments on various melt rock samples and zircon grains, respectively, would be highly desirable in order to firmly establish the age of the Araguainha impact.

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*Popigai – the complex case* 

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The Popigai structure (Russia) is at  $\sim$ 100 km in diameter (e.g., Masaitis et al., 2005), one of the five largest impact structure known on Earth. The age of this crater, reported at  $35.7 \pm 0.2$  Ma [ $\pm$  0.6%] (Bottomley et al., 1997), is also relevant to the debate of the relationship between impacts and mass extinctions, particularly in view of its temporal proximity to the

Eocene/Oligocene boundary (33.9  $\pm$  0.1 Ma; Gradstein et al., 2004) and with respect to the importance of the near-coincidence of this with another of the largest recorded terrestrial impact events close to this time: Chesapeake Bay at ca. 35.8 Ma (Poag et al., 2004). The age of the Popigai structure is based on a 40Ar/39Ar date obtained on melt rock clasts and calculated using a well calibrated standard (Hb3gr hornblende; Jourdan et al., 2006; Jourdan and Renne, 2007). This age is statistically robust with a MSWD of 1.04 and P of 0.40, although we calculated the error on this age to be  $\pm 0.33$  Ma [ $\pm 0.9\%$ ] using Isoplot (Ludwig, 2003). During their experiments, Bottomley et al. (1997) obtained 4 additional plateau (>70% <sup>39</sup>Ar release; P>0.1) and 3 slightly more perturbed mini-plateau (50-70% <sup>39</sup>Ar release; P>0.1) ages ranging from  $35.09 \pm 0.69$  to  $37.50 \pm 0.91$  Ma that are not accounted for in the age estimate for this impact event. Bottomley et al. (1997) justified their choice by proposing that the older dates included an inherited <sup>40</sup>Ar\* component. However, it can be also argued that the age selected is in fact an alteration plateau age or that, like the other ages, it suffers inherited <sup>40</sup>Ar\* and is, thus, a maximum age. Compare with Figure 4 for a summary of the available age data. In the absence of other evidence (e.g., several samples giving the same age, inherited <sup>40</sup>Ar/<sup>36</sup>Ar ratio) it is difficult to choose a single specific date as being the "true age" of the crater. As a test, we choose to calculate the weighted mean of all but one (displaying an ambiguous tilda-shaped age spectrum and a much younger age, e.g. compare with the Araguainha case) plateau and mini-plateau dates calculated from the data of Bottomley et al. (1997). We expanded the error calculation with t student's times the square root of the MSWD. This yields a mean age of  $36.45 \pm 0.50$  Ma [ $\pm 1.4\%$ ] but a rather large MSWD of 3.2 and P of 0.007 indicating significant geological scatter (Fig. 4). The weighted mean of the four plateau ages only is  $36.42 \pm 0.81$  Ma (MSWD = 4.2; P = 0.005). This case demonstrates that interpreting 40 Ar/39 Ar ages is not a straightforward task and underscores the need for analyzing several samples. At this stage, we conclude that the age of the Popigai

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impact structure is still ambiguous, and we tentatively propose an age of  $36.42 \pm 0.81$  Ma [ $\pm$  2.2%] as currently the best age estimate for this impact structure.

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*Bedout – the hoax.* 

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The alleged "Bedout impact structure" (Becker et al., 2004) is not listed amongst the 174 recognized structures of the Earth Impact Database, nor can we include it in our Table 1. However, the age data presented by those authors provide a case example for a statistically invalid age (Renne et al., 2004; Baksi et al., 2007a and 2007b), and merits discussion. The lack of evidence for impact has led many researchers to question the Bedout allegation a priori (e.g., Wignall et al., 2004; Renne et al., 2004; Müller et al., 2005). Here we focus solely on the <sup>40</sup>Ar/<sup>39</sup>Ar age data obtained for the Bedout "impact", as Becker et al. (2004) suggested that the data indicate a  $^{40}$ Ar/ $^{39}$ Ar age at 250.1  $\pm$  4.5 Ma [ $\pm$  1.8%], in temporal coincidence with the Permian-Triassic mass extinction. The <sup>40</sup>Ar/<sup>39</sup>Ar age spectrum obtained on plagioclase (Fig. 3b) displays a pronounced tildeshaped pattern, which in the case of plagioclase crystals, is often (e.g., Verati and Féraud, 2003) interpreted as reflecting plagioclase sericitization. Seritized plagioclase vields <sup>40</sup>Ar/<sup>39</sup>Ar ages corresponding to mixing between the age of the crystal and the hydrothermal event responsible of the sericite formation. Therefore, in most cases sericitized plagioclase will give an age younger than the true age (Jourdan et al., 2003, Verati & Féraud, 2004; Fuentes et al., 2005). Recalculation of the age based on the data published by Becker et al. (2004) failed to yield any plateau age. Using the same steps as proposed in their plateau age calculation and expanding the error by t student's times the square root of the MSWD yields an age of 253  $\pm$ 12 Ma [ $\pm 4.7\%$ ] with a MSWD of 25 and P of 24.6x10<sup>-45</sup> (see also Baksi et al., 2007a). Both the statistical test and age spectrum indicate that the date obtained (even when errors are fully propagated) can by no means be considered valid.

Vredefort, Chixculub, Ries, Jänisjärvi and 7 others – the robust ages updated

The chronological data available for eleven other structures (Table 1) have been assessed and appear to provide robust ages with regard to the strict criteria defined above.

The Vredefort impact structure in South Africa (Gibson and Reimold, 2001, 2008) has a diameter of ~250-300 km. Its age has been determined on zircon using both SHRIMP and TIMS U/Pb techniques. Some grains show evidence of Pb-loss and/or inheritance. However, most of the results cluster on the Concordia and give indistinguishable dates of  $2017 \pm 5$  Ma [ $\pm 0.2\%$ ] (SHRIMP; Gibson et al., 1997) and  $2023 \pm 4$  Ma [ $\pm 0.2\%$ ] (TIMS; Kamo et al., 1996). The SHRIMP results tend to show more Pb-loss perturbation than the TIMS data and, therefore, the TIMS age has been adopted as the age of the Vredefort impact at  $2023 \pm 4$  Ma. Although this age is robust, it might be interesting to reinvestigate the age of this impact structure using the most recent development in the U/Pb dating technique (e.g., CA-TIMS) if one wants to further improve the precision on the existing age.

The Chicxulub impact structure (e.g., papers in MAPS, 2004) is particularly "notorious", as it is generally linked to the K/T boundary mass extinction, although this is still being debated (e.g., Keller, 2005; Arenillas et al., 2006). The age reported at  $64.98 \pm 0.05$  Ma [ $\pm 0.007\%$ ] is based on three statistically robust plateau ages obtained on impact melt rocks, and is corroborated by numerous step-heating and total fusion ages of geochemically-correlated tektites from various locations (Swisher et al, 1992). Although the data are robust, the Chicxulub case is a nice example of systematic error due to inaccurate calibration of the standard used in the measurement (FCs at 27.84 Ma). More recent calibrations (e.g., Renne et

al., 1998; Jourdan & Renne, 2007 with FCs at 28.03 Ma) give older ages at  $65.51 \pm 0.05$  Ma. 618 619 Independent calibration of FCs based on astronomical tuning yields an age of 65.81  $\pm 0.14$  Ma 620 for Chicxulub melt rocks (Kuiper et al., 2008) This recalibration preserves indistinguishability from the age of the Cretaceous/Tertiary boundary (65.99 ±0.12 Ma; Kuiper et al., 2008) 621 622 because both dates are based on the same standard. 623 The Ries crater is a well-preserved 24-km-diameter impact structure in Germany. The age 624 listed for this crater is  $15.1 \pm 0.1$  Ma [ $\pm 0.7\%$ ] (Staudacher et al., 1982). This impact structure is associated with a large continental tektite (moldavite) strewn field. Three recent <sup>40</sup>Ar/<sup>39</sup>Ar 625 626 investigations of suevite and tektites yield statistically robust and indistinguishable plateau 627 and isochron mean ages of  $14.52 \pm 0.14$  Ma (9 plateau ages; Schwartz & Lippolt, 2002; based 628 on standard HD-B1 at 24.21  $\pm$  0.32 Ma), 14.45  $\pm$  0.08 Ma (7 data for step-heated individual 629 grains plotted in a global isochron; Laurenzi et al., 2003 recalculated with the FCT-3 biotite 630 standard calibration of Dazé et al., 2003 at 28.16 Ma), and one statistically significant 631 isochron age at  $14.8 \pm 0.4$  Ma (Buchner et al., 2003; recalculated using an age of  $28.34 \pm 0.28$ 632 Ma for TCs (Renne et al., 2008)). Deriving an age for the Ries impact event based on three 633 different laboratories is interesting, as possible systematic variations associated with each 634 laboratory determination may be cancelled out. We calculated the weighted mean of the three 635 determinations and propose an age at  $14.48 \pm 0.14$  Ma [ $\pm 0.46\%$ ] (MSWD = 0.43; P = 0.65) 636 for the Ries impact structure. As a final example, the age of the Jänisjärvi structure located in Karelia, Russia has been 637 recently reinvestigated by  $^{40}$ Ar/ $^{39}$ Ar step heating and determined to  $683 \pm 4$  Ma [ $\pm 0.6\%$ ] 638 (MSWD = 1.2; P = 0.14; Jourdan et al., 2008a). This age is significantly more robust and 639 reliable than the previous K/Ar and  $^{40}$ Ar/ $^{39}$ Ar determinations at  $700 \pm 5$  Ma (the age listed in 640 641 the impact database, Masaitis, 1999) and  $698 \pm 22$  Ma (Müller et al., 1990). The new <sup>40</sup>Ar/<sup>39</sup>Ar age has been obtained over 5 out of 7 experiments involving single melt rock 642

fragments that have been carefully selected and HF leached prior to irradiation and analysis. The spread along the isochron (S-value of 83%) allows fully resolving the inherited Ar

component trapped in the grains. This result strongly underscores the importance of sample

preparation in dating impact products.

A complete discussion of the age data for all 25 impact structures with purportedly better than  $\pm 2\%$  age precision is beyond the scope of this paper, but a summary for each structure, with proposed age or age range, is given in Table 1.

A review of the accuracy and precision of the 86 ages available for the confirmed impact

# Appraisal of the impact crater age database

structure is far beyond the scope of this paper. Rather, the reviews above and in Table 1 should be considered as a warning signal concerning the poor state of the impact age database.

Some authors are careful about a straight and blind interpretation of the ages they obtained and often give some warning about their results, yet these potentially problematic ages are propagated into the literature without further criticism and with time "become robust" and widely accepted ages. Our review shows that most of the ages of the 25 impact structures that are claimed to be known with a precision better than ±2% are questionable. Only eleven ages seem to be statistically and geologically robust (Table 1). Among the remaining 14 structures whose ages are questionable, we suggest that 12 are at best ambiguous and should be reported with a "~, > or <" sign. Although the dates given are in most cases probably close to the impact ages proposed (as shown above, e.g., for the Araguainha structure), attributing an uncertainty to these ages gives the false impression that they are accurate within errors which is in some cases demonstrably not true. Two structures (Gardnos and Shoemaker, cf.

discussion above) have "ages" known with a "precision" of a few hundred million years and reporting these ages with a precision on the order of a few percent is unrealistic and strongly misleading for the research community. Such a lack of accuracy (and precision) would not substantially compromise the impact flux determination, but this would be fatal if one tries to correlate multiple impacts and/or relationships with mass extinctions or other phenomena. Improving the impact age database in the near future is therefore crucial. This goal can be achieved provided that careful sample preparation including conscientious picking and leaching of samples is carried out. Detailed specific sample preparation techniques to maximize the chance to obtain valid <sup>40</sup>Ar/<sup>39</sup>Ar ages on impact products has been summarized by Jourdan et al (2007a, 2008a). We also recommend that ages proposed for an impact be the result of several different measurements to test the reliability of each of the individual ages obtained. The Roter Kamm case (Hecht et al., 2008) is a case in point. This allows detecting and eliminating problems and/or outlier data which can be obtained frequently for impact products. To avoid a proliferation of invalid ages, rigorous statistical tests (e.g. MSWD, probability) should be provided with each result. Not only the "good" results should be published but also the data that are more difficult to interpret - provided that a clear notification of the poor reliability of the results is given (i.e., results reported with  $\sim$ , > or <without any error bars given in the final result). When the <sup>40</sup>Ar/<sup>39</sup>Ar age determination fails despite careful sample preparation and analytical technique, it may be productive to try different techniques such as (U-Th)/He (e.g., Farley, 2002), whose greater sensitivity to diffusion could help obviate the inherited daughter problem. Like K/Ar dating, (U-Th)/He will be most effective, where the lack of internal reliability checks (i.e., no age spectrum) is compensated by measurements on a large number of samples and that the errors associated with the dispersion are fully propagated into the final age reported. Alternatively, the <sup>4</sup>He/<sup>3</sup>He

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stepwise heating technique (Shuster and Farley, 2004) holds promise for unveiling thermal perturbations due to impact heating.

Dating an impact structure can be challenging due to the nature and quality of the generally complex samples (e.g., impact breccias). Maybe even more challenging is the frequent absence of datable impact products (i.e., melt rock). In the case of relatively old impact structures, material such as tektites or impact melt rock might have been eroded away or covered by recent sedimentary strata. In this case, techniques such as exposure dating could be used, but with one important question in mind: what is worse, to have no age or a misleading date?

## **Conclusions**

This review showed that of 174 listed impact structures, about half of them are not dated but associated with an age bracket given by stratigraphic constraints only. The impact structure age database informs that only 25 structures are known with a precision better than  $\pm$  2%, including 16 structures with a precision better than  $\pm$  1%. A precision lower than  $\pm$  2% is generally inadequate for correlating impact events with mass extinctions or calibrating stratigraphic ages. Such precisions are generally associated with perturbed data and demand skepticism about the validity of the results. We have reviewed the characteristics of the problems that can be encountered during  $^{40}$ Ar/ $^{39}$ Ar and U/Pb dating and give some advice on sample preparation based on our experience that might help to improve the chance to obtain a valid age. We also provide some statistical basis that would allow the non-geochronologist to assess the quality of an age.

A review of the 25 superficially satisfactory ages shows that only 11 can be considered as statistically and geologically robust. Twelve structures have age data that give only an

717	approximation of the true impact age and for which the attributed age precisions are overly
718	generous. These dates should be reported with $\sim$ , $>$ or $<$ . Finally, 2 of the 25 structures have
719	ages known at the $\pm$ hundred of Ma scale, and reporting them with a precision of $\pm$ 2% is
720	strongly misleading.
721	This review should be viewed as a warning that shows the currently poor state of the impact
722	crater age database. Accurate and precise dates for impact events should be seen as a high
723	priority goal for geochronologists.
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725	Acknowledgments
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## Table and figure captions

- Fig. 1: Age precision distribution of the impact ages. This distribution is based on the impact
- age database (http://www.unb.ca/passc/ImpactDatabase/). The 86 structures not dated include
- 1075 ages reported with a  $\sim$ , > or < sign.
- Fig. 2: <sup>40</sup>Ar/<sup>39</sup>Ar inverse isochron plot showing the spread of the data along the isochron. a) a
- case for Tswaing impact glass (sample 58075-10) from Jourdan et al. (2007a). b) A global
- 1079 isochron for Strangways impact melt rock (Spray et al., 1999) replotted using Isoplot
- 1080 (Ludwig, 2003). S-values calculated using eqn (1).

Fig. 3: Perturbed <sup>40</sup>Ar/<sup>39</sup>Ar age spectra. a) Araguainha impact melt rock; results replotted and recalculated; original data from Hammerschmidt and von Engelhardt (1995). b) Bedout plagioclase results replotted and recalculated (original data from Becker et al., 2004). Note the tilde-shaped spectra for a) and b) indicating alteration and/or <sup>39</sup>Ar and <sup>37</sup>Ar recoil.

Fig. 4: Weighted mean plot and calculation of the Popigai  $^{40}$ Ar/ $^{39}$ Ar plateau and mini-plateau age data recalculated from original data by Bottomley et al. (1997). The "official" age of the crater (35.7 ± 0.2 Ma) is indicated by a \*. Our recalculation using Isoplot (Ludwig, 2003) applied to the same raw data indicates an age of 35.71 ± 0.33 Ma. We tentatively propose an age of 36.42 ± 0.81 Ma, based on the weighted mean of four plateau ages.

Table 1: Age results for 25 impact structures reported in the impact database with a precision better than  $\pm$  2%. Only 11 structures have statistically and geologically robust age data. 12 dates are ambiguous, and 2 ages are not known with a precision better than hundreds of millions of years. Recommended ages are based on an age of 28.03 Ma for FCs (Jourdan and Renne, 2007) and decay constants of Steiger and Jager (1977).

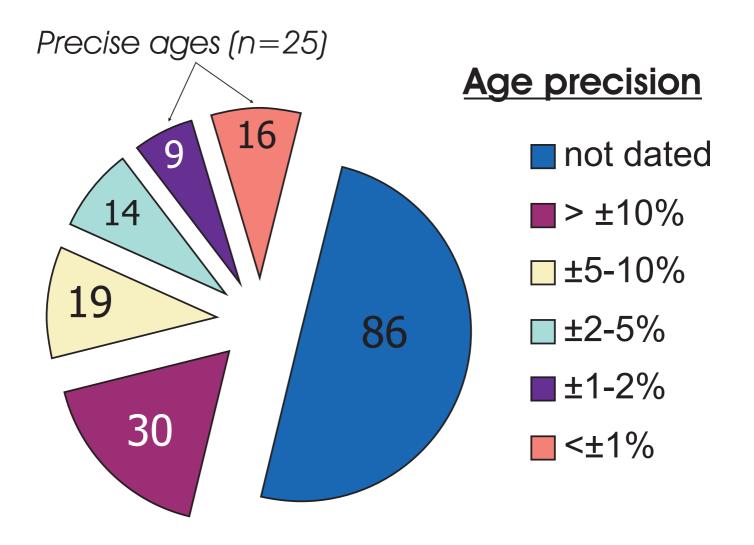


Fig. 1: Jourdan et al.

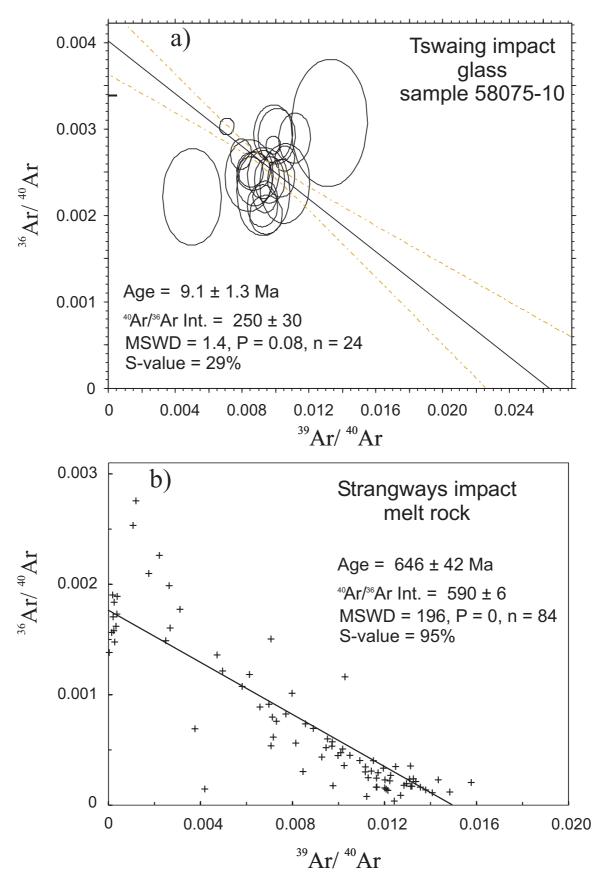


Figure 2: Jourdan et al.

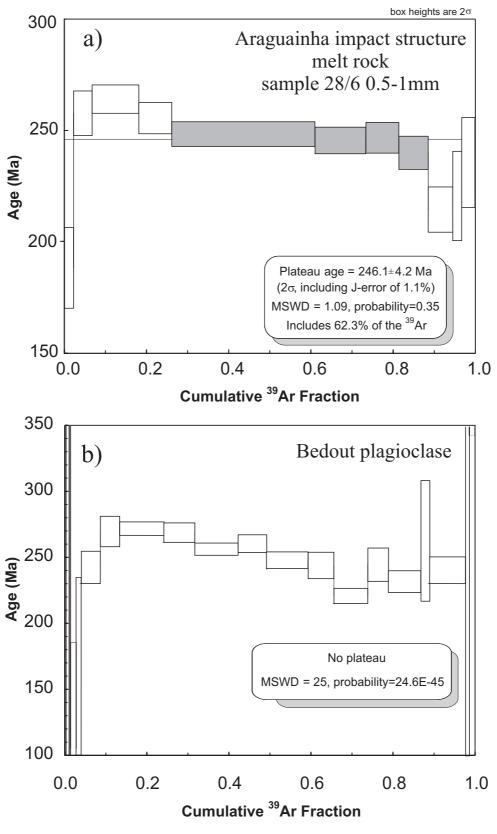


Fig. 3: Jourdan et al.

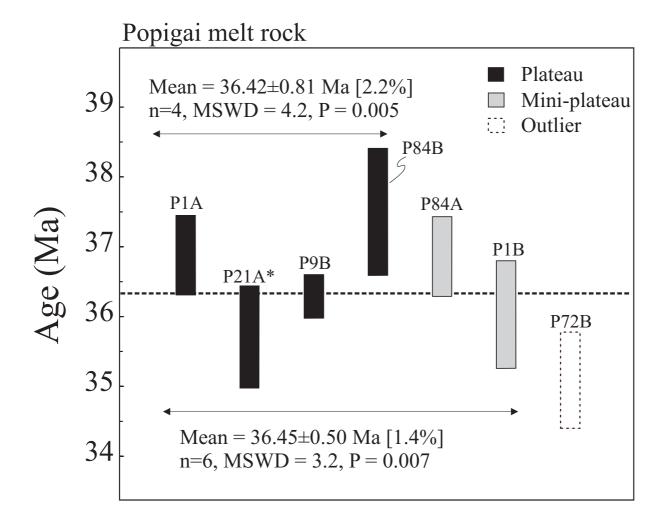


Fig. 4: Jourdan et al.

Crater name	Location	Diameter (km)	Reported age (Ma±; 2σ)	Relative error	Methode	Material	Age based on	Data quality	Observations	Recommended age	References
Araguainha	Brazil	40	244.4 ± 3.25	1.3%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Impact melt rocks	2 plateau ages.	The first plateau includes ~62% of the gas from a perturbed spectra. The second plateau is not statistically valid as it includes only ~30% of <sup>39</sup> Ar.	Only one plateau age with evidence of recoil-induced redistribution of <sup>39</sup> Ar and/or alteration. Additional data are required.	~246 Ma	Hammerschmidt & Von Engelhard, 1995
Boltysh	Ukraine	24	65.17 ± 0.64	1.0%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Impact melt rocks	4 concordant plateau ages.	The four samples behaved differently but give four concordant plateau ages.	Robust age.	65.17 ± 0.64 Ma	Kelley & Gurov, 2002
Chesapeake Bay	Virginia, U.S.A.	90	35.5 ± 0.3	0.8%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Tektites	Concordant plateau and total fusion ages from different studies based on different tektite fields.	Very consistent ages.	Robust age.	35.5 ± 0.3 Ma	Glass et al., 1986; Bottomley, 1982; Obradovich et al., 1989; Horton & Izett, 2005
Chicxulub	Yucatán, Mexico	170	64.98 ± 0.07	0.1%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Glassy melt rocks / tektites	Three plateau ages.	Very consistent ages.	Robust age. Reported at $64.98 \pm 0.05$ Ma. Recalculated using new FCs standard calibration (Jourdan & Renne, 2007).	65.55 ± 0.05 Ma	Swisher et al., 1992
Gardnos	Norway	5	500 ± 10	2.0%	Stratigraphy / <sup>40</sup> Ar/ <sup>39</sup> Ar	Glass / plagioclase	Stratigraphy.	Stratigraphy poorly constrained and <sup>40</sup> Ari <sup>39</sup> Ar experiment failed.	Stratigraphy constrains the age between 500 and 650 Ma.	~500 - 650 Ma	French et al., 1997; Grier et al., 1999
Gosses Bluff	Northern Territory, Australia	22	142.5 ± 1.6	1.1%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Suevite	One age spectrum.	Increasing age spectrum characteristic of Ar loss. No plateau age developed.	Impact age might be older. Additional data are required.	~ 143 Ma or >143 Ma	Milton & Sutter, 1987
Gusev	Russia	3	49 ± 0.2	0.4%	Stratigraphy			Target rocks are end of Maastrichtian and occurrence of Danian foraminifera in the first post- crater sedimentary layer.	Minimum age is beginning of Danian.	End Maastrichtian - Danian (~66 - 62 Ma)	Movshovich et al., 1991
llyinets	Ukraine	8.5	378 ± 5	1.3%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Impact melt rocks	Two integrated ages. No plateau obtained.	Approximate age. Additional data are required.	Two integrated ages of the best behaved samples are 440 ± 4 and 445 ± 4 Ma.Pesonen et al. (2004) have interpreted this age as a maximum age due to excess Ar.	~ 445 Ma or lower (?)	Pesonen et al., 2004
Jänisjärvi	Russia	14	700 ± 5	0.7%	<sup>40</sup> Ar/ <sup>39</sup> Ar- K/Ar	Impact melt rocks	K/Ar not reliable. 5 new <sup>40</sup> Ar/ <sup>39</sup> Ar ages spectra combined in a total isochron age.	The five <sup>40</sup> Ar/ <sup>39</sup> Ar ages and the isochron age are very consistent.	<b>Robust age</b> . MSWD = 1.2; P = 0.14.	682 ± 4 Ma	Jourdan et al., 2008a
Kaluga	Russia	15	380 ± 5	1.3%	Stratigraphy - K/Ar	Impact melt rocks (K/Ar)	Upper and lower stratigraphic constrains.	K/Ar not reliable. Stratigraphic constrain give an Eifelian age (early Middle Devonian).	Age of the Eifelian is between 397.5 ± 2.7 Ma and 391.8 ± 2.7 Ma. Crater is located in the Lower Eifelian.	Middle or Late Eifelian (~398 - 392 Ma)	Masaitis, 2002
Kamensk	Russia	25	49.0 ± 0.2	0.4%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Glass shards	6 total fusion ages.	The six ages are concordant (P=0.94).	<b>Robust age.</b> Weighted mean recalculated at 49.15 ± 0.27 Ma.	49.15 ± 0.27 Ma	Izett et al., 1994

Manicouagan	Quebec, Canada	100	214 ± 1	0.5%	U/Pb; <sup>40</sup> Ar/ <sup>39</sup> Ar	Recristallized zircons	<sup>238</sup> U/ <sup>206</sup> Pb mean ages.	2 concordant fractions plotted on the concordia curve.	<b>Robust age</b> . Zircon ages are indistinguishable from $^{40}$ Ar/ $^{39}$ Ar ages at 213 ± 1 Ma. More recent ages given by Ramenazi et al. (2005) at 214.5 ± 0.5 Ma ( $^{49}$ Ar/ $^{39}$ Ar) and 214.56 ± 0.05 Ma (U/Pb).	214.56 ± 0.05 Ma	Hodych & Dunning, 1992; Ramezani et al., 2005
Manson	Iowa, U.S.A.	35	73.8 ± 0.3	0.4%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Sanidine, microcline and suevite	UV laser spot isochron on a sanidine crystal.	Sanidine gives concordant isochron (~74 Ma) but spread along the isochron is very low. Suevite and microcline give also statistically valid ages at ~65 Ma.	Discrepancy between the sanidine results (~74 Ma) and the suevite and microcline results (~65 Ma). Additional data are required.	65 - 74 Ma ?	Izett et al., 1993; Kunk et al., 1989, 1993
Mien	Sweden	9	121 ± 2.3	1.9%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Impact melt rocks	2 age spectra.	Two discordant age spectra. Age based on the weighted mean of a short portion of the least discordant age spectrum.	Spectra difficult to interpret.	~ 121Ma ?	Bottomley et al., 1990
Mjølnir	Norway	40	142 ± 2.6	1.8%	Stratigraphy		Stratigraphy, micro- and macrofaunas, microfloras, Ir anomaly.	Variety of stratigraphic constraints.	Good for comparison with relative stratigraphy. Absolute age depends on the age calibration of the timescale. We calculate the absolute age by including the error on the timescale age.	Volgian-Ryazanian boundary (~143.7 ± 5 Ma). Updated from Gradstein et al. 2004 and including uncertainty on the Timescale age.	Smelror et al., 2001
Montagnais	Nova Scotia, Canada	45	50.5 ± 0.76	1.5%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Impact melt rock	1 age spectrum?	Perturbed spectrum.	Data difficult to interpret. Additional data are required.	~51 Ma ?	Bottomley & York, 1988
Morokweng	South Africa	70	145 ± 0.8	0.6%	U/Pb; <sup>40</sup> Ar/ <sup>39</sup> Ar	Recristallized zircons	<sup>238</sup> U/ <sup>206</sup> Pb mean ages.	3 concordant fractions plotted on the concordia.	<b>Robust age</b> . Zircon age is indistinguishable from biotite age <sup>40</sup> Ar/ <sup>39</sup> Ar age at 143 ± 4 Ma.	145.2 ± 0.8 Ma	Hart et al., 1997 Koeberl et al., 1997
Pilot	Northwest Territories, Canada	6	445 ± 2	0.4%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Impact melt rocks	Mean between 2 different portions of the spectrum.	No plateau developed.	The age spectrum shows some perturbation. Data difficult to interpret. Additional data are required.	~445	Bottomley et al., 1990
Popigai	Russia	100	35.7 ± 0.2	0.6%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Impact melt rocks	1 plateau age.	The plateau is statistically valid (P=0.4).	Based on 1 plateau, but 4 other plateaus and 2 mini-plateaus are not accounted for in the calculation. Weighted mean of the three plateau ages with error expanded by to \MSWD is proposed instead to account for the data scatter.	36.42 ± 0.81 Ma (?)	Bottomley et al., 1997
Puchezh-Katunki	Russia	80	167 ± 3	1.8%	Stratigraphy		Bajocian pollen present in both the allogenic breccias and post impact crater lake deposits.	Need more documentation (Palfy et al., 2004).	Pollen suggests a Bajocian age. Isotopic ages are given by K/Ar and range from ~200 to ~183 Ma. Additional data are required.	End Triassic - Bajocian (~203 to 168 Ma)	Palfi, 2004; Masaitis and Pevzner, 1999; Schmieder & Buchner, 2008

Ries	Germany	24	15.1 ± 0.1	0.7%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Suevite / Tektites	Plateau, isochron and total fusion ages.	Very consistent ages.	Recent data obtained on various tektites (Graupensand, Lusatian, Bohemian and Moravian fields) by different laboratories give concordant and <b>robust</b> $^{40}$ <b>Ar</b> $^{139}$ <b>Ar ages</b> . Weighted mean age of those tektite ages is 14.47 ± 0.14 Ma (P = 0.65).	14.47 ± 0.14 Ma	Buchner et al., 2003; Laurenzi et al., 2003; Staudacher et al., 1982; Schwartz & Lippolt, 2002
Shoemaker (formerly Teague)	Western Australia, Australia	30	1630 ± 5	0.3%	Rb/Sr	Impact melt rocks	4 analyses.	Samples are variously altered.	The data are not reliable and can reflect various alteration and tectonic overprint processes. SHRIMP data constrain on the maximum age of the target rock at ~2.2 Ga.	Proterozoic	Bunting et al., 1982; Pirajno & Glickson, 1998
Siljan	Sweden	52	376.8 ± 1.7	0.5%	<sup>40</sup> Ar/ <sup>39</sup> Ar	Impact melt rocks	UV laser spot fusion and concordant step-heating experiment.	Three concordant ages are obtained.	Robust age. Weighted mean is expanded by to√MSWD for realistic error propagation by Reimold et al. (2005).	376.8 ± 1.7 Ma	Reimold et al., 2005
Sudbury	Ontario, Canada	250	1850 ± 3	0.2%	U/Pb and <sup>207</sup> Pb/ <sup>206</sup> Pb (TIMS)	Recristallized zircons and baddeleyite from melt rocks and norites	<sup>238</sup> U/ <sup>206</sup> Pb mean ages and upper concordia intercept.	Concordant data.	Robust age. 3 different samples give a concordant weighted mean of 1849.9 ± 1.1 Ma (MSWD=0.05; P=0.95). If we include 2 recent <sup>207</sup> Pb) <sup>206</sup> Pb results in the calculation, this gives a weighted mean of 1849.3 ± 0.3 Ma (MSWD=2.3; P=0.05)	1849.3 ± 0.3 Ma	Ostermann et al., 1994; Krogh et al., 1984; Davies, 2008.
Vredefort	South Africa	300	2023 ± 4	0.2%	U/Pb (TIMS) and SHRIMP); <sup>40</sup> Ar/ <sup>39</sup> Ar	Recristallized zircons from pseudotachylitic breccia and impact melt rock	<sup>238</sup> U/ <sup>206</sup> Pb mean ages and lower concordia intercept.	Concordant data.	Robust age. TIMS U/Pb data at 2023 ± 4 Ma are supported by SHRIMP (2017 ± 5 Ma) and Ar/Ar (2018 ± 14 Ma) data.	2023 ± 4 Ma	Kamo et al., 1996; Gibson et al., 1997; Spray et al., 1995
Wetumpka	Alabama, U.S.A.	6.5	81 ± 1.5	1.9%	Stratigraphy		The youngest target rock in the crater is Mooreville chalk (lower Campanian).	Maximum age.	Poor constraints on the minimum age. Perhaps minimum age is given by the Archola Formation. Campanian starts at 83 +- 0.7 Ma according to more recent timescale (Gradstein et al., 2004).	Lower Campanian or younger (<83 Ma)	King, 1997

Table 1: Jourdan et al.

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F. Jourdan



P.R. Renne



U.W. Reimold (to be updated)