

# ***Interactive comment on “High-resolution records of the beryllium-10 solar activity proxy in ice from Law Dome, East Antarctica: measurement, reproducibility and principal trends” by J. B. Pedro et al.***

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Received and published: 21 May 2011

## Authors' Response to Anonymous Referee #3

We thank the anonymous reviewer for this detailed and constructive review. Comments by the referee are labelled (R) and are followed by the authors' response (A). Text that has been added to the revised manuscript in response to referee comments is emphasised below using italic script. References not listed in the main manuscript can be found at the end of this document.

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Major comments:

### R: 3.1 Concentration and flux

In wet deposition areas such as Law Dome, it is obvious that one should use concentration rather than flux unless there are large climatic transitions. However, in such a case, other meteorological effects possibly affect the  $^{10}\text{Be}$  signals as discussed in an earlier paper (Pedro et al., 2006, JGR). They may influence discussions on the trend performed in Section 3.4.1 (especially, on the lag of  $^{10}\text{Be}$  and NM and an inconsistency between those after 2008), where some additional discussions based on the relation between  $^{10}\text{Be}$  and  $\delta^{18}\text{O}$  are necessary.

A: Following the advice of the referee we have included a new section (Sect. 3.5) in the manuscript that directly tests the relation between the  $^{10}\text{Be}$  and  $\delta^{18}\text{O}$  data in the same way as Pedro et al., (2006). The new text is copied below. We comment explicitly in the new text that the relation with  $\delta^{18}\text{O}$  does not offer an explanation for the divergence between neutron monitor data and  $^{10}\text{Be}$  concentrations after 2008. Note that in order to introduce this new section it was necessary to make some minor changes to the sectional headings and arrangement of subsections.

#### 3.4.4 Relationship between $^{10}\text{Be}$ and $\delta^{18}\text{O}$

*Results from an earlier analysis of the DSS0102-pit suggested an important meteorological influences on  $^{10}\text{Be}$  forced by variability in local meteorology and air mass moisture history (Pedro et al., 2006). This influence was detected in the form of a significant negative correlation ( $r_{xy} = 0.57$ ;  $p < 0.01$ ) between first-differences in  $\delta^{18}\text{O}$  and  $^{10}\text{Be}$  measurements. The relationship can now be tested over the 10-year composite.*

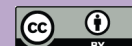
*Following the procedure in Pedro et al., (2006), first-differences in  $^{10}\text{Be}$  concentrations are tested against first-differences in  $\delta^{18}\text{O}$ . This yields  $r_{xy} = -0.14$  with 95% CI of  $-0.38$  to  $0.02$ . This negative relationship is consistent with, although weaker than, that observed in the previous study. Indeed, the 95% CI around  $r_{xy}$  indicates that the*

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*significance of the relation is marginal. Notably, there is no trend in  $\delta^{18}\text{O}$  capable of offering an explanation for the departure of  $^{10}\text{Be}$  concentrations from the neutron counting rate curve in 2008 and 2009.*

*A critical difference with respect to our earlier study that may explain this weaker correlation is the sub-monthly (snowfall event scale) resolution of DSS0102-pit compared to the coarser monthly-resolution of the composite. The implication is that  $^{10}\text{Be}$  and  $\delta^{18}\text{O}$  co-vary at DSS on the snowfall event scale, but that this relation appears to deteriorate with coarser sample resolution. This is also an encouraging result from the perspective of interpreting information about atmospheric production from ice core  $^{10}\text{Be}$ .*

We also include a sentence in the conclusions to summarise these findings:

*Similarly to a previous study at DSS a negative relation is found between  $^{10}\text{Be}$  and  $\delta^{18}\text{O}$ , however the relation is much weaker than that observed previously.*

### R: 3.2 Reproducibility

Despite much smaller (insignificant) than that shown in Moraal et al. (2005), the authors found two types of difference between ice core  $^{10}\text{Be}$  records obtained from very near sites. Rather negligible one is difference regarding a spike in 2005 summer described in the first paragraph in Section 3.2. The difference of the timing of the spike is within the error of the dating. However, since exceeding the measurement error, the authors conclude that the difference in peak values represents a real difference caused by environmental factors. I never exclude such possibility. However, I think that the authors should add an alternative possibility that the difference was brought about by experiments or coring or both (as discussed in the subsequent paragraphs), or simply insert the word "may" before the word "represent" on line 23 of page 688. There is no reason that only this spike was not affected by such effects.

A: This is a fair point; we cannot absolutely exclude experimental factors. We take the reviewers advice and insert the word "may".

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R: Another one is somewhat more serious: that is an offset between snow pits (DSS0102-and DSS0506-pits) and a thermally drilled core (DSS0506-core). The offset is clear over considerable intervals: snow pit data are higher in concentration than thermally drilled core. As the authors are recognizing, this can be expressed in other words: acidified samples are frequently higher in concentration than non-acidified one. I agree with the authors that the releasing of undesirable  $^{10}\text{Be}$  atoms from dusts and micrometeorites has an only negligible effect for Antarctic ices. However, I disagree with their statement that "any loss of  $^{10}\text{Be}$  by absorption to laboratory equipments should be balanced by corresponding loss of  $^9\text{Be}$  carrier". The statement would be right if the chemical forms of the carrier  $^9\text{Be}$  and ice-core  $^{10}\text{Be}$  was practically the same. Since the chemical form of  $^{10}\text{Be}$  in ice (and its melt water) is poorly known, an active dissolution process (such as acidification) is necessary for avoiding selective adsorption of  $^{10}\text{Be}$  atoms to bottle walls, filters (especially, a submicron filter), and dusts. Such behaviour of  $^{10}\text{Be}$  in sample solution is described in details in Finkel and Nishiizumi (1997) and Yiou et al (1997) and should be considered in Sections 3.2 and 3.4.1.

A: This is a very important issue that goes to the principal of using a carrier in AMS measurement of  $^{10}\text{Be}$ . To provide some more details: when ice samples are melted in the presence of  $^9\text{Be}$  carrier (as in our technique) the sample is flooded with  $\sim 10^{13}$  times more  $^9\text{Be}$  atoms than  $^{10}\text{Be}$  atoms. Our assumption is that when this carrier is added the ratio of  $^9\text{Be}$  to  $^{10}\text{Be}$  in the sample is fixed, i.e. that any loss of  $^{10}\text{Be}$  by absorption to experimental equipment and particulates is balanced by loss of  $^9\text{Be}$  carrier, such that  $^{10}\text{Be}:^9\text{Be}$  ratios are unaffected. We have performed experiments that suggest this assumption is well-founded. The reviewer agrees with this statement provided that "the chemical forms of the carrier  $^9\text{Be}$  and ice-core  $^{10}\text{Be}$  [are] practically the same". The reviewer states further that "an active dissolution process (such as acidification) is necessary for avoiding selective adsorption of  $^{10}\text{Be}$  atoms to bottle walls, filters (especially, a submicron filter), and dusts." We can provide some clarification here that we think addresses the reviewers concern.

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1. Even if  $^{10}\text{Be}$  and  $^9\text{Be}$  are in different chemical forms, molecular processes will lead to interchange between  $^{10}\text{Be}$  and  $^9\text{Be}$  atoms. The rate of this exchange depends on reaction kinetics. Given that reaction kinetics are not well understood, we would agree that it is preferable that  $^9\text{Be}$  and  $^{10}\text{Be}$  are in similar chemical forms.
2. The aqueous chemistry of Be is dominated by its tendency to be hydrated and to form hydroxy-complexes (Everest, 1973). The major species of dissolved Be in aquatic systems at neutral to basic pH is  $\text{Be}(\text{OH})_2$ , at pH more acidic than 5.7 the dominant species quickly transitions to  $\text{Be}^{2+}$  (the pH dependence of Be speciation is shown in Fig 1, below). This speciation is important and gets back to the issue raised by the reviewer;  $\text{Be}^{2+}$  is strongly hydrated and will stay in solution, whereas  $\text{Be}(\text{OH})_2$  tends to be adsorbed onto surfaces.
3. Importantly, there is acid in the  $^9\text{Be}$  carriers that we have used for all of the sample sets reported in this paper. Our tests show that the acid in the carrier itself is sufficient to acidify the samples to pH  $\sim 4.2$ . Hence the sample makes a transition from ice to an acidified and  $^9\text{Be}$ -flooded aqueous solution. According to the aqueous speciation of Be (Figure 1) the chemical forms of both carrier  $^9\text{Be}$  and ice core  $^{10}\text{Be}$  at this pH will indeed be the same, i.e. dominated by the  $\text{Be}^{2+}$  form.
4. Note that even at pH more acidic than 5.7 some  $\text{Be}(\text{OH})_2$  will form and some of this  $\text{Be}(\text{OH})_2$  will adsorb to experimental equipment. However, this process affects both  $^9\text{Be}$  atoms and  $^{10}\text{Be}$  atoms, leaving the ratio in solution unchanged.
5. The reviewer refers to Finkel and Nishiizumi (1997) and Yiou et al (1997). These studies did find some evidence for selective adsorption of  $^{10}\text{Be}$ ; however, only for glacial ice with high dust concentrations. In this case, the  $^{10}\text{Be}$  adsorbed to the dust is in a very different chemical form to the  $^9\text{Be}$  added as a carrier. It appears that dust trapped on 0.45 micron filters in these studies acted as a

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substrate for non-equilibrium exchange between ice core  $^{10}\text{Be}$  (of atmospheric origin) and  $^{10}\text{Be}$  attached to dust (of terrestrial origin) (Baumgartner et al., 1997). Both studies reported that Holocene ice with lower dust was negligibly affected by this problem. Since dust levels at DSS are among the lowest at any polar site (Jun et al., 1998), the Finkel and Nishiizumi (1997) and Yiou et al (1997) results for glacial ice with high dust loading do not really apply.

All these points argue that levels of acidification do not offer a satisfactory explanation for the offset between the DSS0102-pit and DSS0506-core. We make revisions to the text as follows. In Sect 2.4 we add the sentence:

*Due to the acidity of the carrier (it was prepared in dilute  $\text{HNO}_3$ ) the samples typically had a pH of  $\sim 4.2$  after melting.*

In Sect 3.2. we expand on our assumption of equilibrium between ice core  $^{10}\text{Be}$  and carrier  $^9\text{Be}$ , the conditions under which it may break down, and why we consider that it does not break down in our study. We include the new/revised text that follows:

*Both sample sets were melted in the presence of  $^9\text{Be}$  carrier, which floods samples with  $\sim 10^{13}$  times more  $^9\text{Be}$  atoms than  $^{10}\text{Be}$  atoms. We assume that any loss of  $^{10}\text{Be}$  by adsorption to experimental equipment is balanced by loss of  $^9\text{Be}$  carrier, such that  $^{10}\text{Be}:$  $^9\text{Be}$  ratios are unaffected. Importantly, this assumption may not hold if the carrier  $^9\text{Be}$  and ice core  $^{10}\text{Be}$  are in different chemical forms and there has not been sufficient time for reaction kinetics to equilibrate  $^9\text{Be}$  and  $^{10}\text{Be}$  atoms between these different forms. There is some evidence that the assumption of equilibrium does break down for Greenland ice samples from the last glacial period with high dust particle concentrations (Finkel and Nishiizumi, 1997; Yiou et al., 1997). This probably relates to non-equilibrium exchange (adsorption and desorption) of  $^{10}\text{Be}$  and  $^9\text{Be}$  between terrestrial dust and meltwater in ways that are not fully understood (Baumgartner et al., 1997). Importantly, Holocene ice samples, with much lower particle concentrations, were negligibly affected by this problem (Finkel and Nishiizumi, 1997; Yiou et al., 1997).*

*The particle concentrations in modern DSS ice are actually among the lowest of all the polar ice core sites (Jun et al., 1998). In addition, recall from Sect. 2.4. that the carrier itself is an acidic solution that typically lowers the sample meltwater pH to  $\sim 4.2$ . The aqueous chemistry of  $^{10}\text{Be}$  dictates that at pH more acidic than 5.7 the dominant species of Be is the strongly hydrated  $\text{Be}^{2+}$ , which tends to remain in solution (Everest, 1973). In the absence of dust we expect the ice core  $^{10}\text{Be}$  and carrier  $^9\text{Be}$  to be in equilibrium in this  $\text{Be}^{2+}$  form. Hence, while we cannot completely rule out some selective loss of  $^{10}\text{Be}$ , we consider it unlikely to have played any major role in the offset between the two DSS records.*

The reviewers concern also prompted us to revisit all the calculations and analysis involved in arriving at the final concentrations in the DSS0102-pit. We have identified two oversights with our reporting of the DSS0102-pit results. This was one of the first records measured by our group and since this time our methods have been refined. Firstly, we made a small error (of 1.7%) in calculating the mass of  $^9\text{Be}$  carrier added to the ice samples from this record (the error was due to failing to correct a calculation to account for the density of the carrier solution). Secondly, we neglected to subtract the  $^{10}\text{Be}$  values of the chemistry blanks from the DSS0102-pit samples. We have now revised the DSS0102-pit data presented in the manuscript (including Table 1, Table 2 and Fig. 3) to account for these errors. The mean concentration in the revised data is  $5.00 \pm 1.91$  (compared to the previous  $5.20 \pm 1.96$ ). Accordingly, the offset between the DSS0102-pit and DSS0505-core data is reduced slightly to 27% (compared to the previous 32%).

In our opinion this 27% offset may be explained by real site-to-site differences at DSS. We show in the paper that similar offsets are seen in other trace chemical records from DSS when viewed over 1-year intervals. Finally, we would like to remind readers and the editor that the DSS0102-pit data is not used in constructing the 10-year composite record (the composite includes only the identically prepared records), as such these small changes do not affect the relation with the neutron counting rate.

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Minor comments:

R: Page 684, lines 8-9. What is the volume of the column filled with resins?

A: The columns contain 10 ml of Dowex 50W-X8 200 mesh cation exchange resin. The volume of resin is listed in the flowchart (Fig. 2.) and now also in the text.

R: Page 684, lines 13-14. Which fraction(s) was (were) collected for the subsequent analysis? If the all, why was the eluent divided into three parts?

A: The text is revised to remove this ambiguity as follows:

*Beryllium was stripped from the columns by a sequence of three washes of 20 mL, 15 mL and 20 mL of 3M HNO<sub>3</sub>. Eluent from the first two washes was combined into a single fraction and then pH adjusted to 7.8 to 8.5 by adding concentrated NH<sub>3</sub>. Full precipitation of beryllium (as Be(OH)<sub>2</sub>) from this fraction was achieved after several hours, whereupon the sample was centrifuged and the supernatant discarded. Typically all beryllium was stripped from the column by the first fraction and neutralisation of the eluent from the final 20 mL 'backup' fraction did not yield any precipitate.*

The reason for a 20 mL and then 15 mL wash rather than a single 35 mL wash is simply due to the volume that can be added to the column at any one time without overflowing it. Also, advice from radionuclide chemist Krista Simon is that the full precipitation takes > 1 hr so we have adjusted the text which previously read 'Full precipitation... was achieved in ~1 hr' to now read '...after several hours'.

R: Page 698, line 20. "a" should be replaced by "and".

A: Done.

R: 2.4 Extraction of <sup>10</sup>Be from ice and AMS measurement I understand that the authors paid special attention to the pretreatment of sample for good boron suppression and the resulting successful AMS measurement. However, it seems to go a bit overboard, because a successful <sup>10</sup>Be determination of 2-13 x 10<sup>-13</sup> level has been realized by

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using ordinary (easier) procedures in many previous works.

A: It is the case that we have paid special attention to boron suppression. This was in response to unacceptable levels of boron contamination in some previous samples from DSS (Pedro et al., 2009). Our new technique has proved very successful and has played an important role in reducing total measurement uncertainties to  $\sim 3\%$ . This is lower than the uncertainties that have been reported for other studies of ice core  $^{10}\text{Be}$  (typically  $\sim 5$  to  $7\%$ : e.g. Beer et al., 1991, Yiou et al., 1997; Finkel and Nishiizumi, 1997; Aldahan et al., 1998; Raisbeck et al., 1990). The trouble with boron contamination in  $^{10}\text{Be}$  analyses is that you never know when it is going to rear its head. If it does, corrections to the data of 15 to 20% may be required (e.g. Aldahan et al., 1998; Finkel and Nishiizumi, 1997; Yiou et al., 1997) or the samples may require complete reprocessing before they can be reliably measured at all (Simon et al., 2011). Since introducing boron suppression techniques to our sample processing we have had no problem with boron contamination; so we are happy to go to this extra effort and we think that the other researchers in this field may also be interested in reading about our technique.

## References

Hinz, I., Koeber, K., I., K., and Kuhn, P.: Gmelin Handbook of Inorganic Chemistry, chap. Be, Supplement Vol. A1, Springer-Verlag, 1986.

Interactive comment on Clim. Past Discuss., 7, 677, 2011.

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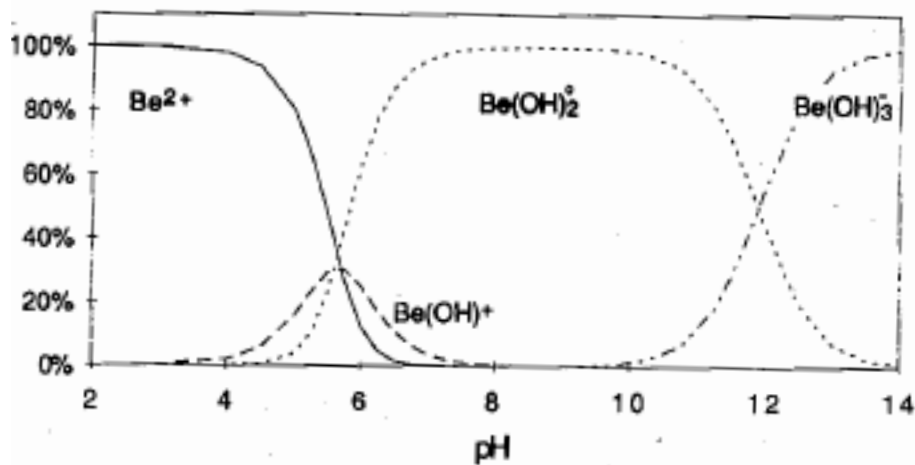


Fig. 1. Aqueous speciation of beryllium as a function of pH, from Hinz et al. (1986)

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