Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Geochimica et Cosmochimica Acta 70 (2006) 5433–5436
Geochimica
www.elsevier.com/locate/gca

Response

Reply to the comment by Desch and Ouellette on "Li and B isotopic variations in an Allende CAI: Evidence for the in situ decay of short-lived ^{10}Be and for the possible presence of the short-lived nuclide ^{7}Be in the early solar system"

Marc Chaussidon [a,*], François Robert [b], Kevin D. McKeegan [c]

[a] *CRPG-CNRS, BP 20, 54501 Vandoeuvre-lès-Nancy, Cedex, France*
[b] *LEME-MNHN-CNRS, 61 rue Buffon, 75005 Paris, France*
[c] *Department of Earth and Space Sciences, UCLA, Los Angeles, CA 90095-1567, USA*

Received 11 August 2006; accepted in revised form 29 August 2006

1. Introduction

That Meteoritics is an interdisciplinary science is evidenced by the careful scrutiny that theoretical astrophysicists Desch and Ouellette (D&O hereafter) have given difficult petrologic and isotopic data. We thank them for this keen interest and for the opportunity to further discuss our interpretation of Li isotopic variations found in an Allende CAI and, hopefully, to clear up some misconceptions regarding the nature of the fossil record that would be left by the in situ decay of the very short-lived radioisotope ^{7}Be. We agree with D&O that the astrophysical implications of the existence of live ^{7}Be in early solar system rocks would be "profound", but we politely remind them that our article was not written to meet a "burden of proof"; in fact, had we intended to claim that such a proof was provided by our data, then we would surely have removed the words "evidence for ... the *possible presence* of ^{7}Be" from the title.

Three points are made by D&O in their comment, namely: (1) they recognize that there exists a correlation between ^{7}Li/^{6}Li and ^{9}Be/^{6}Li ratios, but they claim that because we cannot demonstrate that this correlation is strictly linear according to a statistical test, which assumes that the data scatter only due to random analytical uncertainties, that it necessarily follows that "the radiogenic hypothesis safely can be rejected"; (2) they recognize that the data must be corrected for recent galactic cosmic ray (GCR) spallation and that this correction is significant for only very few (specifically 3) spots with extremely low Li concentrations, but they propose an improved production rate for spallogenic ^{6}Li and ^{7}Li which differs from that used by us by factors of ≈1.56 for ^{6}Li and ≈1.79 for ^{7}Li, but which they nevertheless suggest to have uncertainties of a factor of two or more. Using their preferred "best guess", D&O find that "there is no substantial evidence for supra-chondritic ^{7}Li/^{6}Li ratio in Allende 3529–41"; (3) they recognize that all the analytical spots in 3529–41 cannot be considered equally since a fraction of them has obviously suffered secondary post-magmatic perturbations, but they contest our approach to identify these perturbations and propose that most of the spots should be rejected, in fact all the ones with ^{7}Li/^{6}Li ratios far from chondritic. This of course results in erasing from the data any possible trace of ^{7}Be decay leading D&O to attribute all the Li isotopic variations we found in 3529–41 to secondary alteration of the CAI with Li having lower than chondritic ^{7}Li/^{6}Li ratios.

In the following, we address each of these criticisms in turn, without repeating many details discussed in our article. While fully acknowledging the complexity of the data and their interpretation in terms of the history of the CAI, we nevertheless still maintain that the ^{7}Li/^{6}Li variations in 3539–41 are plausibly explained by the in situ decay of ^{7}Be, which along with low initial ^{7}Li/^{6}Li values constitutes good evidence for significant irradiation processes just before or even during formation of the CAI. We reiterate that our approach has been to try to find the most reasonable explanation of the ^{7}Li/^{6}Li variations

* Corresponding author. Fax: +33 3 83 51 17 98.
E-mail addresses: chocho@crpg.cnrs-nancy.fr (M. Chaussidon), robert@mnhn.fr (F. Robert), mckeegan@ess.ucla.edu (K.D. McKeegan).

0016-7037/$ - see front matter
doi:10.1016/j.gca.2006.08.042

in 3529–41, and that we do not claim to have definitely demonstrated the presence of ^{7}Be. Nothing in the comment by D&O is able to convince us that the analysis of our data as indicating evidence for "… the possible presence of ^{7}Be…" is demonstrably incorrect, but we find that the ad-hoc interpretation that D&O propose for the $^{7}Li/^{6}Li$ variations (alteration of the CAI with Li having a low $^{7}Li/^{6}Li$ ratio) is simply not consistent with the data.

2. Correlation between ^{7}Li/^{6}Li and ^{9}Be/^{6}Li

The first point made by D&O is that the correlation between $^{7}Li/^{6}Li$ and $^{9}Be/^{6}Li$ is not consistent with a line according to a χ^2 test. They argue that "the existence of live ^{7}Be at the time of the CAI's formation is demonstrated *if and only if* the data fit a linear trend with a reduced $\chi^2 < \sim 1.5$ and a slope greater than zero by a significant amount" (*emph. added*). While it is the case that a weighted fit to the data does not pass a χ^2 test, and thus does not sample a single population which scatters about the correlation line due only to random analytical uncertainties, this requirement represents a fundamental misunderstanding by D&O regarding the distinction between the plausible existence of now-extinct radioactivity and theoretically perfect isochronous behavior of parent and daughter isotopes in a CAI. Indeed, a weighted fit to the 37 data of tables 4A and B accounting for uncertainties in both variables, yields an absurdly high reduced $\chi^2 = 17.3$, not 4.3 as miscalculated by D&O (the quoted uncertainties are 2σ and are limited primarily by counting statistics). Clearly, the data do not fit a single line, but it is almost impossible to expect a perfect linear correlation between $^{7}Li/^{6}Li$ and $^{9}Be/^{6}Li$ and this is the reason why such a statistical discussion was not made in our article. Because (i) the half life of 53 days of ^{7}Be is commensurate with the typical duration for cooling of CAIs, from ≈0.1 to ≈10 K/h (Stolper and Paque, 1986) and because (ii) Li has a high diffusivity in crystals (Giletti and Shanahan, 1997; Coogan et al., 2005), there is no way to expect that Li isotopes were not at least partially redistributed in the CAI during or just after the decay of ^{7}Be (in the hypothesis of the presence of ^{7}Be). In this regard, ^{7}Li is very different from other daughter products of short-lived nuclides (e.g., ^{26}Mg, ^{10}B, etc.) and this certainly makes the ^{7}Be–^{7}Li system difficult to study. The predictions that can be made on the redistribution of Li are strongly model dependant, depending for instance on the time at which ^{7}Be was introduced in the CAI or on the cooling history of the CAI. A partial redistribution of Li isotopes during the decay of ^{7}Be would result in obscuring the expected linear correlation in the $^{7}Li/^{6}Li$ vs. $^{9}Be/^{6}Li$ diagram by rotating the ^{7}Be isochron around the average $^{9}Be/^{6}Li$ of the CAI: in such a scenario, the points with extreme $^{9}Be/^{6}Li$ ratios would be the most sensitive to these perturbations. As discussed in our article, the ^{10}Be isochron is much better defined and this is consistent with the much longer half life of ^{10}Be (1.5 Ma) because isotopic closure is achieved well-before any significant ^{10}Be decay.

Of course it would be necessary to demand statistical agreement of the data with a linear fit if the goal was to utilize the correlation as a true isochron, i.e., for constraining relative time of formation. However, to indicate mere plausibility for the former existence of the now-extinct parent nuclide, statistically perfect behavior is not a rigorously necessary condition. For example, if the D&O criteria were applied to Al–Mg system, virtually no Allende CAI for which a reasonable number of sufficiently precise data were measured would pass the test (for examples, see Podosek et al., 1991 and Young et al., 2005). In fact, 3529–41 itself shows scatter in Mg isotopes significantly beyond that which can be attributed to analytical errors with a reduced $\chi^2 = 3.7$ (Podosek et al., 1991). Yet no one would use this non-ideal behaviour to argue against the former existence of ^{26}Al in this or similar objects (or in the solar system generally)! Instead, like Podosek et al., they would (correctly) point out that use of the Al–Mg system as a chronometer can be complicated by poor isotopic closure effects.

Thus, at odds with D&O, we consider that the lack of a perfect linear correlation between $^{7}Li/^{6}Li$ and $^{9}Be/^{6}Li$ is not a sufficient reason to "safely reject the radiogenic hypothesis". On the contrary, this was the starting point of our work: how does one evaluate whether the $^{7}Li/^{6}Li$ variations in 3529–41 can plausibly be due to the in situ decay of ^{7}Be when this cannot be simply demonstrated by a perfect ^{7}Be–^{7}Li isochron? This evaluation depends, in part, on an understanding of the full effects of spallation, i.e., not simply in producing ^{7}Be, a point which is also appreciated by D&O.

3. Correction for spallogenic Li and detection of possible "^{7}Li excess"

D&O checked the correction we made for the recent spallogenic production of ^{6}Li and ^{7}Li in the Allende meteroid and came to production rates which are lower than ours by a factor ≈ 1.56 for ^{6}Li and of ≈1.79 for ^{7}Li. They used exactly the same approach as we did except that they took into account a different data set for the cross-sections (Moshalenko and Mashnik, 2003) that was not known to us. This modifies significantly the corrected $^{7}Li/^{6}Li$ for the three spots with very low [Li]: e.g., spot III.6 which has a very low [Li] of ≈0.4 ppb and a $^{7}Li/^{6}Li$ ratio of 11.99 ± 0.82 was corrected with the cross-sections we used to 13.46 ± 0.82 and is corrected by D&O to12.89 ± 0.89. However, as indicated by D&O in their comment, the precision which can be guessed for such a correction is at best a factor of 2, so that the two corrections easily intersect within errors. This variability in the corrections is certainly not surprising to us and it just illustrates the fact that this correction has a large uncertainty, another source of uncertainty, not mentioned by D&O, being the precision of the determination by ion microprobe of Li concentrations at the ppb level. We think that significant progress on such corrections for Li will come only from the precise calibration of the Li production rates in minerals from meteorites of known exposure histories. This is a matter of ongoing work that we hope to be able to finalize soon. In the present context, it is of course rather frustrating that the spots which would be potentially the most demonstrative for ^{7}Be are those for which the measurement by ion microprobe is the most difficult and those for which the spallogenic correction is the strongest.

D&O make a big case that with their correction, none of our data shows ^{7}Li/^{6}Li ratios higher than the chondritic ratio of 12.02 (e.g., spot III.6 corrected by D&O has a ^{7}Li/^{6}Li ratio of 12.89 ± 0.89) which would, according to them, rule out any trace of the in situ decay of ^{7}Be. Unfortunately, this idea is wrong because it relies on the incorrect assumption that the initial ^{7}Li/^{6}Li ratio of the CAI has to be chondritic. Here again, it is important to stress the differences that Li exhibits relative to other elements. Contrary for instance to ^{26}Al isochrons for which the initial ^{26}Mg/^{24}Mg is always within a few permil chondritic, the initial ^{7}Li/^{6}Li ratio (intercept in a ^{7}Be–^{7}Li diagram), or the initial ^{10}B/^{11}B in a ^{10}Be–^{10}B isochron, is a priori not chondritic. This comes from the fact that all the isotopes of Li, Be and B are produced together during irradiation processes. A simple first order calculation (see Chaussidon et al., 2006; Chaussidon and Gounelle, 2006) demonstrates that the ^{7}Li/^{6}Li ratio of a solid, in which spallogenic Li–Be–B isotopes have been added to reach a ^{10}Be/^{9}Be ratio of 10^{-3}, will be much lower than 12, i.e., from $\approx$11.4 to $\approx$3.4 for a solid having initially a chondritic Li/Be ratio or a typical CAI Li/Be ratio, respectively. This first order conclusion is corroborated by all published Li isotopic analyses of CAIs which show an average initial ^{7}Li/^{6}Li ratio lower than 12, between 11.03 ± 0.42 and 11.81 ± 0.15, (Chaussidon et al., 2001; MacPherson et al., 2003). Thus, even with the spallogenic corrections preferred by D&O, there are spots with high Be/Li that show marginally or even well resolved (at 2σ) values that are elevated from initial ^{7}Li/^{6}Li ratios, which, of course, could plausibly be construed as evidence for ^{7}Be.

4. How to deal with Li isotopic redistribution ?

Finally, D&O contest the approach we proposed to first identify zones in the CAIs where the Li and B distributions inherited from the magmatic history of the CAI were perturbed. They do not however, propose any other petrologic rationale to do this identification even though post-magmatic perturbations are more or less "inescapable" for Li which is present in the CAI as a trace element (in the ppm–ppb range and sometimes below the ppb), again a major difference from the ^{26}Al–^{26}Mg system. We do not wish to contest D&O on whether any given spot is perturbed or not. We are perfectly aware that Li perturbations are widespread in this CAI and that the approach we proposed (consistency of Li and Be distributions with experimentally determined magmatic partitioning of these trace elements) allows us to identify some of these perturbations, but certainly not all of them. This approach has, however, the merit of being a simple and uniform criterion that is independent of the hypothesis regarding a possible correlation in ^{7}Li/^{6}Li vs. ^{9}Be/^{6}Li. D&O also propose a method that is simple and, by their reckoning, unbiased although they admit that it is "somewhat arbitrary". However, arbitrarily dismissing all data from one end (^{9}Be/^{6}Li < 30) of a possible correlation line, while also changing the corrected ^{7}Li/^{6}Li of points with high ^{9}Be/^{6}Li, and then finding that the residual data no longer show a slope significantly greater than zero, seems to us to be steering the analysis more than a truly unbiased approach would indicate. We leave it to the reader to judge the comparison between diagrams showing ^{7}Li/^{6}Li vs. ^{9}Be/^{6}Li for non perturbed and perturbed spots (Figs. 10 and 11 in Chaussidon et al., 2006) as to whether this could be indicative of the existence of possible traces of in situ ^{7}Be decay in 3529–41.

5. Comments and conclusion

A few comments regarding the alternative proposal by D&O that all the ^{7}Li/^{6}Li variations we found in 3529–41 can be explained by the addition to the CAI of "isotopically light Li in spots with low Be/Li ratios" are called for. First, simple mass balance requires that any kind of two components mixing, whatever its complexity and possible redistributions, must produce a linear correlation between ^{7}Li/^{6}Li and 1/[Li] in the CAI. As shown by our data (see Fig. 12 in Chaussidon et al., 2006) this is obviously not the case. On the other hand, there is a trend (though not perfectly linear!) between ^{7}Li/^{6}Li and ^{9}Be/^{6}Li, which is the reason why we invested time in evaluating the possibility of the in situ decay of ^{7}Be since it would be a process able to modify the ^{7}Li/^{6}Li ratios in the CAI without changing significantly the Li concentrations. In addition it is important to stress here that we did not find in 3529–41 traces for Li isotopic fractionation due to diffusion, as we identified recently in pyroxene phenocrysts from lunar and martian meteorites (Barrat et al., 2005; Beck et al., 2006). Second, what D&O call "isotopically light Li" has a name: it is spallogenic Li produced by irradiation processes. This aspect of the implications of the ^{7}Li/^{6}Li variations present in 3529–41 must not be underestimated and is independent of the traces of ^{7}Be decay in the CAI. Because Li is a volatile to moderately volatile trace element with no known mineral carrier in the nebula, it is difficult to envision how strong isotopic heterogeneities could have been maintained in the nebula. The simplest explanation, also in agreement with the limited but significant Li and B isotopic variations found in chondrules (Chaussidon and Robert, 1995, 1998; Robert and Chaussidon, 2003), is that some Li was produced locally by irradiation in the solar system. From mass balance, the contribution of this Li source to solar system Li would be negligible in bulk and accordingly chondrites have the bulk solar system ^{7}Li/^{6}Li of $\approx$12. However, this source of Li would be significant for CAIs which are depleted in Li relative to bulk solar system and which (based on ^{10}Be) likely formed in regions of intense irradiation.

In conclusion, the comment by D&O emphasizes points which were already discussed and evaluated in detail in our article. We reject the assertion that perfect isochronous behavior is a necessary condition in order to merely demonstrate the plausible existence of a short-lived nuclide and we note there is ample precedent for our viewpoint, e.g., for ^{60}Fe (Birck and Lugmair, 1988), ^{36}Cl (Murty et al., 1997), and others. We agree with D&O that the uncertainty in the correction for Li produced by recent GCR spallation of the Allende meteroid is larger than desirable for this type of work. Their proposed value for this correction, based on different cross-sections than the ones we used, is different than ours. However, the two corrections intersect within errors and both suffer unfortunately from large uncertainties at this low level of Li concentrations. The only progress we can foresee in this direction will come from Li analysis in different minerals from meteorite samples with well known exposure histories.

In the end, we are still faced with explaining the ^{7}Li/^{6}Li variations in 3529–41 and what they might indicate regarding its origin. In this respect D&O do not bring anything new in their comment and their proposition of Li isotopic variations resulting from mixing between chondritic Li and isotopically light Li is not substantiated by the data since the ^{7}Li/^{6}Li ratios are not correlated with 1/[Li]. On the contrary, in situ decay of ^{7}Be could explain the positive trend (not a perfect isochron!) observed between ^{7}Li/^{6}Li and ^{9}Be/^{6}Li in zones where the post-magmatic perturbations of Li were minimum as indicated by our approach. We still think that the data, even in their complexity, can be explained by the "possible presence of ^{7}Be". In addition, we note that the ^{7}Be/^{9}Be ratio that we infer from CAI 3529–41, even if high compared with some predictions (Leya et al., 2003), is not inconsistent with other irradiation models (Gounelle et al., 2006). Finally, we emphasize the fact that 3529–41 and CAIs in general have ^{7}Li/^{6}Li ratios lower than chondritic, which in itself is a strong argument in favour of irradiation processes having taken place around the early Sun.

Associate editor: Alexander N. Krot

References

Barrat, J.A., Chaussidon, M., Bohn, M., Gillet, Ph., Göpel, C., Lesourd, M., 2005. Lithium behavior during cooling of a dry basalt: an ion microprobe study of the lunar meteorite Northwest Africa 470 (NWA 479). *Geochim. Cosmochim. Acta* **69**, 5597–5609.

Beck, P., Chaussidon, M., Barrat, J.A., Gillet, P., Bohn, M., 2006. Diffusion-induced lithium isotopic fractionation during the cooling of magmatic rocks: the case of pyroxene phenocrysts from nakhlites meteorites. *Geochim. Cosmochim. Acta.* **70**, 4813–4825.

Birck, J.L., Lugmair, G.W., 1988. Nickel and chromium isotopes in Allende inclusions. *Earth Planet. Sci. Lett.* **90**, 131–143.

Chaussidon, M., Gounelle, M., 2006. Irradiation processes in the early solar system. In: Lauretta, D., Leshin, L. (Eds.), *Meteorites and Early Solar System II*. Arizona University press, pp. 323–339.

Chaussidon, M., Robert, F., 1995. Nucleosynthesis of ^{11}B-rich boron in the pre-solar cloud recorded in meteoritic chondrules. *Nature* **374**, 337–339.

Chaussidon, M., Robert, F., 1998. ^{7}Li/^{6}Li and ^{11}B/^{10}B variations in chondrules from the Semarkona unequilibrated chondrite. *Earth Planet. Sci. Lett.* **164**, 577–589.

Chaussidon, M., Robert, F., McKeegan, K.D., 2006. Li and B isotopic variations in an Allende CAI: evidence for the in situ decay of short-lived ^{10}Be and for the possible presence of the short-lived ^{7}Be in the early solar system. *Geochim. Cosmochim. Acta* **70**, 224–245.

Chaussidon, M., Robert, F., McKeegan, K.D., Krot, A.N., 2001. Lithium and boron isotopic compositions of refractory inclusions from primitive chondrites: a record of irradiation in the early solar system. *LPS*XXXII #1862.

Coogan, L.A., Kasemann, S.A., Chakraborty, S., 2005. Rates of hydrothermal cooling of new upper oceanic crust derived from lithium-geospeedometry. *Earth Planet. Sci. Lett.* **240**, 415–424.

Giletti, B.J., Shanahan, T.M., 1997. Alkali diffusion in plagioclase feldspar. *Chem. Geol.* **139**, 3–20.

Gounelle, M., Shu, F.H., Shang, H., Glassgold, A.E., Rehm, K.E., Lee, T., 2006. The irradiation origin of beryllium radioisotopes and other short-lived radionuclides. *Astrophys. J.* **640**, 1163–1170.

Leya, I., Halliday, A.N., Wieler, R., 2003. The predictable collateral consequences of nucleosynthesis by spallation in the early solar system. *Astrophys. J.* **594**, 605–616.

MacPherson, G.J., Huss, G.R., Davis, A.M., 2003. Extinct ^{10}Be in type A calcium–aluminum-rich inclusions from CV chondrites. *Geochim. Cosmochim. Acta* **67**, 3165–3179.

Moshalenko, I.V., Mashnik, S.G., 2003. Evaluation of production cross sections of Li, Be, B in CR. In: Kajita, T., Asaoka, Y., Kawachi, A., Matsubara, Y., Sasaki, M. (Eds.), *Proc. 28th Intl. Cosmic Ray Conf.*, pp. 1969–1972.

Murty, S.V.S., Goswami, J.N., Shukolyukov, Y.A., 1997. Excess Ar-36 in the Efremovka meteorite: a strong hint for the presence of Cl-36 in the early solar system. *Appl. J. Lett.* **475**, L65–L68.

Podosek, F.A., Zinner, E., MacPherson, G.J., Lundberg, L.L., Brannon, J.C., Fahey, A.J., 1991. Correlated study of initial ^{87}Sr/^{86}Sr and Al-Mg isotopic systematics and petrologic properties in a suite of refractory inclusions from the Allende meteorite. *Geochim. Cosmochim. Acta* **55**, 1083–1110.

Robert, F., Chaussidon, M., 2003. Boron and Lithium isotopic composition in chondrules from the Mokoia meteorite. *LPS*XXXIV #1344.

Stolper, E., Paque, J.M., 1986. Crystallization sequence of calcium-aluminum-rich inclusions from Allende: the effects of cooling rate and maximum temperature. *Geochim. Cosmochim. Acta* **50**, 1785–1806.

Young, E.D., Simon, J.I., Galy, A., Russel, S.S., Tonui, E., Lovera, O., 2005. Supra-canonical ^{26}Al/^{27}Al and the residence time of CAIs in the solar protoplanetary disk. *Science* **308**, 223–227.