

Discussion

Reply to: “Recycled” volatiles in mantle derived diamonds—Evidence from nitrogen and noble gas isotopic data

Cécile Gautheron^{a,b,*}, Pierre Cartigny^c, Manuel Moreira^b,
Jeff W. Harris^d, Claude J. Allègre^b

^a *UMR Interactions et Dynamique des Environnements de Surface (UMR 8148 CNRS),
Université Paris 11, Orsay, 91405 Orsay Cedex, France*

^b *Laboratoire de Géochimie et Cosmochimie (UMR 7579 CNRS), Institut de Physique du Globe de Paris,
Université Paris 7, 4 place Jussieu 75252 Paris cedex 05, France*

^c *Laboratoire de Géochimie des Isotopes Stables (UMR 7047 CNRS), Institut de Physique du Globe de Paris,
Université Paris 7, 4 place Jussieu 75252 Paris cedex 05, France*

^d *Department of Geographical and Earth Sciences, Gregory Building, University of Glasgow,
Glasgow G12 8QQ, Scotland, UK*

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Abstract

In a reinterpretation of our published rare gas data obtained on polycrystalline diamonds from the Orapa kimberlite (Botswana) [C.E. Gautheron, P. Cartigny, M. Moreira, J.W. Harris and C.J. Allègre, Evidence for a mantle component shown by rare gases, C. and N isotopes in polycrystalline diamonds from Orapa (Botswana), *Earth Planet. Sci. Lett.*, 240 (2005) 559–572.], Mohapatra and Honda [R.K. Mohapatra, and M. Honda, “Recycled” volatiles in mantle derived diamonds—evidence from nitrogen and noble gas isotopic data, *Earth Planet. Sci. Lett.*, this issue, 2006.] claim that mixing between a-priori defined proportions of subducted seawater, subducted recycled oceanic crust, recycled sediments, air and the mantle would be more appropriate to account for the observations. This view sharply contrasts with our conclusions that the chemical and isotope compositions of rare gases record diamond formation from mantle-derived fluid(s) together with mantle post-crystallization radiogenic/nucleogenic/fissiogenic ingrowth and preferential diffusion of the lightest atoms out of the diamonds in the mantle [C.E. Gautheron, P. Cartigny, M. Moreira, J.W. Harris and C.J. Allègre, Evidence for a mantle component shown by rare gases, C and N isotopes in polycrystalline diamonds from Orapa (Botswana), *Earth Planet. Sci. Lett.*, 240 (2005) 559–572.]. We present here reasons why the alternative view of Mohapatra and Honda [R.K. Mohapatra and M. Honda, “Recycled” volatiles in mantle derived diamonds—evidence from nitrogen and noble gas isotopic data, *Earth Planet. Sci. Lett.*, this issue, 2006.] is not supportable.

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1. On the subduction of rare gases

The evidence for the mixing model of Mohapatra and Honda [2] is presented in two figures ($^{40}\text{Ar}/^{36}\text{Ar}$ vs. $^{129}\text{Xe}/^{130}\text{Xe}$ and $^{36}\text{Ar}/^{130}\text{Xe}$ and $^{84}\text{Kr}/^{130}\text{Xe}$ vs.

* Corresponding author. Tel.: +33 1 69 15 67 83; fax: +33 1 69 15 48 91.
E-mail address: gautheron@geol.u-psud.fr (C. Gautheron).

$^{129}\text{Xe}/^{130}\text{Xe}$) in which there is a “recycled/subducted” endmember lying on one side, with the other endmember, on the opposite side, being the mantle. Mohapatra and Honda thus agree with our main conclusion, namely that a “mantle component” [1] is present within our samples. The discussion centers on whether some subducted volatiles may or may not be involved during diamond formation. In our view, the recycled endmember(s) assumed by Mohapatra and Honda [2] are weakly constrained, both chemically and isotopically.

The possibility of subducting rare gases from seawater or sediments is uncertain. If any rare gases from either seawater or sediments are partially lost through subduction-related devolatilization process(es), the resulting fractionation of chemical ratios of rare gas (e.g. $^{36}\text{Ar}/^{130}\text{Xe}$ or $^{84}\text{Kr}/^{130}\text{Xe}$) would depend upon the scale of that devolatilization. It is often proposed that subducted oceanic crust would undergo >90% dehydration [3,4]. Therefore how rare gases could be subducted without any relative fractionation is heavily reliant on the assumption that some amount of seawater within the subducting, dehydrating altered oceanic crust remains unmodified. This possibility remains elusive (see [5]). The lack of constraints on the scale of devolatilization is recognized by Mohapatra and Honda [2]. They note that it is “*not feasible to derive reliable [...] chemical ratios ($^{36}\text{Ar}/^{130}\text{Xe}$ and $^{84}\text{Kr}/^{130}\text{Xe}$)*” of the subducted components. These authors then neglect devolatilization and assume unmodified seawater is subducted. We believe that these authors have arbitrarily assumed chemical ratios and a consequence of this approach is that the true mixing hyperbolic curve of their Fig. 1 is very poorly constrained.

In addition, the authors also neglect the importance of time-integrated radiogenic, nucleogenic and fissiogenic ingrowth that would make isotope ratios distinct from modern seawater or present crustal material. As time would lead to isotope ratios far different from modern seawater or present crustal material, the model developed by these authors would only be valid if the polycrystalline diamonds formed almost immediately after the material was subducted and also, that this material spent virtually no time in the mantle before being picked up by the kimberlite en route to the surface. This situation appears unlikely since present evidence shows that diamonds from Orapa have eclogitic and peridotitic inclusions which give genesis ages varying from 1.0 to 2.9 Ga for monocrystalline diamonds. Although these ancient ages may not apply to polycrystalline diamonds (see [1]), similar minerals to those of the inclusions are found on the surfaces of such diamonds. Significant residence times are also required/inferred to account for both advanced N-aggregation state and radiogenic ingrowth from He or Ne [1].

Furthermore, the contribution of subducted material is at odds with the observed mantle-like Xe-patterns that the present authors have taken as a key observation [1]. In summary, the formation of polycrystalline diamonds from subducted volatiles is thus inconsistent with the observations; if the low $^{36}\text{Ar}/^{130}\text{Xe}$ and $^{84}\text{Kr}/^{130}\text{Xe}$ result from mixing, it could only reflect a late stage addition of crustal water rather than subducted volatiles.

2. On the fractionation of stable isotopes at mantle temperatures

It is generally accepted that peridotite-related diamonds form from mantle-related carbon [6,7]. Only some eclogitic diamonds might form from subducted carbon and these would have odd isotopic values (e.g. sulfur, oxygen, carbon) (e.g. [6,7]). In our study [1], the identification of similar mantle-like Xe-patterns within both polycrystalline peridotitic and eclogitic diamonds was taken as further support for derivation from the same source. In addition, both monocrystalline and polycrystalline Orapa diamonds define similar trends in $\delta^{13}\text{C}-\delta^{15}\text{N}$, again suggesting that these diamonds have the same origin and formation ages.

To account for odd carbon and nitrogen isotope among eclogitic diamonds, high temperature fractionation in the mantle (from mantle-related carbon) has been proposed (e.g. [8], including monocrystalline diamonds from Orapa [9]). We also stress that coupled $\delta^{13}\text{C}-\delta^{15}\text{N}$ variations are incompatible with a mixing relationship involving recycled sediments (see [8,9] for reviews). “Evidence for the occurrence of subducted nitrogen” in either the diamond source region or in the sublithospheric mantle cited in [2] (see [10]) refers to studies which omit (despite decades of empirical and experimental demonstrations) the possibility of fractionation of light stable isotopes at mantle temperatures. Such a line of thought will always lead to the conclusion that any stable isotope variation would have to be produced by a mixing process(es); a circular argument which does not develop the subject.

We acknowledge however that some arguments in favor of a limited role of N-stable isotope fractionations at mantle have been presented by Mohapatra and Murty [11]. However, in the light of recent experimental evidence [12], both their data and arguments “*need to be reconsidered with caution*” [12].

3. Conclusions

We thus question the arguments presented by Mohapatra and Honda [2] proposing that there is some obvious subducted component(s) in the rare gases found

in polycrystalline diamonds. The chemical isotopic composition of rare gases in polycrystalline diamonds from Orapa can be best explained on the basis of mantle fluids and post-crystallization radiogenic/nucleogenic/fissionogenic ingrowths and diffusion out of the diamond. We believe that this is the simplest way to account for our observations without having to introduce a-priori assumptions and simplifications that would lead to inconsistencies, as Mohapatra and Honda [2] have done.

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