

Stability of aqueous neodymium complexes in carbonate-bearing solutions from 100-600°C

Corresponding Author: Dr Margaret Reece

This manuscript has been previously reviewed at another Nature Portfolio journal. This document only contains reviewer comments and rebuttal letters for versions considered at Communications Earth & Environment.

This file contains all editorial decision letters in order by version, followed by all author rebuttals in order by version.

Version 0:

Decision Letter:

**** Please ensure you delete the link to your author home page in this e-mail if you wish to forward it to your coauthors ****

Dear Dr Reece,

Your revised manuscript titled "Determination of the Stability of Aqueous Neodymium Complexes in Carbonate-Bearing Solutions from 100-600°C" has now been seen by our original reviewers #1 and #3, whose comments appear below. In light of their advice we are delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Earth & Environment, provided you address the remaining discussion points by Reviewer #3.

We therefore invite you to revise your paper one last time to address the remaining concerns of our reviewer. At the same time we ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work.

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We hope to hear from you within two weeks; please let us know if you need more time.

Best regards,

Carolina Ortiz Guerrero, Ph.D.
Associate Editor,
Communications Earth & Environment
Consulting Editor, Communications Sustainability

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

This review comes after the point-by-point responses and modifications of the manuscript by the authors, following my (and another referee's) review of their original manuscript submitted to Nature Communications.

Here I appreciate the detailed answers provided, and the rephrasing of some parts of the manuscript which makes the conclusion of the work less rigid and more convincing. The permittivity thing remains a point we might not agree about, but I'm totally OK with the way it is formulated now.

The only (very) small recommendation I have would be to reformulate more clearly the last sentence added to the abstract about the 'box model'. Indeed the term "to model the separation of Nd from Th" is a bit too dry. Maybe a few details about the context could be provided (box model, model and comparison to natural settings, etc.).

I reckon this work should now be published, and will add a solid contribution to the topic of REE transport by alkaline carbonate-bearing fluids.

Regards
Denis Testemale

Reviewer #3 (Remarks to the Author):

Dear editor and authors,

I read the manuscript with great interest, including the comments from previous reviewers and the authors' revisions and responses to those comments. I agree that this is a simple but effective study, which reveals the essential role of carbonate during hydrothermal REE mobilization. I would recommend it for publication, but not in its current form. Several major points in this manuscript still need to be revised or strengthened:

(1) This research is focused on REE mobilization in carbonatite systems. Therefore, it is highly necessary to give a brief introduction about the nature of REE ore-forming fluids in carbonatites. I recommend adding one or two sentences in Line 42 (before "Given the importance of carbonate ions ..."), to summarize the temperature ranges, chemical compositions, and REE concentrations in the fluid inclusions from typical carbonatite REE deposits (Maoniuping, Dalucao, Kalkfeld, Okorusu etc., can be easily found in the review made by Walter et al., 2021, ESR), with proper references being included. In particular, emphasizing that carbonate is an important component in REE ore-forming fluid (e.g., all reported REE daughter minerals in fluid inclusions are carbonates). This not only attracts and helps readers to build a general view about the REE ore-forming processes in carbonatites, meanwhile also provides additional supports for interpretation of your experiment results.

(2) The major finding of this research is that NdCO_3OH is the dominant REE complexation species in hydrothermal fluids. This contradicts to the conclusions from several well-known researches in two aspects: a) carbonate, instead of halogens or sulfate, acts as the predominant complexation ligands for REE in hydrothermal fluids. And b) alkalis contribute to REE mobilization, but not in a direct way (I agree with the second reviewer's point, that alkalis are essential at least for enrichment of carbonate anions). However, in the introduction section, the authors emphasized the argument on the role of alkalis (which needs to be revised, see below), but didn't mention the disagreements on REE complexation species in hydrothermal fluids. In my opinion, this is an even more important issue, as the viewpoint that REE mobilization is controlled by complexing with chloride or sulfate ligands has been widely accepted by geologists, whereas in this research, the authors confirmed that REE complexation with chloride contributes negligibly to REE mobilization. I believe this is the case, otherwise REE would be high enriched in Cl-enriched hydrothermal fluids, such as those in porphyry copper deposits, which turned out to be REE-depleted. I recommend the authors adding another one or two sentences to address the current disagreements on REE complexation species in hydrothermal fluids.

(3) Introduction about the disagreements on the role of alkalis in previous researches (Lines 50 - 56), even after revisions, is

still incorrect. Firstly, Anenburg didn't "reject" Louvel's idea, because he published his work BEFORE Louvel. In fact, Anenburg was one of the reviewers and supported Louvel's work during publication (you can find Anenburg's comments on Louvel's work in the supplementary materials). More importantly, Louvel investigated the mobilization of REE (La, Sm, Gd and Yb) in (CO₃²⁻, F- or OH⁻)-bearing fluids with salt concentrations ranging from 0.1 to 4.0 m. Whereas, the experiments by Anenburg only contains H₂O contents no greater than 6.5 wt.%. In other words, Louvel's experiment is about REE mobilization in hydrothermal fluids, but Anenburg's is clearly in relatively dry carbonate melt (the saturation content of water in carbonatite magmas is ~10 wt.%). It is inappropriate to compare the results from these two experiments directly. I suggest rephrasing this part (Lines 50 - 59) as follows:

while Anenburg and Yuan's work enhances the role of alkalis during REE mobilization in carbonatite melts or highly evolved brine-melts, the study by Louvel et al revealed that REE mobilization in hydrothermal fluids can be achieved via complexing with carbonate cations. In this study, we investigated the mechanisms of REE transport in aqueous liquids that falls into the conventional hydrothermal fluid categories.

Some minor revisions are as follows:

Line 12, I am not sure about the journal's policy, but I think it's necessary to give the full name of REE when firstly using this term, same for Nd in Line 20 and Th in Line 26.

Line 14, add "that" between "fluids" and "commonly".

Line 16, replace "researchers" by "researches", as some researchers changed their opinions among different researches.

Lines 17-18, replace "alkali metals control REE behavior ... required for ore formation" by "halogens or sulfate are the principle complexing ligands for REEs". As mentioned above, disagreements on REE complexation species in hydrothermal fluids is a more important issue, and should be included here.

Line 19, delete "the first". You don't need to emphasize that your work is "the first", readers would know.

Line 21, ranging from 100 to 600°C, or in the 100-600°C range.

Lines 24-26, rephrase the last sentence as: ... at temperatures of 500-600°C, which are sufficient to form REE-rich ores. Thermodynamic simulations also suggest that REE complexation with carbonate ligands could be the major cause for separation of REE from thorium (Th).

Lines 31-32, the shortage of REE resources are mainly due to: distribution and exploitation of REE resources being controlled by several countries.

Line 34, delete "pure". It's hard to determine that a REE deposit is "pure" hydrothermal.

Line 41, add "in silicate-associated systems" after "by acidic solutions".

Line 42, add a comma after "hydrothermal systems", this sentence is too long.

Line 98, add "carbocernaite or bastnäsita was used in Yuan's experiment, and" after even though. This should be enhanced, as different experiments using different REE minerals draw the same conclusion.

Lines 103-107, need to be rephrased. As mentioned above, Anenburg's experiment is about REE mobilization in carbonatite melt. Your experiment condition is comparable to that in Louvel's experiment, not Anenburg's.

Table 1, add the logK and logβ values for REE complexation species involving chloride, fluoride, etc., from previous studies by Migdisov et al. for comparison.

Line 128, add subtitles in this section, such as "REE complexation in hydrothermal fluids" before Line 129, "Th-REE separation by hydrothermal surges" before Line 162, and "Application for understanding the REE ore-forming process in Ashram" before Line 210.

Lines 174-186, this part belongs to the "Materials and Methods" section.

Lines 198-200, agreed. REE ore-forming processes in carbonatites and associated hydrothermal fluids are rather complicated, results from experiments provide basic understandings, interpretations for results from natural samples should be made with caution.

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We thank the editors and reviewers that have given their time and suggestions to our submitted manuscript. In this document is the detailed responses to the second round of reviewer comments. Reviewer comments are given below in black, with our responses in green. Full specific changes in the manuscript can be identified in the "full mark-up" file, with edits from this round denoted in red and edits from the previous round of modification in blue. The "clean" version of this work (which is what is referenced with specific line numbers in the following responses) conforms to standards communicated to us from the editorial staff at Communications Earth & Environment.

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

This review comes after the point-by-point responses and modifications of the manuscript by the authors, following my (and another referee's) review of their original manuscript submitted to Nature Communications.

Here I appreciate the detailed answers provided, and the rephrasing of some parts of the manuscript which makes the conclusion of the work less rigid and more convincing. The permittivity thing remains a point we might not agree about, but I'm totally OK with the way it is formulated now.

Thank you.

The only (very) small recommendation I have would be to reformulate more clearly the last sentence added to the abstract about the 'box model'. Indeed the term "to model the separation of Nd from Th" is a bit too dry. Maybe a few details about the context could be provided (box model, model and comparison to natural settings, etc.).

We acknowledge that specificity in the abstract, particularly as you pointed out in the first rounds of edits, helps readers to quickly evaluate an article for relevance. However, the abstract requirements for Comm E&E are less than 150 words (currently our word count is 149), and so we have attempted to keep key specifics of this work while being as concise as possible to conform to editorial standards.

I reckon this work should now be published, and will add a solid contribution to the topic of REE transport by alkaline carbonate-bearing fluids.

Thank you for your feedback, criticisms, suggestions and most importantly your time in helping us make this work what it has become.

Reviewer #3 (Remarks to the Author):

Dear editor and authors,

I read the manuscript with great interest, including the comments from previous reviewers and the authors' revisions and responses to those comments. I agree that this is a simple but effective study, which reveals the essential role of carbonate during hydrothermal REE mobilization. I would recommend it for publication, but not in its current form. Several major points in this manuscript still need to be revised or strengthened:

We are happy to hear that this work captured your interest and thank you for the positive summary.

(1) This research is focused on REE mobilization in carbonatite systems. Therefore, it is highly necessary to give a brief introduction about the nature of REE ore-forming fluids in carbonatites. I recommend adding one or two sentences in Line 42 (before “Given the importance of carbonate ions ...”), to summarize the temperature ranges, chemical compositions, and REE concentrations in the fluid inclusions from typical carbonatite REE deposits (Maoniuping, Dalucao, Kalkfeld, Okorusu etc., can be easily found in the review made by Walter et al., 2021, ESR), with proper references being included. In particular, emphasizing that carbonate is an important component in REE ore-forming fluid (e.g., all reported REE daughter minerals in fluid inclusions are carbonates). This not only attracts and helps readers to build a general view about the REE ore-forming processes in carbonatites, meanwhile also provides additional supports for interpretation of your experiment results.

Thank you for suggesting this reference, we have included a couple of sentences further elaborating carbonatite deposits and their relevance to rare earths on lines 33-34 starting with “Studies of fluid inclusions...” and “Commonly reported brine solutions...” at lines 41-42.

(2) The major finding of this research is that NdCO_3OH is the dominant REE complexation species in hydrothermal fluids. This contradicts to the conclusions from several well-known researches in two aspects: a) carbonate, instead of halogens or sulfate, acts as the predominant complexation ligands for REE in hydrothermal fluids. And b) alkalis contribute to REE mobilization, but not in a direct way (I agree with the second reviewer’s point, that alkalis are essential at least for enrichment of carbonate anions). However, in the introduction section, the authors emphasized the argument on the role of alkalis (which needs to be revised, see below), but didn’t mention the disagreements on REE complexation species in hydrothermal fluids. In my opinion, this is an even more important issue, as the viewpoint that REE mobilization is controlled by complexing with chloride or sulfate ligands has been widely accepted by geologists, whereas in this research, the authors confirmed that REE complexation with chloride contributes negligibly to REE mobilization. I believe this is the case, otherwise REE would be high enriched in Cl-enriched hydrothermal fluids, such as those in porphyry copper deposits, which turned out to be REE-depleted. I recommend the authors adding another one or two sentences to address the current disagreements on REE complexation species in hydrothermal fluids.

Thank you for your discussion of these points. However, we disagree with your conclusion that our data is a contradiction to what has been observed with halogens and sulfate. In our opinion, the limited discussions available for REE mobilization in carbonate-bearing fluids is due largely to the vast absence of thermodynamic information of their speciation in such fluids. Because of this, historical discussions and subsequent models were focused on a narrow range of deposits that were associated with acidic, carbonate-free fluids. Within these systems, indeed the main vehicle of rare earth transport was determined to be chloride and sulfate complexes. However, for carbonate-bearing fluids the main mechanism of transport has been poorly identified. Our conclusions are therefore not contradictory to these assumptions, but complementary. Additionally, the formation and accumulation of carbonate mineral deposits has stalled the investigation of carbonate as a mobilization ligand due to earlier classifications as a deposition ligand. What we have described in this work and what has been described in the four other heavily referenced articles (Nisbet, Louvel, Anenburg, and Yuan) support the perceived

shift of chloride's lower involvement in observed complexes than what has been traditionally accepted.

Towards the suggestion made for the inclusion of this topic in the manuscript, there is more discussion of these complexes in the second introductory paragraph, as the whole of this paragraph was rewritten, we can't point out specific instances. Another cautionary note regarding this matter is included at line 180-183 Inclusion of formation constants (prompted in a minor revision comment below) for these other complexes was also incorporated into the main text file's table. As the reviewer points out, the negligible contribution of chloride was mentioned in the previous submission, at what has now become line 121-123 (in the discussion section) and this study was not the first where this phenomenon was observed.

B) The changes related to this point are addressed in detail with the next reviewer comment.

(3) Introduction about the disagreements on the role of alkalis in previous researches (Lines 50 - 56), even after revisions, is still incorrect. Firstly, Anenburg didn't "reject" Louvel's idea, because he published his work BEFORE Louvel. In fact, Anenburg was one of the reviewers and supported Louvel's work during publication (you can find Anenburg's comments on Louvel's work in the supplementary materials). More importantly, Louvel investigated the mobilization of REE (La, Sm, Gd and Yb) in (CO₃²⁻, F⁻ or OH⁻)-bearing fluids with salt concentrations ranging from 0.1 to 4.0 m. Whereas, the experiments by Anenburg only contains H₂O contents no greater than 6.5 wt.%. In other words, Louvel's experiment is about REE mobilization in hydrothermal fluids, but Anenburg's is clearly in relatively dry carbonate melt (the saturation content of water in carbonatite magmas is ~10 wt.%). It is inappropriate to compare the results from these two experiments directly. I suggest rephrasing this part (Lines 50 - 59) as follows: while Anenburg and Yuan's work enhances the role of alkalis during REE mobilization in carbonatite melts or highly evolved brine-melts, the study by Louvel et al revealed that REE mobilization in hydrothermal fluids can be achieved via complexing with carbonate cations. In this study, we investigated the mechanisms of REE transport in aqueous liquids that falls into the conventional hydrothermal fluid categories.

We understand how the order in which these comments were originally presented can be construed as Anenburg's study being after Louvel's and we thank you for the rewording suggestion.

We have incorporated what we believe are the key messages from the above suggestion into how the second introduction paragraph has been restructured. Additionally, the results section has been reworded to sodium chloride's effect and specific mentions of Anenburg's study removed. The separate effects of sodium and chloride are still discussed briefly in the discussion section.

Some minor revisions are as follows:

Line 12, I am not sure about the journal's policy, but I think it's necessary to give the full name of REE when firstly using this term, same for Nd in Line 20 and Th in Line 26.

Yes, as this was originally a transferred manuscript, a portion of the formatting from the previous submission was incorrect. See our next response.

Line 14, add "that" between "fluids" and "commonly".

Line 16, replace "researchers" by "researches", as some researchers changed their opinions among different researches.

Lines 17-18, replace "alkali metals control REE behavior ... required for ore formation" by "halogens or sulfate are the principle complexing ligands for REEs". As mentioned above,

disagreements on REE complexation species in hydrothermal fluids is a more important issue, and should be included here.

Line 19, delete “the first”. You don’t need to emphasize that your work is “the first”, readers would know.

Line 21, ranging from 100 to 600°C, or in the 100-600°C range.

Lines 24-26, rephrase the last sentence as: ... at temperatures of 500-600°C, which are sufficient to form REE-rich ores. Thermodynamic simulations also suggest that REE complexation with carbonate ligands could be the major cause for separation of REE from thorium (Th).

As mentioned in the response to reviewer #1’s suggestion, much of the abstract had to be more concisely worded to fit within the requirements of this journal. We appreciate the suggestions and incorporated them into the abstract before refining.

Lines 31-32, the shortage of REE resources are mainly due to: distribution and exploitation of REE resources being controlled by several countries.

Added “by a small number of countries” to the end of the sentence; line 28

Line 34, delete “pure”. It’s hard to determine that a REE deposit is “pure” hydrothermal.

Changed purely to “substantially”; line 30

Line 41, add “in silicate-associated systems” after “by acidic solutions”.

Updated as recommended; line 38-39

Line 42, add a comma after “hydrothermal systems”, this sentence is too long.

Sentence split instead for clarity; line 41

Line 98, add “carbocernaite or bastnäsite was used in Yuan’s experiment, and” after even though. This should be enhanced, as different experiments using different REE minerals draw the same conclusion.

Updated as recommended at this line (91), and an additional statement regarding this observation was added to the discussion (sentence starts on line 117-119).

Lines 103-107, need to be rephrased. As mentioned above, Anengurg’s experiment is about REE mobilization in carbonatite melt. Your experiment condition is comparable to that in Louvel’s experiment, not Anenburg’s.

As mentioned above, specific reference to Anenburg’s experiment has been removed and the whole paragraph refocused to NaCl instead of just Na; lines 97-108

Table 1, add the logK and log β values for REE complexation species involving chloride, fluoride, etc., from previous studies by Migdisov et al. for comparison.

Formation constants (log β) are now included in the table for available chloride, fluoride, and sulfate species. Log K values would be misleading since phosphates were not used as a reference mineral in those studies.

Line 128, add subtitles in this section, such as “REE complexation in hydrothermal fluids” before Line 129, “Th-REE separation by hydrothermal surges” before Line 162, and “Application for understanding the REE ore-forming process in Ashram” before Line 210.

We agree subsections would make navigating this section easier to readers, however per the journal’s editorial requirements only the results and methods sections are allowed to have distinguished sub-headings

Lines 174-186, this part belongs to the “Materials and Methods” section.

Updated as recommended; lines 257-269

Lines 198-200, agreed. REE ore-forming processes in carbonatites and associated hydrothermal fluids are rather complicated, results from experiments provide basic

understandings, interpretations for results from natural samples should be made with caution.
Thank you.