Reviewers' Comments:

Reviewer #1 (Remarks to the Author)

This manuscript, submitted by Cerantola and co-authors, is potentially a very nice paper reporting the structures and stability of two "new" tetrahedrally co-ordinated carbonates that form from a $FeCO_3$ precursor at lower mantle conditions. The authors performed laser-heated diamond anvil cell experiments on synthetic single crystals of $FeCO_3$ at a range of PT conditions. Their results include reports of the HS-LS transition in siderite, bracketing of the melting temperature and subsequent dissociation of siderite, in-situ Mössbauer of $FeCO_3$ and its high PT products. These are in addition to the formation conditions and structure of $Fe_4C_3O_{12}$ and $Fe_4C_4O_{13}$ which are the "new and exciting" results of this work, however I note both that the latter carbonate is the iron end-member composition of the tetrahedral carbonate reported by Merlini et al (2015). Additionally, I believe there are some significant omissions, particularly in the methods description and of essential data, which must be provided for publication. These additions are necessary to fully assess the robustness and reliability of the results, which is especially important given the authors appear to demonstrate the structures provided in a previous paper were incorrectly refined. However, both the stability and crystal chemistry of the new phases are reasonable, so I see no reason why this should not, with revisions, become an good publication. Below I outline my suggested amendments and comments.

1. The authors report the discovery of a never-seen-before carbonate phase, with a structure that is, to the authors knowledge, different from any other compounds. The lattice parameters, structure, chemistry and stoichiometry are all determined based entirely on the refinement of a diffraction pattern collected at 97 GPa, however this pattern is not included in this submission. This makes it very hard to truly evaluate the quality of the refinement or the data - I believe this must be added before publication, possibly in supplementary information (SI).

The starting materials in experiments are single crystals of $FeCO_3$, however it is unclear whether the product $Fe_4C_3O_{12}$ is also a single crystal, or a powder. The authors suggest it is a single crystal, but without a 2D diffraction image it seems more likely, especially considering the different stoichiometry of the product, to either be a powder or multiple/twinned crystals.

There is very little information provided in the Methods to indicate how the authors proceeded from a diffraction pattern to full refinement of crystal chemistry. Whilst I understand how this is feasible, some indication of the steps taken, including any assumptions made and the reasons for such assumptions should be described in detail, e.g. did the authors use the refined unit cell volumes to guide stoichiometry, how many missing reflections of the predicted refelctions were there, were there any extra reflections, how did they deal with peaks from unreacted $FeCO_3$ starting materials etc. Some of these assumptions lead to the conclusion that all the iron in this phase is ferric, however, if this is the case why are there four components of the mössbauer spectra in Fig S2a? Surely there should be one from $FeCO_3$ and two from $Fe_4C_3O_{12}$, and the spectra suggests the phase is magnetic unless I am mistaken? The authors should comment on this?

It is also notable that the quality of the refinement for $Fe_4C_3O_{12}$ is significantly worse than that for $Fe_4C_4O_{13}$ (larger GooF, R1). Why is this? This should be discussed. Also, the text says there were ~300 independent reflections, but Table S1 suggests > 1700...

Given this is the first ever report of this structure, it is rather hard to visualise the structure using fig 2 alone. Perhaps more views of the structure could be added in SI.

It is assumed that this phase is produced in addition to diamond, is there any evidence for this in the form of debye rings in the diffraction. The authors do mention Raman spectra, but do not show them, this would be helpful.

2. The methods, in general, are extremely brief. In order to find out several pieces of key information it was necessary to look up other papers, and I remain uncertain of several points. The

authors shouldn't make it hard for readers in this way.
How was it verified that there was no temperature gradient across the sample? For instance, the normal setup on ID-27 (ESRF) uses a 2-5 micron pinhole, and therefore you cannot check this easily. Do the other setups used also collect temperatures using a pinhole, or do they use a 1D slit, collecting a profile across the whole sample? Are there examples of these profiles?
Is it known whether the starting material contain no Fe^{3+}? As there is a mixed singlet/doublet spectrum at RT at 44 GPa, which could be in the starting material, or a partial transition from HS to LS.
Was recovery of the samples attempted? If so, is it known when they become amorphous/back transformed? Is this why chemical analysis using FIB, or other, wasn't attempted? Or was it attempted, as this would significantly strengthen the case for a completely new stoichiometry and chemistry.
How many independent experiments were there, and what was their individual PT paths? This particular info would be very helpful if included in a table.
How many and which diffraction patterns were single crystal, and how many were powder patterns?
The caption of fig S3 says see methods to explain something that isn't present.

3. The structural transformation sequences of the new tetrahedral carbonates are rather confusingly presented at the moment. This isn't helped by the confusing nature of Figure 1, and the poorly defined colours of the various symbols, I think there is an opacity/layering problem that is affecting the printed colours. Perhaps a key would be useful, rather than just a figure caption description? A record of the PT paths of each experiment would also be helpful, perhaps as arrows on the figures.
Are the oxide phases that form in addition to $Fe_4C_4O_{13}$ always consistent? It is mentioned that they can sometimes be refined from xrd, can we see an example pattern.
Line 324 suggests that $FeCO_3$ transforms directly to $Fe_4C_4O_{13}$, which is misleading because throughout other parts of the manuscript it is argued that it forms from reaction of $Fe_4C_3O_{12}$, so without this precursor it would not form.
Is there evidence for the growth of $Fe_4C_4O_{13}$ at the expense of $Fe_4C_3O_{12}$, such as the strengthening/weakening of diffraction peaks.
Are both products always single crystals, as the authors suggest?
Do you ever completely get rid of $FeCO_3$ and $Fe_4C_3O_{12}$ in the high T samples with $Fe_4C_4O_{13}$? If this was the case the final product in the DAC must contain CO_2, diamond and an Fe-oxide (e.g. Fe_3O_4) alongside the $Fe_4C_4O_{13}$. If there are Raman spectra is there evidence of this?

4. The order of discussion is a bit clunky. I wanted discussion of potential decomposition/formation reactions for the various phases to be much earlier, or at least nearer to the description of the results they are relevant to. I would move the discussion about fitting the data of Liu et al to after the interpretation of your own results. Whilst the discussion in 2259-281 seemed like it was out of place.

5. From reading the manuscript it is apparent that, if these tetrahedral carbonate phases are going to form in the mantle, they will have to do so initially from carbonates in cold slabs (if the reactions you propose are correct). But it is also apparent from the structural fit of Liu et al's data, that both phases form extensive solid solutions with Mg endmembers. In the case of tetrairon orthocarbonate, it is clear that Mg significantly expands its stability field at the expense of the diiron diiron tetracarbonate structure, and to higher T. This goes completely unmentioned at the moment. Clearly, given the stability fields of the various carbonates, there is a clear PT path that must be followed for these new phases to form, but once existing they might remain at geotherm temperatures. This should be discussed more, and is one of the most significant implications of this work.

6. In lines 165-183 incongruent melting is discussed. The authors, like previous authors, suggest that dissociation of carbonate produces diamond + oxides. However, in this case, the current

results clearly show this "dissociation" occurs above the melting temperature. The is no clear evidence that this is an equilibrium reaction, or whether it is a quench phenomenon related to the DAC. It is possible it is related to diffusion in a large thermal gradient, that is accelerated in the presence of melt. It is certainly clear that it is not dissociation of siderite, this should be clarified.

7. From the data provided, the values in lines 293 and 294 should be 35.9 and 13.1 respectively.

Line 44: Oceanic sediments are not the only flux of carbon into the mantle, much comes from the oceanic crust and mantle beneath.

Line 46: There is no evidence that the diamond-hosted carbonates (calcite and dolomite) reported in Kaminsky 2012 come from the lower mantle. Those carbonate inclusions are in diamonds with no other reported inclusions. Thus they categorically do not prove that carbonates exist in the lower mantle, and I therefore believe this reference is confusing. The nyerereite and nahcolite inclusions also mentioned in this paper are actually described by Kaminsky (2009, Min Mag) and were reported as "lower mantle" carbonates. There are other references that report lower mantle carbonate inclusions, which may or may not actually be from the LM. Several carbonate microinclusions have been reported in diamonds containing ferropericlase with magnesite exsolution (e.g. Kaminsky, Can Mineralogist, 2015; Kaminsky, Mineral Petrology, 2015); many authors are currently arguing that these must represent lower mantle samples because of magnetite exsolution observed within the inclusions, however this still seems far from clear to me. Magnesite was reported in a diamond with another inclusion interpreted as "former bridgmanite" (Thomson CTMP 2014). Also, Brenker et al (2007) (EPSL) reported carbonates in equilibrium with "former calcium perovskite", which may have been from the lower mantle.

Line 60: I don't think Rohrbach and Schmidt actually show slabs will be more oxidised than surrounding mantle.

Line 361: Kelemen and Manning 2015 actually appear to conclude, based on their figure 5, that somewhere between none and almost all of the carbonate in slabs is subducted into the mantle.

There is at least one mistake in Table S4. The final entry was at 97 GPa.

28th July 2016.

Reviewer #2 (Remarks to the Author)

In this work the authors investigated the behavior of $FeCO_3$ at pressures over 100 GPa and temperatures over 2500 K in a laser-heated diamond anvil cell using a combination of single crystal X-ray diffraction and Mössbauer spectroscopy. The key finding is the discovery of two new Fe-bearing carbonates, $Fe_4C_3O_{12}$ and $Fe_4C_4O_{13}$ which is isostructural with recently reported $Mg_{1.6}Fe_{2.4}C_4O_{13}$ by Merlini et al. (2015). The latter observation suggests that ca. 35% of magnesium may be incorporated in the structure and that this structure may be an important phase to consider in the Erath’s deep interior. The authors conclude that the conditions in the Earth’s lower mantle may not lead to full decomposition of Fe-based carbonates - at least over the time–range of the experiments performed.

While the authors attempt to relate these and other findings to the stability of iron-bearing carbonates in the Earth’s deep interior, I found that the manuscript deviated from this theme and lost its coherency. I suggest, for example, that the details of structure and crystal chemistry of the newly-discovered iron carbonates be published in another manuscript. The details of the spin transition do not need a separate section. The manuscript should focus on the stability and the thermodynamic conditions of the decarbonation process in magnesium and iron-bearing carbonates. However, while this manuscript provides intriguing new details, this remains poorly constrained as seen in Figure 1 which attempts to compile all known data. The reactions depend critically upon the redox conditions and a further discussion of this subject is warranted. Thus, in its existing form, I cannot recommend that the manuscript be accepted for publication.

Reviewer #1

“This manuscript, submitted by Cerantola and co-authors, is potentially a very nice paper reporting the structures and stability of two "new" tetrahedrally co-ordinated carbonates that form from a FeCO3 precursor at lower mantle conditions. The authors performed laser-heated diamond anvil cell experiments on synthetic single crystals of FeCO3 at a range of PT conditions. Their results include reports of the HS-LS transition in siderite, bracketing of the melting temperature and subsequent dissociation of siderite, in-situ Mössbauer of FeCO3 and its high PT products.“

We appreciate that Reviewer #1 recognized the potential significance of our results.

“These are in addition to the formation conditions and structure of Fe4C3O12 and Fe4C4O13 which are the "new and exciting" results of this work, however I note both that the latter carbonate is the iron end-member composition of the tetrahedral carbonate reported by Merlini et al (2015).”

We clearly stated in the paper that $Fe_4C_4O_{13}$ is isostructural with $Mg_2Fe_2C_4O_{13}$, and we provide appropriate reference (ref. 23) (and we also explain why we consider the synthesis of pure iron compound $Fe_4C_4O_{13}$ important). $Fe_4C_3O_{12}$ on the other hand was synthesized by us for the first time. As Reviewer #1 certainly noticed, Dr. Marco Merlini is co-author of the present work, and we are sure he never published findings of the same phase before.

“ The authors report the discovery of a never-seen-before carbonate phase, with a structure that is, to the authors knowledge, different from any other compounds. The lattice parameters, structure, chemistry and stoichiometry are all determined based entirely on the refinement of a diffraction pattern collected at 97 GPa, however this pattern is not included in this submission. This makes it very hard to truly evaluate the quality of the refinement or the data - I believe this must be added before publication, possibly in supplementary information (SI).”

The structures of these novel iron carbonates were determined not from powder, but from single crystal diffraction data. We provide now as supplements CIF files which contain all crystallographic information as required by IUCr.

“The starting materials in experiments are single crystals of FeCO3, however it is unclear whether the product Fe4C3O12 is also a single crystal, or a powder. The authors suggest it is a single crystal, but without a 2D diffraction image it seems more likely, especially considering the different stoichiometry of the product, to either be a powder or multiple/twinned crystals.”

We thank the reviewer to highlight this point. All our structural refinements have been performed on single crystal domains that we identified in the diffraction patterns, see for example the 2D image, Fig. S1 in SI (added in the revised version). For instance, we refined the structure of $Fe_4C_3O_{12}$ at ~74 GPa after heating at ~1750 K, choosing one out of 4 identified single crystal domains. This does not mean we did not observe the signature typical for powder diffraction, however we could identify for all reported data single crystal domains that allowed us to perform single crystal structural refinement.

There is very little information provided in the Methods to indicate how the authors proceeded from a diffraction pattern to full refinement of crystal chemistry. Whilst I understand how this is feasible, some indication of the steps taken, including any assumptions made and the reasons for such assumptions should be described in detail, e.g. did the authors use the refined unit cell volumes to guide stoichiometry, how many missing reflections of the predicted refelctions were there, were there any extra reflections, how did they deal with peaks from unreacted FeCO3 starting materials etc.

It is also notable that the quality of the refinement for Fe4C3O12 is significantly worse than that for Fe4C4O13 (larger GooF, R1). Why is this? This should be discussed. Also, the text says there were ~300 independent reflections, but Table S1 suggests > 1700...”

We appreciate Reviewer #1 advise to include in the paper more methodological and technical details how structural analysis was performed. Fortunately, methodology of single crystal structural analysis at high pressure (and high temperatures) was rapidly developed over last few years, and the way “how the authors proceeded from a diffraction pattern to full refinement of crystal chemistry” is described in numerous publications of some of co-authors of current work and other colleagues (see, for example, refs. 8,16,23,26,27,39,48,), accumulated in special issues (particularly, High Pressure Research, 33, 2013), and in PhD Thesis (see, for example, https://epub.uni-bayreuth.de/2124/). It seems not feasible to summarize all these technological and computational procedures in few sentences. However, the method is currently applied by several groups, and fully established.

We supplement now the manuscript with CIF files (checked by UICr CIFchecker) which is supposed to address Reviewer's #1 concerns regarding assumptions, number of reflections used, etc. Please note that Table S2 (former Table S1, which present some data contained in CIFs) shows the absence of any constrains during structural solution and refinement (it also means that no assumptions were made to refine chemical composition), number of observables are 6 to 10 times larger than number of determined parameters, and we have quite high redundancy factors (i.e. number of observed reflection is 4.5-5 times higher than independent one).

Using additional experimental data and further analysis we improved quality of structural refinement of $Fe_4C_3O_{12}$ as shown in corresponding tables and CIF.

Reviewer #1 is absolutely correct, upon laser heating we get several single crystal domains of the same phase (and we now state it explicitly in the text), but modern crystallographic software (particularly CrysAlisPro which we are using) can handle this specific cases.

"Some of these assumptions lead to the conclusion that all the iron in this phase is ferric, however, if this is the case why are there four components of the mössbauer spectra in Fig S2a? Surely there should be one from FeCO3 and two from Fe4C3O12, and the spectra suggests the phase is magnetic unless I am mistaken? The authors should comment on this?"

As we explain above (and as it is also stated in the paper) the chemical composition of $Fe_4C_3O_{12}$ was determined directly by solving the structure of the material from single crystal X-ray diffraction data, without any additional assumption. Conclusion that all iron is ferric is made based on simple count.

As we explained in the text, the "accurate Mössbauer spectroscopy characterisation of the pure phase is difficult due to presence of other iron compounds in the laser-heated samples". For this reason it is not trivial to address the magnetic components observed in the spectrum. The intense magnetic sextet(s) could represent the two Fe-sites in $Fe_4C_3O_{12}$, because we did not observe any magnetic contribution in the Mössbauer spectrum of $Fe_4C_4O_{13}$ + Fe-oxides that we reported in Fig. S2b. However, since we could not isolate the orthocarbonate from the other phases we prefer to do not speculate on the magnetism of this phase for now. We would like also mention (and this is stated in the text as well) that all components in Mössbauer spectra collected on the samples containing HP-carbonate phases belongs to iron in high-spin state, and this we consider as important (and quit robust) result.

"Given this is the first ever report of this structure, it is rather hard to visualize the structure using fig 2 alone. Perhaps more views of the structure could be added in SI."

As Reviewer #1 proposes we add a new Fig. 2 with other views of the structures. Moreover, with this revised version of the manuscript we provide CIF files, so drawing and visualization of the crystal structure become immediate. Also, with slightly more effort, Table S2 (former Table S1) contains all necessary information to draw models of crystal structures.

"It is assumed that this phase is produced in addition to diamond, is there any evidence for this in the form of debye rings in the diffraction. The authors do mention Raman spectra, but do not show them, this would be helpful."

It seemto be not feasible to identify unambiguously diamond from weak powder diffraction lines in very complex environment of strongly scattering iron-bearing phases. As Reviewer #1 proposes we added Raman spectra in SI (Fig. S3).

" The methods, in general, are extremely brief. In order to find out several pieces of key information it was necessary to look up other papers, and I remain uncertain of several points. The authors shouldn't make it hard for readers in this way.

We fully agree with Reviewer #1 and often we experience the same problems reading papers in journals of Nature series. However, we have to obey Nature Communications rules which stay "*Methods should be written as concisely as possible*". So, we did our best to provide "*all elements necessary for interpretation and replication of the results*". We thank Reviewer #1 for pointing some weaknesses and try to address concerns as best as we can.

"How was it verified that there was no temperature gradient across the sample? For instance, the normal setup on ID-27 (ESRF) uses a 2-5 micron pinhole, and therefore you cannot check this easily. Do the other setups used also collect temperatures using a pinhole, or do they use a 1D slit, collecting a profile across the whole sample? Are there examples of these profiles?"

Temperature gradients in LH-DAC experiments are often present. They can be generated by misalignment between laser and X-ray beam, as well as by difference in sample absorption due to changing sample thickness or surface roughness. Using a small X-ray beam with respect to the laser-heating beam can prevent these situations, proven that they are well align with respect to each other and the sample size is smaller than the laser beam hot spot. In all our experiments we fulfilled these requirements and we feel safe to conclude that in within the measured area we did not have significant (higher than the reported experimental uncertainties) temperature gradients. Moreover, in revised version of the manuscript we explicitly state "*Methodological aspects of the high pressure experiments on these beam-lines are well establishe*[8,16,2326,48]". We explain in the manuscript that "Crystals (as a rule about 10 μm in diameter) were completely 'surrounded' by laser light and there were no measurable temperature gradients within the samples".

The laser heating set-ups at both ID27 (ESRF) and IDD-13 (APS) allow collecting temperature profile through the heated spot, and we have examples of such profiles. There are already many examples of such pictures in publications of our and other groups, and we do not think that adding one more profile (out of hundreds measurements performed during laser heating in this particular work) could contribute to justify the quality of experiments.

“Is it known whether the starting material contain no Fe3+? As there is a mixed singlet/doublet spectrum at RT at 44 GPa, which could be in the starting material, or a partial transition from HS to LS.”

The starting material has no Fe^{3+}. The presence of only Fe^{2+} has been confirmed by Mossbauer spectroscopy (Cerantola et al.[19]) and by single crystal diffraction. In fact, the question raised by Reviewer #1 is addressed in Ref. 19 and we explicitly refer to it.

As reported in the caption of Fig. 4 (former Fig. 3), the spectra at 45 GPa have been collected before (left) and during heating (right) at 570(50) K. The blue doublet corresponds to the high spin of ferrous iron whereas the red singlet stands for low spin state. The intensity (amount) of high spin component increases with increasing temperature.

“Was recovery of the samples attempted? If so, is it known when they become amorphous/back transformed? Is this why chemical analysis using FIB, or other, wasn't attempted? Or was it attempted, as this would significantly strengthen the case for a completely new stoichiometry and chemistry.”

We undertake few attempts to FIB recovered samples, but it proven to be difficult for small laser-heated crystals and material was lost (note we are not dealing with compact samples usually recovered after powder diffraction experiments). We continuously try to get TEM data on recovered materials, but we consider this part of work independent from that we are presenting here and, in fact, of secondary priority: (a) we obtained data about chemistry and structure of materials in situ by employing single crystal diffraction analysis (and Mössbauer spectroscopy as well), and (b) comparison of our results with literature reports show that TEM analyses of the recovered samples (even in combination with in situ powder diffraction) cannot provide the full picture of the chemical processes (for example, not all carbonate and oxide phases were identified) and give information about the crystal structures of the high pressure materials.

“How many independent experiments were there, and what was their individual PT paths? This particular info would be very helpful if included in a table.

How many and which diffraction patterns were single crystal, and how many were powder patterns?"

We provide new Table S1 (in SI) which contains information about all data-points shown on Fig. 1.

"The caption of fig S3 says see methods to explain something that isn't present."

We corrected figures captions and Methods. All necessary references (particularly, #50, #51, #52, #53, #54 and #56) are provided.

"The structural transformation sequences of the new tetrahedral carbonates are rather confusingly presented at the moment. This isn't helped by the confusing nature of Figure 1, and the poorly defined colours of the various symbols, I think there is an opacity/layering problem that is affecting the printed colours. Perhaps a key would be useful, rather than just a figure caption description? A record of the PT paths of each experiment would also be helpful, perhaps as arrows on the figures."

We did our best to improve the presentation; particularly, Table S1 is now added, and Fig. 1 is modified taking in to account Reviewer #1 suggestions.

"Are the oxide phases that form in addition to Fe4C4O13 always consistent? It is mentioned that they can sometimes be refined from xrd, can we see an example pattern."

The 2D image containing diffraction rings of HP-Fe_3O_4 is shown in Fig. 3. In Table S5 (former Table S3) we provide examples of the results of single crystal structural refinements of iron oxides we found in experiment with iron carbonate – $Fe_{13}O_{19}$, HP-Fe_3O_4, Fe_5O_7, and ppv-Fe_2O_3. We report lattice parameters, space groups, number of detected reflections (range from about 160 to over 400), R-factors, etc. Our results can be directly compared with data from ISCD data-base (for reader's convenience ref numbers are also provided), and thus phases identification is unambiguous.

Line 324 suggests that FeCO3 transforms directly to Fe4C4O13, which is misleading because throughout other parts of the manuscript it is argued that it forms from reaction of Fe4C3O12, so without this precursor it would not form.

We did our best to avoid any definite statements if $Fe_4C_4O_{13}$ may be obtained directly from $FeCO_3$. In particular, we wrote: "Laser heating of $FeCO_3$ at temperatures above 1750(100) K at pressures above ~74 GPa resulted in formation not only $Fe_4C_3O_{12}$ and iron oxides (see below) but also a monoclinic (space group *C2/c*, #15) phase". Later we explain: "The monoclinic *diiron(II) diiron(III) tetracarbonate*, $Fe_4C_4O_{13}$ appear only upon prolonged (about one hour) laser heating above 1650(100) K". In the Discussion section we consider different scenario which could lead to formation of $Fe_4C_4O_{13}$, and based on observations propose that it forms through decomposition of $Fe_4C_3O_{12}$. Experimental observations supporting our idea are presented on Fig. 5, where the progressive heating of $FeCO_3$ at different temperatures and constant pressure (~110 GPa) shows the transformation sequence: $FeCO_3 \rightarrow Fe_4C_3O_{12} \rightarrow Fe_4C_4O_{13}$.

Is there evidence for the growth of Fe4C4O13 at the expense of Fe4C3O12, such as the strengthening/weakening of diffraction peaks.

We obviously see some changes in relative intensities of the reflections, but in the complex diffraction patterns from mixtures containing several components (some powdered and some highly spotty polycrystalline) it would be too speculative to draw any conclusions based on such observations.

Are both products always single crystals, as the authors suggest?

Yes they are. But of course we observed powdered (or highly textured polycrystalline) patterns as well. Examples are given i.e. in Fig. 3 (former Fig. 4). See also the new Fig. S1 (added in the revised version) with the example of $FeCO_3$ transformation to $Fe_4C_3O_{12}$ and observation of new diffraction spots.

Do you ever completely get rid of FeCO3 and Fe4C3O12 in the high T samples with Fe4C4O13? If this was the case the final product in the DAC must contain CO2, diamond and an Fe-oxide (e.g. Fe3O4) alongside the Fe4C4O13. If there are Raman spectra is there evidence of this?"

In Fig. 1 we show a region of coexistence between $Fe_4C_3O_{12}$ and $Fe_4C_4O_{13}$. However, we have the case when samples treated at pressures about 100 GPa and temperatures above 2500 K contain $Fe_4C_4O_{13}$ and iron oxide(s) (Fe_3O_4 and Fe_2O_3). We did not observe CO_2 (and did not expect to observe because it is known that CO_2 is not stable at such conditions). We could not find evidences for presence of pure oxygen by diffraction, which is not so surprising – oxygen is low-Z material in comparison with iron-bearing compounds, and may also dissolve/mix with Ne pressure medium. As we mentioned in the text (and as it should be evident from Fig. S3 (which is added in this revised version), Raman spectroscopy in the presence of nanocrystalline diamond (and probably other highly fluorescing products of laser heating experiments) has no chances to spot oxygen.

"The order of discussion is a bit clunky. I wanted discussion of potential decomposition/formation reactions for the various phases to be much earlier, or at least nearer to the description of the results they are relevant to. I would move the discussion about fitting the data of Liu et al to after the interpretation of your own results. Whilst the discussion in 2259-281 seemed like it was out of place."

We thank the reviewer for the advise. As Reviewer #1 suggests we re-arrange the Discussion section, and particularly we wrote a new sub-section which dedicated to incorporation of Mg in CO_4-bearing carbonates.

"From reading the manuscript it is apparent that, if these tetrahedral carbonate phases are going to form in the mantle, they will have to do so initially from carbonates in cold slabs (if the reactions you propose are correct). But it is also apparent from the structural fit of Liu et al's data, that both phases form extensive solid solutions with Mg endmembers. In the case of tetrairon orthocarbonate, it is clear that Mg significantly expands its stability field at the expense of the diiron diiron tetracarbonate structure, and to higher T. This goes completely unmentioned at the moment. Clearly, given the stability fields of the various carbonates, there is a clear PT path that must be followed for these new phases to form, but once existing they might remain at geotherm temperatures. This should be discussed more, and is one of the most significant implications of this work."

We appreciate Reviewer #1 advise to discuss possible stability of Mg,Fe-orthocarbonate along the geotherm, and we followed this suggestion. However, we also feel that unless solid experimental evidences are at hands the idea should be formulated with caution.

"In lines 165-183 incongruent melting is discussed. The authors, like previous authors, suggest that dissociation of carbonate produces diamond + oxides. However, in this case, the current results clearly show this "dissociation" occurs above the melting temperature. The is no clear evidence that this is an equilibrium reaction, or whether it is a quench phenomenon related to the DAC. It is possible it is related to diffusion in a large thermal gradient, that is accelerated in the presence of melt. It is certainly clear that it is not dissociation of siderite, this should be clarified."

We agree with the reviewer that this might not be an equilibrium reaction. Indeed we cannot exclude that after prolonged heating (several hours, days?) $FeCO_3$ will completely decompose to form α-Fe_2O_3 or HP-Fe_3O_4. However, we earnestly described our results. Based on what we observed there are no evidences that dissociation of siderite is an artifact related to laser heating in DACs (at least because results in DACs and multi-anvil apparatuses are essentially the same).

“From the data provided, the values in lines 293 and 294 should be 35.9 and 13.1 respectively.”

Corrected.

“Line 44: Oceanic sediments are not the only flux of carbon into the mantle, much comes from the oceanic crust and mantle beneath.”

Corrected.

“Line 46: There is no evidence that the diamond-hosted carbonates (calcite and dolomite) reported in Kaminsky 2012 come from the lower mantle. Those carbonate inclusions are in diamonds with no other reported inclusions. Thus they categorically do not prove that carbonates exist in the lower mantle, and I therefore believe this reference is confusing. The nyerereite and nahcolite inclusions also mentioned in this paper are actually described by Kaminsky (2009, Min Mag) and were reported as "lower mantle" carbonates. There are other references that report lower mantle carbonate inclusions, which may or may not actually be from the LM. Several carbonate microinclusions have been reported in diamonds containing ferropericlase with magnesite exsolution (e.g. Kaminsky, Can Mineralogist, 2015; Kaminsky, Mineral Petrology, 2015); many authors are currently arguing that these must represent lower mantle samples because of magnetite exsolution observed within the inclusions, however this still seems far from clear to me. Magnesite was reported in a diamond with another inclusion interpreted as "former bridgmanite" (Thomson CTMP 2014). Also, Brenker et al (2007) (EPSL) reported carbonates in equilibrium with "former calcium perovskite", which may have been from the lower mantle.”

We “soften” formulations and provide new references as Reviewer #1 suggests (refs. 6 and 7).

“Line 60: I don't think Rohrbach and Schmidt actually show slabs will be more oxidised than surrounding mantle.”

Rohrbach and Schmidt[14] describe two mechanisms, redox freezing and redox melting, where carbonatite melts reduce and form diamonds (redox freezing) or diamonds oxidize forming CO_2 (redox melting). Both processes might happen at the 660 Km-discontinuity where the subducting lithosphere deflects into the transition zone or stagnate into the lower mantle (redox freezing) or during upwelling, when the lower mantle constituted mainly by Fe^{3+}-rich perovskite oxidizes diamonds due to the sudden increase in Fe^{3+} activity, which is not counterbalanced by an adequate amount for instance of metal iron (redox melting).

In their manuscript, Rohrbach and Schmidt[14] write: " **Starting from a subducting, locally carbonated relatively oxidized mafic to ultramafic lithosphere**, our experiments demonstrate that carbonatite melts will be generated in such lithosphere on thermal relaxation".

"Kelemen and Manning 2015 actually appear to conclude, based on their figure 5, that somewhere between none and almost all of the carbonate in slabs is subducted into the mantle."

We appreciate Reviewer #1 comment and incorporate it in the text.

"There is at least one mistake in Table S4. The final entry was at 97 GPa."

We thank Reviewer #1 for pointing it out, but this is not a mistake – at the moment of data collection of SMS pressure in the cell was 92(2) GPa.

Reviewer #2

"In this work the authors investigated the behavior of FeCO3 at pressures over 100 GPa and temperatures over 2500 K in a laser-heated diamond anvil cell using a combination of single crystal X-ray diffraction and Mössbauer spectroscopy. The key finding is the discovery of two new Fe-bearing carbonates, Fe4C3O12 and Fe4C4O13 which is isostructural with recently reported Mg1.6Fe2.4C4O13 by Merlini et al. (2015). The latter observation suggests that ca. 35% of magnesium may be incorporated in the structure and that this structure may be an important phase to consider in the Erath's deep interior. The authors conclude that the conditions in the Earth's lower mantle may not lead to full decomposition of Fe-based carbonates - at least over the time–range of the experiments performed.

While the authors attempt to relate these and other findings to the stability of iron-bearing carbonates in the Earth's deep interior, I found that the manuscript deviated from this theme and lost its coherency. I suggest, for example, that the details of structure and crystal chemistry of the newly-discovered iron carbonates be published in another manuscript."

We thank Reviewer #2 for the comments, however we do not agree with Reviewer #2 judgment that manuscript deviate from declared subject – stability of iron-bearing carbonates at conditions of deep Earth interiors. In fact, we would argue our work clarify the most fundamental question – could iron carbonates sustain pressure-temperature conditions of lower mantle, and if "yes" in which form they may exist. We demonstrate that self-redox reaction does not lead to the break down of carbonates to oxides (or elements), but instead results in the formation of more complex (and unexpected) compounds. We are fully convinced that without unambiguous identification of the products of the reactions and their phase/structural characterization any possible analysis of the fate of iron-bearing carbonates in the Earth interior would be just speculations. We are glad that Editor explicitly "recommend do keep" "presentation of the new crystal chemistry".

The details of the spin transition do not need a separate section.

As Reviewer #2 proposed we eliminate separate section on the spin crossover.

"The manuscript should focus on the stability and the thermodynamic conditions of the decarbonation process in magnesium and iron-bearing carbonates. However, while this manuscript provides intriguing new details, this remains poorly constrained as seen in Figure 1 which attempts to compile all known data. "

We do not understand why Reviewer #2 believes we have to focus on "decarbonation process". In fact, instead of "decarbonation" we observed formation of novel carbonates. This result is unambiguous and clearly reflected on Fig. 1.

"The reactions depend critically upon the redox conditions and a further discussion of this subject is warranted."

We agree with Reviewer #2 statement. In the revised version of the manuscript we explain that while only reaction (5) explicitly depends on oxygen fugacity, all other processes described in section "*Chemical transformations of* $FeCO_3$ *at high pressures and temperatures*" may be affected by redox conditions (or play role of buffering reactions in more complex process involving iron-bearing carbonates). Moreover, in the view of the recently reported (see for example Refs. 26,42) fundamental changes in the chemical behaviour of iron-oxygen system at pressures above ~70 GPa and high temperatures, our results are also calling for detail investigations of redox processes in lower part of Earth lower mantle and core-mantle boundary. Here we provide important new findings and information but we perfectly understand that the effort of one group is not sufficient to fully resolve the problem, and we hope that publication of our work will promote further studies in the direction also proposed by Reviewer #2.

Reviewers' Comments:

Reviewer #1:
Remarks to the Author:
I have read the revised manuscript and replies to the reviewers' comments, and have found the response convincing for the most part, and the authors have certainly managed to address my technical concerns. The key results of Cerantola et al. manuscript can be summarised as:

- The identification and structure determination of Fe4C3O12, the iron endmember of the high pressure carbonate structure reported by Merlini et al (2015).
- The identification and structure determination of Fe3C3O12 – a new high pressure carbonate mineral constructed from CO4 tetrahedra. It has also been confirmed that "siderite-II" from previous studies likely was this structure.
- That these tetrahedrally coordinated iron carbonates are stable at adiabatic temperatures. Combined with their ability to form partial solid solutions with magnesium-bearing compositions suggests they might exist in the Earth's lower mantle.

The new manuscript appears much improved, and presents a more concise and coherent report of the results. I retain the following issues, which need not necessarily be an impediment to publication of the study:

- In my opinion the authors still do not present a convincing argument demonstrating that there is a mechanism that would allow delivery of oxidised carbon into the deep mantle and thus, do not demonstrate that these new carbonate structures should be expected to be part of the lower mantle assemblage.
- It is not clear whether these structures are stable in mantle bulk compositions, which are much more magnesium-rich even that the study of Merlini et al. (2015). The relevance of endmember iron carbonates is not entirely clear.
- The interpretation of mössbauer spectra remains confusing. In my opinion, the lack of certainty surrounding this aspect of the manuscript acts to raise doubt, rather than support the key arguments.

Reviewer #2:
Remarks to the Author:
The authors have addressed all of the reviewers comments.

The revised manuscript is acceptable for publication in Nature.

Reviewer #1

"I have read the revised manuscript and replies to the reviewers' comments, and have found the response convincing for the most part, and the authors have certainly managed to address my technical concerns.

…

The new manuscript appears much improved, and presents a more concise and coherent report of the results."

We appreciate Reviewer #1 recognized our effort to improve the manuscript following his/her advises. We thank Reviewer #1 for supporting the publication of our manuscript.

"I retain the following issues, which need not necessarily be an impediment to publication of the study:

- In my opinion the authors still do not present a convincing argument demonstrating that there is a mechanism that would allow delivery of oxidised carbon into the deep mantle and thus, do not demonstrate that these new carbonate structures should be expected to be part of the lower mantle assemblage"

Presence of carbonates in lower mantle is not a hypothesis – it is proven by the finding of carbonates inclusions in diamonds (see, for example, Kaminsky F. (2012) Mineralogy of the lower mantle: a review of 'superdeep' mineral inclusions in diamond. Earth Sci. Rev. 110. 127–147, now added as a reference in the main text, Ref. 8) In our manuscript we report two new structures characterized by C-O tetramers with different degrees of polymerization (ortho- and tetracarbonate structures), and clearly demonstrate their stability at lower mantle conditions. Thus we provide evidence that certain form of carbonates may be present in Earth lower mantle. Uncover mechanism of their delivery to deep interiors or primordial nature is behind scope of the work.

"It is not clear whether these structures are stable in mantle bulk compositions, which are much more magnesium-rich even that the study of Merlini et al. (2015). The relevance of endmember iron carbonates is not entirely clear."

We thank Reviewer #1 to point this out, indeed we are aware of this. We performed this study starting from the $FeCO_3$ endmember in order to investigate the ultimate case of possible destabilization of iron-bearing carbonates due to self-redox reaction(s) at conditions of Earth lower mantle. We found that instead of full decomposition, iron carbonate formed novel compounds and thus we address the stability of Fe-carbonates. Of course, the next natural step is to study behavior of Mg-rich materials, and it is in focus of our research now.

“The interpretation of mössbauer spectra remains confusing. In my opinion, the lack of certainty surrounding this aspect of the manuscript acts to raise doubt, rather than support the key arguments.”

We believe Reviewer #1 refers to our attempt to fit the Mössbauer spectrum of the HP-carbonates phases. We fully agree with Reviewer #1 that analysis of very complex Mössbauer spectra reported in Fig. S2 is very difficult due to overlap of components from different phases and different iron species. Still, the data serve its purpose – assignment of possible oxidation states of iron in laser-heated samples. We are convinced that at the moment there is no any way to provide better resolved spectra, or spectra of pure phases, at conditions of our experiments. Thus, we believe that solid experimental data should be reported, with the intent as well to provide basis for further studies/analysis of different groups.

Reviewer #2

“The authors have addressed all of the reviewers comments.

The revised manuscript is acceptable for publication in Nature.”

We thank Reviewer #2 for his support to publish our manuscript in Nature Communications.