Interactive comment on “Turning sunlight into stone: the oxalate-carbonate pathway in a tropical tree ecosystem” by G. Cailleau et al.

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Referee 4

1) The objectives of the study are unclear, and are not well linked to the data that were collected. The below excerpts are the objectives that were stated. However, these are vague. How will the data collected specifically test a hypothesized model?

Intro Question: Does this system work with only the presence of oxalate (supplied by an oxalogenic tree) and soil oxalotrophic bacteria, as observed in Petri dishes, or do other key players need to be involved to make this system an efficient carbon sink?

Objective: Consequently, the aim of this study is to document and challenge our present-day knowledge about the oxalate-carbonate pathway involved in tropical settings. For this purpose, we propose to use microscopic and petrographic investigations, as well as stable isotopic measurements, to test the previously hypothesized model elaborated from experimental data obtained in the laboratory and described by Braissant et al. (2004).

Question in Discussion As a consequence, it seems that this system is unable to work only with both the oxalogenic tree and the soil oxalotrophic bacteria. So how does the system really work? Where does the transformation of oxalate into carbonate take place? To answer these questions, fluxes of matter are described and discussed using all observations made from the field to the microscopic scale.

Authors’ answer: Specifically, petrographic data show that, in absence of wounds on the trunk, the oxalate is not consumed by oxalotrophic bacteria in the wood itself. These data challenge the hypothesized model given by Braissant et al. (2004). From a general point of view, field, SEM, as well as optical observations, show the importance of termites feeding on wood. In the same way, the wood decay involving different guilds of organisms (e.g. termites, saprophytic fungi, etc) has been overlooked in laboratory experiments (currently, the rate of litter decay is being monitoring in order to address the specific point of the calcium oxalate release rate). This study gives a pertinent and extremely useful snapshot of the natural system leading to a refinement of the previous model, which left some unanswered questions. Concerning the questions that recurrently appear in the manuscript, our purpose is to invite the reader to follow our reasoning.

Authors’ answer: We agree.

2) The study needs more context. The previous papers by Braissant and other mentioned should be reviewed in more depth, and used to highlight what gaps are missing in our understanding of this system. It would also be useful to have more context about the study site, climate, soil C:N, soil pH etc.

Authors’ answer: We agree.
To be added in P 1081 in section 3.1

At Biga the site, the mean annual temperature (MAT) is 24.5°C the mean annual rainfall (MAR) is 1500 mm/yr. 5 dry months occur in this semi-deciduous forest belonging to the Guinean domain. At the Kani site, the MAT is estimated as equal to the Biga site, MAR is 1300mm/yr and there is a 6-month dry period occurring in this gallery forest belonging to the Sudanian domain. In the Massangam area (including the Massangam, Machatoum, and Mankaré sites), the MAT is 23°C and the MAR is 1800 mm/yr. These sites take place in the gallery forest belonging to the Guinean domain. The studied soils mainly belong to the reference soil group Ferralsol (WRB 2007).

3) More information about how this system is important in carbon cycling would help justify its importance. How common are trees that have this process? How much of the C sequestered by these trees ends up in carbonate? What is the approximate residence time of the carbonate?

Authors’ answer : As stipulated P1079 L19-20, this part of our work has already been published in Cailleau et al 2004. For instance, 960 kg of pure C as calcium carbonate (c.a. 8 tons) were quantified around a 170+/−30yr old iroko tree (this 14C dating is a revision of the age approximation of 80 yr given in Cailleau et al., 2004). In other words, on average (the system is obviously not working at the same rate throughout the tree’s life), around 5.76 kg of pure carbon were sequestered each year by this tree (half the rate given in Cailleau et al 2004 due to 14C dating revision). Calculation using the iroko distribution leads to the expectation of a potential lack of C sequestration into carbonate, due to deforestation, equal to 1.2x10−4 to 2.6x10−3 Pg/Cyr (see Cailleau’s PhD thesis manuscript available at http://doc.rero.ch/record/5512?ln=en for more information). The carbonate presence associated to iroko trees has been documented in several African countries such as the former Belgian Congo, i.e. the Democratic Republic of the Congo (Adriaens 1934, Plancquaert 1946), Ivory Coast (Carozzi 1967, our works), Uganda (Campbell and Fisher 1932, Harris 1932) and Cameroon (our work). Other trees in Africa seem to trigger the oxalate-carbonate pathway as well, but with a lower efficiency (unpublished data). On the other hand, recent field trips in South America and in India have revealed the presence of the oxalate-carbonate pathway around native trees (unpublished data). Regarding residence time, some recent research we have conducted in Burkina Faso shows that the soil carbonate residence time below the first 10 cm could be of the order of magnitude of 5000 yr.

4) The isotope data is not clearly related to each other between the pools measured. The tree tissues are the most depleted (-24 per mil), with the Ca-oxalate from live tissues and the burned Ca-oxalate also very depleted (-19 to 17 per mil). In contrast, the Ca-carbonate samples measured were less depleted (>−10 per mil) and more similar to CO₂ signature of the air (-6 to -8 per mil). While the isotope measurements were meant to clarify the pathway of carbon from trees to soil, these data do little to satisfy. It’s not obvious to me from this data that the C in Ca-carbonate is from C in Ca-oxalate. Could the authors identify two clear end members? Could another isotope (18O?) or marker be measured for a mixing model?

Authors’ answer : The two possible endmembers are the oxalate and the carbonate, although the soil respiration through the decay of organic matter obviously also contribute to the pool. But, this system is not a conventional system in which, on one hand, OM decay directly influences the soil atmosphere (CO₂), which in turn, is influenced by its diffusion towards the atmosphere. As the iroko system appears to provide huge amounts of oxalate, the rate of oxalate consumption is likely to be of great importance. The effect of burnt wood observed near the trunk is good example of the complexity of this system.
P1079 L20. Potential C sink of what magnitude?
Authors’ answer: see Cailleau et al. 2004 as cited. A revised calculation indicates a potential lack of C sequestration into carbonate due to deforestation over Africa equal to 1.2 x 10^{-4} to 2.6 x 10^{-3} Pg/Cyr (see Cailleau’s PhD thesis manuscript available at http://doc.rero.ch/record/5512?ln=en for more information).

Section 2 P1080-1081. Why not include more of an ecosystem perspective here about C sink potential?
Authors’ answer: The following sentence is added at the end of section 2.2
Recently, these carbonate accumulations were defined within the context of the Ivory Coast sites as a carbon sink (Cailleau et al., 2004). As a NT (Near Threatened) conservation status is attributed to the iroko tree, its related C sink could disappear within the range of the calculated C sequestration.
The following sentence is added at P1086 L24:
The Biga tree age was determined to be 170 ± 30 yr old by 14C dating. This age is about double the first estimate ased on information by locals, who knew that the tree was at least 80 yr old (Cailleau et al. 2004).

P1081 L19 binoculars? Do you mean hand lens?
L19: binocular microscope replaces binocular

P1081 why mention these other sites, but be vague about what you did there?

Authors’ answer: because the 14C age was determined for the Cameroon tree (Machatoum) and this tree provides replicates for oxalate C isotope as well.

P1082 L6 Do you have a citation from the bromoform method? Or is this the first time anyone has done it? Can you provide some validation for this method?

P1083 methods for Ca-oxalate separation. Same problem with validation. Any citations or evidence that this works? After precipitation of Ca-oxalate, how much of the sample was C from oxalate, versus some other source of C? It’s not clear that you removed the other C compounds for isotope analysis.
Authors’ answer: The acid dissolution is the most efficient method to quantify oxalate in wood (Clausen et al., 2008). When dissolved, oxalic acid is assumed to remain stable without C exchanges. After calcium addition and removal of the supernatant, followed by silicagel drying, the Ca-oxalate precipitate is observed under SEM. A single typical habit, a tetrahedral crystal of oxalate has been observed as in Francheschi and Horner (1980). In addition, crystals seemed to be very pure.

P1084 section 4.2–the purpose of the X-ray diffraction on these particular samples is not clear to me. Haven’t previous studies identified Ca-oxalate already in these tissues? The second sentence about Ca-carbonate in former roots does not seem to fit in this section. I think clarification and more details are needed.
P1085 L3 “there is no evidence of dissolution of these crystals”. Explain. In the figure caption you state that “Oxalate crystals (blue arrows) are embedded in the amorphous silica, which postdates the oxalatization.” The reason for your interpretations here are not immediately obvious.

Authors’ answer: First, “amorphous silica postdates oxalatization” means clearly that as described in figure 6, the process of oxalatization starts before the silicification. This does not mean that all the Ca-oxalate crystals are embedded in silica. Moreover, as shown in Figure 2 there are also Ca-oxalate crystals present in the wood tissues. Even if some of them can be observed embedded in Ca-carbonate, this is not the general case of Ca-oxalate crystals. If we consider all the Ca-oxalate crystals observed, there is no evidence of oxalate dissolution in these two types of tissue (bark or wood) except for the specific case of wounds.

Optical observations. Lots of studies have looked at images of Ca-ox crystals, could you emphasize here what is new-found information? Or be more clear about observing Ca-oxalate, versus Ca-carbonate versus silicates. And how do you know which is which from the images?

Authors’ answer: A full description is necessary to understand how and when the different steps occur as the iroko tree has never been studied in the framework of a temporal succession of mineralizations during the oxalate-carbonate pathway. It includes oxalate description, location, etc. How can we be clearer than presenting these phases as temporally displayed in a sequence of significant steps occurring in an oxalotrophic system? This is the newfound information!

Concerning the identification of these 3 phases, first the X-ray diffraction allows the identification of what is present in both bark and wood tissues. There is only silica and Ca-oxalate in the bark. Oxalate has a typical habit easily distinguished (sharp angles, straight edges) from silica, which also has a distinct birefringence hue in crossed polarized light (grey range). UV epifluorescence observations helped as well. X-ray diffraction tells us that only Ca-carbonate and Ca-oxalate are present in wood tissues. As Ca-oxalate has the same habitus in wood tissues as in bark, its identification is easy. Moreover, carbonate is easily distinguishable from oxalate as the two mineral species have distinct refringence and birefringence.

P 1085 L20. Explain Fig 3c also. The front of calcitization looks interesting, and how does it relate to the Ca-ox you saw dissolving?

Authors’ answer: The authors agree. The following sentence is added P 1090 L22 Only one example of oxalate consumption in wood tissue has been observed associated with some oxalate dissolution patterns (Fig. 3c): it is near a wound. It appears that some oxalotrophic bacteria can reach these oxalate crystals even if they are still embedded in wood. The calcitization front could act as a sort of a protection layer… This question remains open.

P1087 L10-12 this information should be in methods.

Authors’ answer: The main isotopic investigation has been conducted at the Biga site. Additional measurements have been performed at other sites in order to get a picture of the variability inside this type of system.

Moved from P1087 L10-12 to P1083 L15

P1087-1088 C isotopes section. It is not clear why these particular samples were
measured and the purpose of the measurement and the comparisons made. Why were averages taken?
Authors’ answer: First the Biga site was the most extensively sampled because it was up until then the most interesting site (in 2002) and also because some field logistical aspects did not allow more samples to be recovered from other sites. The Ivory Coast September 2002 civil war stopped any further investigations. Concerning the choice of the analysed samples, our purpose is to give a general view of the system; averages were calculated when multiple similar samples were available.

P1087 L18-19 which site is this sample from?
L19: (n =1, only from Biga site) replaces (n =1)

P1087 L 23 the average you calculated was based on which 11 samples? You report only 3 sample from Biga above. The average of the four values above does not equal -7.9.
Authors’ answer: Our mistake; the average corresponds to values listed as “Soil sample below the hollow trunk” in Table 1. There are 8 values, giving an average of -7.9‰ below the hollow trunk in figure 7.
L23 : were -7.9 ± 1.0‰ (n =8) replaces have been -7.9 ±09‰ (n =11)

L22 : the replaces these

P1087 L 24 which site was the soil from?

L23 : At the Biga site, in the replaces In the

P1088 L15 It’s not obvious that there is a fractionation occurring when oxalate oxides during incineration if you are not reporting the isotope value before burning. At Biga the Ca-ox isotope value you report is already depleted and was -19 per mil. P1088 L16 Or are these values the isotope values before incineration? Clarify. If so, why were the Ca-ox values from Biga so different?
Authors’ answer: isotopic values for Ca-oxalates extracted from wood are given in P1087 L1-4 as well as in the Table 1 P1101. C isotopic values obtained for carbonate resulting from incineration of extracted Ca-oxalate at 500°C are given in P1088 L10-14 as well as in the Table 1 P1101. If we consider values for each studied site, after incineration, there is an obvious fractionation, which values are given in P1088 L16-18. The authors do not see any problem for that specific point.

P1089 L5-6 What do mean that the system is unable to work with both the oxalogenic tree and the soil oxalotrophic bacteria? And how does this relate to wounds and oxalate dissolution in the tree tissues? Close attention to language and clarity is needed.
Authors’ answer: This means that because Ca-oxalate are not found free from their embedding organic matrix, this system needs another agent (saprophytic fungi, termites,…) to allow soil oxalotrophic bacteria to be in direct contact to Ca-oxalate crystals. The relationship with wounds is that, oxalotrophic bacteria can be put in contact with Ca-oxalate crystals in the wood itself in this specific case. Until now, the oxalotrophic process was only studied in laboratory experiments in which oxalotrophic bacteria were inoculated on plates with a Ca-oxalate enriched medium. This kind of work obviously cannot give insight into the true nature of the studied system. This is more than a simple process; this story is about a highly complex ecosystem.
More questions are being asked in the Discussion. The questions of your research should be clear before now.

Authors' answer: We do not agree. In the introduction we ask the question “Does this system work with only the presence of oxalate (supplied by an oxalogenic tree) and soil oxalotrophic bacteria, as observed in Petri dishes, or do other key players need to be involved to make this system an efficient carbon sink?”. As a reiteration acting as a transition sentence, we ask the question “how does the system really work?” which is not a new question. As clearly stated in the introduction “the aim of this study is to document and challenge our present-day knowledge about the oxalate-carbonate pathway involved in tropical settings.”

“In addition, at this step, oxalic acid excretion by roots is also a possible source.” This sentence seems out of order and should come after the following sentence. Also, not sure what you mean by “at this step”

Authors’ answer: The authors would not hide a process that undoubtedly should happen, even if they do not investigate this particular point, which is difficult to address.

Oxalate flux into the soil is not limited to the input of calcium oxalate crystals through litter renewal. Indeed, oxalic acid excretion by roots is also a possible source.

“In addition, at this stage, oxalic acid excretion by roots is also a possible source. Indeed, oxalate flux into the soil is not limited to the input of calcium oxalate crystals through litter renewal.”

“Milestones” does not seem to be the appropriate word for this section.

The most highly mineralized trees (hardened by calcite) are very often observed associated with traces of termite activity on the trunk. This is clearly expressed at the Mankaré and Biga sites cited in the present study where the trees had hollow trunks.

The most mineralized trees (hardened by calcite) are always observed associated with important concomitant termite effects on the trunk.

This paragraph is muddled. It sounds like termites do three things 1) consume wood tissue and release carbonates as they eat the surrounding wood, and 2) cause more of the tree to release more organic matter in general to the soil (like big slabs of wood) and 3) there is some association between termites and more carbonate production of the tree. I’m not sure if that is entirely correct?

The termites are doing these things, that’s true: by consuming wood tissue (bearing Ca-oxalate and carbonate) on the outer part of the tree itself, they produce wood slabs as well as “sawdust” flux (in doing this, termites increase the “normal litter forming organic matter flux”) to the soil. As a consequence, more carbonate is added to the soil. The increased oxalate flux to the soil will in consequence possibly increase the oxalotrophic effect on the soil with a consequence to possibly increase the rate of carbonate accumulation.
The writing in this section needs improvement to better guide the reader. The visualization jumps from live trees, to soil, back to live trees, back to soil and back to trees.

Authors’ answer:

How does the carbonate biomineralization take place inside the tree tissues? Thin section observations show that calcite biomineralization of the tree is not a consequence of an in situ oxalate consumption, i.e. in the wood tissues (Fig. 3a, b). According to Verrecchia et al. (2006), carbonate ions resulting from the oxalate oxidation are present in the aqueous soil solution. The oxalate oxidation takes place in the soil after the oxalate release from its embedding organic matter (Figs. 3e, 4a, b). This actually leads to a carbonate ion enrichment of the soil solution surrounding the oxalogenic tree. The calcitization of wood tissues is consequently induced by this soil solution (i.e., xylem sap) pumped through the roots.

Replaces

How does the carbonate biomineralization take place inside the tree tissues? According to Verrecchia et al. (2006), carbonate ions resulting from the oxalate oxidation are present in the aqueous soil solution. Thin section observations show that calcite biomineralization of the tree is not a consequence of an in situ oxalate consumption, i.e. in the wood tissues (Fig. 3a, b). The oxalate oxidation takes place in the soil after the oxalate release from its embedding organic matter (Figs. 3e, 4a, b). This actually leads to a carbonate ion enrichment of the soil solution surrounding the oxalogenic tree. The calcitization of wood tissues is consequently induced by this soil solution (i.e., xylem sap) pumped through the roots.

P1091 L1 “Lumberjacks” is a colloquial term, not sure it’s appropriate. Maybe try “those who harvest”

Authors’ answer:
P1091 L1: Lumberman replaces lumberjack

P1091 L11-19 “must be the result” of diffusion process of carbonate…. I’m still not clear how carbonate stays in solution in the sap and then precipitates at a certain point. L13 authors write “(and eventually Ca2+)” though, I cannot see why there is a time lag in Ca2+ uptake and movement in xylem sap. It seems that the arrival of Ca2+ would initiate Ca-carbonate precipitation, so what is here in parentheses is actually quite important and should be elaborated on.

Authors’ answer: Concerning the remark about “eventually Ca2+”, we speak about an XX-enriched sap, stating that this sap does not have to be enriched in Ca2+ but can be enriched. This is not a prerequisite for carbonate precipitation as long as the sap saturation index with respect to calcium carbonate allows its precipitation.

P1091 L20-P1092 L1-10 Some of the above comment is addressed here, although not very clearly. Is there a time-lag in Ca2+ in the xylem, or are both carbonate and Ca ions continually present but precipitation happens under dry conditions? These two sections need to be clarified and improved in writing.

Authors’ answer: As answered before, we do not imagine a time-lag but as mentioned by the referee, an hydric stress is more likely to enhance carbonate precipitation. The authors do not agree with the last referee’s remark

P1093 L13-15 This paragraph does not have any interesting information in it. Delete or explain.
There must be several alternative explanations that you did not address.

Regarding this point, we invite the referee to keep in mind that the presence of charcoal grains have been identified by Cailleau et al. (2005).

"confirms" is too strong language

This supports the assumption that calcite pseudomorphosis on wood tissues could be related to sap.

Replaces

This confirms that calcite pseudomorphosis on wood tissues is related to sap.

"DIC"... what do you mean by DIC?

dissolved inorganic carbon (DIC) replaces DIC

clarify language here and in the rest of the paragraph. There are two processes that change with depth, 1) CO2 in the soil decreases with depth and 2) oxalate concentrations from the tree decreased with depth. Are you saying that these two processes have opposite effects on DIC concentrations?

There is no mention of concentration, this paragraph only deals with isotopic signature. As a consequence, we discuss the influence of both “DIC” in equilibrium with organic matter oxidization (basic concept found in soil C isotopic investigations) and oxalotrophy, which in the context of the iroko tree, seems to be very important. So, the paragraph hypothesizes that the oxalotrophy strongly influences the DIC due to its assumed important rate.

what do you mean by variations?

We mean that some particular carbonate form present in very small amounts in some horizons correspond to unique features such as pseudomorphosed tissues or needle fibre calcite (NFC). NFC shows very depleted 13C signature (large standard deviation compared to mean value). See Cailleau et al 2009 as mentionned

section 5.4 It is less of a concern to define the tree itself as a micro-ecosystem than to describe the importance of this study to a larger ecosystem. For example, how much C is involved when you include the tree density of the larger ecosystem? How much of the tree’s C sequestration via photosynthesis ends up in calcite versus more rapidly decomposing pools?

For instance, 960 kg of pure C as calcium carbonate (c.a. 8 tons) were quantified around a 170+/−30yr old iroko tree (14C dating allowed the age approximation of 80 yr given in Cailleau et al., 2004 to be revised). In other words, on average (the system obviously does not work at the same rate throughout the tree’s lifetime) around 5.76 kg of pure carbon are sequestrated each year by the tree (the biomass is not taken into account). Calculation using the iroko distribution leads to the expectation of a potential lack of C sequestration into carbonate due to deforestation equal to 1.2×10^4 to 2.6×10^3 Pg/Cyr (see Cailleau’s PhD thesis manuscript available at http://doc.rero.ch/record/5512?ln=en for more information). Concerning the last question, we do not have any available data yet.
The conclusions may not be appropriate in that there is little clear mechanistic data in this study that sufficiently describes the functioning of this system. There is a proposed model, but I don't think that the pathways between measured pools were either illustrated/quantified/described with data as evidence.

Authors' answer: This model is based on multiscalar observations (field and thin section observations) described on pages 1084 to 1086. Some flux outputs are observed (e.g. termite role organizing wood tissues flux to the soil, litter formation, decay leading to the oxalate crystal release, etc.), others are assumed (atmosphere equilibration with aerial secretions, etc.).

General comment: Throughout the manuscript and especially the figures, you use all the terms: carbonate, calcite, CaCO3 and DIC. Please minimize the use of multiple words that mean the same thing. If there is a specific reason you are using one word over the other, you may want to explicitly alert the reader to the reason.

Authors' answer: Well, all these terms have different meanings: carbonate is a chemical species, calcite a mineral, CaCO3 a chemical formula of a compound, and DIC, the various carbonate species in solution (CO2\*, HCO3-, CO32-). We tried to use each term when appropriate.

Fig 6 This figure is not well described in the text. How do you know that this is a sequence of events?

Authors' answer: Observations give all the needed information to build this temporal sequence of events. This is one of the strengths of sedimentary petrography. See result section.

Fig 5 and Fig 7 Figure 7 is much more complicated. Can it be used instead of Fig 5, but first take the time to explain all the fluxes between the pools? Are all the same processes represented in both figures?

Authors' answer: Indeed, figure 7 is based on figure 5, which is the result of all the observations made during this study. This figure is designed in order to give to the reader a "naturalistic" view of the system. Figure 7 attempts to place all the C isotopic data obtained at the most studied site in an observational-based model. This gives a pertinent snapshot of such a system.

Fig 7 "Photosynthesis CO2 uptake d13C ∼ -6 to -8 per mil" was this measured? It's not mentioned in the methods. Is this the signature of CO2 in the air or of plant tissues?

Authors' answer: No, this is an assumption.

P1108: added in the caption: δ13C signature from atmospheric CO2 is given as an illustration, no measurement was performed.

Why just the isotope data from Biga? How does this related to the isotope data from the other sites? Can you add data (ex. From the wound secretion) from the other sites to fill in some of the missing pools, as an estimation?

Authors' answer: The Biga site was the most thoroughly investigated site. Due to polit-
cal issues (civil war), it has not been possible to conduct new field missions. Moreover, in contrast to the case of Ca-oxalate, for which we gave C isotopic signatures from all the visited sites, our approach concerning the carbon isotope from carbonate is different. Oxalate compounds are the direct result of photosynthetic processes and local atmospheric CO2 signatures (which can be considered as stable/known). There are numerous processes (i.e. oxalotrophy, DIC equilibrium reactions, as well as some other unknown processes such as bacterial induction for carbonate precipitation, etc) when considering the case of carbonate precipitation throughout the whole oxalate-carbonate pathway. In consequence, we do not wish (and we do not think it is not relevant) to give one piece of datum coming from a different site with a different setting.

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