Manuscript Number: GCA-D-15-00678R1

Title: Paired stable isotopes (O, C) and clumped isotope thermometry of magnesite and silica veins in the New Caledonia Peridotite Nappe

Article Type: Article

Corresponding Author: Mr. Benoit Quesnel, PhD

Corresponding Author's Institution: Géosciences Rennes, University of
Rennes1, UMR6118

First Author: Benoit Quesnel, MSc

Order of Authors: Benoit Quesnel, MSc; Philippe Boulvais, Ph.D; Pierre
Gautier, Ph.D; Michel Cathelineau, Ph.D; Cédric M John, Ph.D; Malorie
Dierick, MSc; Pierre Agrinier, Ph.D; Maxime Drouillet, MSc

Abstract: The stable isotope compositions of veins provide information on the conditions of fluid-rock interaction and on the origin of fluids and temperatures. In New Caledonia, magnesite and silica veins occur throughout the Peridotite Nappe. In this work, we present stable isotope and clumped isotope data in order to constrain the conditions of fluid circulation and the relationship between fluid circulation and nickel ore-forming laterization focusing on the Koniambo Massif. For magnesite veins occurring at the base of the nappe, the high $\delta^{18}\text{O}$ values between 27.8‰ and 29.5‰ attest to a low temperature formation. Clumped isotope analyses on magnesite give temperatures between 26°C and 42°C that are consistent with amorphous silica - magnesite oxygen isotope equilibrium. The meteoric origin of the fluid is indicated by calculated $\delta^{18}\text{O}_{\text{water}}$ values between -3.4‰ to +1.5‰. Amorphous silica associated with magnesite or occurring in the coarse saprolite level displays a narrow range of $\delta^{18}\text{O}$ values between 29.7‰ and 35.3‰. For quartz veins occurring at the top of the bedrock and at the saprolite level, commonly in association with Ni-talc-like minerals, the $\delta^{18}\text{O}$ values are lower, between 21.8‰ and 29.0‰ and suggest low-temperature hydrothermal conditions (~40-95°C). Thermal equilibration of the fluid along the geothermic gradient before upward flow through the nappe and/or influence of exothermic reactions of serpentinization could be the source(s) of heat needed to form quartz veins under such conditions.

Dear Editor,

Please find attached the revised version of manuscript #GCA-D-15-00678, entitled “Paired stable isotope (O, C) and clumped isotope thermometry of magnesite and silica veins in the New Caledonia Peridotite Nappe”, by B. Quesnel, P. Boulvais, P. Gautier, M. Cathelineau, C.M. John, M. Dierick, P. Agrinier and M. Drouillet, which required moderate revisions before final acceptance for publication in *Geochimica et Cosmochimica Acta*.

You can find on this file our answers (in red below) to reviewer’s comments.

Accordingly to these comments, the text and some figures have been modified. For the text, we have let these changes visible on the manuscript to make easier your lecture. Note also that we have taken into account the minor editorial suggestions of reviewers (for example those noticed in yellow boxes in pdf files); these changes do not appear in the new version. We have also built new tables that could be useful for the geochemists community; these calculations have been suggested by reviewers 1 and reviewer A. Gilg (we now present a temperature range for quartz formation of 40-95°C, instead of 40-80°C in the previous version; conclusions remain unchanged). These tables are introduced as electronic supplements to preserve the ms as short and clear as it was.

Best regards,
Benoit Quesnel and co-authors

Dear Editor,

Please find attached the revised version of manuscript #GCA-D-15-00678, entitled “Paired stable isotope (O, C) and clumped isotope thermometry of magnesite and silica veins in the New Caledonia Peridotite Nappe”, by B. Quesnel, P. Boulvais, P. Gautier, M. Cathelineau, C.M. John, M. Dierick, P. Agrinier and M. Drouillet, which required moderate revisions before final acceptance for publication in *Geochimica et Cosmochimica Acta*.

You can find on this file our answers (in red below) to reviewer’s comments.

Accordingly to these comments, the text and some figures have been modified. For the text, we have let these changes visible on the manuscript to make easier your lecture. Note also that we have taken into account the minor editorial suggestions of reviewers (for example those noticed in yellow boxes in pdf files); these changes do not appear in the new version. We have also built new tables that could be useful for the geochemists community; these calculations have been suggested by reviewers 1 and reviewer A. Gilg (we now present a temperature range for quartz formation of 40-95°C, instead of 40-80°C in the previous version; conclusions remain unchanged). These tables are introduced as electronic supplements to preserve the ms as short and clear as it was.

Best regards,
Benoit Quesnel and co-authors

Reviewer #1:

This is a very interesting paper that combines clumped isotope and stable isotope measurements in magnesite and quartz veins to constrain fluid conditions in the Peridotite Nappe of New Caledonia. The unique field location studied allows continuous sampling from the Serpentine Sole up through the laterite profile, which enables the authors to make conjectures about the nature of fluid circulation through the nappe and questions earlier models of fluid circulation during laterization. The combination of clumped isotope data in magnesite and $\delta^{18}\text{O}$ data in quartz not only allows the authors to draw conclusions about the temperatures and fluid $\delta^{18}\text{O}$ involved in the alteration events that occurred at this location, but may also provide some constraints on the most applicable choices of isotope fractionation factors for magnesite and quartz in similar environments. This study will be highly attractive to researchers whose interests include clumped isotopes, the formation of magnesite, laterization, peridotite alteration, and low-temperature hydrothermal circulation.

The paper was overall, well-organized and well-written, with the exception of a few typos and awkward phrasings. Overall, I think this is good work, but felt that some points required clarification and would like to see more details in some places, such that readers will be able to reproduce their calculations. Since line numbers were not provided, my line-by-line comments are not listed here, but are provided as comments on the attached pdf. The main points I would like to see addressed are as follows:

1) I am not convinced that you can be confident in the temperatures obtained from quartz $\delta^{18}\text{O}$. How do you know the $\delta^{18}\text{O}$ of the fluid from which the quartz formed?

Many quartz occurrences are associated with garnierite in fractures, at the base of the lateritic level. As a result, it is more than likely that garnierite and quartz veins formation is linked to the laterization process and record the downward circulation of meteoric fluid. This idea is largely defended in the literature.

The section 6.2 has been modified accordingly, and now specifies the range of $\delta^{18}\text{O}$ values from which the quartz formed.

Why should the $\delta^{18}\text{O}$ of the fluid that formed amorphous silica in the serpentine sole be the same as that which formed quartz in the saprolitic level?

Amorphous silica and quartz veins did not precipitate under similar conditions. However, a meteoric origin of the fluid for both the quartz veins (see above) and for the amorphous silica (which is in equilibrium with magnesite veins that derived from meteoric waters) is established. There is no reason to consider distinct $\delta^{18}\text{O}$ values for both types of silica.

What is the fluid $\delta^{18}\text{O}$ value that you used for your temperature calculations? It should be explained more clearly how you arrived at this value and perhaps how uncertainty in this value would translate into uncertainty in the temperature estimates.

Reviewer 1 is right. This point is now specified in section 6.2.

Why do you choose the quartz-water fractionation of Sharp & Kirschner 1994/ Zheng 1993? You demonstrated that these fractionation factors were inconsistent with the $\delta^{18}\text{O}$ and clumped isotope results obtained on coexisting magnesite and silica.

If the magnesite-quartz and magnesite-water fractionation of Zheng 1999 imply a quartz-water fractionation that is not consistent with other Sharp & Kirschner 1994/ Zheng 1993, how do you justify using different fraction factors in different parts of the discussion? It's not a fault of yours that these fractionation factors are not particularly well-constrained, but you should try to be as consistent as possible and discuss how your temperature estimates are affected by uncertainties due to the choice of fractionation factors.

In fact the oxygen fractionation factor between quartz and magnesite of Zheng (1999) is a combination of the oxygen fractionation factor between quartz and H_2O of Zheng (1993) and the oxygen fractionation factor between magnesite and H_2O of Zheng (1999). Thus, we used the oxygen fractionation factor between quartz and H_2O of Zheng (1993) in order to estimate the ranges of temperatures of formation of amorphous silica and quartz veins.

The section 6.2 has been clarified with respect to this point. If ever useful, what we believe for the geochemists community, we provide an electronic supplement S5 where various oxygen fractionation factor between silica and H_2O are compared.

2) Provide more details of clumped isotope methods and calculations:

-A little bit more of a short, introductory overview of what clumped isotopes are early on might be helpful too, since I imagine there will be readers who are very interested in the implications of this study for lateritization, hydrothermal circulation, etc, who are not familiar with the technique.

Right. A sentence has been added in the Introduction.

-Add supplementary table with all analyses, including each replicate analysis, standards, gases, raw data, and transfer function, such that data could be re-processed by other researchers if desired.

We have added an Electronic Supplement (S1) in which the detailed clumped isotope data are presented.

-If you have done work to demonstrate that 90°C digestion of magnesite for 1 hour results in complete digestion (e.g., same yield as for same number moles of calcite and/or that replicates with longer digestion times do not result in different stable and clumped isotope results), show that here as 1 hour is not always sufficient for complete digestion of magnesite.

In fact, the reaction time does not have influence on the $\delta^{18}\text{O}$ value (Das Sharma et al., 2002). Unfortunately, no publication on the influence of the reaction time on the Δ^{47} value is available to date in the literature. This work has however been done by Tobias Kluge and Pablo Del Real on magnesite samples at Imperial College of London (where the data presented in the present paper have been obtained); these researchers show that there is no influence on the Δ^{47} value. The corresponding publication is now submitted.

-I agree that using the calibration of Kluge et al 2015 is the best approach, but because that calibration is derived in the same laboratory as your magnesite data, not because it is similar to Bristow et al 2011. (The conclusion of Falk & Kelemen 2015 was not that Bristow et al 2011 provides the best calibration for magnesite generally, but that there is not a significant difference between magnesite, calcite, and dolomite so whatever calibration seems to apply in a particular lab for calcite should also apply for magnesite.)

Right. Text has been simplified accordingly (sentences deleted in section 6.1.1)

3) Try to make it as clear as possible where samples came from and what the sample materials are.

-In a few places, it can be a little confusing when you talk about brown silica whether you are talking about brown amorphous silica or brownish microcrystalline quartz.

Right. Throughout the ms, we have replaced “brownish micro-crystalline silica” by “brown micro-crystalline quartz” and “brown amorphous silica” by “brown opal”. This point was also raised by reviewer 3 A. Gilg.

-Perhaps add to Table 1 a column indicating what level of the nappe the sample is from (serpentine sole, moderately serpentinized peridotite, saprolitic level, etc), so readers do not have to refer to the map repeatedly.

Done.

4) Fix typos (Mis-numbered sections starting with "Oxygen isotopes in quartz veins and amorphous silica," some minor spelling and grammar issues as noted in pdf)

Done.

YELLOW BOXES

Introduction:

Another sentence or two introducing clumped isotopes may be helpful for readers not familiar with this technique.

Added

lower case?

Text modified : “a very promising tool, **particularly** in Earth Sciences”

allows temperatures of formation of carbonate to be estimated

Text modified.

Ni talc-like minerals, Ni serpentine-like minerals

Text modified (throughout the ms)

Is this list only intended to apply to magnesite formed in association with quartz/silica or also to any magnesite formed via carbonation of peridotite? If the latter, then Oman should also be included on the low temperature / meteoric list.

As you note, in Oman, some magnesite is formed via carbonation at hydrothermal conditions (Falk and Kelemen, 2015), but most magnesite veins in Oman are thought to form at low temperatures from fluid of meteoric origin (Kelemen et al. 2011, Streit et al. 2012).

Right. Oman added in the low temperature list. Streit et al. added in the reference list.

While it remains true that the carbonation events described in Beinlich at all likely did occur at hydrothermal conditions, their temperature estimates based on $\delta^{18}\text{O}$ isotopes were calculated incorrectly and using the correct forms of the equations for the fractionation factors that they

cite would have suggested that their mineral pairs were actually out of equilibrium. (Just noting that for your reference, not that you need to change anything here because of that).

Ok. Thanks for the precision.

Geological Setting:

Ni talc-like minerals

Text modified (throughout the ms).

You describe the saprolitic level as being part of the laterite profile and containing quartz and silica, while the peridotite below contains no silica, but on your map in figure 2, almost all quartz sampling locations are placed in the "Moderately serpentinized peridotites" section of the Peridotite Nappe. This is confusing.

Figure 2 has been modified; the saprolitic level now appears in the map.

Sampling and Samples

Pirogues River = Foue Peninsula + Kone??

nodular magnesite from Foue Peninsula??

trydimite from Bien Sur mine??

Figure 1, Table 1 and text have been modified.

Are these fibrous textures associated with monomineralic magnesite veins or are they associated with serpentine- or talc-like minerals?

Monomineralic. Text modified.

REF?

« Suggesting growth under mechanical stress » has been deleted. This sentence was not necessary.

optical microscopy or other techniques?

This is now specified in the ms.

Make sure you have consistent terminology throughout the text, as it can be slightly confusing whether "brown silica" refers to microcrystalline quartz or brownish amorphous silica, and if "quartz" refers only to "the clearer yellow, whitish to clear quartz."

Now specified throughout the ms.

Analytical techniques:

REF e.g., Ghosh et al. 2007

Really 2007? We have added Ghosh et al. 2006.

The phrase "in practice" seems a little odd here.

Text modified.

A few more details would be good.

Sample size? Common acid bath? Continuously trapped presumably?

Text modified.

Have you done any tests to demonstrate that magnesite is completely reacted? It would be good to show that the expected yield is achieved (e.g., bellows filled to the same percent as when an equal number of moles of calcite are reacted) and/or that the isotopic composition does not change for replicates reacted for even longer times.

See general comment #2 above.

What do you mean by "manually extracted"?

Deleted

Results:

Would be good to add supplementary table of all analyses, raw data, standards, gases, transfer function, etc.

We have added an Electronic Supplement (S1) in which the detailed clumped isotope data are presented.

This means between yellow/clear quartz and brownish-red microcrystalline quartz, right?

This could be slightly confusing to readers since you also describe brown amorphous silica.

Modified. See general comment #3 above.

Discussion :

6.1.1

Falk & Kelemen suggest that the Bristow calibration (on calcite and dolomite) provides the best agreement with magnesite formed at known temperatures not because it is the best calibration for magnesite generally, but because it is the calibration based on clumped isotope measurements made at Caltech and the clumped isotope data in Falk & Kelemen (2015) was also collected at Caltech. That is, inter-laboratory differences are important, but differences between different carbonate minerals are not. Therefore, you are correct in using Kluge et al (2015) for your clumped isotope temperature estimates, but this is because Kluge et al (2015) is calibration based in the same lab, not because it is similar to the calibration of Bristow et al. (2011) which worked well for magnesite in another lab.

(It is also good that you are using the same acid fractionation factor as Kluge et al 2015; both Bristow et al 2011 and Falk & Kelemen 2015 used an acid fractionation factor of 0.081. It is not clear what acid fractionation factor is true, but probably best to maintain consistency with the calibration used.)

Text modified. See general comment #2 above.

Useful outcome!

Indeed!

It would be much more convincing that magnesite + silica are in isotopic equilibrium and that your choice of fractionation factors is really the most applicable if you had multiple samples like this.

Unfortunately, we have only one sample with both magnesite and amorphous silica. Text has been slightly modified.

Yes - all the possible combinations can be quite frustrating!

Right. A supplementary material is now provided. Text has been adjusted accordingly.

Reviewer 3 A. Gilg also raised this point.

6.2 now 6.1.3

Why wouldn't this also fractionate oxygen isotopes?

At high pH, the C isotope system may well be affected by kinetic fractionation whereas the O isotope one may not (this is discussed in the references we indicate in the ms). Note also that we have moved this section in a new paragraph (#6.1.3 instead of 6.2) to lower its factual importance (this is clearly not the main point of our paper).

6.3 now 6.2

But didn't these quartz-water fractionations yield improbable temperatures for your magnesite-silica vein when combined with the magnesite water fractionation of Zheng 1999, which you used to estimate the d18O of the fluid, right?? Explain more precisely what the steps are involved here. What is the constant value of d18O that you are using and how did you calculate that? You previously discuss d18O fluid values calculated using clumped isotope temperatures and the magnesite-water fractionation of Zheng 1999. Are you just using the average value of those results? 1) If so, then aren't you combining two mineral-water fractionations that you previously noted were inconsistent? 2) If not, how are you estimating the d18O of the fluid? Using the 26C temperature from the magnesite quartz fractionation + the quartz-water fractionation of Zheng1993 / Sharp & Kirschner1994? That would be slightly odd to do because if you accept both the magnesite-quartz and magnesite-water fractionations of Zheng 1999, there is an implied quartz-water fractionation in there as well...

See answer to general comment #1 above.

Why should the fluid that formed the quartz in the coarse saprolite level have the same d18O as the fluid that formed the magnesite+silica in the sole?

See answer to general comment #1 above.

"So," sounds informal.

Replaced by "To summarize"

What do you mean by "even at the temperatures prevailing during of intense laterization"?

Aside from the typo including both "during" and "of", it is still not clear what you mean.

Right. The sentence has been deleted

6.4 now 6.3

REF?

Estimating the paleo-gradient of temperature in the New Caledonia ophiolite after its obduction probably would deserve a long discussion. We have taken a low value in order to estimate the lowest paleo-gradient of temperature in the ophiolite and check if this could be consistent with our temperature estimations. Overall, we think that no reference is needed here.

Very awkward phrasing.

Text modified.

Figures:

If it doesn't clutter up the figure too much, consider labeling minerals directly on the image, so that they can still be distinguished by readers looking at black & white version or by color-blind readers.

Actually, this makes the figure very difficult to read... Since the names of the samples are indicated in fig 4, the readers can refer directly to the Table 1 to check the mineralogy.

Reviewer #2:

This paper discusses new clumped and traditional isotope analyses of quartz and magnesite veins in the Peridotite nappes of New Caledonia, an important Ni-Ore deposit. This is an

interesting contribution worth publishing after some moderate revisions which I specify below.

The description of the analytical methods needs to be improved.

Oxygen and carbon isotopes in magnesite: the analytical method should be described in a bit more details (e.g. what apparatus was used for the digestion?).

Right. Some development has been added in the text.

The isotopic composition should be reported against VPDB and VSMOW and the standardization procedures in the laboratory should be described: Which international standard were used for calibration? How was the analytical uncertainty and reproducibility estimated?

Right. Some precisions have been added (most were already given actually)

Clumped isotopes in Magnesite: did you get 100% yield with one hour at 90°C? In my experience one hour is not enough to get 100 % yield., please specify.

Right. See general comment #2 of reviewer 1.

end of section 6.1.1

It is not clear what the authors want to say with this paragraph. That the fractionation curves are somehow wrong?

We have deleted this paragraph. A supplementary material is now provided. Text has been adjusted accordingly.

The fact that the combination of magnesite—water and quartz-water fractionation factors does not give reasonable temperatures, could also mean that these minerals have not precipitated in equilibrium and/or are not cogenetic. This should be discussed, the arguments why the GBMS-Si-1 magnesite and silica are cogenetic should be explained in more detail. The fact that they are "intimately associated" is not enough of a criteria to prove that they are precipitated in equilibrium from the same fluid.

Right. We have slightly modified the text. See also answer to specific comment of reviewer 1 above.

6.2 now 6.1.3

Line 4: why should a composition of -9 represent an atmospheric CO₂ contribution ? values of -9 are found in many environments and soils do not necessarily indicate an atmospheric source of the CO₂, it is also due to organic matter respiration. Please explain.

Right. This paragraph has been modified (as also suggested by reviewer 3 A. Gilg). Kinetic fractionation associated to direct hydroxylation of CO₂ is a possibility to reach low $\delta^{13}\text{C}$ but these low values are only reached when CO₂ is absorbed directly from the atmosphere, and are also commonly associated with very negative oxygen isotope compositions. This was actually first noted by O'Neil, J.R., Barnes, I., 1971. C₁₃ and O₁₈ compositions in some fresh-water carbonates associated with ultramafic rocks and serpentinites: western United States. *Geochimica et Cosmochimica Acta* 35, 687-697. Thus if this mechanism is envisaged as a cause of the low $\delta^{13}\text{C}$, then also the oxygen isotopes would be out of equilibrium, (and probably also the clumped isotopes) invalidating the calculations of the composition of the water. I do not think this is a dominant process because the oxygen isotopes do not show a large variation, but should be taken into consideration in the revision of the discussion.

As specified above, C isotopes may be kinetically fractionated at high pH whereas O isotopes may be not. Reviewer 2 is right only for extremely high pH, conditions under which both C and O isotopes are fractionated.

While the production of hydrocarbons by Fisher-Tropsch like reactions is a possibility, the $\delta^{13}\text{C}$ of abiogenic methane e.g in the lost city system (Proskurowski et al. 2008) is only -10 to -13‰ so to explain the low values in the magnesites it would mean that most of the carbon forming the magnesite would have to be derived from the fluids. I am not sure this is possible. I think the interpretation of the carbon isotopes requires substantial revision.

Right. Actually, there is a tremendous literature on the possible causes of C isotope fractionation in such low-temperature conditions. The reviewers are not convinced by this idea of Fisher-Tropsch reactions as a possible mechanism. They may well be right, as we are... Nevertheless, we have decided to simply remove this part from the discussion to make clearer

the important message of the paper, based on the oxygen isotope system.

6.3 now 6.2

The authors attribute the variability of the oxygen isotope composition of the amorphous silica to variations in composition of the water, but how about the possibility that what they are seeing is disequilibrium precipitation? Would silica first precipitate as a hydrated form and then convert to an anhydrous phase? Could that produce changes in its isotopic composition?

Actually, we attribute the variability of the oxygen isotope composition of the amorphous silica to variations in temperature, not in composition of the water (see the end of first paragraph of new section 6.2). Concerning the possible conversion of a hydrated form to an anhydrous one, we have no evidence of this process and thus not discuss the isotopic consequences.

The use of "Ni talk-like": The authors should always use "Ni Talk-like minerals" instead of only Ni talk-like.

Text modified throughout the ms.

YELLOW BOXES

Introduction:

Phyllosilicates

We now write "Ni talc-like minerals"

Geological Setting :

Is

We prefer the word « reaches » given that the thickness of the laterite profile is known to be spatially variable.

Quartz veins and amorphous silica :

by microscopy

We now write "using optical and electronic microscopies (MET; MEB)"

Analytical techniques:

Should follow the new procedures VSMOW VPDB

Done.

To avoid confusion you should specify that this is the value before acid fractionation correction because it is different from the published one in Meckler et al.

Done

again isotope data should be reported against VSMOW and the value obtained for NBS28 should e reported as well.

Done

Discussion:

this formulation is somewhat unclear, the Falk and kelemen calibration would be the one of Bristow, not a new one. Pleas reformulate the sentence to make this clear.

We have modified the text following the proposition of the reviewer 1.

This could mean that magnesite and quartz are not cogenetic and not in equilibrium.

That is exactly the point we reach in the paper : quartz and magnesite are out of equilibrium.

Magnesite and amorphous silica are likely in equilibrium on the contrary, at least in the sample where we have both species.

Reviewer #3:

The manuscript reports on new stable O and C isotope data of magnesites, quartz and other silica phases and clumped isotope thermometry of seven magnesite samples from the Koniambo Ni laterite district, New Caledonia. The authors conclude that syntectonic magnesite veins that occur mostly (exclusively?) at the base of the Peridotites Nappe and occasionally contain amorphous silica phases, formed at low temperatures of about 25 to 40°C from meteoric waters, while quartz veins that exist only in the "coarse" saprolites developed at higher structural levels of the nappe within the only moderately serpentinized peridotites formed at higher temperatures of about 40 to 80°C. The presence of a low-temperature hydrothermal system within the Ni laterite is thought to be related to either upward flow of warm waters from the base of the nappe or to exothermic serpentinization

reactions. The classical per descensum model for Ni laterites is challenged.

The manuscript is clearly structured and generally well-written, but needs some minor revision of the style by a native English-speaker.

Some references used in the text are missing in the reference section (e.g. Butt & Cluzel 2013 or Oelkers et al. 2013).

We have not checked all references but the authors should do so.

The isotope data are new, original and in my view very interesting as they have potentially significant implications on vein formation conditions in the New Caledonian Ni laterites but possibly also on the correct oxygen isotope fractionations between quartz and magnesite, or between magnesite and water. I strongly support the publication of the manuscript after some moderate revision, as there are several aspects that need some clarification:

1) Characterization of silica phases.

The authors distinguish between quartz, "amorphous silica" and "brown silica" or "poorly crystallized brown silica", "brownish amorphous silica" and even "micro-crystalline brownish reddish silica". The authors state that they used microscopies [sic] and Raman spectroscopy to distinguish silica phases. They do not report what kind of Raman bands have been observed in their samples and how the attribution to amorphous silica (opal?) or microcrystalline silica (quartz) has been made in praxis. In one sentence, they state the presence of tridymite (chapter 4.2) but not in which sample. All this is not acceptable. I strongly suggest that silica phases are primarily identified by XRD (and then additionally by Raman spectroscopy if more than one phase is present) and the use of the nomenclature of Jones and Segnit 1971 or Flörke et al. 1991 for silica phases.

Note that this is not only just a terminological problem. If the samples are dominated by truly X-ray amorphous silica phases, i.e. opal-A, then these may contain significant amounts of water in the form of isotopically easily exchangeable OH groups which potentially influence the oxygen isotope values. The water content of the silica phases should be measured in that case and the water-rich samples may require specific analytical procedures to get "useful" oxygen isotope values; see the literature of opal oxygen isotope analyses, e.g. Labeyrie & Julliet 1982; Matheney & Knauth 1989; Brandriss et al. 1998, and many others. Thus any applied pre-fluorination step should be mentioned in the analytical protocol and oxygen yields as well.

Right. As also (strongly) suggested by reviewer 1 and 2, we now specify the nature of the silica products : throughout the ms, we have replaced "brownish micro-crystalline silica" by "brown micro-crystalline quartz", "brown amorphous silica" by "brown opal", "translucent amorphous silica" by "translucent opal". Reviewer 3 is likely right saying that an even more detailed mineralogical characterization of amorphous silica would be useful, but we do think that our isotopic results on these species, largely distinct from the well-crystallized quartz, allows us to propose that amorphous silica formed under distinct conditions to quartz.

2) Use of oxygen isotope fractionation factors for magnesite and silica phases
I strongly suggest to include all published magnesite-water, including Golyshev et al. 1981; Aharon 1988; Schauble 2006, and silica-water including also opal-water, not only quartz-water, in the discussion and interpretation of oxygen isotope values. This might be rewarding as it will shed some light of the correct fractionation equations for magnesite and the silica phase.

Done, by introducing a new table as supplementary materials including all the fractionation cited above (and even more). Text has been modified accordingly.

3) Kinetic effects on clumped isotope temperatures

The authors suggest that magnesite veins formed primarily syntectonically in the serpentine sole (see also Quesnel et al. 2013). If serpentinization is coeval with the magnesite formation

at the base of the nappe, then these fluids should be alkaline or even hyperalkaline (as they are today) and kinetic isotope effects during carbonate precipitation should be quite common. The authors do not discuss kinetic isotope effects in the alkaline environment on clumped isotope temperatures (see Watkins & Hunt 2015 EPSL 432, 152ff).

Actually, Watkins and Hunt (2015) and also Hill et al (2014) show that precipitation of calcite in alkaline to hyperalkaline environment have minor effect on the D47 composition. This can lead to slightly overestimate or underestimate of several °C the temperature of mineral growth. In our case, this does not change the final message, i.e the magnesite formed at low temperature.

Watkins and Hunt (2015) and Hill et al (2014) have been added in the reference list and we have slightly modified the text at the end of the section 6.1.3.

4) Relative timing of serpentinization, magnesite vein formation, lateritization, hydrothermalism with quartz vein formation only in the saprolites and Ni concentration. I had big problems in understanding the relative timing of all these processes, even after having read the manuscript several times. The authors conclude from the isotope results that the syntectonic magnesite veins formed at temperatures of about 25 to 40°C and their abundance imply a high aqueous fluid flux through the ultramafic rocks apparently far from the surficial laterites. At the same time they argue that temperatures at the base of the nappe with an estimated minimum thickness of 500 to 2000 m were at least 35 to 75°C. If both is correct, this would mean that the nappe had already been strongly eroded to 500 m or even less when it was thrust onto the basement at the sampling sites Koniambo 1-4, but much thicker at sites 6 to 11 in the east. Correct? Why were the temperatures at the base of the nappe during magnesite formation so low, especially as the authors invoke serpentinization reactions as the alternative major heat source and the serpentine sole is the most intensely serpentinized area? So the low-temperatures of the magnesite veins seem to contradict all possible heat sources suggested by the authors unless these processes occurred at very different times. All that seems a bit unclear to me.

Is it possible that cool surface-derived fluids from the basement terranes were injected into the overriding warm peridotites during nappe emplacement and that these cool fluids were responsible for the cool magnesite vein formation?

We agree with reviewer 3's concerns, notably because we actually share the same ones! He is right saying that one inference of the reasoning is that the processes should have "occurred at very different times". It remains that in the present paper, we document "anomalously" high temperature of quartz formation in the saprolitic level, and we think that this information is a robust brick to add in the general wall that would represent the general model of "serpentinization, magnesite vein formation, lateritization, hydrothermalism with quartz vein formation only in the saprolites and Ni concentration" in the New Caledonian realm.

The relationship of Ni enrichment with magnesite or quartz vein formation is also very unclear as the authors do not report on the Ni concentrations at the various sample sites. Are all sampling sites in the Koniambo area economic Ni ore zones or only the "coarse saprolites" in the "highlands"?

In Figure 2, I can see low-level laterites near the Koniambo sampling sites 1 and 2. Do these laterites have a coarse saprolite zone containing quartz veins or are they economically mineralized?

Only the coarse saprolite level in the "highlands" is presently mined.

Why are the low-T hydrothermal quartz veins only occurring in the moderately serpentinized peridotites if serpentinization is a major heat source?

The most likely reason is that the serpentinization event responsible for the heat in the saprolite level was synchronous with lateritization and did not correspond to the early events which led to pervasive serpentinization of the Nappe (especially at the sole).

A synthetic geological section through the Koniambo area with the location of magnesite veins, quartz veins, laterites at the various elevations, serpentinization intensity and location of economic Ni mineralization would be useful for the reader to better understand the relative succession of processes.

We added a reference to the recently published Quesnel et al. (2016), a paper dedicated to the analysis of deformation (another brick in the wall...), where such a cross-section through the Koniambo massif is available. Here, we now present the structural positions of the samples in Table 1 and we represent the saprolite level in figure 2.

5) The location "Koniambo" area should be mentioned at least in the abstract, if not in the title.

Right. Added in the abstract

I have attached an annotated pdf with some minor comments and suggested corrections.

H. Albert Gilg, TUM, Munich, 15/11/2015

YELLOW BOXES:

Abstract:

? Some veins may form without significant fluid-rock interaction. Stable isotopes may not distinguish between the various mechanisms and thus "origins" of vein formation. better: origin of fluids and temperatures.

We have modified accordingly..

? Is this a mineral? Please use IMA conform mineral names,

We prefer to write "Ni talc-like mineral"; we do not use the IMA conform mineral names given that IMA does not recognize kerolite as a mineral phase.

We discuss this point in details in the publication:

Cathelineau, M., Quesnel, B., Gautier, P., Boulvais, P., Couteau, C., Drouillet, M. (2015b) Nickel dispersion and enrichment at the bottom of the regolith : formation of pimelite target-like ores in rock block joints (Koniambo Ni Deposit, New Caledonia). Mineralium Deposita, 1-12.

Introduction:

? What do mean with "given fluid-rock ratio"? The fluid-rock interaction may change the stable isotope composition of the fluid as mentioned just before. So stable isotope compositions of vein minerals depend on these factors:

-fluid isotope composition that may be influenced by fluid-rock interaction

-temperature (and pressure in the case of hydrogen isotopes)

-salinity of the fluid

-precipitation under equilibrium (slow) or kinetic (fast) conditions.

If the equilibrium fractionation factors between mineral and water as a function of temperature is not well established as in the case of magnesite, it imposes another critical problem.

For clarity, we have deleted "at given fluid/rock ration".

or other geothermometers

Modified.

only one deposit?

Indeed, here we consider the New-Caledonian Ni laterite as a unique deposit.

? you mean talc-like mineral? Please add a reference that highlights the nomenclature problems of minerals in Ni laterites.

References added.

What do you mean with amorphous silica: opal-A opal-C opal-CT or even chalcedony?

Raman analyses show a large band between 300cm⁻¹ and 500cm⁻¹ and in some case a band at 460cm⁻¹. Our amorphous silica are opal however, it is difficult to say what type of opal. We change the text and the Table 1 accordingly. See also general comment #1above.

Most of these studies refer to magnesite deposits which are not related to Ni laterites! So you should distinguish between processes related to Ni laterites and those not related to them.

There may be more than process of magnesite vein formation.

In fact only few studies link the magnesite formation to the Ni laterite formation. We present these studies here in order to show that the meteoric origin of the fluid from which magnesite formed via carbonation of serpentinized peridotites is the most common conclusion in the literature.

We have nevertheless slightly modified the text.

based on what kind of argumentation? Only stable isotope data?

Indeed. We have modified the text accordingly.

Geological setting:

or rather distinct episodes of tectonic quiescence!

We are not convinced that episodes of tectonic quiescence are needed to form laterites. This is not the debate here but we have added “and/or epeirogenic movements” because, indeed, laterite formation is the combined result of climate and vertical movements.

how much Ni is in high grade ores?

The Ni content of garnierite is variable (10 wt.% to 50 wt.%). We cite two papers which deal with the characterization of this ore.

succession or association? If the former what was forming first and what came later?

“Succession” replaced by “association”.

If this is the Mineralium Deposita article, then I cannot find any characterisation of silica in it,

In this article (Cathelineau et al, 2015b), we describe the association between Ni talc-like minerals and silica in the same veins. Indeed, there is no mineralogical characterization of the silica phases in this paper. But since we described the field evidence of this association we consider that this reference is adapted here. We have modified “quartz and poorly...” by “silica” in the new version.

please use IMA-conform mineral terms!

We write Ni talc-like mineral. We do not use the IMA conform mineral names given that IMA does not recognize kerolite as mineral phase. See above.

Sampling and Samples:

what is the vertical extent in meter of this (composite?) section? It would be very useful to have a figure showing a composite section with a scale and all sampling sites.

Please refer to major comment #4.

? I would say the rather the last fluid event if vein filling occurs from rim to core. Are the veins syntaxial?

Right. We have deleted this sentence because ambiguous.

what kind of microscopes? Be more precise here.

Done.

Why not XRD?

What kind of Raman spectrometer? Which range of wave numbers? Which Raman bands have been used to identify the silica minerals? Show examples!

See major comment #1. We have deeply modified this section and we have specified the various bands.

Do the quartz veins occur in saprolites formed on the Serpentine Sole and the moderately serpentinised top of the nappe? Or only in the latter?

The structural level is now indicated in the Table 1 and we now represent the saprolite in the figure 2.

There is a difference between microcrystalline and amorphous silica.

Which minerals form "brown silica" microcrystalline quartz and/or opal-A and/or opal-C and/or opal-CT?

The text has been modified. See again answer to major comment #1 above.

Analytical techniques:

It is recommended (Kim et al. 2015, GCA 158, 276ff) to use the VSMOW and VPDB scales. As I suspect that you do not use original Peedee Formation belemnites as reference materials.

Done.

Is that an acid fractionation factor for calcite or magnesite? It will most probably not be the same for the two minerals.

The acid fractionation for clumped isotopes has been demonstrated several times to be independent of mineralogy, unlike what happens for $\delta^{18}\text{O}$. This has been documented for instance in Kluge et al 2015, and in Defliese et al 2015 (in both cases comparing aragonite and calcite). There is also data showing that there is no difference in acid fractionation between calcite and dolomite (Bonifacie et al, under review), and that siderite and calcite have the same acid fractionation factor (Fernandez et al, 2014). So there is no reason to

believe magnesite would be different, although we cannot formally demonstrate this here of course.

5.2

The mineralogy of "amorphous silica" is not well characterised. Here the authors come up with "tridymite" (which sample, all?) which is a very high temperatures polymorph of SiO₂. I suspect the authors mean opal-CT.

What is the difference between "brown silica" and "brownish amorphous silica"? Unclear terminology! I recommend a proper mineralogical description. As amorphous silica may contain significant amount of water as isotopically easily exchangeable OH groups, the water content of the non-quartz silica phases must be presented.

We modified the section 3.3 and 6.2 (former 5.2 section) in order to provide a more accurate description of the various silica phases. See also our answer to major comment #1.

Discussion:

Low Temperature geochemistry:

I recommend here to present all published oxygen isotope fractionation factors for magnesite including Aharon, Golyshev et al and Steele for example in a $100 \ln \alpha$ versus $10^6/T^2$ plot between 100 and 0 °C. The various proposed fractionation factors are either right or wrong and not "more applicable" in one or another setting! You might also compare other proposed fractionation equations (or values) proposed by Golyshev et al 1981, Aharon 1988, Steele, Schauble et al. 2006.

We now provide electronic supplement (S2, S3) where the different oxygen fractionation factors between magnesite and H₂O are presented (Golyshev et al., 1981; Zheng, 1999; Chacko and Deines, 2008; Aharon, 1988 and Schauble et al, 2006). It is proposed to add also the fractionation factor of Steele (<http://www.the-conference.com/JConfAbs/1/593.html> "Theoretical Determination of Isotope Fractionation Factors in Sedimentary Carbonates, D. Fraser Steele") but unfortunately we only find an abstract with no values that could be used. This section has been rewritten accordingly.

This is not true for opal-A, a very common amorphous silica species (see Labeyrie, Brandriss et al.). Thus the exact nature and water content of the amorphous silica phases studied here is important,

See our answer to the major comment #1.

What about opal-water oxygen isotope fractionation?

We have added the electronic supplement S4 and S5 where the various combinations between fractionation factors silica-H₂O and magnesite-H₂O are presented and where we present the various oxygen fractionation between silica and H₂O.

Discussion: Meteoric origin of the fluid:

As far as I can see almost all magnesite come from the "Serpentine Sole", none from the moderately serpentinized peridotites, Or do you mean magnesites from laterites versus unweathered rocks? Unclear.

Right, we have deleted "irrespectively of the nature of the host rock".
old lateritic soil or recent soil?

Recent soil. We have modified.

Are such high temperatures realistic in a vegetation covered lateritic soil environment on Earth? I doubt that.

This is the maximum temperature recorded by magnesite. Clearly, such temperatures can be attained at the surface.

Discussion: Fractionation in the carbon isotope system

? In the paragraph, you conclude with a significant variation oxygen isotope composition of the fluid precipitating magnesite related to evaporation ($\delta^{18}\text{O}$ VSMOW = -3.2 to +1.5 permil).

The sentence was unclear. We suggest here that all the magnesite (veins and nodules) are all formed from fluid with meteoric origin. We modified the text accordingly..

maybe but a very small one. There are supergene magnesites in a tectonically stable environment with very high $\delta^{13}\text{C}$ values, see Rao et al. 1999

Features and genesis of vein-type magnesite deposit in the Doddakanya area of Karnataka, India Journal of the Geological Society of India

Reviewer 2 also raised this point. We modified the text.

Yes, but kinetic isotope fractionation in a strongly alkaline environment also influences very strongly oxygen isotope values (refs.) leading to strongly correlated O and C isotope values. I cannot see any such correlation in the data presented here. Thus I think the low C isotope values in magnesites are not related hyperalkaline fluids but rather to the carbon source.

See answer to the comment of reviewer 2.

single step (Sabatier) or two-step process? See McCollom 2013 RevMinGeochem.

This paragraph has been deleted (see our answer to the comment of reviewer 2).

How is CO produced in such a low-T environment?

This paragraph has been deleted (see our answer to the comment of reviewer 2).

Discussion: Conditions of quartz veins and amorphous silica formation:

Why would you exclude different types of fluids involved with such a large oxygen isotope variation?

See our answer to the comment #1 of reviewer 1.

You mean paleo-latitude here.

Yes; we have specified the text.

How do you know anything about the paleo-elevation evolution of the island? This also influences oxygen isotope values of precipitation.

There is no quantitative constraints on the evolution of the elevation of the island through geological time.

Evaporation effects and also analytical factors should not be excluded. Amorphous silica may have a lot of hydroxyl-groups that may show postformational isotope exchange.

See answer to the major comment #1.

I think the clumped isotope value of 35 ± 6 °C should be used here!

We deleted this sentence because it was useless.

Discussion: Heat sources for quartz veins formation:

? What is a "homogeneous" condition? I do not understand. You mean for example constant temperatures?

Indeed, since we consider the fluid composition as constant, we talk about temperatures here. The text has been modified.

All the magnesite samples are from the Serpentine Sole level. I am not sure if they occur (and in what amount) in the moderately serpentinized level and in the laterites and saprolites,

Right, magnesite occurs at the sole, but amorphous silica may occur at various levels. This is what is written here.

Why not upward circulation from a water-rich cool lower plate?

The more evident source of magnesium needed to form magnesite is the laterization process (and/or the in situ dissolution of serpentine). Moreover, we document carbon isotope compositions consistent with carbon coming from atmosphere and biogenic soil. However, it is true that we cannot formally exclude the possibility of upward circulation of cool fluid from lower plate.

Nevertheless, in this section, we simply remind what was the model proposed in Quesnel et al (2013).

indicates variable conditions and distinctly higher temperatures!

The text has been modified.

But these would suggest also quartz veins in the Serpentine Sole, but there are none!

Not necessarily. Actually, no quartz occurrences have been observed in the Massif elsewhere than at the saprolite level. To discuss that, we wrote the following suggestion in the paper:

“The question of mechanism of precipitation of quartz in the saprolitic structural level remains. The first possibility consists in the precipitation of quartz lead by a change of pH condition. Indeed quartz solubility is function of pH increasing rapidly from pH>9. The pH measured in New Caledonian resurgences of water at the base of the nappe are basic with pH up to 11 (Monin et al., 2014) whereas pH in coarse saprolite level is around ~8 (Trescases, 1975). This abrupt decrease of pH at the saprolitic interface could explain quartz precipitation. Moreover, an additional mixing with *per descensum*

Well maybe but all the quartz vein samples come from saprolites (**indeed**) developed on only moderately serpentinized peridotites and not from saprolites developed on the highly serpentinized Serpentine Sole.

Right. Please refer to our answer to the major comment #4 of reviewer 3 A. Gilg.

Does this serpentinization heat really raise the water temperatures significantly if the fluid-rock ratios are so high as you propose earlier? I would not believe that without a realistic back-on-the-envelope-model calculation.

The source of heat is clearly a point that would need to be addressed in a specific study. For example, if Fritsch et al. (in press) invoke such high temperatures (we now refer to their work in the introduction ; this reference has been added in the reference list), their explanation is weird. On the other hand, Guillou-Frottier et al. (reference already cited) more convincingly argue for a temperature increase in association with serpentinization. Here, in our paper, we document abnormally high temperatures in the saprolitic level using the isotopic tools, and simply discuss the cause of temperature increase.

which temperature range do you mean here?

In the Massif du Sud, at the “Bain des Japonais” the temperature of the resurgences can reach 37°C (Monnin et al, 2014). We have added this temperature in the text.

but again isn't serpentinization in these levels with quartz veins only moderate?

See our answer to major comment #4

Conclusion:

Only true for quartz vein formation but not for the "amorphous silica" formation that occurs at the same temperatures as Mg carbonates!

Right. We have modified.

~25 to 40°C

We have modified.

only magnesite not amorphous silica?

Right. We have added amorphous silica.

So far it is not clear to me where the high economic Ni concentrations are really located in the laterites of the Serpentine Sole (sample locations 1-3) or in the laterites of the moderately serpentinized peridotite (locations 6-11)? This statement need data on Ni concentrations that I cannot find here!

The Ni mineralization is localized only in the saprolite level, so developed on the moderately serpentinized peridotite. The saprolite level is now represented on the figure 2.

See also our answer to the major comment #4.

Ok, but which one is related to Ni accumulation?

The fluid circulation linked to the quartz veins formation.

maybe but not with temperature estimates based on the Nappe thickness (600 to 2000m and normal geothermal gradients: 35 to 70°C) see chapter 5.4. 2 paragraph above).

This is why we say “two distinct fluid circulation systems”

Why does that not happen during magnesite vein formation?

See our answer to the major comment #4.

Figures and figure captions

Table 1

What means x here? Why not leave it blank?

We now leave it blank.

Numbers are missing here. From where do these sample come exactly?

These samples come from another study, we just know that they come from the saprolite level of the Koniombo Massif, not the exact location. But we have here the essential information.

Fig.1

Add scale bar and/or latitude-longitude

Ok, we have added scale bar.

Fig.2

Could you indicate the location of economic Ni deposits in the map?

In fact, all the laterites occurring on the upper part of the massif are mined. So the economic Ni deposits are the laterites.

Laterites has the same color as the sea. Chnage the color to be unambiguous.

Ok we have changed it and we have also added the saprolite level in this map.

Fig 4

What is Figure 4H? Needs explanation.

Legend completed as “H: hand sample GBMS-Si-1 where magnesite and amorphous silica are cogenetic”.

Fig.5

add some more tick marks here

Done

large binning interval

We have modified.

References:

We modified following your suggestion and we have checked the consistency between the text and the references list.

Paired stable isotopes (O, C) and clumped isotope thermometry of magnesite and silica veins in the New Caledonia Peridotite Nappe

Benoît Quesnel*, Philippe Boulvais, Pierre Gautier

Géosciences Rennes, Université Rennes1, UMR 6118 CNRS, 35042 Rennes Cedex, France; benoitquesnel@hotmail.fr, philippe.boulvais@univ-rennes1.fr, pierre.gautier@univ-rennes1.fr

Michel Cathelineau

Géoressources, Université de Lorraine, UMR 7359 CNRS, CREGU, 54506 Vandoeuvre-lès-Nancy, France. michel.cathelineau@univ-lorraine.fr

Cédric M. John

Department of Earth Science and Engineering and Qatar Carbonate and Carbon Storage Research Centre (QCCSRC), Imperial College London, Prince Consort Road, London SW7 2AZ, UK. cedric.john@imperial.ac.uk

Malorie Dierick, Pierre Agrinier

Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ Paris Diderot, UMR 7154 CNRS, F-75005 Paris, France. dierick@ipgp.fr, agrinier@ipgp.fr

Maxime Drouillet

Service géologique, Konimbo Nickel SAS, 98883 Voh, New Caledonia. mdrouillet@koniambonickel.nc

** corresponding author*

Keywords: Peridotite, weathering, magnesite, silica, stable isotopes, clumped isotope thermometry, laterite, low temperature hydrothermalism.

Abstract

The stable isotope compositions of veins provide information on the conditions of fluid-rock interaction and ~~their origin on the origin of fluids and temperatures~~. In New Caledonia, magnesite and silica veins occur throughout the Peridotite Nappe. In this work, we present stable isotope and clumped isotope data in order to constrain the conditions of fluid circulation and the relationship between fluid circulation and nickel ore-forming laterization focusing on the Koniambo Massif. For magnesite veins occurring at the base of the nappe, the high $\delta^{18}\text{O}$ values between 27.8‰ and 29.5‰ attest to a low temperature formation. Clumped isotope analyses on magnesite give temperatures between 26°C and 42°C that are consistent with amorphous silica - magnesite oxygen isotope equilibrium. The meteoric origin of the fluid is indicated by calculated $\delta^{18}\text{O}_{\text{water}}$ values between -3.4‰ to +1.5‰. Amorphous silica associated with magnesite or occurring in the coarse saprolite level displays a narrow range of $\delta^{18}\text{O}$ values between 29.7‰ and 35.3‰. For quartz veins occurring at the top of the bedrock and at the saprolite level, commonly in association with Ni-talc-like minerals, the $\delta^{18}\text{O}$ values are lower, between 21.8‰ and 29.0‰ and suggest low-temperature hydrothermal conditions (~40-~~80~~95°C). Thermal equilibration of the fluid along the geothermic gradient before upward flow through the nappe and/or influence of exothermic reactions of serpentinization could be the source(s) of heat needed to form quartz veins under such conditions.

1. INTRODUCTION

Carbonate and silica veins occur in various geological contexts, and are the marker of past geological fluid circulation. Understanding the conditions of veins formation is of primary importance to decipher the role of fluids in the transfer of heat and matter, the transport and deposition of metals, and the mechanical properties of shear zones and faults. Stable isotopes are one of the historical tools used in the characterization of fluid-rock interactions (Urey, 1947; McCrea, 1950; Epstein et al., 1953; Emiliani, 1966; Craig and Boato, 1955). Theoretically, stable isotopes give access to the fluid stable isotopic composition and the temperature of precipitation of minerals ~~at a given fluid/rock ratio~~. However, estimates of temperature and fluid composition are interdependent. That is the reason why stable isotopes studies have to be undertaken with a strong knowledge of the local geology and in association with complementary

65 methods of fluid characterization, like fluid inclusions studies or other
66 geothermometers-for example.

67 The recent development of the carbonate clumped isotope thermometer has rapidly
68 been considered as a very promising tool in Earth Sciences (Eiler, 2007). This method
69 is based on the thermodynamic phenomenon of “clumping” which consists in the
70 preferential bonds formation between the heavy isotopes of carbon and oxygen in
71 carbonate minerals. Unlike conventional carbonate thermometers, the clumped
72 isotope thermometer allows _temperatures of formation of carbonate to be estimated
73 estimating the temperatures of formation of carbonate independently of the initial
74 fluid isotopic composition. By extension, it can provide an estimate of the $\delta^{18}\text{O}$ value
75 of the parent fluid since the $\delta^{18}\text{O}$ of the carbonate and temperatures are measured
76 independently on the same aliquot of sample. .

77 For the last two decades, the study of carbonate and silica veins developed in
78 ultramafic rocks has attracted a renewed interest given the implications of this process
79 for permanent carbon capture and storage through CO_2 mineralization (Kelemen and
80 Matter, 2008; Kelemen et al., 2011; Oelkers et al., 2013; Ulrich et al., 2014), and in
81 the understanding of lateritic nickel ore formation (Butt and Cluzel, 2013 and
82 references herein). The New Caledonia Peridotite Nappe hosts one of the largest
83 lateritic nickel ore deposit representing around 30% of the global reserves in nickel,
84 thus making New Caledonia the 7th nickel producer in the world. In New Caledonia as
85 in many other places worldwide (Caribbean, South America, Balkans, Russia, West
86 Africa, South East Asian, Australia) Ni-laterites result from the intense weathering of
87 ultramafic rocks exposed at the surface under hot and humid climate. Their
88 development requires the dissolution of protolith minerals leading to i) the export of
89 soluble elements and ii) the in-situ authigenesis of mineral phases hosting the
90 insoluble elements. In the case of peridotites in New Caledonia, Si and Mg are
91 exported whereas the laterites are enriched in iron oxi-hydroxides. Ni, with an
92 intermediate behavior, is concentrated at the base of the lateritic profile where it
93 reaches economic concentrations as Ni-bearing goethite (Trescases, 1975; Freyssinet,
94 2005). The erratic nickeliferous high-grade ore is located along fractures; it is known
95 as garnierite, a mix of Ni-rich serpentine, Ni talc-like minerals -and Ni-sepiolite (e.g.
96 Faust, 1966; Brindley and Hang, 1973; Villanova-de-Benavent et al., 2014;
97 Cathelineau et al., 2015b; Fritsch et al., in press) commonly associated with silica.

Formatted: Font: 12 pt, Not Bold

98 In New Caledonia (Fig. 1), numerous magnesite (MgCO_3), quartz and amorphous
99 silica veins occur at different levels in the peridotite nappe and are thought to
100 represent by-products of the laterization process (Glasser, 1904; Trescases, 1975). A
101 *per descensum* model of fluid circulation was proposed in which Si and Mg are
102 exported downward along fractures cutting through the nappe (Trescases, 1975).

103 Many studies have concentrated on the mineralogical characterization of the Ni
104 bearing phases (Brindley and Hang, 1973; Villanova-de-Benavent et al., 2014;
105 Cathelineau et al., 2015b; Dublet et al., 2015; Fritsch et al., in press), but only few
106 studies focused on the understanding of the physical and chemical conditions of Si,
107 Mg and Ni mobility. Based on stable isotope analyses ($\delta^{18}\text{O}$) of Ni talc-like minerals
108 in garnierite from Morocco (Bou Azzer), Ducloux et al (1993) showed that they could
109 form between 25°C and 100°C. Part of this large spread in temperature is due to
110 uncertainties in the oxygen isotope fractionation factors between Ni talc-like minerals,
111 Ni serpentine-like minerals and water. These authors consider that this temperature
112 range is consistent with a low temperature hydrothermal origin.

113 For silica occurrences from New Caledonia, Saboureau and Trichet (1978) focused on
114 fluid inclusions included in quartz. They identified two generations of quartz,
115 respectively crystallized at <30°C and >120°C. Unfortunately, these samples were
116 collected in soils and represent transported relicts of dismantled quartz occurrences. It
117 is consequently difficult to place them in their genetic context. Recently, Fritsch et al
118 (in press) invoked conditions of low-temperature hydrothermalism to explain the
119 succession of Ni-bearing phases filling fractures and ending with quartz. A
120 temperature of about 70°C is estimated for quartz precipitation by analogy with quartz
121 formed in sandstones.

122 For magnesite formed via carbonation of peridotite variously serpentinized, on the
123 basis of stable isotopes analyses (C and O), most authors argue that carbonation
124 occurs at low temperature and that the fluid is of meteoric origin but rarely propose to
125 link carbonation and laterization processes (Oman: Kelemen et al., 2011; Streit et al.,
126 2012; West California: Barnes et al., 1973; Poland: Jedrysek and Halas, 1990;
127 Balkans: Fallick et al., 1991; Jurkovic et al., 2012; Greece: Gartzos, 2004; East
128 Australia: Oskierski et al., 2013; New Caledonia: Quesnel et al., 2013). On the other
129 hand, some authors argue that few carbonation events likely occurred at hydrothermal
130 conditions (on the basis of stable isotopes analyses (Balkans: Fallick et al., 1991;

Formatted: Not Highlight

Formatted: Not Highlight

Norway: Beinlich et al., 2012) and clumped isotope thermometry (Oman: ~~–~~Falk and Kelemen, 2015).

In this study, we perform stable isotopes analyses on magnesite and silica veins and clumped isotope analyses on magnesite veins from New Caledonia, with a special attention to the Koniambo massif (Fig. 1,2) where the recent development of a mining site allows the access to numerous and exceptional outcrops. We show how the two isotopic methods are complementary and can help to constrain the conditions of veins formation. We also question the *per descensum* model of fluid circulation proposed to explain the vertical distribution of the different mineralization in the peridotite nappe.

2. GEOLOGICAL SETTING

New Caledonia is located in the southwest Pacific Ocean, 1300 km east of Australia (Fig. 1). Peridotites are abundant on the island as a consequence of the Eocene obduction of a sliver of oceanic lithosphere (Cluzel et al., 2012). The Peridotite Nappe sub-horizontally overlies the substratum which is comprised of several volcano sedimentary units (Cluzel et al., 2012). The New Caledonian Peridotite Nappe is exposed in the “Massif du Sud” and as a series of klippen along the northwestern coast (Fig. 1).

Laterite occurs at the top of the peridotites (Fig. 1). Several planation surfaces attest to distinct episodes of weathering and/or epeirogenic movements during the Cenozoic (Latham, 1986; Chevillotte et al., 2006; Sevin et al., 2012). Capping the laterite profile, a ferricrete composed of indurated iron oxides (hematite) mainly occurs as relicts 1 to 2 m thick. Below the ferricrete, the limonitic level is mainly composed of oxi-hydroxides (goethite) and reaches about 20 m in thickness. In this level, the structure of the rock is totally erased. At the base of the profile, the saprolitic level consists in an intermediate state of alteration between limonite and the underlying peridotite. This level reaches around 30m thick. The highly fractured structure of the protolith is preserved. The saprolite level hosts a diffuse Ni mineralization as well as an erratic nickeliferous high-grade ore (Cathelineau et al., 2015a and b; Fritsch et al., in press), known as garnierite veins.

Garnierite occurs as fracture infillings and consists in an ~~succession-association~~ of Ni-rich serpentine and Ni talc-like minerals often associated with silica quartz and poorly

~~crystallized brownish silica~~ (Trescases, 1975; [Cluzel and Vigier, 2008](#); Cathelineau et al., 2015b). Some garnierite occurrences formed syn-tectonically (Cluzel and Vigier 2008) and occur occasionally as hydraulic breccia where ~~a quartz silica~~ cement hosts clasts of serpentine and Ni talc-like [minerals](#) (Myagkiy et al., 2015). Fractures can also be filled solely by [quartz silica](#).

Beneath the saprolite, the main part of the nappe consists of peridotites in which no silica occurs. Peridotites are highly fractured. Serpentinization is intensive in the deformed zones. At the base of the nappe, peridotites are pervasively serpentinized and highly sheared, constituting the so-called Serpentine Sole.

The sole hosts numerous magnesite veins (Quesnel et al., 2013) commonly associated with amorphous silica (Ulrich et al., 2014). Elsewhere in New Caledonia, silica also occurs as infillings of late normal faults of regional extent, as pervasive silicification at the base of the nappe, locally known as the “Mur de silice” and as veins spatially associated to the Saint Louis and Koum Oligocene granitoid intrusions (Paquette and Cluzel, 2007; Jacob, 1985; Aye et al., 1986).

These occurrences are not studied here as they do not relate to the supergene alteration system of the Koniambo Massif. This massif (Fig. 2) corresponds to one of the klippen occurring along the northwestern coast (Fig. 1). As everywhere on the island, the nappe is capped by a highly dissected and partly reworked lateritic profile (Maurizot et al., 2002). At lower elevations, laterites of the westerly-dipping Kaféaté plateau probably belong to a younger planation surface (Latham, 1977; Chevillotte et al., 2006).

3. Sampling and Samples

3.1 Strategy

In the Koniambo massif, a recently opened mining site allows the sampling of the Peridotite Nappe nearly continuously from the Serpentine Sole to the lateritic profile ([Quesnel et al., 2016](#)). The Serpentine Sole is well exposed along cross-sections several hundreds of meters long and a few tens of meters high. The intermediate levels of the Nappe can be observed along an access road reaching the summit of the mining face where mining operations presently expose the laterite and the transition to the fractured peridotite. The veins have been collected at all levels in the Peridotite Nappe in order to get information on the circulation of fluids at the nappe scale

(~800m thick) on the 1D vertical direction. On each sampling site (Fig. 2), the nature of the structure hosting veins has been described when possible. ~~Samples have been collected in the core of veins to avoid host-rock buffering effects and to obtain the signature of the main fluid circulation event.~~

To obtain a first estimate on the representativeness of the Koniambo Massif with regards to the whole New Caledonia Peridotite Nappe, some samples have been collected at other locations within New Caledonia (Fig. 1): magnesite veins in the nearby Kopéto Massif (Foué peninsula and Koné), quartz veins from the coarse saprolite level from Thio Plateau and Monéo and amorphous silica from Népoui ~~and from the Pirogues river.~~

3.2 Magnesite

In the Koniambo massif, magnesite occurs mainly as veins in the Serpentine Sole (Fig. 3a, b). Some magnesite veins occur along fractures up to a few hundred of meters above this level (sampling sites 3 and 5, Fig. 2 and Table 1). In many cases, magnesite veins display a cauliflower texture which attests of a non-oriented growth. Some occurrences show a coarse fibrous texture where fibers of monomineralic magnesite are orthogonal to vein walls (Fig. 3b,c) ~~suggesting growth under mechanical stress~~. At the Serpentine Sole level, magnesite veins occur preferentially within and along the margins of meter-thick low-dipping shear zones that are also marked by the development of serpentine (Fig. 3a,b). These veins are locally folded or offset by subsidiary shear planes (Fig. 3a). Most of the veins occurring outside the main shear zones have an orientation and coarse fibrous texture suggestive of tension gashes opened during the same shear regime (Fig. 3b,c; see also Quesnel et al., 2013). In soils (Fig. 3d), magnesite appears as nodules that can reach a few tens of cm in width. In general, magnesite samples are mono-mineralic but locally intimately associated with amorphous silica at the Serpentine Sole level.

3.3 Quartz veins and amorphous silica

Quartz and amorphous silica samples have been examined using optical and electronic microscopies (MEB), and the nature of silica polymorphs has been checked by Raman spectroscopy. In the coarse saprolite level and the underlying bedrock, quartz veins occur as fractures infillings. These infillings correspond to the re-opening

Formatted: Highlight

Formatted: Highlight

of ancient fractures commonly filled by serpentine, and in some cases by nickel-rich (or nickel-bearing) serpentine and/or talc-like minerals (Fig. 4c,d,f). They can occur as large branched networks of veins (Fig. 4a), as massive veins (Fig. 4c) or as thin films (Fig. 4d). Locally, quartz occurs as brown micro-crystalline ~~brownish-reddish silica~~quartz infillings (Fig. 4b, f; “~~brown-silica~~ Mic Qz” in Table 1), generally preceding the clearer yellow, whitish to clear quartz (Fig. 4b, c, d f; “Qz” in Table 1). The brown color is due to the presence of micron-size inclusions of goethite and hematite. Raman analyses of these various types of quartz show systematically three main bands around 130 cm⁻¹, 205 cm⁻¹ and 465 cm⁻¹.

Two types of amorphous occurrences were studied: i) ~~brownish amorphous silica~~opal occurs as very late coating or drapery-like on blocks of the coarse saprolite level, which constitutes a rather rare case, (Fig. 4e; “~~amorphous-silica~~brown opal” in Table 1); ii) translucent ~~amorphous-silica~~opal closely associated with magnesite at the Serpentine Sole, as micro-spherule (Koniambo; Fig. 4g,h; first three rows in Table 1) or as microfracture infillings (Nepoui). Raman analyses show a large band between 300 and 500 cm⁻¹ and in some case a band at 460 cm⁻¹.

Similar quartz ~~and amorphous-silica~~opal samples were collected in other New Caledonian occurrences for comparison (Fig. 1 and Table 1).

4. Analytical techniques

4.1 Oxygen and carbon isotopes in magnesite

The isotopic analysis of 21 magnesite samples has been performed at the stable isotope laboratory of the University of Rennes 1, France. Samples were finely crushed in a boron carbide mortar, then reacted with anhydrous phosphoric acid at 75°C for 24h. The experimental fractionation factor between magnesite and CO₂ is $\alpha_{\text{CO}_2\text{-Magnesite}}=1.009976$ at 75°C (Das Sharma et al., 2002). CO₂ was analyzed on a VG OPTIMA triple collector mass spectrometer. In the absence of magnesite standard, in-lab calcite standard (Prolabo Rennes) samples were analyzed together with the magnesite samples under identical conditions in order to control the general reliability of the protocol. The analytical uncertainty is estimated at $\pm 0.3\text{‰}$ for oxygen and

Formatted: Superscript

±0.2‰ for carbon by duplication of several analyses. The results are reported using the δ notation relative to VSMOW for O and to VPDB for C.

4.2 Magnesite clumped isotopes

The clumped isotope value of a carbonate sample can be deduced by measuring CO₂ following acidification, and using the Δ_{47} notation (in ‰) that compares the abundance of the rare ¹³C-¹⁸O bonds within a sample relative to a calculated stochastic distribution (Eiler and Schauble, 2004; Affek and Eiler, 2006):

$$\Delta_{47} = \left[\frac{R^{47}}{2R^{13} \cdot R^{18} + 2R^{17} \cdot R^{18} + R^{13} \cdot (R^{17})^2} - \frac{R^{46}}{2R^{18} + 2R^{13} \cdot R^{17} + (R^{17})^2} - \frac{R^{45}}{R^{13} + 2R^{17}} + 1 \right] \cdot 1000 \quad (1)$$

The Δ_{47} value is calculated from the measured ratios (R^i) of masses 45, 46 and 47 to mass 44 and by calculating R^{13} (¹³C/¹²C) and R^{18} (¹⁸O/¹⁶O) from R^{45} and R^{46} assuming random distribution. R^{17} is calculated from R^{18} assuming a mass-dependent relationship between ¹⁸O and ¹⁷O. The higher the Δ_{47} is, the lower the temperature of formation of the mineral (e.g. Ghosh et al. 2006).

Clumped isotope analyses were performed on 7 samples of magnesite in the Qatar Stable Isotopes Laboratory at Imperial College, London, UK. Magnesite was finely crushed and samples of ~5 mg were digested online in a common acid bath composed of 105% ortho-phosphoric acid at 90°C during 1 hour. The liberated CO₂ gas was continuously trapped and purified by passage through a conventional vacuum line with multiple cryogenic traps and Porapak-Q trap held at -35°C (Dennis and Shrag, 2010) and was analyzed using a Thermo Finnigan MAT-253 gas source mass spectrometer. The analysis protocol followed procedures described by Huntington et al. (2009) and Dennis et al. (2011) comprising measurements that consisted of 8 acquisitions with 7 cycles per acquisition and an integration time of 26 s. Each cycle included a peak center, background measurements and an automatic bellows pressure adjustment aimed at a 15V signal at mass 44. The sample gas was measured against an Oztech reference gas standard ($\delta^{13}\text{C} = -3.63$ ‰ VPDB, $\delta^{18}\text{O} = -15.79$ ‰ VPDB). Each sample was measured at least three times using separate aliquots to improve counting statistics. An internal standard (Carrara marble, “ICM”, 0.312‰), a

published inter-laboratory standard ("ETH3", Meckler et al., 2014, 0.634‰ before acid fractionation correction) and heated gases were analyzed regularly in order to correct for non-linearity (Huntington et al., 2009) and to transfer the measured values in the absolute reference frame (Dennis et al., 2011). Finally, an acid fractionation factor of 0.069‰ was added to the Δ_{47} values in the absolute reference frame to account for acid fractionation at 90°C (Guo et al., 2009, Wacker et al., 2013). The analytical uncertainties of the Δ_{47} measurements were added by Gaussian error propagation using standard error of the mean.

4.3 Oxygen isotopes in quartz veins and amorphous silica

The isotopic analysis of 26 silica samples has been performed at the stable isotope laboratory of Institut de Physique du Globe de Paris, France. Samples were finely crushed and reacted with BrF_5 as an oxidizing agent overnight in Ni tubes at 550°C following the method of Clayton and Mayeda (1963). O_2 was directly analyzed on a Thermo-Fisher Delta V mass spectrometer. During the course of the analyses, the measurements of 14 NBS28 quartz standard allowed to control the general reliability of the protocol (mean = 9.67 ± 0.1 ‰, $n = 14$).

Thirteen other silica samples have been analyzed at the stable isotope laboratory of Géosciences Rennes (University of Rennes 1, France). Samples were and finely crushed and O_2 was liberated from minerals through reaction with BrF_5 at 670°C overnight following the method of Clayton and Mayeda (1963). O_2 was then converted into CO_2 by reaction with hot graphite. Isotopic ratios were measured on a VG SIRA 10 triple collector. NBS 28 quartz standard and in-house A1113 granite standard were routinely analyzed together with samples; the analytical uncertainty is ± 0.2 ‰. The O isotope composition is reported using the δ notation relative to VSMOW.

5. RESULTS

5.1 Magnesite

The stable isotopes compositions of magnesites (Fig. 5 a,b and Table 1) are comparable to those obtained by Quesnel et al. (2013). The oxygen isotope compositions of magnesites are homogeneous, with $\delta^{18}\text{O}$ values in the range of

27.8‰ - 29.5‰. The small variation in $\delta^{18}\text{O}$ values does not correlate with any structural or textural characteristics of magnesite. The $\delta^{13}\text{C}$ values vary between -15.3‰ and -9.1‰ (Fig. 5b,c and Table 1). The highest $\delta^{13}\text{C}$ values correspond to nodular magnesite from soil. The low values between -15.3‰ and -12.1‰ correspond to veins from the Serpentine Sole or from highly serpentinized peridotite (sample GMAR-5).

The Δ_{47} values and clumped isotope temperatures in magnesite are reported in Table 1 and illustrated in Figure 5d. The detailed clumped isotope data are presented in the Electronic Supplement S.1. The clumped isotope temperatures presented here are calculated using the Δ_{47} calibration for calcium carbonate of Kluge et al. (2015), because to date, no Δ_{47} calibration exists for magnesite. The temperatures range between 26-42°C (Fig. 5d and Table 1) with an average temperature of $30 \pm 5^\circ\text{C}$ for the magnesite veins from the Serpentine Sole and a temperature of $42 \pm 2^\circ\text{C}$ for a nodular soil magnesite.

5.2 Quartz veins and amorphous silica

The oxygen isotope compositions of quartz veins and amorphous silica display a large range of $\delta^{18}\text{O}$ values between 21.8‰ and 35.3‰ (Fig. 5a and Table 1). The values higher than 30‰ correspond to translucent or brownish opal amorphous silica and tridymite. Quartz veins from the coarse saprolite level have a total range of $\delta^{18}\text{O}$ values between 21.8‰ and 29.0‰, most values being between 24‰ and 28.5‰.

There is no systematic difference between quartz and brown micro-crystalline silicag quartz.

Formatted: Not Highlight

Formatted: Not Highlight

6. DISCUSSION

6.1 Conditions of carbonation

6.1.1 Low temperature geochemistry

The oxygen isotope composition of magnesite samples are included in the range ($27.4\text{‰} \leq \delta^{18}\text{O}_{\text{Magnesite}} \leq 29.7\text{‰}$), similar to the results of Quesnel et al. (2013). A first range of temperature of formation of magnesite veins between $\sim 40^\circ\text{C}$ - 80°C was

estimated by Quesnel et al. (2013) using the oxygen fractionation factor between magnesite and water of Chacko and Deines (2008) and a $\delta^{18}\text{O}$ range of fluid composition between -1‰ and -7‰ which correspond to values of rainwater on isolated island at inter-tropical latitude and low elevation (IAEA database: http://www-naweb.iaea.org/napc/ih/IHS_resources_gnip.html). ~~If the other oxygen fractionation coefficient factors of Zheng (1999) had would have been used (see details in Electronic Supplement S.2 and S.3) in the Quesnel et al. (2013) study instead,~~ the calculated temperature range would be lower, the lowest range (~2°C and 40°C) being reached with the fractionation factor of Aharon (1988) between 10°C and 40°C. Clumped isotope thermometry is particularly useful in such situation when i) ~~two several~~ distinct fractionation factors do not converge towards the same range of temperature of mineral formation and ii) uncertainties on the initial fluid composition is particularly large. To calculate the clumped temperature from Δ_{47} values, Falk and Kelemen (2015) ~~used the calibration of Bristow et al. (2011) but in our case, we favor the use of the recent laboratory calibration for calcium carbonate of Kluge et al. (2015) performed in the same laboratory than our study. showed that the calibration employed by Bristow et al. (2011) is in better agreement with magnesite whose temperatures of precipitation are known than other calibrations (Gosh et al., 2006; Guo et al., 2009; Dennis and Schrag, 2010; Dennis et al., 2011). However, the recent laboratory calibration for calcium carbonate of Kluge et al. (2015) for a temperature range between 25 and 250°C gave a similar fit of the data to the one presented by Falk and Kelemen (2015). Actually,~~ for our samples, the clumped isotope temperatures calculated using these two calibrations are similar, taking into account the uncertainties of the measurements. The clumped isotope temperatures obtained using the calibration of Kluge et al. (2015) average around 30°C, and would suggest that the magnesite-water fractionation factors of Aharon (1988; Magnesite 1) and Zheng (1999) are the most consistent with our results. ~~of Zheng (1999) is more applicable in the New Caledonian setting than the fractionation factor described in Chacko and Deines (2008).~~

We use the isotopic equilibrium between amorphous silica and magnesite to test the validity of the calculated clumped temperature of magnesite formation. We were able to obtain the $\delta^{18}\text{O}$ of magnesite, $\delta^{18}\text{O}$ of amorphous silica and Δ_{47} on magnesite measurements for one sample (GBMS-Si-1, Fig.4g,h and Table 1) where magnesite

Formatted: Font:

and amorphous silica are intimately associated and are interpreted as cogenetic. At the serpentine sole level where sample GBMS-Si-1 was collected, pervasive development of amorphous silica linked to magnesite formation by serpentine dissolution is documented (Ulrich et al., 2014). The isotopic fractionation between silica and magnesite ($\Delta^{18}\text{O}_{\text{Amorphous silica-Magnesite}}$) measured on this sample is 4.2‰. Actually, there is no published isotopic fractionation factor between these two species. We therefore combine the various oxygen fractionation factors between silica forms and H₂O and magnesite and H₂O available in the literature in order to obtain the corresponding temperature (Electronic supplement S.4). Only three different combinations provide realistic temperatures, around 25°C for two of them and around 40°C for the third. ~~Considering that there is no significant fractionation between amorphous silica and quartz (Kita et al., 1985; Zheng, 1993; Sharp and Kirschner, 1994), this measured value is consistent with the theoretical value of the $\Delta^{18}\text{O}_{\text{Quartz-Magnesite}}$ of 4.2‰ at 26°C (Zheng, 1999).~~ On the same sample GBMS-Si-1, the Δ_{47} measurement allows calculating a temperature of $35 \pm 6^\circ\text{C}$ (Table 1), broadly consistent with the 26°C value these temperatures estimated above. It thus appears that both methods agree with each other, despite the lack of a specific Δ_{47} calibration for magnesite. More generally, the range of clumped isotope temperatures between 26 ± 4 and 42 ± 2 calculated for magnesite confirms its low temperature of formation in the Koniambo massif.

~~It should be noted that when combining quartz-water and magnesite-water fractionation factors available in the literature to get the fractionation between quartz and magnesite, one obtains unrealistic estimates. For example, using the magnesite-water fractionation of Zheng (1999) and the quartz-water fractionation of Sharp and Kirschner (1994), one obtains a temperature of 136°C; and using the magnesite-water fractionation factor of Chacko and Deines (2008) with any of the quartz-water fractionation factor available in the literature, one obtains negative $\Delta^{18}\text{O}_{\text{Amorphous silica-Magnesite}}$ values.~~

6.1.2 Meteoric origin of the fluid

Since clumped isotope thermometry allows estimating the temperatures of formation of carbonate independently of the knowledge of the fluid composition, we can

calculate the $\delta^{18}\text{O}$ of the fluid from which magnesite formed. The fact that magnesite veins are commonly decimeter thick and abundant on the studied outcrops implies that a large amount of fluid has been involved in their formation. This suggests a high fluid/rock ratio during the fluid circulation through the nappe. The observation that the $\delta^{18}\text{O}$ values of magnesite are homogeneous, ~~irrespective of the nature of the host rock,~~ (Fig. 5a) pleads for such conditions. Consequently, we consider that the calculated $\delta^{18}\text{O}$ value of the fluid represents its initial composition and not a composition buffered by the host rock during its circulation through the nappe. Given the consistency between temperature estimate using quartz-magnesite equilibrium and clumped isotopes, we use here the oxygen fractionation between magnesite and water from Zheng (1999). The calculated fluids for the 7 magnesite samples have $\delta^{18}\text{O}$ values ranging from -3.4‰ to +1.5‰ (Table.1). The 6 negative $\delta^{18}\text{O}$ values have an average of -2.5‰ with a minimum at -3.4‰ and a maximum at -0.6‰. They correspond to magnesite veins occurring at the Serpentine Sole. The highest value ($\delta^{18}\text{O} = +1.5\text{‰}$) corresponds to a nodular magnesite occurring in a recent soil (DECH1). The oxygen isotope compositions of the fluid are homogeneous and consistent with the present day composition of rainwater on isolated island at inter-tropical latitude and low elevation ranging from -7‰ to -1‰ (AIEA database: http://www-naweb.iaea.org/naweb/ih/IHS_resources_gnip.html). For the nodular magnesite, the positive oxygen fluid composition is interpreted as evaporation at surface conditions which leaves residual water enriched in ^{18}O . The higher clumped temperature of 42°C calculated for this sample seems consistent with the slightly higher temperature needed to precipitate magnesite through evaporation of surface waters.

6.1.3 Fractionation in the carbon isotope system

Whereas the $\delta^{18}\text{O}$ values of magnesite veins are homogeneous and suggest a single meteoric origin ~~unicity~~ of the fluid from which they formed, the large spread of $\delta^{13}\text{C}$ values implies several sources of carbon and/or specific fractionation effect in the carbon isotope system. The highest $\delta^{13}\text{C}$ values, around -9‰, could result from various sources of carbon. An atmospheric CO_2 contribution could, at least in part, explain these high values. A biogenic soil source could also be dominant. ~~suggest an atmospheric CO_2 contribution. Indeed, t~~ This would be ~~is~~ consistent with the fact that

magnesite with such $\delta^{13}\text{C}$ values are nodular magnesites from soil and are probably formed in-situ by evaporation as previously explained for sample "DECH1". Most of the magnesite samples from the Serpentine Sole have lower $\delta^{13}\text{C}$ values between -15.3‰ and -12.1‰. An organic carbon contribution from surface soil or from decarboxylation of deep seated organic matter-rich sediments could explain such low values.

Independently, several resurgences of hyperalkaline fluid with pH up to 11 related to present day serpentinization (Barnes et al., 1978, Monin et al., 2014) occur in New Caledonia (Launay and Fontes, 1985). ~~At least two~~ Among the processes involving such fluid that could explain low values of $\delta^{13}\text{C}$, ~~The first one consists in the~~ kinetic isotopic fractionation of C isotopes is known during hydroxylation of dissolved CO_2 when carbonate forms by diffusive uptake of dissolved CO_2 (Dietzel et al., 1992). Such process has been proposed to explain the extreme depletion of ^{13}C measured in various carbonate occurrences, without important effect on the oxygen isotope compositions, as calcite travertine deposit in Oman (Clark et al., 1992), sediments cemented by calcite from central Jordan (Fourcade et al., 2007) and also for magnesite deposits in Australia (Oskierski et al., 2013).

Recently, Hill et al. (2014) and Watkins and Hunt (2015) showed that kinetic fractionation in alkaline to hyperalkaline environment have minor effect on the $\Delta 47$ composition of carbonate. This can lead to underestimate the clumped isotope temperature of mineral growth by a few °C. Even if such effect would have existed during magnesite formation, this thus would not change the conclusion that magnesite formed at low temperature, around 30°C.

~~The second type of processes consists in abiotic carbon production by Fisher-Tropsch reaction during serpentinization. This reaction consists in the catalytic reaction between H_2 , produced by serpentinization, and CO to form CO_2 or light hydrocarbons. This reaction induces an increase of pH due to the occurrence of free OH^- (Holm, 1996) and produces organic products depleted in $\delta^{13}\text{C}$ (McCollom and Seewald, 2006). Often described as a reaction occurring at high temperature hydrothermal conditions (Berndt et al., 1996; Potter et al., 2004; McCollom and Seewald, 2006; Tara et al., 2007) some studies showed that it can also happen at low temperature (Charlou et al., 1991; Proskurowski et al., 2008; Neubeck et al., 2011;~~

~~Etiope et al., 2011), consistently with the low temperature formation of the New Caledonian magnesite veins.~~

6.2 Conditions of quartz veins and amorphous silica formation

At the island scale, the $\delta^{18}\text{O}$ values of quartz veins and amorphous silica spread over a range of $\sim 15\text{‰}$. The fact that all quartz veins and amorphous silica occur in the peridotite and commonly in deformation zones (at the serpentine sole or as fractures or faults infillings) suggest that they are probably genetically linked to a unique fluid reservoir. We argued in section 6.1.2 that an amorphous silica sample ($\delta^{18}\text{O} = 33\text{‰}$) formed in isotopic equilibrium with magnesite (sample GBMS-Si-1) from a meteoric water at low temperature. By inference, we consider that all amorphous silica occurrences formed from a meteoric fluid. For the quartz veins, their structural position (i.e. at the base of the laterite profile, in the saprolite) and their association with garnierite strongly suggest that the fluid from which they formed also have a meteoric origin. Considering the low variability of ~~paleogeography~~ paleo-latitude of New Caledonia during the 30 last million years (Paleomap project: <http://gcmd.nasa.gov/records/PALEOMAP-Serf.html>) and by consequence the limited variation of the isotopic composition of rainwater during that period, variations in temperature are the most likely factor at the origin of the large spread in $\delta^{18}\text{O}$ values recorded by silica species.

Given that quartz veins are commonly decimeter thick and abundant in the coarse saprolite level it is likely that the system worked under conditions of large fluid/rock ratios, in which case fluids keep their initial isotopic compositions during interaction with rocks. By consequence, the $\delta^{18}\text{O}$ of silica materials directly reflect the temperature of formation, as the $\delta^{18}\text{O}$ of the fluid is considered as constant. As no oxygen isotope compositions of present-day rainwaters in New Caledonia are available, we use the mean value of the $\delta^{18}\text{O}$ values calculated for the meteoric fluid from which magnesite veins formed (mean $\delta^{18}\text{O}_{\text{meteoric-fluid}} = -2.5\text{‰}$, see Table.1) to calculate the temperatures of formation of amorphous silica and quartz veins. The use of various oxygen fractionation factors between silica and H_2O (Electronic Supplement S.5) provide similar range of temperature; only the fractionation factor of Bandriss et al. (1998) was unable to provide a temperature consistent with the oxygen isotopic equilibrium between quartz and magnesite for sample GBMS-Si-1 (See

[section 6.1.1 and Electronic Supplement S.4\).](#)

The $\delta^{18}\text{O}$ values of amorphous silica samples range between 29.7‰ and 35.3‰, which correspond to temperatures between $\sim 15^\circ\text{C}$ and $\sim 40^\circ\text{C}$. The quartz veins occurring in the coarse saprolite level have $\delta^{18}\text{O}$ values between 21.8‰ and 29.0‰, which correspond to temperature between $\sim 40^\circ\text{C}$ and ~~$\sim 8095^\circ\text{C}$~~ , with most samples recording temperatures between $\sim 40^\circ\text{C}$ and ~~$\sim 8065^\circ\text{C}$~~ .

To summarize, the main information obtained from the isotope systematics on quartz veins from the saprolitic level is that they formed under conditions of low-temperature hydrothermalism rather than at surface temperatures, ~~even at the temperatures prevailing during of intense laterization.~~

6.3 Heat sources for quartz veins formation

Magnesite and amorphous silica have ranges of oxygen composition narrower than that of quartz veins (Fig. 5a, c) which suggests more ~~homogeneous—constant conditions—temperatures~~ of formation. The clumped isotope temperatures for magnesite formation are between $26 \pm 4^\circ\text{C}$ and $42 \pm 2^\circ\text{C}$, which is consistent with the range of temperature estimated for amorphous silica formation between $\sim 15^\circ\text{C}$ and $\sim 40^\circ\text{C}$. Even if all amorphous silica are not intimately related to magnesite (typically brown ~~opalish—amorphous~~ silica is not), the fact remains that both their similar temperature of formation and their narrow ranges of $\delta^{18}\text{O}$ values suggest that they are genetically linked to the same low temperature fluid. Following Quesnel et al. (2013), we can thus propose that magnesite and amorphous silica occurring at different levels of the nappe record the fluid pathway through the nappe where rapid downward circulation was enhanced by active tectonics.

For quartz veins from the coarse saprolite level the large range of temperature between $\sim 40^\circ\text{C}$ and ~~$\sim 9580^\circ\text{C}$~~ indicates ~~distinct conditions of formation~~ variable conditions and distinctly higher temperatures of formation. The range of temperature estimated for the quartz veins from the coarse saprolite level appears particularly high given their structural position. A first possibility is to invoke upward ~~circulation movements~~ of hot fluids coming from depth. Even if it is difficult to estimate the past thickness of the nappe at the time of fluid circulation, the present-day topographic constraints allow estimating a minimum thickness. The mean elevation in the island scale is $\sim 640\text{m}$ as reported by Chevillotte et al. (2006) and the Mont Panié, located on

the northern part of the East coast, culminates at 1628m. Considering a surface temperature of $\sim 25^{\circ}\text{C}$, a past thickness of the nappe between ~ 500 and $\sim 2000\text{m}$ and a paleo-gradient of temperature in the peridotite nappe of $20^{\circ}\text{C.km}^{-1}$, temperatures of $\sim 35\text{--}75^{\circ}\text{C}$ may have been reached at the base of the nappe. Rapid upward migration of fluids equilibrated at these temperatures might explain the temperatures recorded by the quartz veins. Occurrences of hydraulic breccia where quartz cements serpentine and garnierite clasts in the coarse saprolite level (Myagkiy et al., 2015) are consistent with this idea.

The question of mechanism of precipitation of quartz in the saprolitic structural level remains. The first possibility consists in the precipitation of quartz lead by a change of pH condition. Indeed quartz solubility is function of pH increasing rapidly from $\text{pH} > 9$. The pH measured in New Caledonian resurgences of water at the base of the nappe are basic with pH up to 11 (Monin et al., 2014) whereas pH in coarse saprolite level is around ~ 8 (Trescases, 1975). This abrupt ~~change-decrease~~ of pH at the saprolitic interface could explain quartz precipitation. Moreover, an additional mixing with *per descensum* meteoric water with pH ~ 7 (Trescases, 1975) and at surface temperature is also possible and could lead to quartz precipitation.

Nevertheless, unlike the conditions of syn-tectonic magnesite formation, no clear evidence of syn-tectonic quartz veins formation is recorded and precludes associating the fluid overpressure to tectonic activity. Consequently, even if the upward fluid circulation linked to fluid overpressure may be in agreement with our data, it remains difficult to identify the cause of such large-scale upward migration of fluid.

An alternative hypothesis to explain the $\sim 40\text{--}9580^{\circ}\text{C}$ temperature range of formation of quartz veins at the coarse saprolite level is to invoke exothermic reactions of serpentization. Indeed, such reactions are known to produce heat (Fyfe, 1974) and may explain elevated temperature of fluid in ultramafic-hosted hydrothermal systems (Kelley et al., 2001, Lowell and Rona, 2002, Schroeder et al., 2002). Even if serpentization reactions can explain only a part of the heat contribution for high temperature hydrothermal systems, they could be sufficient for low temperature hydrothermal system like Lost City type (Mével, 2003). In New Caledonia, several present-day resurgences of low-temperature ~~(reaching 37°C)~~ and hyperalkaline fluid with pH up to 11 are interpreted as evidence of present-day serpentization (Barnes et al., 1978, Monin et al., 2014). A recent study (Guillou-Frottier et al., 2015) proposes that such reactions could occur in the coarse saprolite during the weathering

of the peridotite. These authors argue that serpentinization reactions should trigger convective fluid circulation by i) increasing of temperature by several tens of degrees and ii) increasing of permeability and porosity by fracturation induced by volume expansion (Kelemen and Hirth, 2012). This model could explain the relatively high temperatures identified for the quartz veins formation and the local occurrences of hydraulic breccia where quartz cements serpentine and garnierite (Myagkiy et al., 2015). Our observation and isotopic data are consistent with this model.

7. CONCLUSION

On the basis of stable oxygen isotope data and clumped isotope analyses, we argue that carbonation at the base of the nappe and silicification at the saprolite level of the New Caledonia Peridotite Nappe occurred under different temperature conditions. First, stable isotopes and clumped isotope analyses of magnesite and ~~amorphous silica~~opal display a narrow range of $\delta^{18}\text{O}$ values attesting for formation under homogeneous conditions, at temperature of ~~~30~~25 to 40°C for magnesite and between ~~~15~~20°C and ~40°C for amorphous silica. The oxygen isotope compositions estimated for the fluid at the origin of magnesite and amorphous silica is—are consistent with meteoric water compositions. Second, the $\delta^{18}\text{O}$ values of quartz veins from the coarse saprolite level display a large range, which is indicative of formation between ~40°C and ~~~95~~80°C, typical temperatures of low temperature hydrothermalism.

These results lead to question the classical *per descensum* model of Ni-laterites ore deposit where silica, magnesium and nickel leached during supergene alteration of peridotite are exported by downward fluid circulation along fractures cutting through the nappe. Indeed, our results tends to show that carbonation of the Serpentine Sole and quartz veins formation at the coarse saprolite level are the results of two distinct fluid circulation systems. If the low-temperatures conditions of magnesite formation, specified here using clumped isotope thermometry, are consistent with the tectonically enhanced downward meteoric water circulation model previously proposed in Quesnel et al. (2013), higher temperatures of quartz veins formation would imply that a refinement of the classical *per descensum* model is needed. Thermal equilibration of the fluid along a normal geothermic gradient through the

nappe or influence of exothermic reactions of serpentinization could explain such temperatures. Regardless of the exact explanation, it means that nickel lateritic mineralization, with which the quartz veins studied here are associated, developed under conditions of low-temperature hydrothermalism. This inference may be of importance with regards to the properties of migration of ~~this element~~nickel during mineralization.

ACKNOWLEDGEMENTS

This study constitutes a part of B. Quesnel PhD which is supported financially and technically by Koniambo S.A. This study has benefited from equipment purchased by the Qatar Carbonate and Carbonate Storage Research Center sponsored by Qatar Petroleum, Shell, and the Qatar Science and Technology Park. PB and MC thank Emmanuel Fritsch for the geological tour he organized in the CNRT framework. Mineralogical investigations carried out at Nancy were done within the framework of Labex Ressources 21 (supported by the French National Research Agency through the national program “Investissements d’avenir”, reference ANR-10-LABX-21-LABEX RESSOURCES 21).

FIGURES

Figure 1- Simplified geological map of New Caledonia. Ultramafic rocks are from Maurizot and Vendé-Leclerc (2009) and laterites are adapted from Paris (1981).

Figure 2- Geological map of the Koniambo massif adapted from Maurizot (2002). Numbers indicate sampling location and are reported in Table 1 for all samples coming from the Koniambo massif.

Figure 3- Field observations of magnesite occurrences. A-C: Field views of magnesite veins occurring at the serpentine sole. A: field view illustrating relationship between magnesite veins and shear zone. The thickest vein occurs in the main shear band whereas the thinnest occur in C'-type shear bands. B,C: field view illustrating the

Formatted: Justified, Line spacing:
1.5 lines

fibrous texture of magnesite veins. D: field view of nodular magnesite occurring in a soil. Sample numbers are indicated and are reported in Table 1.

Figure 4- A,C,D: field view of quartz veins occurring in the coarse saprolite level of Koniambo massif. B,F: sawed sections through two hand specimen showing complex textural relationships between B: ~~brownish-silica~~brown micro-crystalline quartz and yellow and white quartz and F: ~~brownish-silica~~micro-crystalline quartz, translucent quartz and clasts of serpentine (in green). G,E: field view of amorphous silica. G: translucent ~~amorphous-silica~~opal associated with magnesite at the Serpentine Sole. H: hand sample GBMS-SI-1 where magnesite and amorphous silica are cogenetic. E: ~~brownish amorphous-silica~~opal occurring as late coating on blocks of the coarse saprolite. Sample locations are indicated by a ~~yellow-white~~ star and are reported in Table 1.

Figure 5- The light grey color represents samples from the Koniambo massif, those in dark grey are from elsewhere on the island. All the sample locations are reported in the figures. 1,2 and in Table 1. The isotopic values are given versus VSMOW (Vienna Standard Mean Ocean Water) for $\delta^{18}\text{O}$ and versus VPDB (Vienna PeeDee Belemnite) for $\delta^{13}\text{C}$. A: histogram of $\delta^{18}\text{O}$ values of magnesite samples (veins and nodules) B: $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ diagram of magnesite samples. C: histogram of $\delta^{18}\text{O}$ values of quartz veins amorphous silica. D: diagram showing the temperature calculated from Δ_{47} analyses using the calibration of Kluge et al. (2015) as a function of the $\delta^{18}\text{O}$ values of 7 magnesite samples.

Table 1- Δ_{47} , $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of magnesite samples and $\delta^{18}\text{O}$ values of silica samples. “n” indicates the number of replicate samples analyzed by clumped isotope thermometry. T (Δ_{47}) uncertainty is estimated on the basis of the 1SE analytical uncertainty in measured Δ_{47} propagated through the Kluge et al. (2015) equation. The $\delta^{18}\text{O}$ of the fluid from which magnesite formed is calculated using the clumped isotope temperature and the oxygen fractionation factor between magnesite and H_2O of Zheng (1999).

REFERENCES

685

686 Affek, H.P., Eiler, J.M. (2006) Abundance of mass 47 CO₂ in urban air, car exhaust,
687 and human breath. *Geochim. Cosmochim. Acta* **70**, 1–12.

688

689 Aharon, P. (1988) A stable-isotope study of magnesites from the rum jungle uranium
690 field, Australia : implications for the origin of strata-bound massive magnesites.
691 *Chemical Geology* **69**, 127-145

Formatted: English (United States)

Formatted: French (France)

692

693 Aye, F., Bonnemaison, M., Jacob, M. (1986) Etude gîtologique et géochimique des
694 indices et anomalies en Sb, W, As, Au de la côte Est de la Nouvelle-Calédonie-
695 programme CORDET-Rapport final du projet A4 (1983-84). Bureau des Recherches
696 Géologiques et Minières report 85 NCL 079 GMX.

697

698 Bandriss, M.E., O'Neil, J.R., Edlund, M.B., Stoermer, E.F. (1998) Oxygen isotope
699 fractionation between diatomaceous silica and water. *Geochimica et Cosmochimica*
700 *Acta* **62**, 1119-1125,

Formatted: English (United States)

Formatted: English (United States)

701

702 Barnes, I., O'Neil, J. R., and Trescases, J. J. (1978) Present day serpentinization in
703 New Caledonia, Oman and Yugoslavia. *Geochimica et Cosmochimica Acta* **42**, 144–
704 145.

705

706 Barnes, I., O'Neil, J.R., Rapp, J.B., White, D.E. (1973) Silica-carbonate alteration of
707 serpentine: wall rock alteration in Mercury deposits of the California Coast Ranges.
708 *Economic Geology* **68**, 388-398.

709

710 Beinlich, A., Plümper, O., Hövelmann, J., Austrheim, H., Jamtveit, B. (2012) Massive
711 serpentinite carbonation at Linnajavri, N-Norway. *Terra Nova* **24**, 446-455.

712

713 ~~Berndt, M.E., Allen, D.E., Seyfried, W.E. (1996) Reduction of CO₂ during~~
714 ~~serpentinization of olivine at 300°C and 500 bar. *Geology* **24**, 351-354.~~

715

716 ~~Boschi, C., Dini, A., Dallai, L., Ruggieri, G., Gianelli, G. (2009) Enhanced CO₂-~~
717 ~~mineral sequestration by cyclic hydraulic fracturing and Si-rich fluid infiltration into~~
718 ~~serpentinites at Malenrata (Tuscany, Italy). *Chemical Geology* **265**, 209–226.~~
719
720 Bristow T. F., Bonifacie M., Derkowski A., Eiler J. M. and Grotzinger J. P. (2011) A
721 hydrothermal origin for isotopically anomalous cap dolostone cements from south
722 China. *Nature* **474**, 68–71. <http://dx.doi.org/10.1038/nature10096>.
723
724 Brindley, G.W., ~~Bish, D., Wan, H.M~~Hang, P.T.: (1973~~9~~) ~~Compositions, structures,~~
725 ~~and properties of nickel-containing minerals in the kerolite–pimelite series~~The nature
726 ~~of garnierites—I—Structures, chemical compositions and color characteristics.~~ ~~*Am-*~~
727 ~~*Mineral*~~*Clays and Clay Minerals* **21**~~64~~,27615–40625.
728
729 Butt, C.R., Cluzel, D. (2013) Nickel laterite ore deposits: weathered serpentinites.
730 *Elements* **9**, 123–128.
731
732 Cathelineau, M., Caumon, M-C., Massei, F., Brie, D., Harlaux, M. (2015a) Raman
733 spectra of Ni-Mg kerolite: effect of Ni-Mg substitution on O-H stretching vibrations.
734 *Journal of Raman Spectroscopy*, Proceedings GEORaman 2014 (11th), St Louis
735 (USA)
736
737 Cathelineau, M., Quesnel, B., Gautier, P., Boulvais, P., Couteau, C., Drouillet, M.
738 (2015b) Nickel dispersion and enrichment at the bottom of the regolith : formation of
739 pimelite target-like ores in rock block joints (Koniambo Ni Deposit, New Caledonia).
740 *Mineralium Deposita*, 1–12.
741 ▲
742 Chacko T., Deines P. (2008) Theoretical calculation of oxygen isotope fractionation
743 factors in carbonate systems. *Geochim. Cosmochim. Acta* **72**, 3642–3660
744 doi:10.1016/j.gca.2008.06.001.
745
746 Charlou, J.L., Bougault, H., Appriou, P., Nelsen, T., Rona, P.A. (1991) Different
747 TDM/CH₄ hydrothermal plume signatures: TAG site at 26°N and serpentinized
748 ultrabasic diapir at 15°05'N on the Mid-Atlantic Ridge. *Geochim. Cosmochim. Acta*
749 **55**, 3209–3222.

Formatted: English (United States)

Formatted: Font: Not Bold, English (United States)

Formatted: Superscript

Formatted: English (United States)

Formatted: Not Highlight

Formatted: English (United States)

Formatted: Font: Italic

Formatted: French (France)

750

751 Chevillotte, V., Chardon, D., Beauvais, A., Maurizot, P., Colin, F. (2006) Long-term
 752 tropical morphogenesis of New Caledonia (Southwest Pacific): Importance of positive
 753 epeirogeny and climate change. *Geomorphology* **81**, 361-375.

754

755 Clark, I.D., Fontes, J.C., Fritz, P. (1992) Stable isotope disequilibria in travertine from
 756 high pH waters: laboratory investigations and field observations from Oman.
 757 *Geochim. Cosmochim. Acta* **56**, 2041-2050.

758

759 Clayton, R., Mayeda, K. (1963) The use of bromine pentafluoride in the extraction of
 760 oxygen from oxides and silicates for isotopic analyses. *Geochim. Cosmochim. Acta*
 761 **27**, 43-52.

762

763 Cluzel, D., Maurizot, P., Collot, J., Sevin, B., (2012) An outline of the geology of
 764 New Caledonia; from Permian-Mesozoic Southeast Gondwanaland active margin to
 765 Cenozoic obduction and supergene evolution. *Episodes* **35**, 72–86.

766

767 Cluzel, D., Vigier, B. (2008) Syntectonic Mobility of Supergene Nickel Ores of New
 768 Caledonia (Southwest Pacific). Evidence from Garnierite Veins and Faulted Regolith.
 769 *Resource Geology* **58**, 161–170. doi:10.1111/j.1751-3928.2008.00053.x

770

771 Craig, H., Boato, G. (1955) Isotopes. *Annual review of physical chemistry* **6**, 403-432.

772

773 Das Sharma, S., Patil, D.J., and Gopalan, K. (2002) Temperature dependence of
 774 oxygen isotope fractionation of CO₂ from magnesite–phosphoric acid reaction.
 775 *Geochim. Cosmochim. Acta* **66**, 589–593. doi:10.1016/S0016-7037(01)00833-X.

776

777 Dennis K. J., Affek H. P., Passey B. H., Schrag D. P. and Eiler J. M. (2011) Defining
 778 an absolute reference frame for ‘clumped’ isotope studies of CO₂. *Geochim.*
 779 *Cosmochim. Acta* **75**, 7117– 7131. <http://dx.doi.org/10.1016/j.gca.2011.09.025>.

780

781 Dennis, K., Schrag, D. (2010) Clumped isotope thermometry of carbonatites as an
 782 indicator of diagenetic alteration. *Geochim. Cosmochim. Acta* **74**, 4110-4122.

783

784 Dietzel, M., Usdowski, E., Hoefs, J. (1992) Chemical and $^{13}\text{C}/^{12}\text{C}$ - and $^{12}\text{O}/^{16}\text{O}$ -
785 isotope evolution of alkaline drainage waters and the precipitation of calcite. *Applied*
786 *Geochemistry* **7**, 177-184.

787

788 Dublet, G., Juillot, F., Morin, G., Fritsch, E., Fandeur, D., Brown Jr., G.E. (2015)
789 Goethite aging explains Ni depletion in upper units of ultramafic lateritic ores from
790 New Caledonia. *Geochim. Cosmochim. Acta* **160**, 1-15. [http://dx.doi.org/10.1016/](http://dx.doi.org/10.1016/j.gca.2015.03.015)
791 [j.gca.2015.03.015](http://dx.doi.org/10.1016/j.gca.2015.03.015).

792

793 Ducloux, J., Boukili, H., Decarreau, A., Petit, S., Perruchot, A., Pradel, P. (1993) Un
794 gîte hydrothermal de garnierites: l'exemple de Bou Azzer, Maroc. *Eur. J. Mineral.*
795 **5**, 1205-1215.

796

797 Eiler J.M. (2007) "Clumped-isotope" geochemistry—The study of naturally-
798 occurring, multiply-substituted isotopologues. *Earth and Planetary Science Letters*
799 **262**, 309–327. doi: 10.1016/j.epsl.2007.08.020.

800

801 Eiler, J.M., Schauble, E. (2004) ^{18}O - ^{13}C - ^{16}O in Earth's atmosphere. *Geochim.*
802 *Cosmochim. Acta* **68** (23), 4767–4777. Doi:10.1016/j.gca.2004.05.035

803

804 Emiliani, C. (1966) Isotopic paleotemperatures. *Science* **154**, 851-857

805

806 Epstein, S., Buchsbaum, R., Lowenstam, H.A., Urey, H.C. (1953) Revised carbonate-
807 water isotopic temperature scale. *Bulletin of the geological society of America* **64**,
808 1315-1326.

809

810 ~~Etiope, G., Schoell, M., Hosgörmez, H. (2011) Abiotic methane flux from the~~
811 ~~chimaera seep and Tekirova ophiolites (Turkey): understanding gas exhalation from~~
812 ~~low temperature serpentinization and implication for Mars. *Earth and Planetary*~~
813 ~~*Science Letters* **310**, 96-104.~~

814

815 Fallick, A.E., Ilich, M., and Russell, M.J. (1991) A stable isotope study of the
816 magnesite deposits associated with the Alpine-type ultramafic rocks of Yugoslavia.

817 *Economic Geology and the Bulletin of the Society of Economic Geologists* **86**, 847–
818 861. doi:10.2113/gsecongeo.86.4.847.

819

820 Falk, E.S., Kelemen, P.B. (2015) Geochemistry and petrology of listvenite in the
821 Samail ophiolite, Sultanate of Oman: complete carbonation of peridotite during
822 ophiolite emplacement. *Geochim. Cosmochim. Acta* **160**, 70-90.
823 <http://dx.doi.org/10.1016/j.gca.2015.03.014>

824

825 Faust, G.T. (1966) The hydrous nickel-magnesium silicates—the garnierite group.
826 *The American mineralogist* **51**, 279-298.

827

828 Fourcade S., Trotignon L., Boulvais P., Techer I., Elie M., Vandamme D., Salameh
829 E., Khoury H. (2007) Cementation of kerogene-rich marls by alkaline fluids released
830 during weathering of thermally metamorphosed marly sediments. Part I: Isotopic (C,
831 O) study of the Khushaym Matruk natural analogue (central Jordan). *Applied*
832 *Geochemistry* **22**, 1293-1310.

833

834 Freyssinet P., Butt C.R.M., Morris R.C., Piantone P. (2005) Ore-forming processes
835 related to lateritic weathering. In: Hedenquist JW, Thomson JFH, Goldfarb RJ,
836 Richards JP (eds), *Economic Geology 100th Anniversary Volume*. Economic
837 Geology Publishing Company, New Haven, Connecticut, pp 681-722\$

838

839 Fritsch, E.M., Juillot, F.A., Dublet, G.A., Fonteneau, L., Fandeur, D., Martin, E.,
840 Caner, L., Auzende, A-L., Grauby, O., Beaufort, D. (2015) An alternative model for
841 the formation of hydrous Mg / Ni layer silicates (“ deweylite ”/“ garnierite ”) in
842 faulted peridotites of New Caledonia: I . Texture and mineralogy of a paragenetic
843 succession of silicate infillings. *European Journal of Mineralogy*, in press, doi:
844 10.1127/ejm/2015/0027-2503

845

846 Fyfe, W.S. (1974) Heats of chemical reactions and submarine heat production.
847 *Geophysical journal of the Royal Astronomical Society.-J. R. stra. Soc.* **37**, 213-215.

848

849 Gartzos, E. (2004) Comparative stable isotopes study of the magnesite deposits of

Formatted: Font: Italic

Formatted: Font: Bold

850 Greece. *Bulletin of the Geological Society of Greece* **36**, 196–203.

851

852 Glasser E. (1904) Rapport à M le Ministre des Colonies sur les richesses minérales de

853 la Nouvelle- Calédonie. Paris, Annales des Mines, 560 p.

854

855 Ghosh P., Adkins J., Affek H., Balta B., Guo W., Schauble E. A., Schrag D. and Eiler

856 J. M. (2006) ^{13}C – ^{18}O bonds in carbonate minerals: a new kind of paleothermometer.

857 *Geochim. Cosmochim. Acta* **70**, 1439–1456.

858

859 Golyshev, S.I., Padalko, N.L., Pechenkin, S.A. (1981) Fractionation of stable oxygen

860 and carbon isotopes in carbonate systems. *Geokhimiya* **10**, 1427-1441 (in Russia)

861

862 Guillou-Frotier, L., Beauvais, A., Bailly, L., Wyns, R., Augé, T., Audion, A-S.

863 (2015) Transient hydrothermal corrugations within mineralized ultramafic laterites.

864 In: Proceedings of the 17th Biennial SGA (Society for Geology Applied to Mineral

865 Deposits) meeting, 24-27 August 2015, Nancy, France, vol.3, 1169-1172.

866

867 Guo, W. F., Mosenfelder, J. L., Goddard, W. A. and Eiler, J. M. (2009) Isotopic

868 fractionations associated with phosphoric acid digestion of carbonate minerals:

869 insights from first-principles theoretical modeling and clumped isotope

870 measurements. *Geochim. Cosmochim. Acta* **73**, 7203–7225. [http://dx.doi.org/](http://dx.doi.org/10.1016/j.gca.2009.05.071)

871 [10.1016/j.gca.2009.05.071](http://dx.doi.org/10.1016/j.gca.2009.05.071).

872 Hill, P.S., Tripathi, A.K., Schauble, E.A. (2014) Theoretical constraints on the effects

873 of pH , salinity , and temperature on clumped isotope signatures of dissolved

874 inorganic carbon species and precipitating carbonate minerals. *Geochim Cosmochim*

875 *Acta* **125**, 610–652.

876 ~~Holms N. G. (1996) Serpentinization of oceanic crust and Fischer-Tropsch type~~

877 ~~synthesis of organic compounds. *Origins Life* **26** (3–5), 205–206.~~

878

879 Huntington K. W., Eiler J. M., Affek H. P., Guo W., Bonifacie M., Yeung L. Y.,

880 Thiagarajan N., Passey B., Tripathi A., Daëron M., and Came R. (2009) Methods and

Formatted: Normal (Web),
Widow/Orphan control, Adjust space
between Latin and Asian text, Adjust
space between Asian text and numbers

Formatted: Font: Italic

Formatted: Font: Bold

limitations of ‘clumped’ CO₂ isotope (Δ_{47}) analysis by gas-source isotope ratio mass spectrometry. *J. Mass. Spectrom.* **44**, 1318–1329.

Jacob, M. (1985) Etude géologique, minéralogique et géochimique des anomalies en As, Sb, Au et W et indices minéralisés liés aux fractures regionals de la côte sud-est de la Nouvelle-Calédonie. Ph.D thesis, University Paul Sabatier, Toulouse, n°3138, 155p.

Jedrysek, M.O., and Halas, S. (1990) The origin of magnesite deposits from the Polish Foresudetic Block ophiolites: Preliminary $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ investigations. *Terra Nova* **2**, 154–159. doi:10.1111/j.1365-3121.1990.tb00057.x.

Jurkovic, I., Palinkas, L.A., Garasic, V., and Strmic Palinkas, S. (2012) Genesis of vein-stockwork cryptocrystalline magnesite from the Dinaride ophiolites. *Ofioliti* **37**, 13–26.

Kelemen, P.B., Hirth, G. (2012) Reaction-driven cracking during retrograde metamorphism: Olivine hydration and carbonation. *Earth and Planetary Science Letters* **345-348**, 81-89.

Kelemen, P.B., Matter, J. (2008) In situ carbonation of peridotite for CO₂ storage. *PNAS* **105(45)**, 17295-17300

Kelemen, P., Matter, J., Streit, E.E., Rudge, J.F., Curry, W.B., Blusztajn, J. (2011) Rates and mechanisms of mineral carbonation in peridotite: natural processes and recipes for enhanced, in situ CO₂ capture and storage. *Annual Review of Earth and Planetary Sciences* **39**, 545–576. doi:10.1146/annurev-earth-092010-152509

Kelley, D.S., Karson, J.A., Blackman, D.K., Früh-Green, G.L., Butterfield, D.A., Lilley, M.D., Olson, E.J., Schrenk, M.O., Roe, K.K., Lebon, G.T., Rivissigno, P., AT3-60 shipboard party (2001) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30°N. *Nature* **412**, 145-149.

914 Kita, I., Taguchi, S., Matsubaya, O. (1985) Oxygen isotope fractionation between
 915 amorphous silica and water at 34-93°C. *Nature* **314**, 83-84.

916

917 Kluge, T., John, C.M., Jourdan, A.L., Davis, S., Crawshaw, J. (2015) Laboratory
 918 calibration of the calcium carbonate clumped isotope thermometer in the 25-250°C
 919 temperature range. *Geochim. Cosmochim. Acta* **157**, 213-227.
 920 doi:10.1016/j.gca.2015.02.028

921

922 Launay, J., Fontes, J.C. (1985) Les sources thermales de Prony (Nouvelle-Calédonie)
 923 et leurs précipités chimiques. Exemple de formation de brucite primaire. *Géologie de*
 924 *la France* **1**, 83-100.

925

926 Latham, M. (1977) On geomorphology of northern and western New Caledonian
 927 ultramafic massifs. International symposium on geodynamics in south-west Pacific,
 928 Nouméa, Technip Paris éd, 235-244.

929

930 Latham, M. (1986) Altération et pédogenèse sur roches ultrabasiques en Nouvelle-
 931 Calédonie: Editions de l'ORSTOM (Office de la Recherche Scientifique et Technique
 932 Outre-Mer), Collection Etudes et Theses.

933

934 Lowell, R.P., Rona, P.A. (2002) Seafloor hydrothermal systems driven by the
 935 serpentinization of peridotite. *Geophysical research letters* **29** (11).

936

937 McCrea, J. M. (1950) On the isotopic chemistry of carbonates and a paleotemperature
 938 scale. *Journal of Chemical Physics* **18**, 849-857.

939

940 ~~Marques, J.M., Carreira, P.M., Rosário Carvalho, M., Matias, M.J., Goff, F.E., Basto,~~
 941 ~~M.J., Graça, R.C., Aires-Barros, L., Rocha, L. (2008) Origins of high pH mineral~~
 942 ~~waters from ultramafic rocks, Central Portugal. *Applied Geochemistry* **23**, 3278-3289.~~
 943 ~~doi:10.1016/j.apgeochem.2008.06.029~~

944

945 Maurizot, P., Lafoy, Y., and Poupée, M. (2002) Cartographie des formations
 946 superficielles et des aléas mouvements de terrain en Nouvelle-Calédonie, Zone du
 947 Koniambo: Bureau de Recherches Géologiques et Minières Public Report RP51624-

Formatted: English (United States)

Formatted: English (United States)

Formatted: French (France)

948 FR, 45 p.
949
950 Maurizot, P., Vendé-Leclerc, M. (2009) New Caledonia geological map, scale
951 1/500000, DIMENC-SGNC, BRGM. Explanatory note by Maurizot, P. and Collo, J.
952
953 ~~McCollom, T.M., Seewald, J.S. (2006) Carbon isotope composition of organic~~
954 ~~compound produced by abiotic synthesis under hydrothermal conditions. *Earth and*~~
955 ~~*Planetary Science Letters* **243**, 74-84.~~

956 Meckler, A.N., Ziegler, M., Millan, M.I., Breitenbach, S.F.M., Bernasconi, S.M.
957 (2014) Long-term performance of the Kiel carbonate device with a new correction
958 scheme for clumped isotope measurements. *Rapid Commun. Mass Spectrom.* **28** (15),
959 1705-1715.

960 Mével, C. (2003) Serpentinization of abyssal peridotites at mid-ocean ridges. *C.R.*
961 *Geosciences* **335**, 825-852.
962
963 Monin, C., Chavagnac, V., Boulart, C., Ménez, B., Gérard, M., Gérard, E.,
964 Quéméneur, M., Erauso, G., Postec, A., Guentas-Dombrowski, L., Payri, C., Pelletier,
965 B. (2014) The low temperature hyperalkaline hydrothermal system of the Prony bay
966 (New Caledonia). *Biogeosciences Discuss.* **11**, 6221-6267.
967
968 Myagkiy, A., Cathelineau, M., Golfier, F., Truche, L., Quesnel, B., Drouillet, M.
969 (2015) Defining mechanisms of brecciation in Ni-Silicate bearing fractures
970 (Koniambo, New Caledonia). In: Proceedings of the 13th Biennial SGA (Society for
971 Geology Applied to Mineral Deposits) meeting, 24-27 August 2015, Nancy, France,
972 vol.3, 1181-1194.
973 ~~13th SGA meeting, Nancy (France)~~

974
975 ~~Neubeck, A., Thanh Duc, N., Bastviken, D., Crill, P., Holm, N.G. (2011) Formation~~
976 ~~of H₂ and CH₄ by weathering of olivine at temperatures between 30 and 70°C.~~
977 ~~*Geochemical Transactions* **12**(6).~~
978

979 Oelkers, E.H., Sigurdur, R.G., Matter, J. (2008) Mineral carbonation of CO₂.
 980 *Elements* 4, 333-337.
 981
 982 Oskierski, H.C., Bailey, J.G., Kennedy, E.M., Jacobsen, G., Ashley, P.M., and
 983 Dlugogoski, B.Z. (2013) Formation of weathering-derived magnesite deposits in the
 984 New England Orogen, New South Wales, Australia: Implications from mineralogy,
 985 geochemistry and genesis of the Attunga magnesite deposit. *Mineralium Deposita* **48**,
 986 525–541. doi:10.1007/s00126-012-0440-5.
 987
 988 Paquette, J.L., and Cluzel, D. (2007) U-Pb zircon dating of post-obduction volcanic-
 989 arc granitoids and a granulite-facies xenolith from New Caledonia: Inference on
 990 Southwest Pacific geodynamic models. *International Journal of Earth Sciences* **96**,
 991 613–622. doi:10.1007/s00531-006-0127-1.
 992
 993 Paris, J.P. (1981) Géologie de la Nouvelle-Calédonie: un essai de synthèse. *Mémoire*
 994 *du BRGM (Bureau de Recherches Géologiques et Minières)* **113**.
 995
 996 ~~Potter, J., Rankin, A.H., Treloar, P.J. (2004) Abiogenic Fischer-Tropsch synthesis of~~
 997 ~~hydrocarbons in alkaline igneous rocks; fluid inclusion, textural and isotopic evidence~~
 998 ~~from the Lovozero complex, N.W. Russia. *Lithos* 75, 311–330.~~
 999 ~~doi:10.1016/j.lithos.2004.03.003~~
 1000
 1001 ~~Proskurowski, G., Lilley, M., Seewald, J.S., Früh-Green, G.L., Olson, E.J., Lupton,~~
 1002 ~~J.E., Sylva, S.P., Kelley, D.S. (2008) Abiogenic hydrocarbon production at Lost City~~
 1003 ~~hydrothermal field. *Sciences* 319, 604–607. doi:10.1126/science.1151194~~
 1004
 1005 Quesnel B., Gautier P., Boulvais P., Cathelineau M., Maurizot P., Cluzel D., Ulrich
 1006 M., Guillot S., Lesimple S., Couteau C. (2013) Syn-tectonic, meteoric water-derived
 1007 carbonation of the New Caledonia peridotite nappe. *Geology* **41**, 1063–1066.
 1008 doi:10.1130/G34531.1
 1009
 1010 Quesnel, B., Gautier, P., Cathelineau, M., Boulvais, P., Couteau, C., Drouillet, M.
 1011 (2016) The internal deformation of the Peridotite Nappe of New Caledonia : a

Formatted: Subscript

Formatted: French (France)

Formatted: English (United States)

[structural study of serpentine-bearing faults and shear zones in the Koniambo Massif. *Journal of Structural Geology* **85**, 51-67.](#)

Formatted: French (France)

Formatted: French (France)

Sabouraud, C., Trichet, J. (1978) Confirmation, par l'étude des inclusions intracristallines, de l'origine superficielle de quartz pyramides. *Geoderma* **20**, 191-199.

Sevin, B., Ricordel-Prognon, C., Quesnel, F., Cluzel, D., Lesimple, S., and Maurizot, P. (2012) First palaeomagnetic dating of ferricrete in New Caledonia: New insight on the morphogenesis and palaeoweathering of 'Grande Terre'. *Terra Nova* **24**, 77-85, doi:10.1111/j.1365-3121.2011.01041.x.

[Schauble, E.A., Ghosh, P., Eiler, J.M. \(2006\) Preferential formation of \$^{13}\text{C}\$ - \$^{18}\text{O}\$ bonds in carbonate minerals, estimated using first-principle lattice dynamics. *Geochimica et Cosmochimica Acta* **70**, 2510-2529.](#)

Schroeder, T., [John, B., Frost, R.B.](#) (2002) Geologic implications of seawater circulation through peridotite exposed at slow-spreading mid-ocean ridges. *Geology* **30**, 367-370.

Sharp, Z.D., Kirschner, D.L. (1994) Quartz-calcite oxygen isotope thermometry: a calibration based on natural isotopic variations. *Geochim. Cosmochim. Acta* **58(21)**, 4491-4501.

Streit, E., Kelemen, P., Eiler, J. (2012) Coexisting serpentine and quartz from carbonate-bearing serpentinized peridotite in the Samail Ophiolite, Oman. *Contrib. Mineral. Petrol.* **164(5)**, 821-837. doi:10.1007/s00410-012-0775-z

Formatted: French (France)

~~Taran, Y.A., Kliger, G.A., Sevastianov, V.S. (2007) Carbon isotope effects in the open system Fischer-Tropsch synthesis. *Geochim. Cosmochim. Acta* **71**, 4474-4487. doi:10.1016/j.gea.2007.06.057~~

1045 Trescases, J.J. (1975) L'évolution géochimique super- gène des roches ultrabasiques
 1046 en zone tropicale: Formation des gisements nickélifères de Nouvelle-Calédonie.
 1047 Mémoires ORSTOM (Office de la Recherche Scientifique et Technique Outre-Mer)
 1048 78, 259 p.
 1049

1050 ~~Ulrich M., Muñoz M., Guillot S., Chauvel C., Cluzel D., Picard C. (2011) Weathering~~
 1051 ~~effects on the mineralogical and geochemical composition of the New Caledonia~~
 1052 ~~ophiolite. *Mineralogical Magazine* **75**(3), 2049~~
 1053

1054 Ulrich, M., Muñoz, M., Guillot, S., Cathelineau, M., Picard, C., Quesnel, B.,
 1055 Boulvais, P., Couteau, C. (2014) Dissolution-precipitation ~~nm~~ processes governing the
 1056 carbonation and silicification of the serpentine sole of the New Caledonia ophiolite.
 1057 *Contrib. Mineral. Petrol.* **167**, 952.
 1058

1059 Urey, H.C. (1947) The thermodynamic properties of isotopic substances. *Journal of*
 1060 *the Chemical Society*, 562-581.
 1061

1062 Villanova-de-Benavent C., Proenza J.A., Galí S., García-Casco A., Tauler E., Lewis
 1063 J.F., Longo F. (2014) Garnierites and garnierites: textures, mineralogy and
 1064 geochemistry of garnierites in the Falcondo Ni-laterite deposit, Dominican Republic.
 1065 *Ore Geol Rev* **58**, 91–109.
 1066

1067 Wacker U., Fiebig J., Schoene B. R. (2013) Clumped isotope analysis of carbonates:
 1068 comparison of two different acid digestion techniques. *Rapid Commun. Mass*
 1069 *Spectrom.* **27**, 1631-1642.

1070 Watkins, J.M., Hunt, J.D. (2015) A process-based model for non-equilibrium clumped
 1071 isotope effects in carbonates. *Earth Planet Sci Lett* **432**, 152–165

1072 Zheng, Y.-F. (1993) Calculation of oxygen isotope fractionation in anhydrous silicate
 1073 minerals. *Geochim. Cosmochim. Acta* **57**, 1079-1091.
 1074

1075 Zheng, Y.F. (1999) Oxygen isotope fractionation in carbonate and sulfate minerals.
 1076 *Geochemical Journal* **33**, 109-126.

Table1
Click here to download high resolution image

Sample	Localization	Nature	Silica	Magnesite								
			$\delta^{18}\text{O}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}_{\text{calc. magnesite}}$	$\Delta\epsilon$	Standard error	$T^{\circ}\text{C}(\Delta\epsilon)$	n°	$\delta^{18}\text{O}$ fluid	
KONIAMBO MASSIF												
GBMS-Si-1	Koniambo 1: Sole	Magnesite vein+translucent opal	33.1	28.9	-13.5	4.2	0.671	0.016	33±6	3	-0.6	
BMS-Si-1'	Koniambo 1: Sole	Magnesite+translucent opal	32.9									
BMS-Gio-15*	Koniambo 1: Sole	Magnesite vein+translucent opal	29.7	29.1	-13.8							
GBMS-2-13	Koniambo 1: Sole	Magnesite vein		28.3	-14.3							
GBMS-3-13	Koniambo 1: Sole	Magnesite vein		28.8	-14.3							
GBMS-4-13	Koniambo 1: Sole	Magnesite vein		29.0	-12.7							
GBMS-5-13	Koniambo 1: Sole	Magnesite vein		28.2	-14.3							
BMS-Gio-9*	Koniambo 1: Sole	Magnesite vein		28.6	-14.3		0.695	0.012	26±4	3	-3.1	
BMS-Gio-3*	Koniambo 1: Sole	Magnesite vein		28.8	-13.8		0.689	0.016	28±5	4	-2.4	
BMS-Gio-12*	Koniambo 1: Sole	Magnesite vein		27.8	-15.2		0.675	0.024	33±8	3	-2.2	
GVAV-1-13	Koniambo 2: Sole	Magnesite vein		28.7	-13.2							
GVAV-2-13	Koniambo 2: Sole	Magnesite vein		28.8	-15.3							
VAV-Gio-9*	Koniambo 2: Sole	Magnesite vein		27.8	-14.4		0.691	0.020	28±7	4	-3.4	
GMAR-2	Koniambo 3: High. Serp.	Magnesite vein		28.2	-14.5		0.693	0.006	27±2	2	-3.2	
GMAR-3	Koniambo 3: High. Serp.	Magnesite vein		28.8	-12.8							
GMAR-5	Koniambo 3: High. Serp.	Magnesite vein		29.5	-13.6							
GMAR-4	Koniambo 3: High. Serp.	Nodular magnesite in soil		29.5	-9.1							
CR-1	Koniambo 3: High. Serp.	Nodular magnesite in soil		28.9	-9.4							
KNB3a	Koniambo: Sapolite	Qtz	25.0									
MG1a	Koniambo: Sapolite	Qtz	25.9									
MG5c	Koniambo: Sapolite	Qtz	28.3									
MG5a	Koniambo: Sapolite	Qtz	24.6									
FQZ-1	Koniambo 7: Sapolite	Qtz	25.9									
Qtz pit 1	Koniambo 7: Sapolite	Qtz	26.0									
BAV-Qtz-1	Koniambo 7: Sapolite	Qtz	25.9									
Si j 3	Koniambo 9: Sapolite	Qtz	29.0									
Si Cl 3	Koniambo 9: Sapolite	Qtz	28.1									
Si Cl Br 1	Koniambo 9: Sapolite	Qtz	28.5									
FQZ-2	Koniambo 10: Sapolite	Qtz	25.4									
Si Cl 1	Koniambo 10: Sapolite	Qtz	27.5									
Si Cl 2	Koniambo 10: Sapolite	Qtz	26.5									
Si j 4	Koniambo 11: Sapolite	Qtz	28.0									
Test Pit	Koniambo 8: Sapolite	Mic Qtz	25.1									
KNB3b	Koniambo: Sapolite	Mic Qtz	27.6									
Si br 4	Koniambo 6: Sapolite	Mic Qtz	23.9									
Pit 207 haul	Koniambo 7: Sapolite	Mic Qtz	25.3									
Kon Hau Test Pit	Koniambo 8: Sapolite	Mic Qtz	25.1									
Si br 6	Koniambo 9: Sapolite	Mic Qtz	27.5									
Si br 2	Koniambo 10: Sapolite	Mic Qtz	27.2									
Si R 1	Koniambo 10: Sapolite	Mic Qtz	24.8									
BMS-Si-13.2	Koniambo 1: Sole	Brown opal	33.4									
Si-Br-late	Koniambo 4: High. Serp.	Brown opal	32.6									
Core Si-1	Koniambo 4: High. Serp.	Brown opal	30.4									
NEW CALEDONIA												
FOUJ-Gio	Food peninsula	Magnesite vein		29.1	-12.1							
Bellevue-Gio-1	Konté	Nodular magnesite in soil		29.2	-9.1							
DECH-1*	Konté	Nodular magnesite in soil		29.5	-9.1		0.652	0.005	42±2	3	+1.5	
NIP-4	Nepoui	Opal	35.3									
MONEO	Mondo	Mic Qtz	26.3									
Thio-SP5	Thio Plateau	Mic Qtz	21.8									
"Tasseo-cargende"	Thio Plateau	Qtz	24.9									
BEV3-a	Thio Plateau	Qtz	25.2									
3TX1-a	Thio Plateau	Qtz	24.5									
Th-PT-3	Thio Plateau	Qtz	25.1									
Th-PT-6	Thio Plateau	Qtz	25.9									
Th-PT-9	Thio Plateau	Qtz	25.8									
Th-PT-10	Thio Plateau	Qtz	25.4									
Th-PT-11	Thio Plateau	Qtz	25.5									

Figure1

[Click here to download high resolution image](#)

Figure2

[Click here to download high resolution image](#)

Figure3
[Click here to download high resolution image](#)

Figure4
[Click here to download high resolution image](#)

Figure5

[Click here to download high resolution image](#)

Electronic Annex

[Click here to download Electronic Annex: Electronic Supplement.xlsx](#)