Answer to first reviewer
(the reviewer's comments are in italic).

Evaluation of manuscript “The low temperature hyperalkaline hydrothermal system of the Prony bay (New Caledonia)” by C. Monnin and others
The paper reports new and interesting fluid compositional data for the Bay of Prony alkaline springs, which are of considerable interest to a growing group of geochemists and geobiologists. The main conclusions of the paper are:
1) fluids reflect mixing between seawater and alkaline groundwater
2) brucite precipitation starts at pH>9.5, when a critical superaturation threshold is reached
3) carbonate supersaturation peeks at pH 10 and fluid mixing plays a key role in carbonate formation

Conclusions 2 and 3 are not supported very well by the way the data is reported. Brucite saturation state is not plotted (see below), so it is difficult to verify what is stated in the text.

> There has been an error during the editing of our manuscript for BGD: Figs 8 and 9 were the same… The brucite saturation sate is indeed not shown. We have posted an erratum on the BDG discussion section with the right Figure 8, but this was understandably unnoticed by the reviewer. We apologize.

Brucite precipitation suggested to occur at pH>9.5 would result in non-conservative behavior of Mg. However, Mg looks like it behaves conservatively in Figure 5. This needs to be investigated in greater detail, perhaps in a blow up diagram that examines the relation of Mg vs. Cl at low concentrations.

> We tried several ways of plotting the data, with no success. Unfortunately a blow up diagram (a log-log plot of the Mg concentration versus that of Cl) does not show much more.

Likewise, sulfate appears to behave conservatively. Does this mean that all the mixing takes place during sampling?

> We do not exactly know what the reviewer means. It is a common feature of all underwater springs (including the ocean bottom high temperature vents) that when a fluid discharges into an aqueous environment, it always mixes with the waters in the immediate environment. So mixing is not an artefact of the sampling.

Or is sulfate indeed not consumed? Is there any evidence for increased sulfide? There is certainly enough hydrogen dissolved in the alkaline waters to drive sulfate reduction. Also, from the published work (Pisapia et al.) what metabolic reactions would one expect to take place and are these reactions reflected in the composition of the vent waters?

> This remark relates to the bacterial sulfate reduction (BSR) where in this case dissolved hydrogen would be the electron donor (in marine sediment the electron donor would be what is commonly called organic matter). It is indeed highly interesting to measure aqueous sulfide that would give an idea of the extend of sulfate reduction. It has to be carried out either on site or very rapidly after sampling because of rapid oxidation, which unfortunately we have not done. Nonetheless molecular ecomogy provided clues for BSR in the different concretions (Quemeneur et al., 2014, Env. Microbiol. Rep)
> The other remark about metabolic reactions is at the heart of the investigation of environments like the alkaline springs of the Prony Bay at the interface between the inorganic world and biology. Our paper aims at describing the main chemical features of the springs. The elucidation of the mechanisms at play is everybody's long term goal that we mention in the last sentence of our paper ("Lastly, the carbonate concretions and the hyperalkaline springs of the Prony hydrothermal system provide a unique example of the interface between a continental ultramafic formation and the marine environment, with peculiar links between geology, fluid chemistry and microbial activity"). A wealth of additional information is provided in companion papers already published (Quemeneur et al., 2014) or very close to be submitted at the time (July 2014) we write this answer to the reviewer (Postec et al, in prep; Pisapia et al, in prep.).

No attempt is being made to match the fluid chemistry with precipitate mineralogy in order to test the hypothesis that the highest supersaturation in the mixed fluids drives carbonate precipitation. It would be interesting to learn more about the carbonate mineralogy, which apparently has been worked up in related studies.

> Our paper describes the general environment of the springs. The description of the mineralogical assemblages deserves a detailed investigation that will indeed be reported elsewhere (Pisapia et al., in preparation). We have already reported the first observations at conferences. Nonetheless, to fulfill the reviewer's concern, we added a few sentences in section VI to describe the general features of the concretion mineralogy.
> Pisapia C., Gérard E., Gérard M., Erauso G., Postec A., Monnin C., Payri C., Pelletier B., Ménez B. - Organomineralization drives early chimney edification at the hyperalkaline hydrothermal field of the Prony Bay (New Caledonia). Proc. Nat. Acad. Sciences, in preparation.

Gas concentrations should be reported for the individual fluids. Just reporting averages in Table 3 is not very helpful. The authors state that Eh is controlled by hydrogen. I don't think this is correct, because the Eh-sensor is fairly insensitive to dissolved hydrogen.

> We have never said that Eh is controlled by hydrogen. What we have written (page 13 of our manuscript) is that "These results indicate that water is indeed reduced to hydrogen at surface temperature conditions, but only at very high pH values (above 11.5) that are not reached in the Prony bay."

It would actually be interesting to see H2(aq) concentrations computed from the partial pressures of H2 in the gas phase. I am pretty sure that those H2 concentrations would correspond to Eh-values that are much lower than the measured ones.

> There are two different reactions. The first one is the solubility of hydrogen:
>
> $$H_2(g) = H_2(aq)$$
>
> The second one is the reduction of water (we here write the half-reaction as we do not know what the other redox couple may be).
>
> $$H_2O(l) + e^- = \frac{1}{2} H_2(aq) + OH^-(aq)$$
>
> There is no reason why these two reactions should be at equilibrium at the same time. Computing the solubility of H2(g) would not give any insight into the redox state of the system.
>
> The first reaction involves degasing that can take place at depth and not at the springs where bubbling in observed. Difference in pathways of gas and fluids is commonly investigated in the study of oil and gas reservoirs.
> Redox disequilibrium is also very common (think of the metastable mixture of gaseous hydrogen and oxygen at room temperature). Also the calculation of the gas partial pressures is not trivial as it requires the partial pressure of water that can indeed be calculated (we have measured the composition of dried gases).
> We nevertheless agree with the reviewer that it would be quite interesting to compute the conditions for degasing as well those for redox equilibrium. But, in order to make sense, such calculations require a fully detailed investigation.

The slope in the Eh-pH diagram is also too steep of H2(aq) control. The authors may want to speculate about which redox reaction would correspond to the trend displayed in Figure 4.

> Again we have not attributed the trend depicted by our measurements reported in Fig. 4 to a control by a redox equilibrium. Instead we have written that "The linear trend depicts the dilution of the reduced hydrothermal fluid by local oxidized seawater. It extrapolates into Eh–pH values reported for a serpentinizing environment (the Cedars site in California, Morrill et al., 2013) that lie on the hydrogen-water redox equilibrium line".

A more detailed comparison between the endmember compositions of the waters with those from CaOH-type water from other sites would be helpful.

> We agree, but such a detailed comparison is also a separate investigation by itself. Our Table 1 is the first step toward such a comparison. For now it only situates the type of the Prony Bay springs amongst serpentinizing environments.

Figure 3 shows a positive correlation between temperature and pH. I don't think the two usually correlate with each other. Mixing it proposed to be responsible for the correlation, but I would not expect a straight mixing diagram in a log-lin diagram.

> These are simple observations that are easily explained by mixing between the high pH fluid and seawater.

In general, I think it would be really helpful (in particular when looking at Fig. 3 and, more so, Figs. 6 and 7) if the authors computed conservative mixing lines between seawater and the BdJ spring endmember.

> In order to compute such mixing lines, we have to define the composition of the endmembers. There is a first difficulty for the saline low pH seawater type side. We show that the waters collected at the Bain des Japonais define a trend different from the waters collected at the other sites. There is a contribution of the nearby Rivière du Carénage that makes the samples collected at BdJ the result of mixing of three water types (high pH fluid, lagoon seawater and river water). We do not have any composition of the river water. A such it is difficult to characterize the low pH endmember of the Bain des Japonais.
> For the deep sites, there is some scatter in the element concentration values at the highest pHs so that the definition of an endmember composition would be ambiguous. This is why we have not attempted it yet. We state in the text that indeed the composition of the endmember fluid at each site is a highly valuable quantity as its variation form one site to the other would help tracing the hydrologic pathways.

I think that the authors could improve the significance of this communication a lot if these comments were addressed in a revised version

Other quibbles:
The term "Ca-OH type water" is used in abstract but nowhere else in the manuscript. Please explain the term in the introduction or omit using it in the abstract.

> We think that the term is rather explicit. Is it necessary to add a sentence saying that a Ca-OH water is a water where Ca and OH are the dominant ions?

Figure 7: What do the dashed lines represent?

> It is written in the figure caption*:* "The dashed line represents the value for standard seawater".

Figure 8 and 9 obviously plot the same data. I suspect both show calcite saturation state.

> Yes they do. It is an error. See our comment at the beginning of this letter.

It is hard to imagine that brucite is oversaturated in pH 8.5 fluids.

> We agree. It is not.

Figure 11: Why do the flow paths for the ST11 fluids cross the basal thrust? Is there any evidence for water interaction with continental crustal rocks?

> This figure should not be taken at face value. See the caption of figure 11: " The arrows tentatively indicate the pathways of the fluid percolation and point to the question of the nature of the geological formations leached by the waters: ophiolite nappe, continental basement and/or coral formations". See also the same type of drawing and the discussion in Chavagnac et al. (2013b).

Table 2: Sample W8 from ST12 is obviously seawater. How can it have only 0.4 mmol/kg DIC. Is this a typo?

> Yes indeed it is an outlier in Fig. 6. We checked our files. It does not seem to be a type. We do not have any explanation for this.

Neal and Shand (2002) and Fujii et al. (2010) references Boschetti and Toscani (2008) in Table 1 are missing from list of references

> Sorry about the omissions. This will be corrected in the revised version of the manuscript.

Quéméneur et al. (2014) is also not in the list of references

> Yes it is. This paper is now in press.