Reply to: Anonymous Referee #1
On the manuscript: "Characterisation of the magmatic signature in gas emissions from Turrialba volcano, Costa Rica"

General comments

This manuscript reports the chemical composition and SO2 flux emitted from Turrialba volcano using a scanning ultra violet spectrometer, FT-IR and Multi-gas sensors and suggested the progressive dying up leading the eruption. Although the data reported by this manuscript are limited in number and overlap with the published data obtained only a week before, addition of such data is important in order to evaluate a short-term fluctuation of the gas emission and the major subject of this manuscript is different from the previous study, which aims to estimate the CO2 flux from the volcano. However, the discussion in this manuscript is poor in quality and sometimes misleading, in particular 1) comparison with the previous data are incomplete, 2) the estimate of the oxygen fugacity is misleading, and 3) discussion of the current state is not supported by the data. Therefore the present manuscript is not acceptable for publication and resubmission of the manuscript after full reconsideration of the discussion is suggested.

"…and suggested the progressive dying up leading the eruption" → nowhere do we suggest that the drying of the hydrothermal system is leading to an eruption.

Specific comments

1) Comparison with the previous studies

1-1) Conde et al. (2014)

The data given in this manuscript largely overlap with those obtained only a week before by Conde et al. (2014). Although their data are cited in the text, similarity and difference of these data sets are not fully discussed in the manuscript. In particular, the possible causes of the four-times difference of the SO2 flux and the five-times difference of the CO/SO2 ratio at 2012 vent. Although the large CO2/SO2 ratio of the 2012 vent is attributed to the large error of the FT-IR measurement, such a conclusion cannot be justified without a quantitative error evaluation. And similar evaluation should be performed for other data sets to quantify the errors of other data. It is also necessary to clarify the progress after Conde et al. (2014).

"…the possible causes of the four-times difference of the SO2 flux" → see reply to similar comment below.

"and the five-times difference of the CO/SO2 ratio at 2012 vent" → We do not report the CO/SO2 ratio at the 2012 vent, neither do Conde et al 2014. We do report the CO/SO2 ratio for the 2010 vent while Conde et al., 2014 do not.

"large CO2/SO2 ratio of the 2012 vent is attributed to the large error of the FT-IR measurement, such a conclusion cannot be justified without a quantitative error evaluation" The CO2/SO2 ratio we report for the 2012 vent does carry a large error (self-evident from the regression statistics R^2= 0.29) and which we already discuss at length. The 95% confidence intervals are calculated and shown on each scatter plot.

"It is also necessary to clarify the progress after Conde et al. (2014)." As stated by the reviewer, the focus of this contribution is quite different from the work of Conde et al., 2014, they report CO2/SO2 ratio only and provide a comparison of two instruments (Multigas and FTIR). This manuscript on the other hand, provides the chemical composition of the Turrialba plume in terms of all major volcanic gas species (H_2O, CO_2, SO_2, HCl, CO, H_2),and identifies a clear magmatic signal in the gas emissions which is interpreted in terms of evolution of the magmatic-hydrothermal system. We see little overlap between these two contributions.

1-2) Conde et al. (2013) Int. J. Earth Sci., doi 10.1007/s00531-013-0958-5
Conde et al. (2013) reported the SO_2 flux data during 2008-2012. This reference should be cited and discussed. In particular, they reported the high flux (~1500 t/d) before the Jan, 2010 eruption, which contradicts the discussion in the present study.

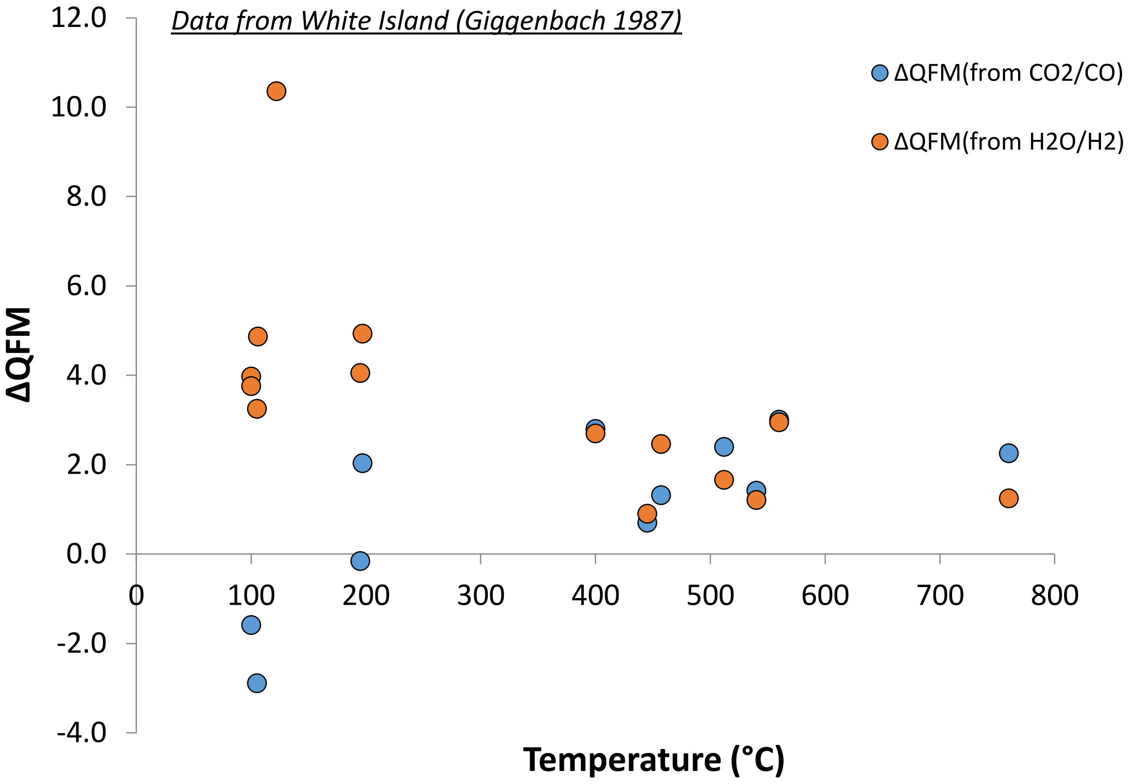
SO_2 flux estimates provided by Conde et al 2013 are derived from Novac network stations. These stations are located 10km away from the summit and are particularly prone to error from processes such as light dilution (See Kern et al. 2010 Bull of Volc.), carry a large error on the determination of the plume height and especially on wind speed. A 1:1 correlation was actually shown between the SO_2 flux estimates at Turrialba from the Novac network and wind speed by Avard et al., (IAVCEI 2013 Scientific Assembly). We also point out that the daily variability in SO_2 flux reported by Conde et al 2013 span three orders of magnitude, and that the high average flux of 1500 t/d prior to the 2010 eruption mentioned by the reviewer is reported with an associated standard deviation of over 1000 t/d. Furthermore, the high fluxes reported by Conde et al 2013 are contradictory to those reported by Campion et al. 2012 (cited in the main text). Given the large uncertainty on the flux measurements reported by Conde et al. 2013, we feel that our discussion of low SO_2 fluxes prior to eruptions is valid. However, it was an oversight to omit the Conde et al. 2013 results from our discussion, and we have now cited this paper.

ADDED: “Conde et al.,(2013) reported SO_2 fluxes intermittently for the period 2008 to 2012 using stations from the Novac network. The high uncertainty on their reported dataset (with daily variations in SO_2 flux spanning up to three orders of magnitude and standard deviations similar or larger than the reported values) makes it unideal however for comparison purposes.”

2) Oxygen fugacity estimation
The oxygen fugacity estimation is misleading. This method is applicable to the gasses, which discharged directly from magma to the atmosphere, such as those of lava lakes, as we can assume the gas composition quenching just after the discharge. Compositions of fumarolic gases, however, vary with outlet temperature and the condition of the magma degassing (such as oxygen fugacity of the magma) cannot be estimated. In particular, the H_2/H_2O and CO/CO_2 ratios are commonly decreases with outlet temperature and the decreasing trend is commonly the result of shift of chemical equilibrium under a control of the major redox pair of SO_2/H_2S, which is known as the gasbuffer (Giggenbach, 1987, Applied Geochemistry, vol. 2, 143-161).

As explained in Giggenbach 1987’s paper: 1. Deviation of the gas redox state from its original magmatic value typically happens when discharge temperature falls below 400°C and 2. The CO_2-CO redox couple (which we use here to derive the fO_2) is the least responsive to changes in the SO_2-H_2S redox buffer. Citing here Giggenbach 1987: “In contrast to H_2/H_2O, which was found to adjust rapidly to conditions dictated by the major fluid phase buffer H_2S/SO_2, CO/CO_2 ratios obviously respond more slowly and, therefore, reflect equilibration conditions at greater pressures and depths.”
The reviewer is referred to Fig. 9 in Giggenbach 1987 which shows that the CO_2/CO ratio is parallel to the FeO-$FeO_{1.5}$ or Fayalite-magnetite line and only deviates at temperatures < 200°C.

If this isn't clear please consider the following diagram reporting data from White Island presented in Table 1 in Giggenbach 1987. The redox state is calculated using the H2O/H2 and CO2/CO ratios and expressed as deviation from the Quartz-fayalite-magnetite buffer plotted against the measured discharge temperature. What is noticeable from this plot is that the redox state recorded by gases between 400 and 800°C is broadly similar. Deviation from the QFM buffer occurs at temperature <400°C and for the CO2/CO ratio, closer to temperatures <200°C.



Considering the above, and given the high temperatures of the gases being measured, we consider that our discussion of the oxygen fugacity estimation is valid and reasonable. However, in view of the reviewer's comment, we have now added a figure (new Fig. 6) showing the correspondence between oxygen fugacity and gas equilibration temperature for the measured CO2/CO ratio.

3) Current state of the degassing
The discussion is poorly supported by the data.
The low SO2 flux is suggested to be indicative of a preparation of eruptions. However, Conde et al. (2013) reported the increase of the flux several months before the 2010 eruption and several low flux periods regardless of the occurrence of eruptions; those observations disagree with the present conclusion.

Although the possibility of low SO2 fluxes prior to eruptions is mentioned in the discussion, it is not presented as a conclusion of the study. Indeed, we acknowledge in the text that "the current dataset is too disparate to conclude with any confidence [that this is a eruption precursor]". While some discussion is made of a potential mechanism for a reduction in SO2 flux prior to an eruption, care has been taken to present this as speculative rather than conclusive.

As discussed above, the SO2 flux data presented by Conde et al. 2013 have very large uncertainties associated with them (the daily variability is always greater than any long term trend they observe), and we therefore feel that although there is disagreement with our findings/discussion it is not sufficiently compelling to discount what we have presented.

If we compare the SO2 flux data we obtained (or even the flux determined by Conde et al., 2014) to the flux measured using OMI (Campion et al 2012) we see that the March 2013 flux are comparable to the value measured just prior to the 2010 eruption.

However, as previously acknowledged, the findings of Conde et al. 2013 should not have been omitted from the original manuscript and are now referenced in the discussion.

The similarity of the 2008 gas composition and the 2013 gas composition is concluded based on the comparison of the S/CO2 and (HCl+HF)/CO2 ratios. However, other compositions, such as HF/HCl, H2/SO2 and CO2/CO ratios are different and the general similarity cannot be concluded.

We use the S/CO2 and (HCl+HF)/CO2 ratios because they are sensitive to hydrothermal vs magmatic contributions to the gas phase.

The CO2/CO ratio is a redox ratio which follows temperature, comparing this ratio between the 2008 measurements from fumaroles at 80 to 280°C to those obtained from the current vent (T>400°C) does not make sense. Also see previous graph for deviation to HT redox state at low temperature. The same comment applies for using ratios with H2.

We were not able to measure HF and therefore did not present a HF/HCl ratio. A comparison of this ratio with the Vaselli et al., 2010 study is therefore not possible.

The progressive drying is suggested based on the gas composition. Although the gas composition indicates the limited contribution of hydrothermal system, this does not suggest the progressive change as there is no composition data after the previous eruption.

We’re talking about a long term change, initiated in 2002 with the first detection of SO2 (Vaselli et al., 2010) and subsequent increase in fumarrolic activity followed by several small eruptions opening the 2010 and 2012 vents. The dataset from Vaselli et al., (2010) and Tassi et al., (2004) shows an evolution of the fumaroles chemistry from 1998 to 2008, evolving from a hydrothermal to magmatic end member.

Other comments
Table 3 and relating discussion are suggested to be removed, as they are not relevant to the major subject of this manuscript.

Disagreed, this table and the related discussion where suggested by an earlier review and do help understanding the data presented.

Fig. 3 is not necessary as any detail of the SO2 flux variation is not discussed in the text.

Fig. 3 shows the quality of the SO2 flux data obtained, notice how little variability there is within and between days, with little deviation from the mean 200 t/day.