Author's response

The author would like to thank both reviewers for their time and effort in reviewing our manuscript. We believe both reviewers have made some valid points. Both suggested a major overhaul of the manuscript itself, with the specific demand to add more data comparing our model with other, existing models. We agree this improves the manuscript and have mostly followed the excellent suggestions for reworking the manuscript.

Below is an overview of the comments and remarks made by the reviewers followed by our response in italic (and if applicable the corresponding changes):

Comments from referees

Referee #1

General comments:

1. The first requirement of a new routine allowing the calculation of XRD patterns from complex mixtures of disordered/interstratified phyllosilicates is consistency with available routines. Although these routines may not all be easily accessible, some of them are and I think an essential step would be to use to developed program to fit XRD patterns calculated with a different calculation algorithm (for a complex mixed layer) to make sure that ALL structural parameters (for both phases and components) are introduced and considered in the right way in the new algorithm.
   We have included a comparison with output from Sybilla for a large number of discrete (pure and mixed-layered) phases and a number of mixtures to confirm PyXRD is producing similar results. We have chosen to restrict the comparison only with this model because of the similar mathematical background, resulting in an almost identical parametrisation. We also think the manuscript would become too bulky by adding more comparisons.

2. In addition I think that refinement of at least one experimental dataset (for example a known mixture of pure clays, or published datasets with determined structural parameters) would be a convincing evidence for the performance of the reported program.
   Although we agree this would be a very good example, we did not include it to prevent the article from becoming too bulky. PyXRD has been used on soil samples in a previous paper (Dumon et al. 2013. Quantitative clay mineralogy of a Vertic Planosol in southwestern Ethiopia: Impact on soil formation hypotheses, Geoderma) showing it can be used for this purpose. We also believe the very similar results obtained in the comparison with Sybilla and the numerous papers using this model serve as an indirect proof for the performance of PyXRD.

3. A second important feature of the multi-specimen approach is its ability to deal with swelling layers which may behave differently depending on experimental data collection conditions: A mono- or bi-hydrated layer in the AD state may for example incorporate 1 or 2 planes of ethylene glycol upon solvation. From the Tables, it seems that all swelling layers are considered as a unique layer type in PyXRD, but precisions are clearly needed with respect to this major and specific aspect. This is especially important for ordered mixed layers (Reichweite parameter >= 1, which are not dealt with in the reported examples) because of the implications on junction probabilities.
   PyXRD indeed supports differently swelling layers by adding several components with different hydration or intercalation states. The weight fractions and junction probabilities for these components can either be set to be identical to each other across the different states or set to different values. This can be done on a parameter-level. This means it is for example possible to have an Illite/Smectite mixed layer represented by two phases, one for the AD and one for the EG state both having two types of smectite. You can then share the weight fraction of illite among the AD and EG state, but have different amounts for the two smectite layer types. We have added some more information in the section on the model structure to clarify this important aspect.

4. Third, I think that the conclusions as to the ability of the proposed refinement algorithm to determine relevant structural (and quantitative) parameters from a single XRD pattern is misleading and should be modified. The main objective of the multi-specimen approach, as described in the abundant devoted literature is NOT to determine better or more accurate parameters but rather to release possible identification ambiguities from different structure models leading, for one of the data collection conditions, to similar XRD patterns. If this

was not the case, the multi-specimen approach (and thus the present program) would be essentially useless, the more common and faster refinement of a single pattern being sufficient… Starting from computed XRD patterns, the ambiguity is easily overcome but this may not be the case when dealing with natural samples. Accordingly, all sections (including conclusion and the abstract) dealing with this aspect should be re-written. I agree with the authors however that refinement of a single pattern may be sufficient once possible identification ambiguities are released (by using the multi-specimen approach).
We did not claim the multi-specimen method was originally intended to determine better or more accurate parameters, but we wanted to see if it is possible to use it in this way. We have re-formulated the hypothesis we are testing and the conclusion to avoid any confusion on this aspect and modified the relevant parts in the manuscript where needed.

5. Finally, reference list is far from being complete. XRD profile modeling has developed significantly over the last two decades because of the increased availability of computing resources and calculation routines. Most of the latter had however been developed and used in the 1970's, and it would be reasonable to cite these pioneering works. It is for example striking that Newmod is cited as one of the available calculation routines with no reference to its original author (R.C. Reynolds, Jr.).
We agree the reference list in the manuscript was a bit lacking. The reason for this was that the complete mathematical deduction is given in the manual. We also feel it is not neccesary to add these deductions in the manuscript, because it would make it too long, and we are not presenting a new development on that front. However, we have added more references in the manuscript including the specific ones mentioned by the reviewer.

Minor remarks:

6. p. 2497: Avoid acronyms in the title
Changes made accordingly
7. p. 2499, l. 1-4: References needed
Changes made accordingly
8. p. 2499, l. 8-11 / p. 2499, l. 21-25: Additional (older) references could be added. In particular reference to the original modeling works of Reynolds (for Newmod), and of the Russian group (Drits and Sakharov) from early 1970's could be included.
Changes made accordingly
9. p. 2500, l. 16-17: References to Meunier and Lanson are not relevant (at least not as presently written) here as they essentially review existing literature.
Changes made accordingly
10. p. 2500, l. 27-28: This statement contradicts the conclusions of the article (as the authors show that it is possible to obtain equally good structural/quantitative determination from a single XRD pattern). From the previous lines, one interest would be to obtain a faster refinement and an improved consistency of the structure models derived from different XRD patterns.
We did not state this is the case, rather we check this hypothesis. We have made some changes to these lines to clarify this.
11. p. 2502, l. 17-18: Probably not necessary to consider ionic species the effect being strongly correlated with thermal motion.
We agree it might not influence the calculation, but include this information anyway.
12. p. 2503, l. 10-12: This is wrong as Newmod also includes uniform (or custom) distribution, MLM2C/3C Ergun's distribution, …
We fail to see what the reviewer is considering wrong here. The lines he refers to are dealing with distributions implemented in PyXRD, not in other models. We are not stating the other models only have these implementations.
13. p. 2503, l. 18: Projection is along c* not c
Changes made accordingly

14. p. 2504, l. 12-14: This possible constrains appear similar to those that were considered inadequate for other programs (see for example p. 2500, l. 8-11)
    We did not claim these constrains are inadequate, we claim the models are not constrained well enough for an automatic refinement without them. We have made changes to clarify our statement.
15. p. 2505, l. 9-20: I am not sure all acronyms are necessary especially as they are (very) seldom used in the rest of the article. Remove acronyms.
    Changes made accordingly
16. p. 2507, l. 5: Why not just consider statistical counting noise [sqrt(I0)]
    Because the patterns considered are not actual measured patterns and are not expressed on an absolute scale (often with decimal values instead of integer counts). We agree this would be the logical approach for real life data.
17. 2507, l. 8: Such a noise level corresponds to ~40000 counts which is seldom achieved experimentally on mixed layers.
    If you would consider statistical counting noise this would indeed translate to this level of counts. However we also wanted to include detector noise (which we acknowledge has improved greatly with recent detectors, but can still be an issue for older XRD equipment) and noise resulting from sample fluorescence, which used to be a problem for us when working on Fe-rich samples with a Cu X-ray source. Modern detector technology can now largely overcome this problem. We have made some small modifications to clarify the motivation behind this.
18. p. 2508, l. 10-11: Systematic discrepancies should be described and an explanation sought.
    Changes made to accordingly.
19. p. 2509, l. 1-2: Meaning unclear.
    Changes made to clarify.
20. p. 2510, l. 26-27: Again, XRD profile modelling was used before 2010!
    We never stated this is the case, and believe it is more relevant to give recent examples, illustrating the currently used approaches and methods.

Referee #2

General comments:

1. Although the interest of the program is undeniable, the article is not sufficiently clear to explain the aims of the program. In addition, the comparison of the program with those are currently used is not developed and the interest of the development proposed by PyXRD v0.6.2 are not enough supported by the discussion.
   We believe the currently reworked manuscript addresses these issues by adding a more thorough comparison and by clarifying the tested hypothesis.
2. Moreover, the “test case simulations” exposed are not enough discussed in details to be considered relevant for a test of sensitivity.
   We never stated these test case simulations are a test of sensitivity. We do mention parameter sensitivity when trying to explain why the used refinement strategy did not converge for a few parameters.
3. First part of the introduction presents a short paragraph about clay minerals. This part is not enough detailed and too restricted to clay minerals by contrast to the title in which the used of the program is generalized to “layered minerals”. If PyXRD v0.6.2 can provide XRD calculation of 00l reflections from different types of layered minerals, the authors should enlarge this first part to other types of layered structures such as layered double hydroxides or layered carbon. If the program provides XRD calculation for only clay minerals, the authors should change the title.
   Although PyXRD can, in theory, produce X-ray diffraction patterns for any kind of layered material, it is geared towards using it for clay minerals. Therefore, we have changed the title to indicate this.
4. The second paragraph deals with the previous programs that were developed to performed XRD calculation in order to identify and quantify clay minerals. This part seems not enough detailed and the differences between XRD calculations from powders and from oriented preparations is not clear. These approaches are complementary but the authors do not explain their own interest. Development of XRD calculation for powders has been used in first for the identification of crystal structure and then has been applied to quantify the contribution of each mineral in a mixture or a sample. Nevertheless, even powerful, this approach was not able to refine structure for layered mineral when mixed layering structures are present. For this reason, XRD calculation of the 00l reflections of layered minerals has been developed in the aim to first determine the structural defect due to mixed layering and second, quantify the contribution of such MLMs in a sample. Thus, the development of profile fitting of 00l reflections from oriented sample is mainly due to the difficulty to identify and quantify MLMs from powder samples and remains the main interest of this type of XRD calculation. This is no mentioned in this paragraph and a background part could be dedicated to this topic in the paper in order to highlight the interest of the program proposed. The authors should split the two types of calculation approaches (powder and oriented sample) after their presentation and focus on the programs that were developed for the calculation of 00l reflections. There are several other programs than those given in the text (NEWMOD, MLM3C, Sybilla) and the authors should give a complete overview of them, they have been developed since the 70’s. Particular attention should be paid to their ability to calculate XRD patterns from complex MLMs with more than 2 types of constitutive layers. Note that the authors present some drawbacks about XRD calculation of oriented samples that are not improved in the manuscript because they cannot. This has a limited interest for the reader.
   We have clarified this paragraph by elaborating on the differences between powder and oriented samples, and by adding some more background as to why modelling of oriented samples is important for mixed-layer minerals. We disagree that we should add a complete overview of all the models that have been developed since the '70, since we are not writing a

review paper. We believe we have included the most commonly used, well known and recent models in our introduction and this should be sufficient. We agree on the reviewers point that the mentioned drawbacks and advantages are perhaps not very relevant and have removed them from this paragraph.

5. The last paragraph is about the ability of the programs to automatically refine parameters for XRD calculation. As for the second paragraph, this paragraph should develop with more details the differences between the automatic approaches used because the automatic procedure is the main input of the program proposed.
   We would again like to point out we are not writing a review paper, and do not feel it is appropriate to give a very detailed description of all the different methods for automatic parameter refinement. We have added some more detail to this paragraph which we believe should help the reader in understanding the significance of the choice without going too far off-topic.
6. About the multi-specimen approach, the authors should explain deeper this procedure because this procedure is traditional in the study of clay minerals for their qualitative identification, and was added latter as a constraint for their XRD calculation.
   Changes were made accordingly.
7. Materials and methods: The main problem of this part is the lack of explanation about the calculation of XRD patterns for layered structures. The authors present the different components of their program but there is no explanation and no calculation that could validated the part that concerns the calculation of the layered structures themselves. This is fundamental because before work on mixture of layered minerals, the authors must prove that their program well reproduced experimental XRD patterns of layered structures from which, the crystal structure as well as the chemistry is know. The author should develop a large part about the parameters computed and give some example that validate the XRD calculation for know layered structures, discrete and MLMs (this could be the first section of the results part). In addition, the authors should compare their resulting calculations with XRD patterns calculate and validate from other software that used a similar approach (Sybilla, MLM3C. . .). In such case, they should compare the direct XRD calculation from simple to complex layered structures, such as discrete to 3 components MLMs with complex stacking order (R2).
   The lack of explanation about the calculations is not relevant, since these are included in the manual of the program, as also mentioned in the manuscript. We have made the suggested comparison. We compared our model with Sybilla, since it was readily available to us and MLM3C is not. Also see the remarks below.
8. Test case simulations The cases tested do not appear relevant except for the automatic refinement. Indeed, the authors test solely their automatic refinement procedure by using theoretical mineral assemblage from their own program. The first test proposes in the comment about “Materials and methods” part seems to be a first step before the case proposed. There are several possibilities to evaluate the program and the choice is too restricted and do not allow to judge the validity and the limits of the automatic refinement procedure. I would suggest to the authors an example of gradual test for the result part:
   - First section: validity of the XRD calculation. Comparison with the results obtained from other programs with a gradual increase of the complexity of the layered structures (discrete clay without swelling layers in air dried state; discrete swelling layers under various treatments such as air dried and after glycolation; R0 two component MLMs without swelling layers; R0 two component with swelling layers; R0 three component MLMs without swelling layers; R0 two component with swelling layers; R1 and R2 three component MLMs with or without swelling layers to finally validate the calculation of parameters for the stacking order).
   - Second section: Validity of the quantitative results from mixture of layered structures: Based on the same idea (comparison with Sybilla results for example), the contribution

of discrete and complex MLMs could be compared on a set of examples which have been validated in the first section. A gradual complexity of the mixture that can reach the complexity of **natural** soil samples could be proposed (from mixture with two clay minerals to mixture with eight or ten clay minerals with 3 or 4 types of R0 three component MLMs). One example with mixture that mimics the clay paragenesis of diagenitic rocks could be also interesting for the geologist. Indeed, such types of samples were, and are, the most studied and such example could allow enlarging the audience. One or two samples from the Golf coast series seem to be good examples (with R0 and R2 MLMs, see the XRD calculations performed in Lanson, B. et al, 2009. Diagenetic smectite-to-illite transition in clay-rich sediments: a reappraisal of X-ray diffraction results using the multi-specimen method. Am. J. Sci. 309, 476–516.).

- Third section: assessment of the automatic refinement based on multi-specimen approach. Based on the same examples than those proposed in the second section, the automatic refinement could be assessed. The main interest of the automatic refinement is for complex mixtures because for less complex mixtures with two or three clay phases (even with R0 2 components MLMs like assemblage 1 and 4 presented in the article), a reliable structure can be find very fast (about one hour) with the manual trial and error approach. Thus, two complex structures, one that mimic <2 µm fraction of soil sample (high number of discrete and R0 3 components MLMs) and one that mimic diagenetic sample (lower number of clay minerals but with R2 MLMs) could be interesting. In such cases, the interest of the multi specimen approach should be more evident because the presence of 3 component MLMs with swelling layers (that can have heterogeneous hydration or swelling behaviours) need to be constraint by using various treatments. One additional interesting example could be the original XRD calculation from which the multi specimen approach was developed for XRD profile modelling (Sakharov, B.A. et al, 1999. Determination of illite–smectite structures using multispecimen X-ray diffraction profile fitting. Clay Clay Miner. 47, 555–566).
- Results and discussion: The “Test case simulations” part could be removed and replaced by a results and discussion part. The different sections proposed below could be discussed in order to demonstrate that the program proposed is relevant for i) XRD calculation of complex layered structures (first section), ii) relevant for the quantification of complex layered structures in mixture (second section), iii) the automatic refinement proposed based on the multi-specimen approach is relevant to rapidly obtain coherent structural models (third section).

We have tried to address most of the suggestions made by the reviewer. More specifically, we have added a direct comparison of PyXRD and Sybilla output for 13 discrete phases (first section) and for 5 mixtures (second section). We have kept the original data regarding the assessment of the automatic parameter refinement with and without the multi-specimen approach. We have not added the examples as suggested by the reviewer, due to time constraints. Nonetheless we believe the currently included comparison is sufficient to illustrate the validity of PyXRD's output.