

Interactive comment on “PyXRD v0.6.2: a FOSS program to quantify disordered, layered minerals using multi-specimen X-ray diffraction profile fitting” by M. Dumon and E. Van Ranst

Anonymous Referee #2

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General comment

In this manuscript, the authors proposed a new program PyXRD v0.6.2 to identify and quantify layered minerals from experimental X-ray diffraction data. This software allows calculating XRD patterns from mixture of discrete layered minerals and mixed layered minerals (MLMs). In the aim to obtain the best fit between the experimental XRD patterns and the calculated one, the parameters used for the calculated XRD pattern are refined by using complex refinement algorithms. The main advantage of this program is to provide one set of parameters and thus, one mixture of layered mineral structure that can fit experimental XRD patterns from various treatments, which is named “multi-specimen” approach in mineralogy. Although the interest of the program is undeniable,

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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. Moreover, the “test case simulations” exposed are not enough discussed in details to be considered relevant for a test of sensitivity. For these reasons, this paper cannot be published in Geoscientific Model Development as proposed. The article should be partly rewritten and several additional explanations and results seem to be needed. I’m aware that the suggestions will require a consequent work nevertheless I’m convinced that these modifications of the text as well as the addition of parts will increase the audience and to strengthen the manuscript for the use of this promising program.

Major comment

Introduction

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 use 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. The second paragraph deals with the previous programs that were developed to perform 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

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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 not 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. 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. 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 later as a constraint for their XRD calculation.

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 validate the part that concerns the calculation of the layered structures themselves. This is fundamental

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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 known. The author should develop a large part about the parameters computed and give some example that validate the XRD calculation for known 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 calculated and validated 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).

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 proposed 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 does 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 contribu-

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tion 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 diagenetic 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 found very fast (about one hour) with the manual trial and error approach. Thus, two complex structures, one that mimic $<2 \mu\text{m}$ 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 constrained 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

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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).

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