Simulations of Theoretical 2D and 1D X-Ray Diffraction Patterns of Palygorskite

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INTRODUCTION

Palygorskite is a modulated phyllosilicate mineral with a structure formed by 2:1 layer type polysomes which are linked by periodical inversions of the apical oxygen of the continuous tetrahedral sheet, and the octahedral sheets is the modulated component, having the following structural formula: $Si_8(Mg_2Al_2)O_{20}(OH)_2(OH_2)_4.4H_2O$. In the literature we can find several structural models of palygorskite, belonging all of them either to monoclinic (Bradley, 1940; 1963; Drits and Sokolova, 1971) or orthorhombic (Preisinger, 1963) groups. Christ et al., (1969) performed a comparative study of palygorskites from different localities, concluding that the structure of the samples studied varied from orthorhombic to monoclinic, stablishing two regions of interest comprised between 4.5 – 4.0 Å and 2.6 – 2.5 Å. Chisholm (1992) performed simulations of powder diffraction considering both a monoclinic *C2/m* space group and an orthorhombic *Pbmn* space group, defining a new region of interest, along with the ones defined by Christ et al., (1969), comprised between 3.3 – 3.05 Å. Interestingly, looking at the region comprised at 4.5 – 4.0 Å, hereafter referred to as "Chisholm zone", one may visually determine whether the palygorskite is monoclinic or orthorhombic. Recent studies of the Rietveld refinement (Chiari et al., 2003; Giustetto and Chiari, 2004; Post and Heaney, 2008) agree that palygorskite is a mixture of, at least, two different phases a monoclinic and an orthorombic, as already proposed by Preisinger (1963) and Chisholm (1992) for some palygorskite samples.

The aim of this work is to perform theoretical simulations of the 2D and 1D diffraction patterns of palygorskite, according to the structural models proposed by Chisholm (1992), prior to their comparison with experimental data.

MATERIALS AND METHODS

We have performed both powder and fiber XRD simulations of palygorskite, according to the proposed structural models corresponding to the *Pbnm* and *C2/m* space groups , with the *β* values for monoclinic palygorskite by Chisholm (1992), but allowing some variation. Chisholm considers all octahedral positions occupied by Mg, while we consider that the M1 site is vacant, and therefore is definitely removed from the structural model, the M2 site is occupied by Al, and the M3 by Mg; in agreement with Guven *et al*., (1992). Fiber simulations were performed having three different orientations, being one of the *a*, *b* and *c* axes perpendicular to the beam in each of the cases.

The ANAELU software package (Fuentes-Montero et al., 2011) was used for the fiber simulation of the ideal 2D diffraction patterns. This software outputs the 2D diffraction pattern of all the possible reflections of a crystal with axial texture from the inverse pole figure and builds the direct pole figures out of them.

XOP/XPOWDER software (Sánchez del Río and Dejus, 2011) was employed for the simulation of powder 1D diffractograms. The XOP/XPLOT software was used for the visualization of all the data generated.

The simulations were performed matching our experimental conditions, as the final objective is the comparison with experimental data in a later study. Powder simulations were calculated for a wavelength of 0.619 Å, while fiber simulations were calculated for a wavelength of 0.861 Å.

RESULTS AND DISCUSSION

Powder diffraction

We observe that our simulations are in good agreement with those of Chisholm (Fig. 1), although there are some differences for some *β* values (105.20º and 106.11º) of monoclinic palygorskite, where the relative intensities of the 040 and 310 + 22 $\bar{1}$ reflections are inverted.

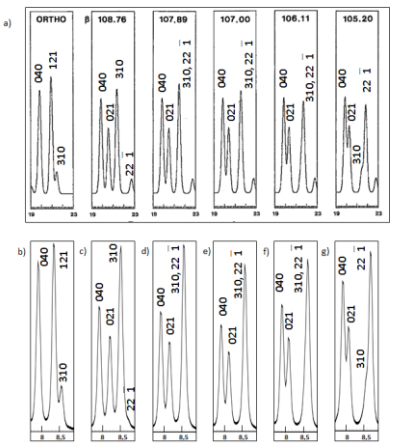

fig 1. *A) Diffraction patterns in the "Chisholm zone" simulated by Chisholm (1992) for CuKα radiation. B) to G) Simulation for palygorskite with a wavelength of λ=0.619 Å for different structures: orthorhombic (B), and monoclinic with β=108.76° (C), β=107.89° (D), β=107.00° (E), β=106.11° (F) and β=105.20° (G).*

The small differences found may be due to several reasons. One is that we considered the ideal structure of palygorskite with a vacant on the cell origin in M1 position, Al in M2 position,

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and Mg in M3, while Chisholm considers all positions occupied by Mg as in the model of Bradley (1940). We performed the simulations using this structure and obtained the same results, thus concluding that was not the cause of the differences. Another fact is that we simulated the diffractograms for a different wavelength but, again, the simulations with the CuKα wavelength gave very similar results in peak intensities. The only other reason could be the different atomic tabulations of the atomic factors used to build the structure factor. We used data from Kissel (2000) parametrized as described in Waasmaier and Kirfel (1995), but data used by Chisholm are not referred.

Fiber diffraction

We simulated the fiber diffraction in three conditions: with the *a* axis perpendicular to the beam, with the *b* axis perpendicular to the beam and with the *c* axis perpendicular to the beam, for the monoclinic and the orthorhombic structures. We observed not significant differences between monoclinic and orthorhombic 2D simulations when the *a* and the *b* axes are perpendicular to the beam, contrary to the case of *c* axis perpendicular to the beam. In the latter case, we observed for the monoclinic simulations that the *0k0* reflections remain aligned with the equator axis, whereas the other *hk0*, with $h \neq 0$, are split azimuthally, as expected considering $\alpha = \gamma = 90$ deg and $\beta \neq 90$ deg (Fig.2).

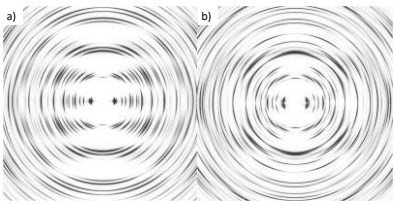

fig 2. *A) Simulated 2D fiber diffraction pattern for orthorhombic palygorskite with beam perpendicular to the c axis. B) Simulated 2D fiber diffraction pattern for monoclinic palygorskite (β = 106.11°) with beam perpendicular to the c axis.*

The powder diffraction patterns obtained by performing azimuthal integration of these 2D diffraction patterns, show remarkable differences in the relative intensities of the reflections located in the "Chisholm zone" as a function of the different orientations of the fiber (Fig. 3). When the *b* axis is perpendicular to the beam, the two types of palygorskite show similar relative intensities. Orthorhombic palygorskite shows similar relative intensities when the *a* and *c* axes are perpendicular, being the 121 the most intense reflection, but differing in the least intense reflection, being the 040 in the first case and the 310 in the second case. This also happens for monoclinic palygorskite, being the combination of the 310 and the $22\overline{1}$ the most intense in both cases, while the 021 and the 040 reflections are the least intense respectively.

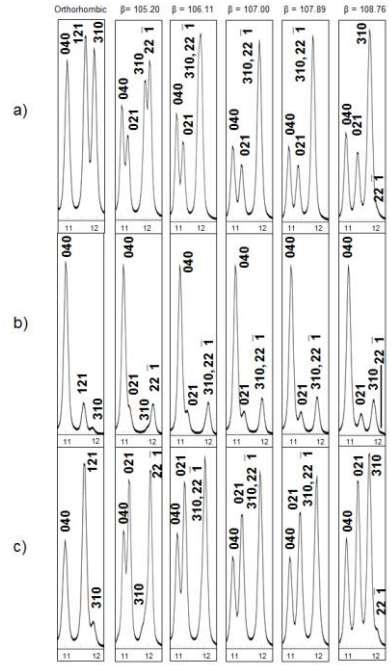

fig 3. *Simulated fiber diffractograms of the "Chisholm Zone" with λ=0.861Å for orthorhombic and monoclinic palygorskite with different orientations of the axis respect to the beam: A) Oriented with the a axis perpendicular to the beam. B) Oriented with the b axis perpendicular to the beam. C) Oriented with the c axis perpendicular to the beam.*

CONCLUSIONS

Powder simulations, according to Chisholm (1992), indeed give a discrimination criteria between monoclinic and orthorhombic palygorskite at the region of interest comprised between 4.5 - 4 Å.

Fiber 2D simulated patterns are similar when the *a* and the *b* axes are perpendicular to the beam, but the pattern is very different when the *c* axis is perpendicular to the beam.

Indeed, the powder diffraction 1D diffractograms obtained from the fiber simulations show remarkable differences and can be used as a discrimination criteria among the three possible orientations considered.
Thus, we can conclude that these simulations will help the discrimination between monoclinic and orthorhombic palygorskite when it comes to experimental data.

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