REAPPRAISAL OF THE CLAY MINERALOGY OF ORGUEIL BY X-RAY DIFFRACTION PROFILE MODELLING. J.-C. Viennet[1], F. Hubert.[2], P. Beck[3], E.E. Alp[4], B. Lavina[4,5], M.Y. Hu[4], J. Zhao[4], S. Bernard.[1], C. Le Guillou[6]., M. Gounelle[1], L. Remusat[1], M. Roskosz[1].

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Introduction: Tracking water from the formation of the solar system to present Earth ocean is a major axe of return-sample missions (Hayabusa 2 and OSIRIS Rex). Clay minerals, the main water carriers in meteorites, are pivotal in this context. CI carbonaceous chondrites represent an invaluable insight into the protoplanetary disk from which the solar system formed and are extremely rich in clay minerals. This is particularly true of the Orgueil meteorite [1]. For this reason, Orgueil has been studied to decipher the interactions between water, organic matter and clay minerals in the early solar system and to describe the pervasive aqueous alteration processes on parent bodies and planetesimals [2]. The presence of both fine-grained Mg-rich smectite and coarse Mg-rich serpentine has been repeatedly described by microscopy studies [3]. Smectites are generally interpreted as the alteration product of the coarse serpentines on the parent body [4]. Yet, microscopic and spectroscopic techniques do not allow determining quantitatively the crystal chemistry of clay minerals (nature, number and stacking mode of the layers within a crystal and proportion of the different clay phases). X-Ray diffraction profile modelling allows this [5, 6]. Here we reappraise the clay mineralogy of Orgueil using this technique in order to better identify the geochemical processes that presided to the formation of this unique object.

Methods: Recent advances in X-ray diffraction developed in soils were applied to the Orgueil meteorite. This approach combines particle size separation and modelling of X-Ray patterns. The Orgueil meteorite was Na-saturated and washed in dialysis tubing. Then, the fraction larger than 50 µm was separated using a sieve and the sub-fractions were obtained by (ultra)centrifugation (< 0.02 µm, 0.02-0.05, 0.05-0.2, 0.2-2, 2-50 µm). Finally, all sub-fractions were Ca-saturated using four saturation cycles and washed by dialysis. The X-Ray patterns were collected on oriented preparations after air drying (Ca-Ad) and ethylene-glycol solvation (Ca-Eg). The X-ray profile modelling was performed using the Sybilla software [7]. Finally, note that size separation made possible to determine the reaction pathways of clay mineral formation as a function of their particle size.

Results: The table 1 shows the relative mass of each sub-fractions after the sequential fractionation of the meteorite of Orgueil.

< 0.02 µm	0.02-0.05 µm	0.05-0.2 µm	0.2-2 µm	2-50 µm	> 50 µm
5	10	23	29	31_t	2

Table 1: *Relative mass in weight percent of each sub-fraction.*

The XRD patterns of the sub-fractions are presented in figure 1. Note that the > 50 µm size fraction is essentially made of a mixture of olivine and magnetite (data not shown). The 2-50 µm fraction is dominated by magnetite with some clay minerals. Magnetite is only present as a minor component in other fractions. Discrete serpentine is detected by the typical almost rational 00*l* reflections at 7.28 and 3.62 Å in both Ca-Ad and Ca-Eg treatments. The presence of swelling layers, corresponding to smectite, is demonstrated by the shift of the XRD patterns between the Ca-Ad and Ca-Eg treatments. In the Ca-Ad, the rational series of peaks at 15.00, 4.99, and 3.01 Å could correspond to the 001, 003 and 005 reflections of smectite. Yet, after Ca-Eg treatment, this series of peak shifts to 17.16, 8.20, 5.61, 3.41 and 2.81 Å. These are not rational, which shows that smectite is not a discrete but instead a mixed-layer-mineral (MLM). Such positions and displacements of the 00l reflections between the two treatments could indicate the presence of smectite-rich serpentine MLM.

The 00*l* reflections of the discrete serpentine decrease in intensities and become wider as the particle size decreases. This change corresponds to a decrease of the proportions and of the coherent scattering domain sizes (CSDS). Turning to the 00*l* reflections of the smectite-rich MLM, we note that they become broader and only the 001 reflection shifts to lower angles with the decrease of particle size. This could be due to a decrease of CSDS without modification of the nature and proportion of the layers within this MLM. Note that, the wide and large band found between 27 and 37° 2Θ in the <0.02 µm fractions do not correspond to any 00*l*

reflection of typical discrete clay minerals. This band is interpreted as another MLM that do not exhibit evidence of 001 reflection as observed in soil fractions [5, 6].

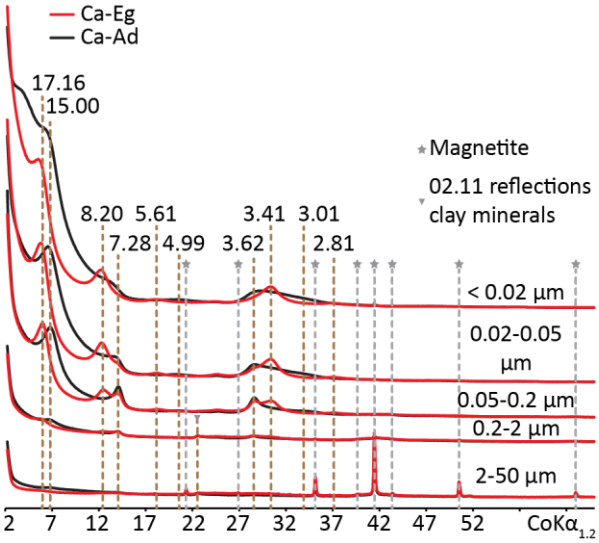

Fig. 1: *Experimental XRD patterns of the sub-fractions after Ca-Ad (black) and Ca-Eg (Red) treatments.*

Figure 2 presents the first result of the X-Ray profile modelling of the 0.02-0.05 µm size fraction. The serpentines are successfully modelled by a discrete serpentine and the smectite-rich serpentine MLM are modelled by a random stacking of layers (R0, [see 5, 6]) made of R0 smectite-serpentine (80-20) MLM. The large band between 27 and 37° 2Θ was reproduced by a R0 serpentine-smectite-10Å (50-30-20) MLM.

From this modelling a first striking result is that more than 80% of Orgueil's clay minerals are not described by microscopy such as TEM or SEM (Fig. 2). On top of the phases rich in smectites and serpentines (classically described), the MLM made of serpentine-smectite-10Å represents more than 80% of the sample. This MLM has never been described in the literature even on terrestrial rocks. A second critical result of our analysis is that the structure of the clay minerals does not seem to vary as a function of the particle sizes (data not shown).

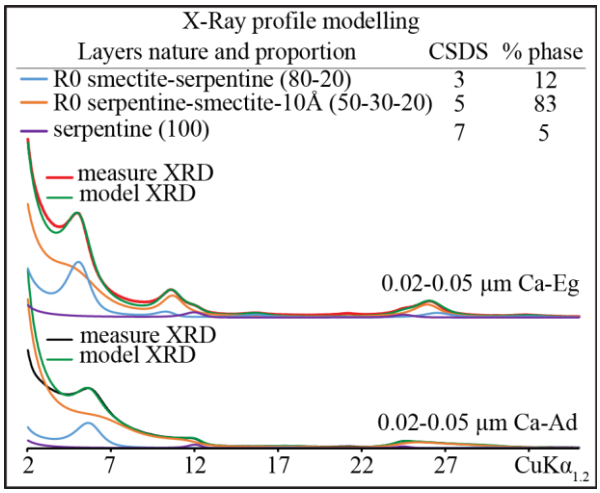

Fig. 2: *Comparison of calculated and experimental XRD patterns obtained after Ca-AD and Ca-Eg.*

Discussion: The formation of such MLMs with no clear particle-size dependence brings its share of answers and questions. The lack of such size-dependence appears inconsistent with the conventional view of fine smectites formed from the alteration of coarse serpentines. Because there is no clear particle-size dependence, it could indicate that these MLMs form in a single step, from a homogeneous medium.

Yet many questions still holds: What is the crystal chemistry of the 10Å layers? How did this 10Å layer formed? Do serpentine or smectite layers originate from the alteration of the 10Å layers or *vice-versa*? Why is there only an increase in proportion of the discrete serpentine with the increase of the particle size? What does the structure of these minerals tell us about the pH/redox/fluid temperature conditions? Were liquid water and/or vapor present during the formation of these MLMs? In other words, are these MLMs an indicator of fluid circulation on the asteroids or the product of gas-grain reaction within the disk? We will discuss these questions to better understand the geological history of Orgueil from the proto-planetary disk to the parent body processes.

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