

## **Supplementary information**

### **Structure and composition of the first biosourced Mn-rich catalysts with a unique vegetal footprint**

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## S1. Syn-M<sub>1</sub> synthesis

Syn-Mn<sub>1</sub> was synthesized by mixing commercial metallic chloride salts. The objective was to determine if an Eco-Mn catalyst and a mixture of chloride salts can have the same structure, composition and catalytic activity.

Metallic elements present in manganese accumulating plants leaves have been identified by ICP-MS analysis. Taking into account the elemental composition of *Grevillea exul* ssp. *rubiginosa* leaves, it was possible to calculate the relative weight percentage of each metallic element in these leaves thanks to **equation (1)**.

**Equation (1):**

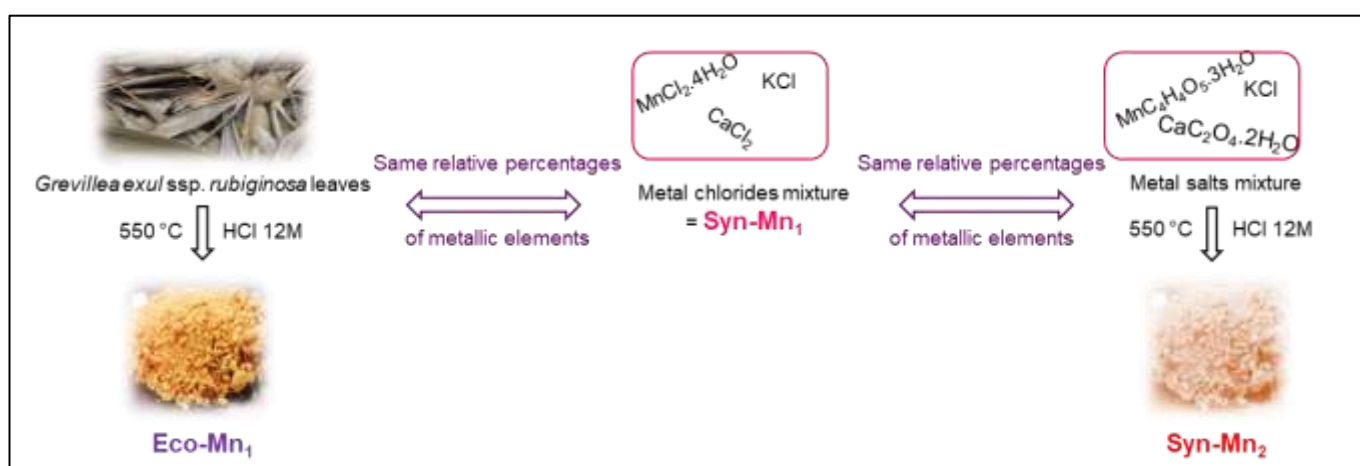
$$\text{Relative \% metallic element } i = \frac{\text{ppm metallic element } i \text{ (determined by ICP - MS)}}{\sum_{i=1}^n \text{ppm metallic element } i \text{ (determined by ICP - MS)}} \times 100$$

The relative percentages of metallic elements in *Grevillea exul* ssp. *rubiginosa* leaves are presented in **Supplementary Table 1**:

	Relative percentages of metallic elements (%)							
	Na	Mg	Al	K	Ca	Mn	Fe	Ni
<i>Grevillea exul</i> ssp. <i>rubiginosa</i>	7.96	15.87	1.13	29.04	15.51	26.52	3.24	0.72

**Supplementary Table 1.** Relative weight percentages of metallic elements present in *Grevillea exul* ssp. *rubiginosa* leaves.

Syn-Mn<sub>1</sub> was produced by mixing commercial metal chlorides, so that the relative percentages of metallic elements in Syn-Mn<sub>1</sub> and in *Grevillea exul* ssp. *rubiginosa* leaves are exactly the same (**Supplementary Fig. 1**).



**Supplementary Figure 1.** Scheme presenting the synthetic catalysts Syn-Mn<sub>1</sub> and Syn-Mn<sub>2</sub>

The selected metal chlorides to produce Syn-Mn<sub>1</sub> are: MnCl<sub>2</sub>.4H<sub>2</sub>O, MgCl<sub>2</sub> (anhydrous), CaCl<sub>2</sub> (anhydrous), NaCl, KCl, NiCl<sub>2</sub>.6H<sub>2</sub>O, FeCl<sub>3</sub>.6H<sub>2</sub>O et AlCl<sub>3</sub> (anhydrous). Experimental details are presented in Methods part.

## S2. Syn-M<sub>2</sub> synthesis

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Syn-Mn<sub>2</sub> was produced in two steps. First, well-chosen commercial or easily synthesized metallic salts were mixed all together. Then, the salts mixture was thermally and chemically treated following the same experimental procedure as the one used to produce Eco-Mn<sub>1</sub>. Syn-Mn<sub>2</sub> was produced in order to determine whether it is possible or not to reproduce the structure, the composition and the catalytic activity of an Eco-Mn catalyst, starting with a mixture of metallic salts.

The chosen salts are mixed so that the relative percentages of metallic elements in the starting mixture and in *Grevillea exul* ssp. *rubiginosa* leaves are exactly the same. The calculation of the relative percentages of metallic elements in *Grevillea exul* ssp. *rubiginosa* leaves is detailed in Supplementary Information 2.

Chosen salts that comprise Syn-Mn<sub>2</sub> starting mixture are as close as possible to the metallic complexes naturally observed in Mn-accumulating plants. Indeed, a bibliographic study was performed in order to have an insight of the chemical environment around metallic elements in Mn-accumulating plants. Thanks to this information, we chose commercial or easily synthesized metallic complexes which are as close as possible to the real metallic species present in Mn-accumulating plants.<sup>1-5</sup> For sure, the real chemical environment around metallic elements in plants is much more complex than in commercial salts, but this approach was a criterion to choose a salt rather than another.

A sample of our bibliographic study is detailed below, with the salts that have been chosen to produce Syn-Mn<sub>2</sub>.

Fernando *et al.* have demonstrated that Mn is mainly under the form of manganese malate in vacuoles of *Garcinia amplexicaulis* and *Grevillea exul* (ssp. *exul* /*rubiginosa*).<sup>6</sup> **Manganese malate trihydrate MnC<sub>4</sub>H<sub>4</sub>O<sub>5</sub>.3H<sub>2</sub>O**, was thus chosen to produce Syn-Mn<sub>2</sub> and was synthesized in the lab.

Sigel *et al.* report that 75 % of magnesium is essential for protein synthesis in plants, and is often linked to phosphate groups of RNA.<sup>7</sup> Thus, **magnesium phosphate Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.xH<sub>2</sub>O**, which is a commercial salt, was chosen.

Calcium oxalate concentrations are significant in numerous plants.<sup>8,9</sup> Besides, Leon *et al.* have highlighted the presence of calcium oxalate in *Grevillea exul* ssp. *rubiginosa* seeds.<sup>10</sup> Thus **calcium oxalate  $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$**  was selected.

Potassium plays, among others, a role in osmotic regulation of plant cells. Potassium associated anions in this phenomenon are for example chloride anions.<sup>11</sup> That is why, **potassium chloride  $\text{KCl}$**  was chosen to produce Syn-Mn<sub>2</sub>.

Sodium is not essential, but can replace potassium, for instance in osmotic regulation.<sup>12</sup> Thus **sodium chloride  $\text{NaCl}$** , was also selected.

Iron is partly stored in chloroplasts under the form of Ferritin protein, in which iron is close to phosphate groups.<sup>8,13</sup> **Iron phosphate  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$**  was thus chosen, all the more so as it is a commercial salt.

Nickel is often associated with organic acids in plants.<sup>8,14</sup> It has been shown by our team that nickel sulfate is significantly present in nickel accumulating plants of New Caledonia.<sup>15</sup> By analogy, and because nickel is only present as traces in *Grevillea exul* ssp. *rubiginosa* we preferred to choose  **$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$**  which is readily and commercially available to produce Syn-Mn<sub>2</sub>.

Finally, aluminium is also present in trace concentrations in *Grevillea exul* ssp. *rubiginosa* leaves. Few data are reported in literature concerning aluminium, except that aluminium is often associated to organic acid such as oxalic acid in Al accumulating plants.<sup>16</sup> **Aluminium oxalate  $\text{Al}_2\text{C}_6\text{O}_{12} \cdot x\text{H}_2\text{O}$** , has thus been chosen.

Experimental details concerning Syn-Mn<sub>2</sub> are presented in Methods part.

### **S3. Metallic compositions by ICP-MS analyses**

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Uncertainties on the concentrations of metallic elements determined by ICP-MS analyses, are inherent in biologic origin and in complexity of studied samples, which are composed of various elements in a wide range of concentrations. Three samples of Eco-Mn<sub>1</sub> were analysed separately, in order to get three concentration values for each element. A relative standard deviation was calculated for each element (it was obtained by dividing the standard deviation by the average of the three measures). The maximum relative standard deviation obtained in this case is 15 %. Among the three measures obtained for each

element with Eco-Mn<sub>1</sub>, the maximum gap observed between two measures is 25 % (the gap is defined as the difference between both considered measures, divided by the highest measure).

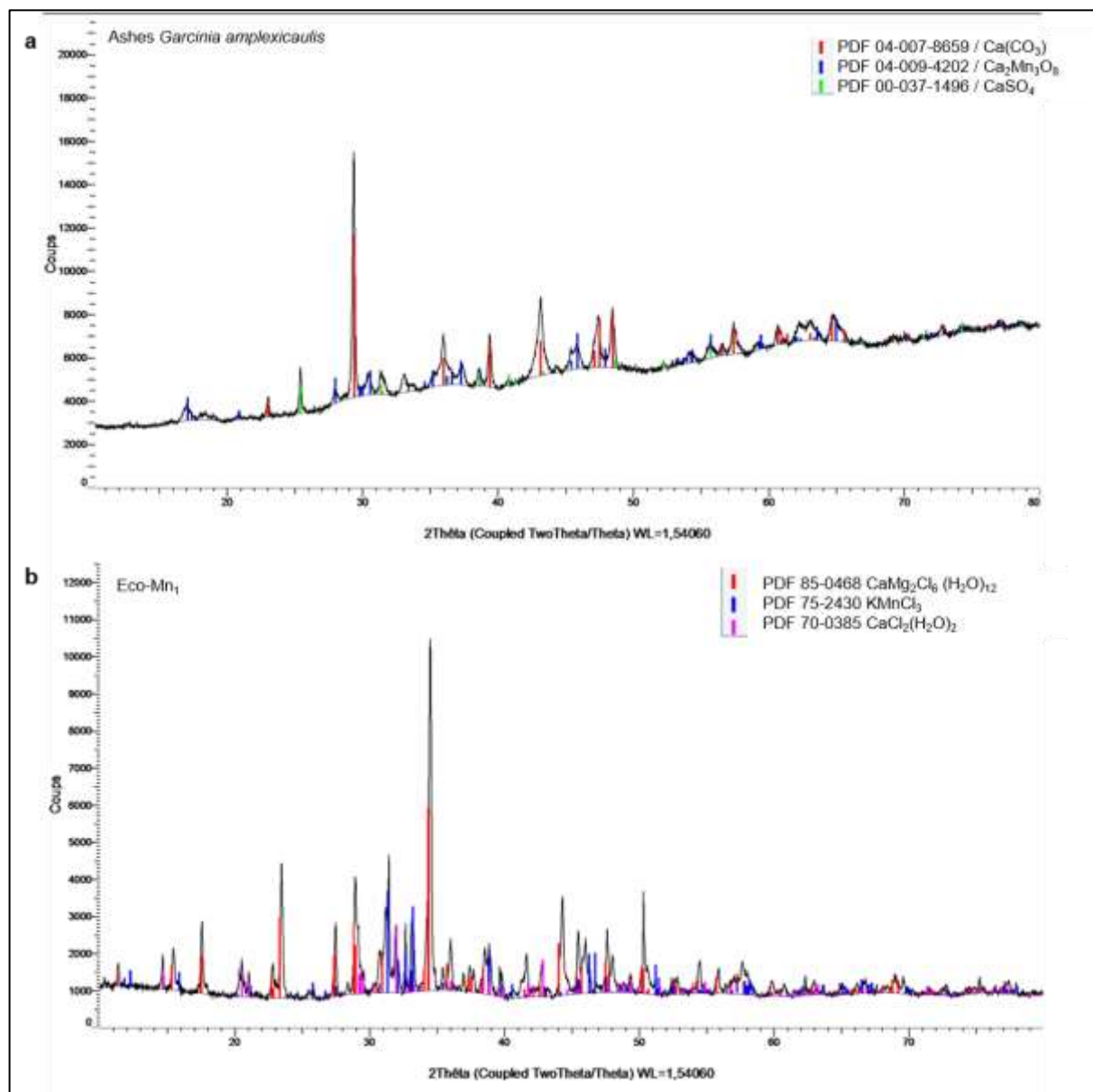
This gives an insight of the uncertainties on ICP-MS analysis and was useful to compare catalysts' compositions and to highlight principal results.

#### **S4. XRD analysis**

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Crystalline species have been identified by comparing the diffraction pics on our XRD patterns with several XRD database (Crystallography Open Data Base 2016, and PDF 2011, 2017 or 2018). Identification has been made by taking into account ICP-MS analysis.

Two examples of diffraction patterns are presented in Supplementary Figure 2, one for ashes of *Garcinia amplexicaulis*, and another for Eco-Mn<sub>1</sub>. Diffraction patterns presented here have been chosen for their readability, with a limited number of species identified on the patterns. Due to the hygroscopic nature of studied catalysts, we had to reduce the acquisition time of XRD patterns, at the expense of their quality. Baselines of XRD patterns are not straight: this is probably due to the presence of amorphous or nanocrystalline phases that cannot be identified by XRD analysis, but that induce background noise on XRD patterns.



**Supplementary Figure 2.** Diffraction patterns of **a**, *Garcinia amplexicaulis* ashes and **b**, Eco-Mn<sub>1</sub> (*Grevillea exul* ssp. *rubiginosa*, HCl 12M). Crystalline species are identified in colour.

## S5. Reference compounds selection for XAS analysis

### S5.1. Chosen salts

Reference compounds are necessary to interpret XAS spectra. As Eco-Mn, Syn-Mn and Tem-Mn catalysts are produced through an HCl activation, metal chlorides were obviously chosen as reference compounds: **anhydrous  $\text{MnCl}_2$** ,  **$\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$** ,  **$\text{KMnCl}_3$** ,  **$\text{K}_3\text{NaMnCl}_6$** ,  **$\text{MnMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$** ,  **$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$**  and  **$\text{K}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$** .

Sulphur has been identified in Eco-Mn catalysts by C,H,N,S analyses (not reported in this paper), thus manganese sulphate and iron sulphate were also selected ( **$\text{MnSO}_4 \cdot \text{H}_2\text{O}$**  and  **$\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$** ).

Besides, plants naturally contains phosphorous,<sup>8</sup> and Eco-Mn might contain phosphorous salts, such as **MnHPO<sub>4</sub>·3H<sub>2</sub>O** and **FePO<sub>4</sub>·2H<sub>2</sub>O**, that have been chosen as reference compounds.

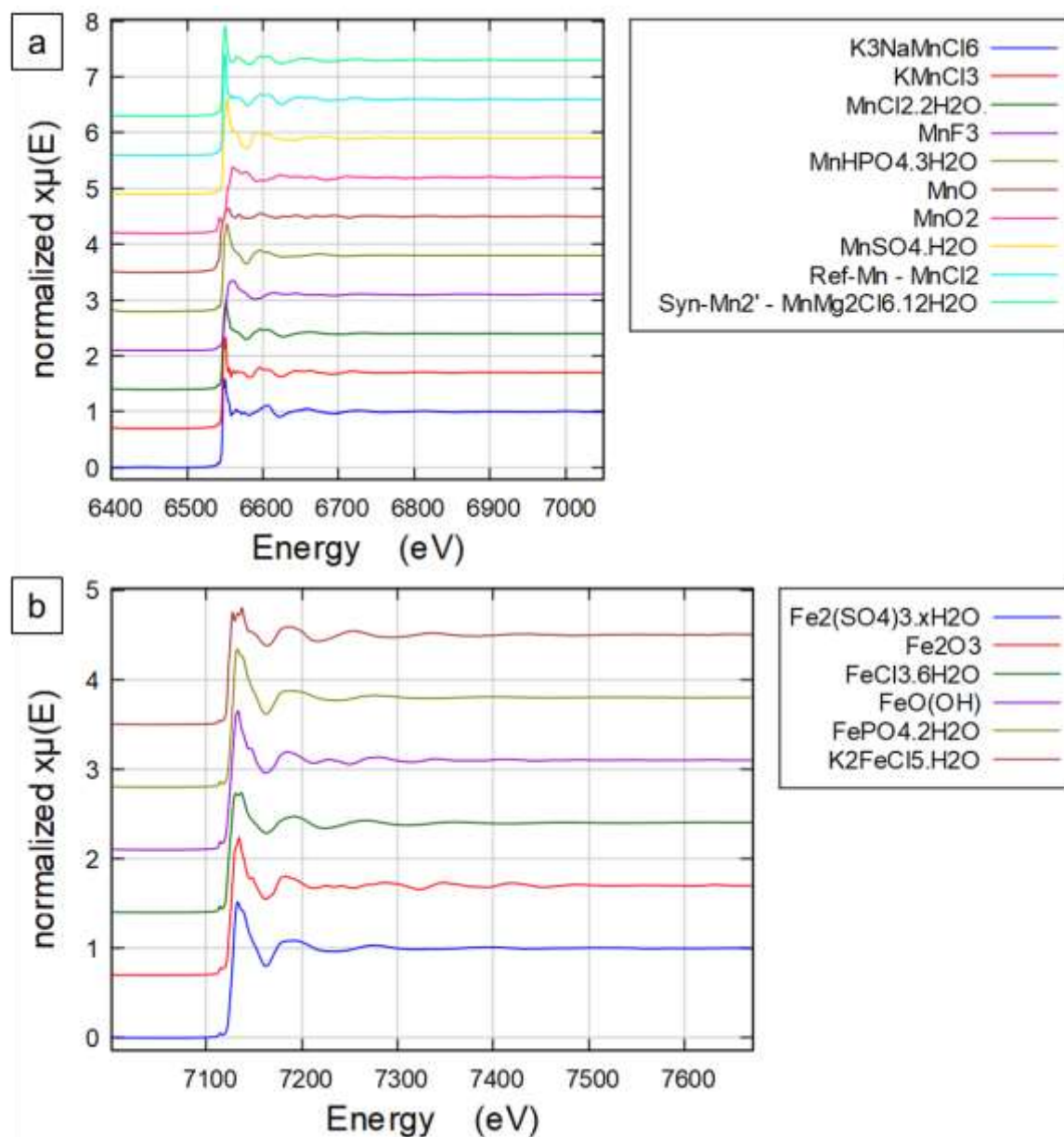
It was also necessary to select Mn salts with higher oxidation states. **MnCl<sub>3</sub>** would be ideal, but is not stable enough, that is why **MnF<sub>3</sub>** was finally chosen. Likewise, as halogen salts with Mn under the oxidation state IV are not stable, **MnO<sub>2</sub>** is used as a reference compound.<sup>17</sup>

In addition, the yellow colour of **K<sub>3</sub>NaMnCl<sub>6</sub>** crystals identified by XRD analyses in Eco-Mn is reported to be due to the presence of akaganeite, an iron oxide-hydroxide compound.<sup>18</sup> That is why **FeO(OH)** was selected as reference compound for XAS studies.

Finally, compounds with oxygen-rich environment around Mn and Fe were chosen: **MnO**, and **Fe<sub>2</sub>O<sub>3</sub>**.

X-ray absorption spectra of reference compounds are presented in Supplementary Figure 3.





**Supplementary Figure 3.** Normalized X-ray absorption spectra of **a**, Mn-rich reference compounds at the Mn K-edge, and **b**, Fe-rich reference compounds at the Fe K-edge.

### S5.2. Mn- and Fe-rich reference compounds synthesis and analyses

MnCl<sub>2</sub>·2H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, MnSO<sub>4</sub>·H<sub>2</sub>O, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O, FePO<sub>4</sub>·2H<sub>2</sub>O, MnF<sub>3</sub>, MnO<sub>2</sub>, FeO(OH) are commercial salts.

To determine the hydration state of MnCl<sub>2</sub>·2H<sub>2</sub>O, the XAS spectrum of this compound was fitted with Artemis software, see **Supplementary Table 2**, and **Supplementary Fig. 4**.

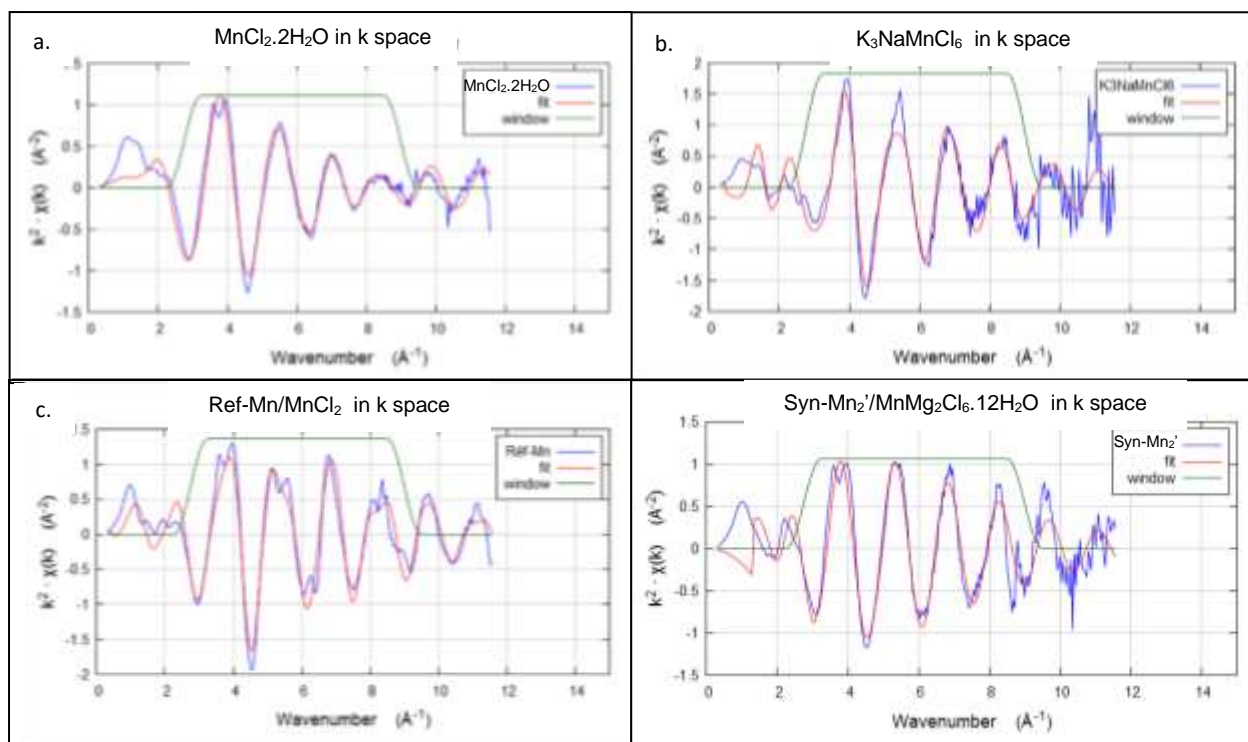
KMnCl<sub>3</sub>, K<sub>3</sub>NaMnCl<sub>6</sub>, K<sub>2</sub>FeCl<sub>5</sub>·H<sub>2</sub>O, MnHPO<sub>4</sub>·3H<sub>2</sub>O were synthesized in the laboratory. Their structure was checked by XRD analysis (**Supplementary Fig. 5**). In case of K<sub>3</sub>NaMnCl<sub>6</sub>, XAS spectrum was also fitted with Artemis software (**Supplementary Table 2 and Supplementary Fig. 4**).

Anhydrous  $\text{MnCl}_2$  and  $\text{MnMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  were produced in a different way. As Fernando *et al.* have highlighted the presence of manganese malate trihydrate in Mn (hyper)-accumulating plants from New Caledonia,<sup>6</sup> we thermally and chemically treated manganese malate trihydrate with the same experimental conditions as those used to produce Eco-Mn<sub>1</sub>. The powder resulting from the thermal and chemical treatment of manganese malate trihydrate is called Ref-Mn. XAS spectrum of Ref-Mn was fitted with Artemis software, which proved that **Ref-Mn is in fact anhydrous  $\text{MnCl}_2$**  (**Supplementary Table 2** and **Supplementary Fig. 4**).

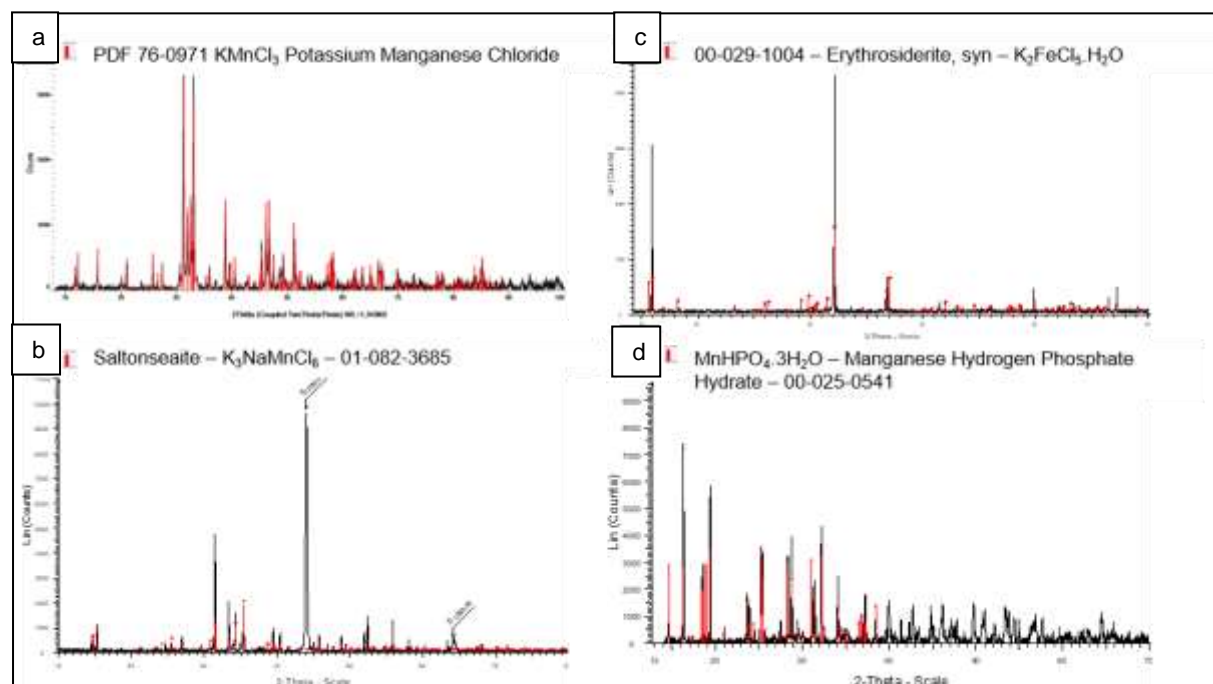
$\text{MnMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  has been shown by XRD analysis in Syn-Mn<sub>2</sub>. However, this Mn species is not pure in Syn-Mn<sub>2</sub>, but is mixed with other manganese salts. Thus, we produce a Syn-Mn<sub>2</sub>' catalyst, where  $\text{MnMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  is supposed to be the only Mn species. Syn-Mn<sub>2</sub>' was produced by adding more magnesium salt in the starting mixture used to prepare Syn-Mn<sub>2</sub>. The exclusive presence of  $\text{MnMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  in Syn-Mn<sub>2</sub>' has been proven by fitting its Mn K-edge XAS spectrum with Artemis software (**Supplementary Table 2**, and **Supplementary Fig. 4**).

	Type of neighbours	Coordination number N	Distance R (Å)	$\sigma^2 (\pm\Delta) (\text{Å}^2)$	E0 (eV)	Residual factor
<b><math>\text{MnCl}_2 \cdot 2\text{H}_2\text{O}</math></b>	Mn-O	2	2.10 ( $\pm 0.03$ )	0.002 ( $\pm 0.006$ )	-1.17	0.010
	Mn-Cl	4	2.48 ( $\pm 0.02$ )	0.006 ( $\pm 0.004$ )		
	Mn-Mn	2	3.62 ( $\pm 0.03$ )	0.011 ( $\pm 0.004$ )		
<b><math>\text{K}_3\text{NaMnCl}_6</math></b>	Mn-Cl	6	2.54 ( $\pm 0.02$ )	0.005 ( $\pm 0.003$ )	0.85	0.033
	Mn-Na	2	3.55 ( $\pm 0.09$ )	0.007 ( $\pm 0.018$ )		
	Mn-K	6	3.99 ( $\pm 0.03$ )	0.011 ( $\pm 0.006$ )		
<b>Ref-Mn = anhydrous <math>\text{MnCl}_2</math></b>	Mn-Cl <sub>1</sub>	6	2.54 ( $\pm 0.01$ )	0.005 ( $\pm 0.001$ )	0.78	0.033
	Mn-Mn	6	3.75 ( $\pm 0.02$ )	0.010 ( $\pm 0.003$ )		
	Mn-Cl <sub>2</sub>	2	4.45 ( $\pm 0.08$ )	0.005 ( $\pm 0.001$ )		
	Mn-Cl <sub>3</sub>	6	4.63 ( $\pm 0.03$ )	0.005 ( $\pm 0.001$ )		
<b>Syn-Mn<sub>2</sub>' = <math>\text{MnMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}</math></b>	Mn-Cl	6	2.56 ( $\pm 0.01$ )	0.006 ( $\pm 0.001$ )	6.69	0.019

**Supplementary Table 2.** Structural parameters obtained by fitting XAS spectra of four reference compounds with Artemis software



**Supplementary Figure 4.** Figures obtained by fitting XAS spectra of four reference compounds, **a**,  $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ ; **b**,  $\text{K}_3\text{NaMnCl}_6$ ; **c**,  $\text{Ref-Mn/MnCl}_2$ ; **d**,  $\text{Syn-Mn}^{2+}/\text{MnMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ .



**Supplementary Figure 5.** XRD patterns of four reference compounds, **a**,  $\text{KMnCl}_3$ ; **b**,  $\text{K}_3\text{NaMnCl}_6$ ; **c**,  $\text{K}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  and **d**,  $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$

## S6. PCA analysis of XAS spectra at Mn K-edge, and Target Transformation analysis

Principal component analysis (PCA) aims at determining the number of pure Mn species present in studied catalysts. The starting point consists in recording XAS spectra of several catalysts in exactly the same experimental conditions.

Each spectrum can be represented as a vector, and all the spectra can be represented under the form of a matrix  $D$ , where each column represents a spectrum, and where each line corresponds to a value of energy. The value indicated on the  $i^{\text{th}}$  line and the  $j^{\text{th}}$  column, corresponds to the value of the linear absorption coefficient  $\mu(E)$  associated to the  $i^{\text{th}}$  energy on the spectrum of the  $j^{\text{th}}$  catalyst.<sup>19,20</sup>

PCA consists in representing the whole dataset with another basis of orthogonal vectors, called **principal components**. In other word the  $D$  matrix can be written as the following product:

$$D = U \cdot S \cdot V^t$$

Where:  $U$  is the orthogonal matrix of principal components

$S$  is a diagonal matrix, with eigenvalues on the diagonal which represent the relative importance of principal components

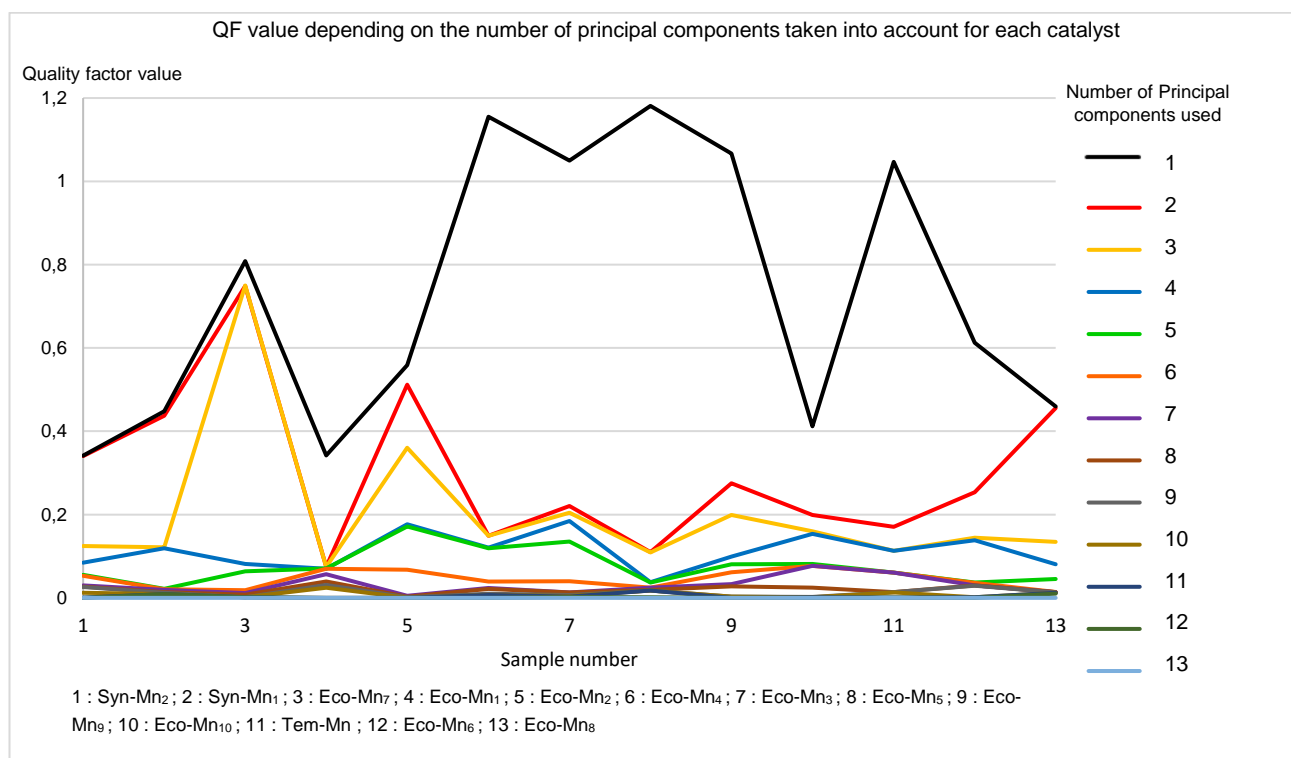
$V^t$  is an orthogonal matrix, which represents the contribution of each principal component to reconstruct each XAS spectrum.

This is the Singular Value Decomposition Algorithm.

Once principal components have been found, it is necessary to identify the minimum number of principal components required to fit all the catalysts' experimental XAS spectra. This minimum number of principal components coincides with the number of pure Mn species present inside Eco-Mn catalysts.

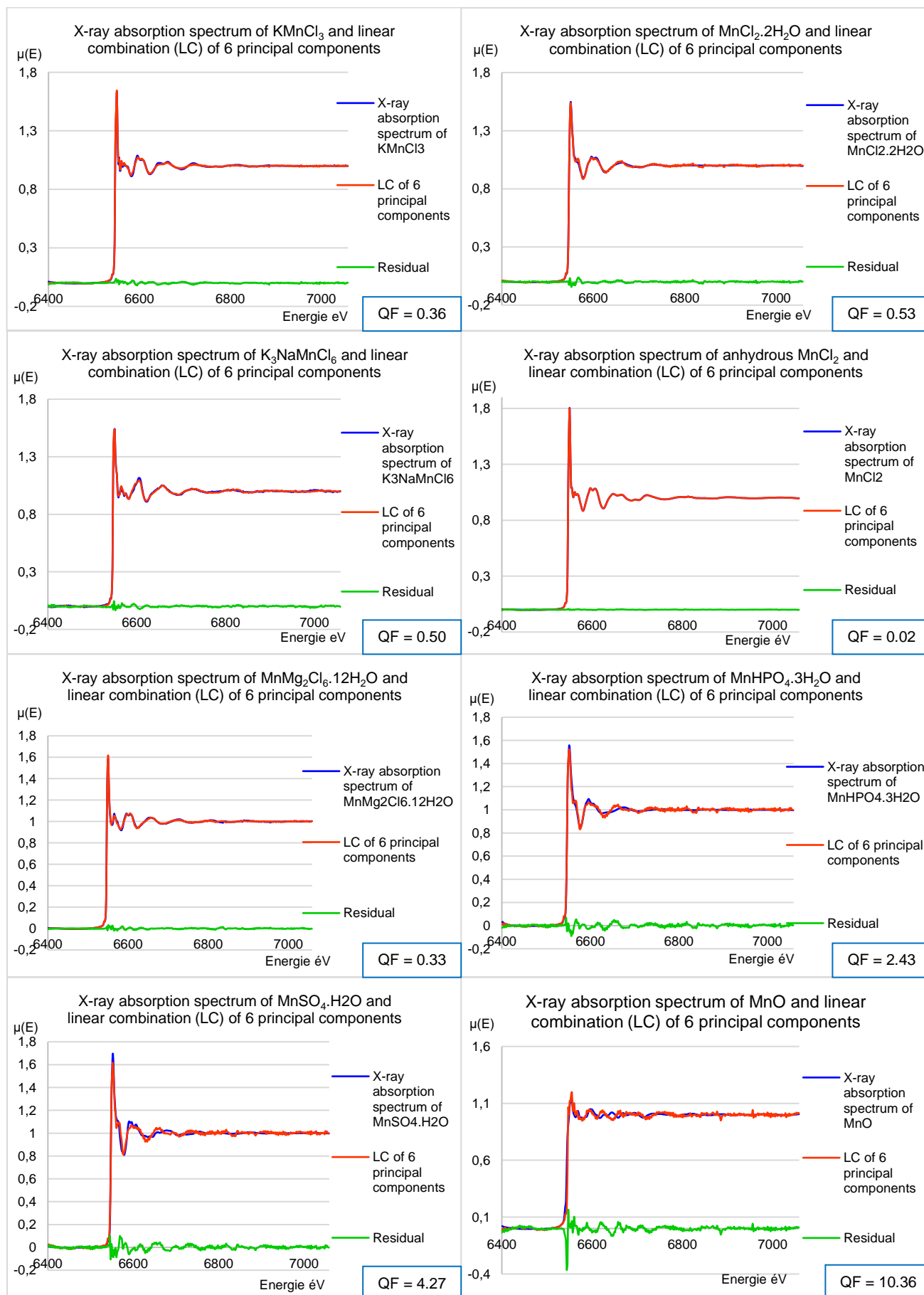
Malinowski indicators are often used to determine the number of principal components that should be taken into account.<sup>19,21</sup> The StraightNoChaser software developed by Michalowicz *et al.*<sup>22,23</sup> also puts forward a quality factor (QF) calculation. The lower is the QF, the better is the fitting of experimental XAS spectra with the considered principal components.

We used the QF factor in this study (**Supplementary Fig. 6**). According to the QF factor, it seems that Eco-Mn, Syn-Mn and Tem-Mn XAS spectra can be fitted with six principal components. Considering more than 6 principal components does not significantly improve the QF value. Thus, Eco-Mn, Syn-Mn and Tem-Mn catalysts are mainly composed of 6 pure Mn species.



**Supplementary Figure 6.** PCA: number of principal components to choose indicated by the QF value

Target Transformation enables to select among all the studied reference compounds the most likely present in Eco-Mn catalysts. This method consists in determining which reference compounds' XAS spectra can be properly fitted with a linear combination of principal components.<sup>19,20</sup> Experimental XAS spectra of reference compounds, and linear combinations of principal components are presented in **Supplementary Figure 7**.



**Supplementary Figure 7.** Target Transformation of reference compounds; QF is a quality factor given by StraightNoChaser software: the lower is the QF, the better is the target transformation.

We put forward two groups of reference compounds: the reference compounds whose XAS spectra can be fitted with a linear combination of 6 principal components and a QF value lower than 1, and the reference compounds whose spectra is fitted with a QF value higher than 1. We can deduce that, **chlorinated reference compounds (MnCl<sub>2</sub>, MnCl<sub>2</sub>.2H<sub>2</sub>O, KMnCl<sub>3</sub>, K<sub>3</sub>NaMnCl<sub>6</sub>, MnMg<sub>2</sub>Cl<sub>6</sub>.12H<sub>2</sub>O) are most likely present in Eco-Mn, Syn-Mn and Tem-Mn catalysts.**

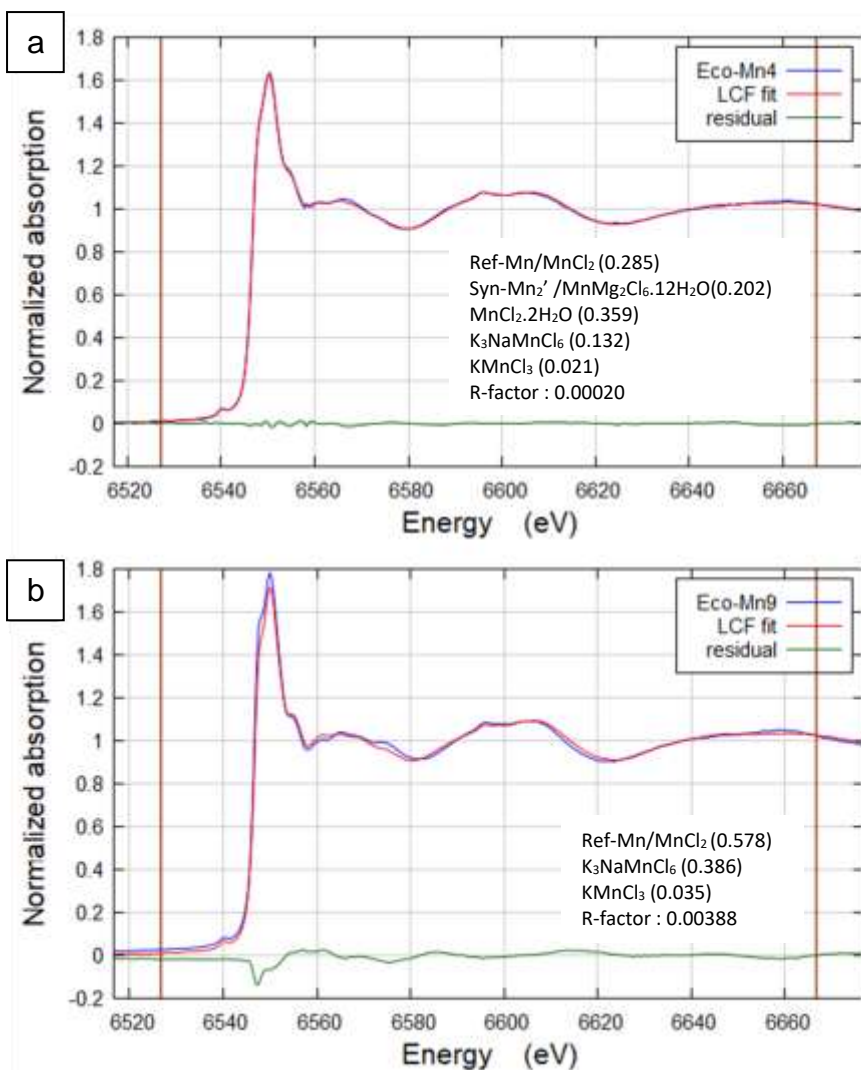
### **S7. Linear combination fitting on XANES spectra at Mn K-edge**

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Linear combination fitting (LCF) aims at fitting experimental XAS spectra of studied catalysts with linear combinations of reference compounds' XAS spectra. Thanks to PCA analysis a restricted number of reference compounds is selected to perform LCF. LCF aims at determining the nature and proportions of pure Mn species that comprise studied catalysts.

LCF has been performed on XANES spectra of all the studied catalysts. Coefficients of linear combinations are given in **Supplementary Table 3**. Comparisons between experimental spectra and spectra obtained with linear combination fitting, are presented in **Supplementary Figures 9 and 10**.

Two examples of linear combination fitting (on XANES spectra of Eco-Mn<sub>4</sub> and Eco-Mn<sub>9</sub>) are presented in **Supplementary Figure 8**.



**Supplementary Figure 8.** Two examples of LCF with Athena software on XANES spectra of **a**, Eco-Mn<sub>4</sub> and **b**, Eco-Mn<sub>9</sub>

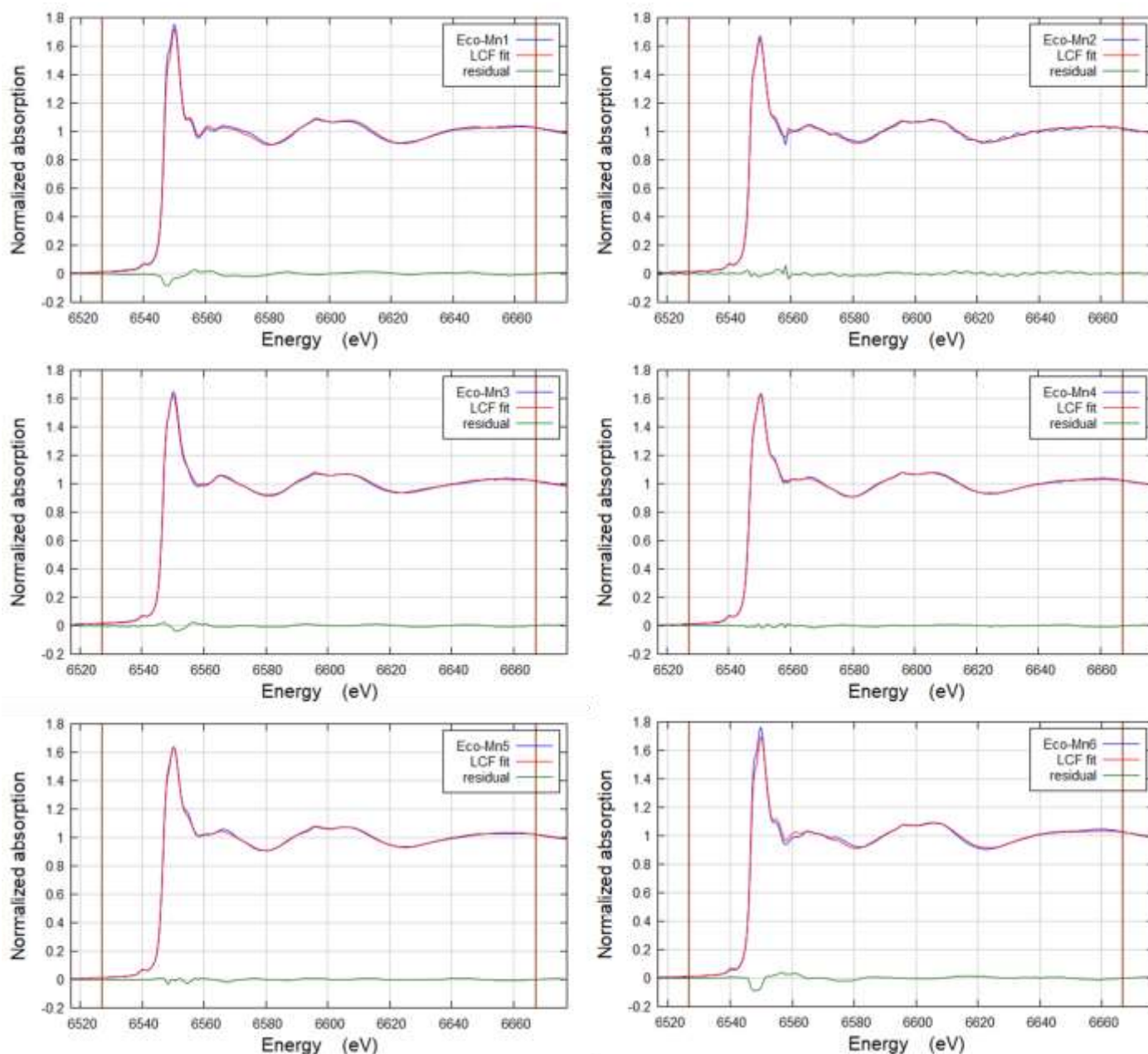
	Catalysts	K <sub>3</sub> NaMnCl <sub>6</sub>	KMnCl <sub>3</sub>	Ref-Mn / MnCl <sub>2</sub>	Syn-Mn <sub>2</sub> ' / MnMg <sub>2</sub> Cl <sub>6</sub> ·12H <sub>2</sub> O	MnCl <sub>2</sub> ·2H <sub>2</sub> O	R-factor	Reduced chi- square
1	Eco-Mn <sub>1</sub>	0.14 (±0.02)	0.33 (±0.05)	0.52 (±0.02)			0.00177	0.000227
2	Eco-Mn <sub>2</sub>	0.23 (±0.04)	0.19 (±0.02)	0.21 (±0.01)	0.34 (±0.02)		0.00081	0.000099
3	Eco-Mn <sub>3</sub>			0.17 (±0.01)	0.65 (±0.01)	0.16 (±0.03)	0.00053	0.000065
4	Eco-Mn <sub>4</sub>	0.13 (±0.03)	0.02 (±0.01)	0.28 (±0.01)	0.20 (±0.01)	0.35 (±0.01)	0.00020	0.000025
5	Eco-Mn <sub>5</sub>	0.04 (±0.01)		0.28 (±0.01)	0.35 (±0.01)	0.31 (±0.01)	0.00028	0.000035
6	Eco-Mn <sub>6</sub>	0.35 (±0.02)	0.19 (±0.04)	0.45 (±0.02)			0.00224	0.000290
7	Eco-Mn <sub>7</sub>		0.71 (±0.01)	0.13 (±0.01)	0.07 (±0.03)	0.08 (±0.01)	0.00066	0.000079
8	Eco-Mn <sub>8</sub>	0.04 (±0.05)	0.03 (±0.01)	0.90 (±0.01)	0.01 (±0.01)		0.00024	0.000031
9	Eco-Mn <sub>9</sub>	0.38 (±0.03)	0.03 (±0.06)	0.57 (±0.03)			0.00388	0.000494
10	Eco-Mn <sub>10</sub>	0.12 (±0.02)	0.22 (±0.04)	0.64 (±0.02)			0.00226	0.000285
11	Syn-Mn <sub>1</sub>	0.03 (±0.01)	0.19 (±0.01)	0.75 (±0.01)		0.01 (±0.01)	0.00014	0.000017
12	Syn-Mn <sub>2</sub>	0.43 (±0.01)		0.40 (±0.01)	0.16 (±0.05)		0.00102	0.000130
13	Tem-Mn		0.34 (±0.04)	0.65 (±0.03)			0.00381	0.000487

**Supplementary Table 3.** LCF results on XANES spectra. Uncertainties are indicated in parentheses. Phases below 10% have been reported, but their contribution can be neglected or not supported by XANES fitting alone.

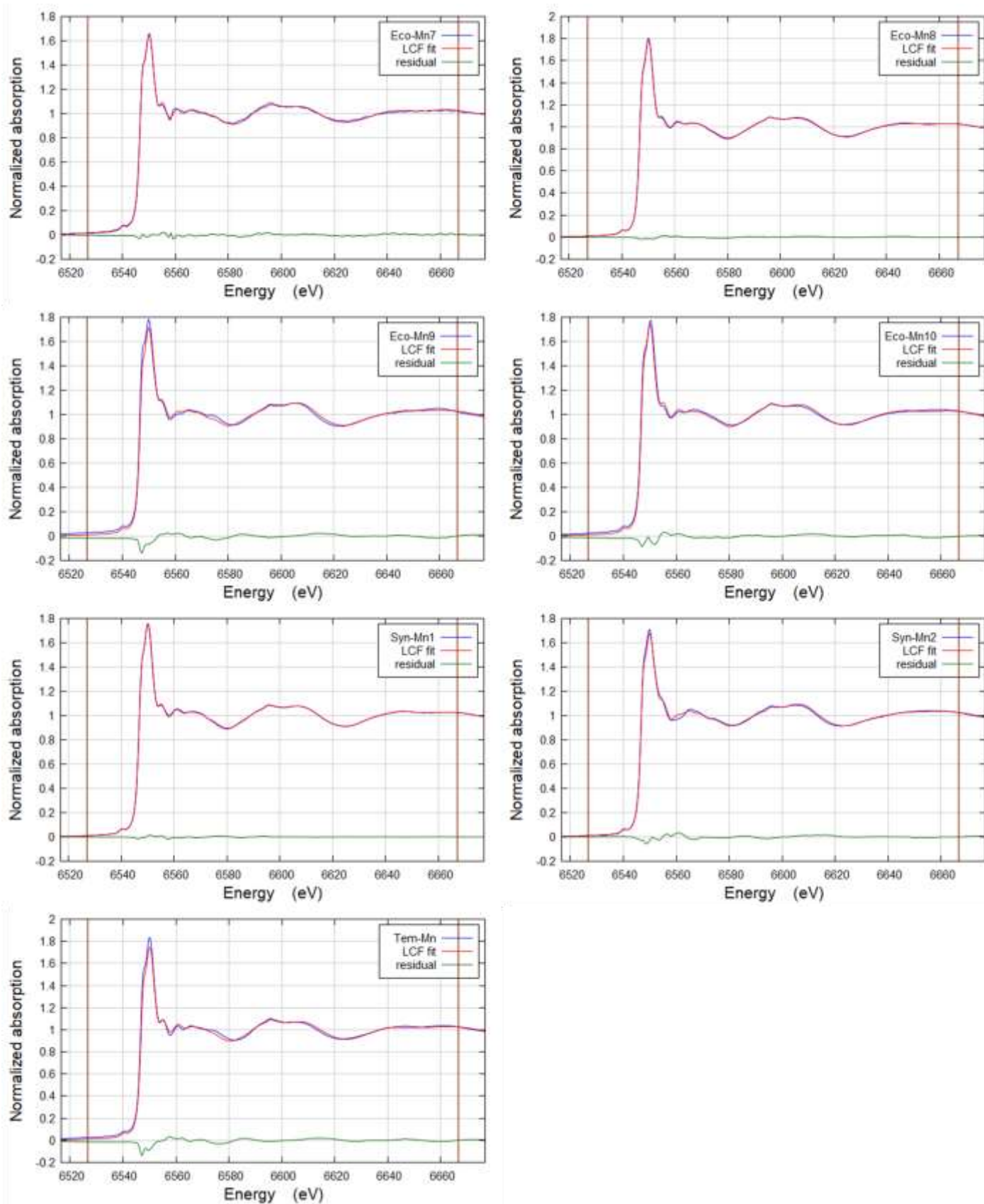


Blanks in Table 5 mean that when one species is not present in a catalyst, Athena software does not take it into account in the linear combination.

In case of Eco-Mn<sub>2</sub> and Eco-Mn<sub>7</sub>, XAS spectra are quite noisy, thus the LCF analysis is not very precise, and results have to be considered carefully.



**Supplementary Figure 9.** XANES spectra of Eco-Mn<sub>1</sub> to Eco-Mn<sub>6</sub> and corresponding linear combination fitting performed with Athena software.



**Supplementary Figure 10.** XANES spectra of Eco-Mn<sub>7</sub> to Eco-Mn<sub>10</sub>, Syn-Mn<sub>1</sub>, Syn-Mn<sub>2</sub> and Tem-Mn with corresponding linear combination fitting performed with Athena software.

Linear combination fitting highlights Mn-rich compounds that comprise Eco-Mn catalysts. Eco-Mn<sub>1</sub>, Eco-Mn<sub>6</sub> and Eco-Mn<sub>10</sub> are made up of K<sub>3</sub>NaMnCl<sub>6</sub>, KMnCl<sub>3</sub> and MnCl<sub>2</sub>. Eco-Mn<sub>9</sub> mainly contains K<sub>3</sub>NaMnCl<sub>6</sub> and MnCl<sub>2</sub>. Tem-Mn mainly contains KMnCl<sub>3</sub> and anhydrous MnCl<sub>2</sub>.

Three main species compose Eco-Mn<sub>3</sub>, Eco-Mn<sub>4</sub> and Eco-Mn<sub>5</sub>: MnCl<sub>2</sub>, MnCl<sub>2</sub>·2H<sub>2</sub>O and MnMg<sub>2</sub>Cl<sub>6</sub>·12H<sub>2</sub>O. Eco-Mn<sub>4</sub> also contains K<sub>3</sub>NaMnCl<sub>6</sub>.

Eco-Mn<sub>8</sub> is mainly composed of MnCl<sub>2</sub>. It is the same for Syn-Mn<sub>1</sub>, which is logical since Syn-Mn<sub>1</sub> was produced by mixing among other metal chlorides MnCl<sub>2</sub>. However, linear combination fitting highlights also the presence of KMnCl<sub>3</sub> in Syn-Mn<sub>1</sub>, even though KMnCl<sub>3</sub> was not used as starting material to produce Syn-Mn<sub>1</sub>. One hypothesis can explain the presence of KMnCl<sub>3</sub> in Syn-Mn<sub>1</sub>. Indeed, Pawelke *et al.* have reported the mechanochemical synthesis of KMnCl<sub>3</sub> from MnCl<sub>2</sub> and KCl by ball-milling.<sup>24</sup> Syn-Mn<sub>1</sub> was synthesized in this study by magnetically stirring MnCl<sub>2</sub>·4H<sub>2</sub>O and KCl during several hours to obtain a fine and homogeneous powder. Thus MnCl<sub>2</sub>·4H<sub>2</sub>O and KCl were mechanically mixed together, which might have led to partly produce KMnCl<sub>3</sub>.

Contrary to Eco-Mn<sub>1</sub>, Syn-Mn<sub>2</sub> contains MnMg<sub>2</sub>Cl<sub>6</sub>·12H<sub>2</sub>O: complexes that comprise synthetic catalysts and Eco-Mn catalysts are different.

### S8. XANES spectrum of Eco-Mn<sub>1</sub> at the Fe K-edge and identification of [A<sup>+</sup> FeCl<sub>4</sub><sup>-</sup>]

XAS spectra of Eco-Mn<sub>1</sub> at the Fe K-edge has been compared to reported XAS spectra in literature. It appears that Eco-Mn<sub>1</sub> probably contains Fe-rich species under the form A<sup>+</sup> [FeCl<sub>4</sub><sup>-</sup>].

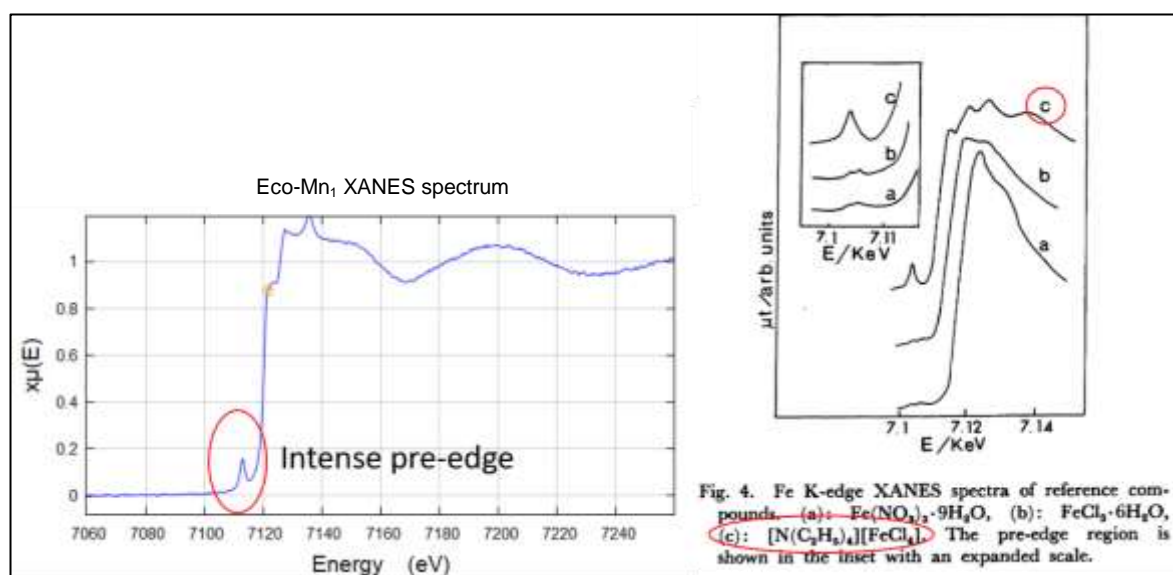


Fig. 4. Fe K-edge XANES spectra of reference compounds. (a): Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, (b): FeCl<sub>3</sub>·6H<sub>2</sub>O, (c): [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>][FeCl<sub>4</sub>]. The pre-edge region is shown in the inset with an expanded scale.

Supplementary Figure 11. XANES spectrum of Eco-Mn<sub>1</sub> and comparison with [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>][FeCl<sub>4</sub>] spectrum in literature.<sup>25</sup>

### S9. Linear combination fitting on XANES spectra at the Fe K-edge, with Athena software

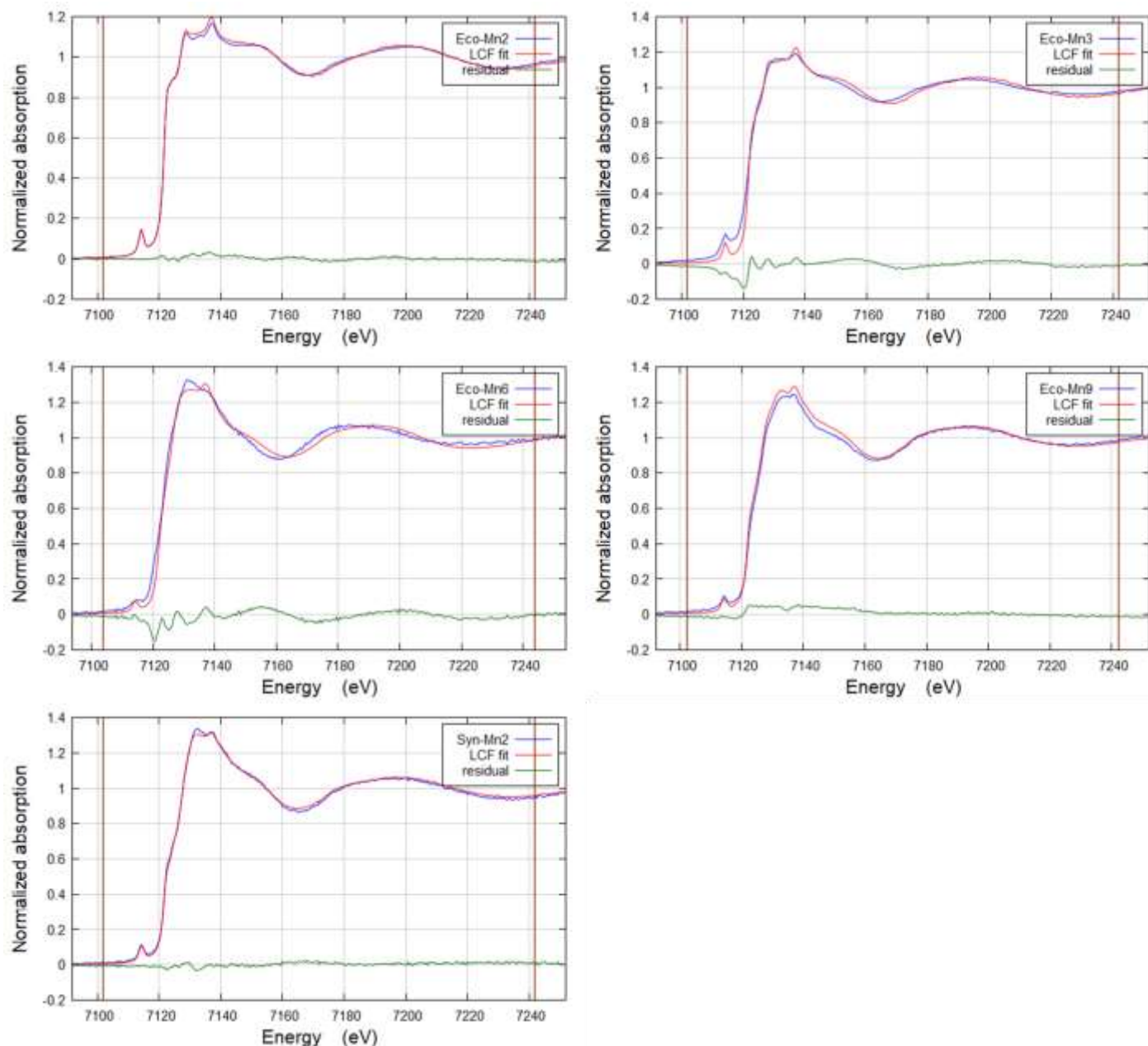
As only few XAS spectra have been recorded at the Fe K-edge, PCA and Target Transformation cannot be used. However, LCF was performed, by using XAS spectra of reference compounds.

Eco-Mn<sub>1</sub> was considered in this case as a « pseudo-reference » compound due to the particular shape of its spectrum, and is used to perform LCF analysis. According to the results at the Mn K-edge, only chlorinated reference compounds were used at the beginning with Eco-Mn<sub>1</sub> to perform LCF (FeCl<sub>3</sub>.6H<sub>2</sub>O and K<sub>2</sub>FeCl<sub>5</sub>.H<sub>2</sub>O). Linear combinations of these three species do not fit properly all Eco-Mn XANES spectra, thus Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.xH<sub>2</sub>O and FePO<sub>4</sub>.2H<sub>2</sub>O were also taken into account in the LCF analysis. Results are presented in **Supplementary Table 4**. Associated figures are presented in **Supplementary Figure 12**. Iron oxide reference compounds are not taken into account here. It is unlikely that iron oxides compose Eco-Mn catalysts regarding their synthesis, but this has to be checked. A Target Transformation analysis should be performed for instance.

These results give insight to the chemical environment around Fe atoms in Eco-Mn catalysts. Some Fe-rich species are still unidentified, but research is ongoing.

	Eco-Mn <sub>1-A</sub>	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .xH <sub>2</sub> O	FePO <sub>4</sub> .2H <sub>2</sub> O	FeCl <sub>3</sub> .6H <sub>2</sub> O	K <sub>2</sub> FeCl <sub>5</sub> .H <sub>2</sub> O	R-factor	Reduced Chi-square
Eco-Mn <sub>2</sub>	0.89 (±0.01)				0.10 (±0.01)	0.00079	0.000089
Eco-Mn <sub>3</sub>	0.66 (±0.02)			0.08 (±0.04)	0.25 (±0.04)	0.00752	0.000787
Eco-Mn <sub>6</sub>	0.12 (±0.07)			0.64 (±0.04)	0.23 (±0.04)	0.00891	0.000984
Eco-Mn <sub>9</sub>	0.41 (±0.01)	0.30 (±0.01)			0.28 (±0.03)	0.00450	0.000524
Syn-Mn <sub>2</sub>	0.53 (±0.01)		0.45 (±0.01)	0.01 (±0.02)		0.00095	0.000120

**Supplementary Table 4.** LCF results on XANES spectra at the Fe K absorption edge. Uncertainties on each coefficient are indicated in parentheses. Phases below 10% have been reported, but their contribution can be neglected or not supported by XANES fitting alone.



**Supplementary Figure 12.** Linear combination fitting on XANES spectra of catalysts at the Fe K-edge.

## S10. DFT analysis of Mn mixed salts

The most stable conformer of molecules in the ground state were optimized by the Density functional theory (DFT) using the Gaussian 09<sup>®</sup> computational package.<sup>26</sup> The B3LYP functionals with the 6-311++G(2d,p) basis set was used to optimize geometry and electronic structure in Gaussian 09<sup>®</sup>. Energy and frequency calculations were performed on fully optimized geometries. B3LYP functionals are relevant to study metals and are widely used. To estimate partial atomic charge, three different models have been applied: Mulliken,<sup>27</sup> Natural Bond Orbital (NBO)<sup>28,29</sup> and Merz–Kollman (MK).<sup>30</sup> We also estimate the HSAB theory (hard and soft Lewis acids and bases).<sup>31</sup>

## **S11. XAS and ICP-MS data comparison**

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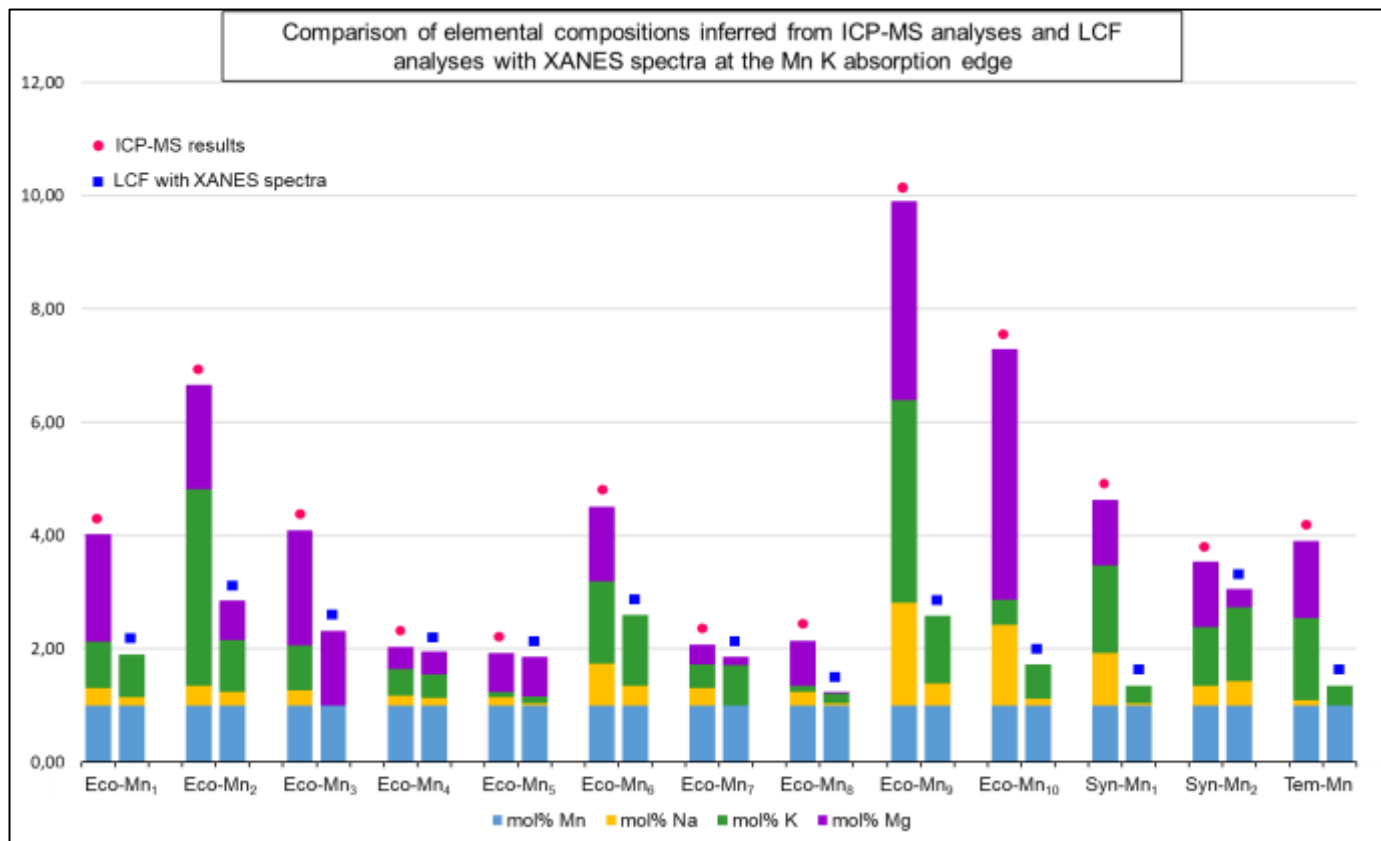
Thanks to LCF analyses performed at the Mn K-edge, it was possible to get molar percentages of K, Na, Mg, and Mn present in Mn species in Eco-Mn, Syn-Mn and Tem-Mn catalysts. Molar percentages of K, Na, Mg and Mn have also been deduced from ICP-MS analyses. Considering molar percentage of Mn equal to one, the relative percentages of K, Na and Mg against Mn have been calculated, and are presented in **Supplementary Figure 13**. XAS analyses only give proportions of K, Na and Mg present in Mn environment: these percentages ought to be lower than percentages of K, Na and Mg in the entire catalyst determined by ICP-MS analyses. Thus, relative percentages of K, Na and Mg inferred from XAS analyses ought to be lower or equal to those obtained from ICP-MS analyses. All the data are reported in the histogram (**Supplementary Fig. 13**).

It appears that results from ICP-MS and XAS analyses are overall coherent. Results are perfectly coherent in case of Eco-Mn<sub>1</sub>, Eco-Mn<sub>2</sub>, Eco-Mn<sub>3</sub>, Eco-Mn<sub>4</sub>, Eco-Mn<sub>6</sub>, Eco-Mn<sub>9</sub>, Syn-Mn<sub>1</sub> and Tem-Mn.

Results obtained with ICP-MS and LCF analysis in case of Eco-Mn<sub>7</sub> are not coherent probably due to its noisy XAS spectrum.

In case of Eco-Mn<sub>5</sub>, Eco-Mn<sub>8</sub>, Eco-Mn<sub>10</sub> and Syn-Mn<sub>2</sub> the amount of potassium deduced from LCF analyses is a bit high compared to ICP-MS analysis. These results might suggest the presence of another species still unidentified or the overstatement of the amount of one manganese-potassium mixed salt.

These studies enable us to determine, at least qualitatively, the Mn species comprised in each catalyst, as presented in **Supplementary Table 5**.



**Supplementary Figure 13.** Comparison of elemental compositions inferred from ICP-MS analyses and LCF analyses with XANES spectra at the Mn K absorption edge.

	LCF analysis on XANES spectra (main Mn-rich species)	XRD analysis (crystalline Mn-rich species)
Eco-Mn <sub>1</sub> Eco-Mn <sub>6</sub> Eco-Mn <sub>9</sub> Eco-Mn <sub>10</sub>	K <sub>3</sub> NaMnCl <sub>6</sub> KMnCl <sub>3</sub> (minor in Eco-Mn <sub>9</sub> ) Anhydrous MnCl <sub>2</sub>	KMnCl <sub>3</sub> (Eco-Mn <sub>1</sub> ) K <sub>3</sub> NaMnCl <sub>6</sub> (Eco-Mn <sub>6</sub> and Eco-Mn <sub>9</sub> )
Tem-Mn	KMnCl <sub>3</sub> Anhydrous MnCl <sub>2</sub>	/
Eco-Mn <sub>3</sub> Eco-Mn <sub>4</sub> Eco-Mn <sub>5</sub>	MnMg <sub>2</sub> Cl <sub>6</sub> ·12H <sub>2</sub> O MnCl <sub>2</sub> ·2H <sub>2</sub> O Anhydrous MnCl <sub>2</sub> (K <sub>3</sub> NaMnCl <sub>6</sub> in Eco-Mn <sub>4</sub> )	MnCl <sub>2</sub> ·2H <sub>2</sub> O (Eco-Mn <sub>4</sub> and Eco-Mn <sub>5</sub> ) KMnCl <sub>3</sub> (Eco-Mn <sub>3</sub> and Eco-Mn <sub>4</sub> )
Eco-Mn <sub>8</sub>	Anhydrous MnCl <sub>2</sub>	MnCl <sub>2</sub> ·2H <sub>2</sub> O
Syn-Mn <sub>1</sub>	Anhydrous MnCl <sub>2</sub> KMnCl <sub>3</sub>	
Syn-Mn <sub>2</sub>	K <sub>3</sub> NaMnCl <sub>6</sub> Anhydrous MnCl <sub>2</sub> MnMg <sub>2</sub> Cl <sub>6</sub> ·12H <sub>2</sub> O	MnMg <sub>2</sub> Cl <sub>6</sub> ·12H <sub>2</sub> O
Eco-Mn <sub>2</sub>	K <sub>3</sub> NaMnCl <sub>6</sub> KMnCl <sub>3</sub> Anhydrous MnCl <sub>2</sub> MnMg <sub>2</sub> Cl <sub>6</sub> ·12H <sub>2</sub> O	K <sub>3</sub> NaMnCl <sub>6</sub>
Eco-Mn <sub>7</sub>	KMnCl <sub>3</sub> Anhydrous MnCl <sub>2</sub>	KMnCl <sub>3</sub>

**Supplementary Table 5.** Summary of the Mn-rich species that comprise the studied catalysts

Eco-Mn<sub>1</sub>, Eco-Mn<sub>6</sub> and Eco-Mn<sub>9</sub> seem to be made up of the same Mn species MnCl<sub>2</sub>, K<sub>3</sub>NaMnCl<sub>6</sub> and KMnCl<sub>3</sub> (except for Eco-Mn<sub>9</sub>), which is logical since these catalysts come from the same plant species.

Eco-Mn<sub>5</sub> and Eco-Mn<sub>8</sub>, both produced from *Garcinia amplexicaulis*, only contain traces of K<sub>3</sub>NaMnCl<sub>6</sub> or KMnCl<sub>3</sub> which is in accordance with their very small proportion of potassium. The major Mn species in Eco-Mn<sub>10</sub> (also produced from *Garcinia amplexicaulis*) is MnCl<sub>2</sub> but contrary to Eco-Mn<sub>5</sub> and Eco-Mn<sub>8</sub> it also contains K<sub>3</sub>NaMnCl<sub>6</sub> and KMnCl<sub>3</sub> which seems in accordance with its higher potassium content.

In case of Eco-Mn<sub>3</sub>, KMnCl<sub>3</sub> is likely to be present according to XRD analysis, even if XAS analyses does not highlight its presence.

Finally, it has to be noticed that some catalysts with very close metallic composition (determined by ICP-MS analysis) such as Eco-Mn<sub>1</sub> and Eco-Mn<sub>3</sub> are not comprised of the same Mn species. To explain these results, we have to consider all metallic cations present in catalysts. Indeed, XAS studies have proved that iron is associated with potassium in Eco-Mn catalysts, and XRD analysis has demonstrated that calcium is often associated with magnesium. There is a competition between all the metallic cations which associate together differently depending on the catalysts, and the whole metallic composition of the catalysts has to be taken into account.



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