Letter to the Editor on the paper by Diop and collaborators

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In this letter to the editor we question the origin of the figures in the paper published by M.A.Diop and collaborators [1], on line since June 28th 2021 on the web site of *Metallurgical and Materials Transactions B* https://doi.org/10.1007/s11663-021-02223-5.

The PhD thesis of Kelly Machado entitled « *Chimie des Bains pour l'Electrolyse de l'Aluminium : Étude RMN Haute Température et Modélisation* », which translates to « *Chemistry of molten baths for aluminum electrolysis : a combined study by high temperature NMR and modeling* » was defended October 19th 2017 at the Université d'Orléans, France. The manuscript was available since then and freely available for download from the *tel.archives-ouvertes.fr* server since December 18th 2018 at the following address: https://tel.archives-ouvertes.fr/tel-01952928 [2]

In their paper M.A.Diop and coworkers[1], are presenting figures that are strongly reminiscent to those of the above mentioned thesis[Figs. 1-8], showing identical symbols, colors and error bars for what they claim to be original new data obtained by themselves. The French labels and captions were translated word for word for most of them and a few extra legends introduced. When the origin of the figures is not acknowledged and the thesis itself not cited, a great part of this materials have been published in recognized journals[3-6] that are not even recognized for their contents even if cited[3, 6 – respectively references 40 and 45] by the authors [note that in ref 45 of their papers the initials and last names have been interchanged].

Considering the extensive use of the materials coming from the PhD thesis here above we not only question the duplication of the figures themselves but also question the reality of the experimental work that is reported in this article.

References

[1] M.A. Diop, S.A. Bousso, T. Wenju, L. Aimin, Structural Studies in Cryolite-Alumina Melts Investigated by Molecular Dynamics Simulations and High-Temperature NMR Data, Metall. Mater. Trans. B. (2021). https://doi.org/10.1007/s11663-021-02223-5.

[2] K. Machado, « Chimie des Bains pour l'Electrolyse de l'Aluminium : Étude RMN Haute Température et Modélisation », PhD Thesis at Université d'Orléans, France, October 19th 2017 https://tel.archives-ouvertes.fr/tel-01952928.

[3] K. Machado, D. Zanghi, V. Sarou-Kanian, S. Cadars, M. Burbano, M. Salanne, C. Bessada, Study of NaF-AlF3 Melts by Coupling Molecular Dynamics, Density Functional Theory, and NMR Measurements, J. Phys. Chem. C. 121 (2017) 10289–10297. https://doi.org/10.1021/ACS.JPCC.7B01530 .

[4] K. Machado, D. Zanghi, M. Salanne, V. Stabrowski, C. Bessada, Anionic Structure in Molten Cryolite-Alumina Systems, J. Phys. Chem. C. 122 (2018) 21807–21816. https://doi.org/10.1021/ACS.JPCC.8B06905 .

[5] A.E. Gheribi, A. Serva, M. Salanne, K. Machado, D. Zanghi, C. Bessada, P. Chartrand, Study of the Partial Charge Transport Properties in the Molten Alumina via Molecular Dynamics, ACS Omega. 4 (2019) 8022–8030. https://doi.org/10.1021/ACSOMEGA.9B01110 .

[6] K. Machado, D. Zanghi, M. Salanne, C. Bessada, Structural, Dynamic, and Thermodynamic Study of KF-AlF3 Melts by Combining High-Temperature NMR and Molecular Dynamics Simulations, J. Phys. Chem. C. 123 (2019) 2147–2156. https://doi.org/10.1021/ACS.JPCC.8B11907 .

Please find below a detailed comparison of some of the figures…

The legends were translated from French to English with possible addition of lettering and reorganization of the figure elements in some cases. All symbols and colors are identical.

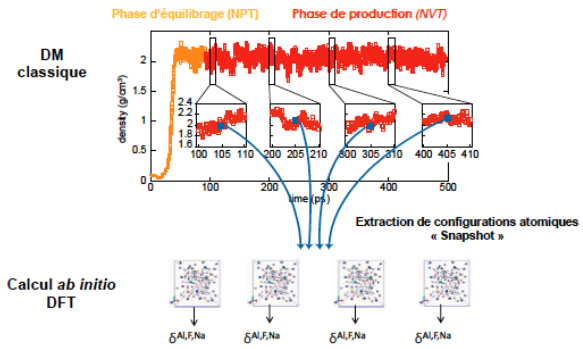
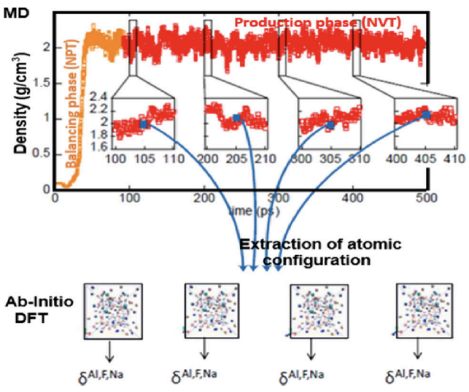
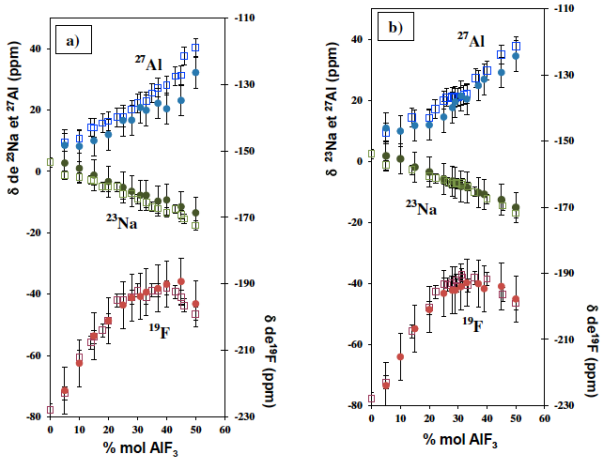
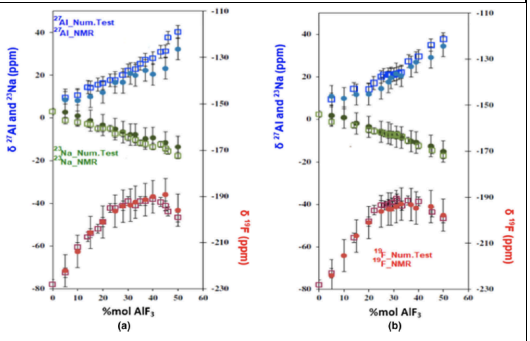
Kelly Machado PhD Thesis 2017	Diop et al. 2021
	
Figure II-13 : Schéma de la procédure d'extraction des instantanés (« snapshots ») issus de la simulation par dynamique moléculaire.	Fig. 1—Diagram of the procedure for extracting snapshots from the simulation by molecular dynamics.
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Figure III-9 : Comparaison des déplacements chimiques des noyaux ^{27}Al, ^{23}Na et ^{19}F calculés (marqueurs pleins) et mesurés par RMN (marqueurs vides) [31], [48], [152] en fonction du pourcentage molaire d'AlF_3 pour: a) surchauffe de 20°C et b) 1032°C.	Fig. 2—Comparison of the chemical shifts of the ^{27}Al, ^{23}Na, and ^{19}F nuclei calculated (solid markers) and measured by NMR (empty markers)[30,40,41] as a function of the molar percentage of AlF_3 for: (*a*) superheat of 20 °C and (*b*) 1032 °C.

Fig. 1 : comparison of figures 1 and 2 of Diop's paper 2021 with originals from the PhD thesis of Machado 2017.

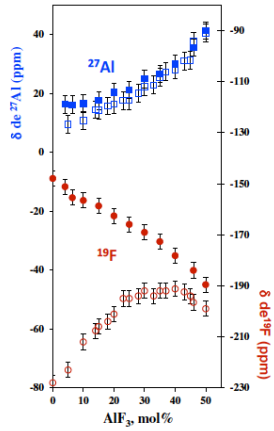
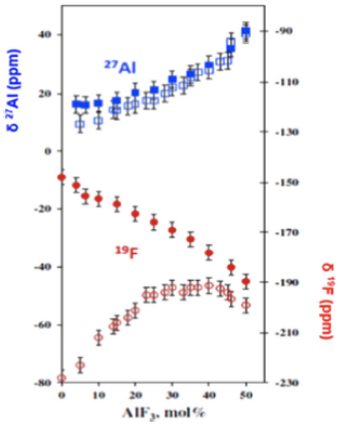
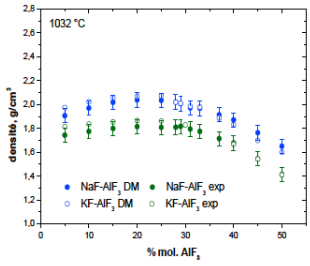
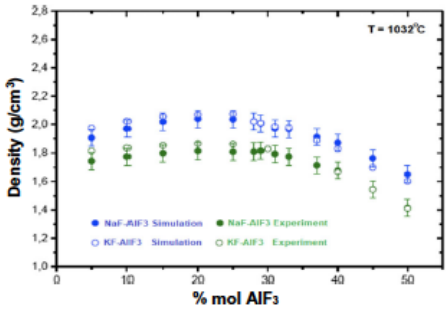
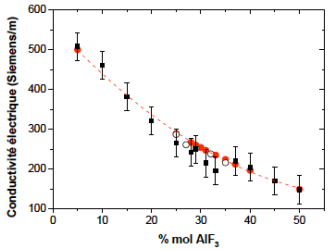
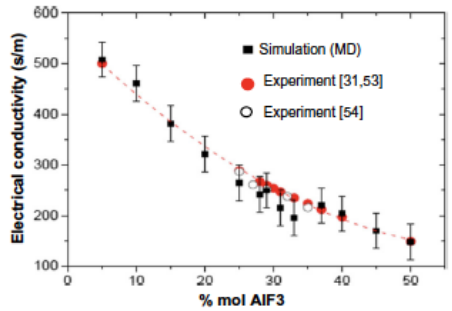
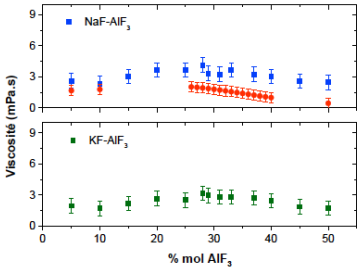
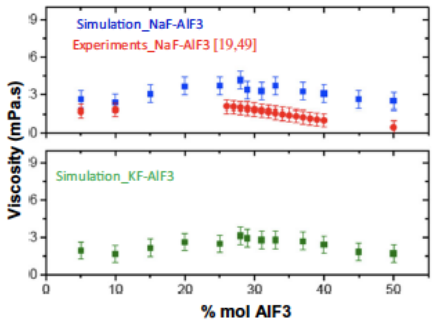
Kelly Machado PhD Thesis 2017	Diop et al. 2021
	
Figure III-3 : Déplacements chimiques à surchauffe constante de 20°C entre 0 à 50 % mol d'AlF$_3$ dans le système NaF-AlF$_3$ (symboles vides) et KF-AlF$_3$ (symboles pleins).	Fig. 3—Chemical shifts at constant superheat of 20 °C between 0 to 50 mol pct of AlF$_3$ in NaF-AlF$_3$ system (open symbols) and KF-AlF$_3$ (full markers).
	
Figure III-8 : Densité des bains fondus obtenue par simulation de dynamique moléculaire (points) et expérimentalement [5], [151] (cercles vides) à 1032°C	Fig. 5—Density of molten baths obtained by MD simulations and experimentally[50] at 1032 °C.
	
Figure III-30 : Conductivité électrique des bains fondus NaF-AlF$_3$ à 1032 °C. Les carrés noirs sont les résultats de la dynamique moléculaire; Les cercles vides sont des données expérimentales de la référence. [164] et les cercles rouges sont des données expérimentales issues des références [5], [151].	Fig. 6—Electrical conductivity of NaF-AlF$_3$ molten baths at 1032 °C between MD and experiments.[30,52,53]
	
Figure III-33 : Viscosité des bains fondus MF-AlF$_3$ (M=Na, K) calculée à partir de la dynamique moléculaire à 1305 K (■ pour Na et ■ pour K). En rouge les données expérimentales [5], [151], [167] pour le système NaF-AlF$_3$ (panneau supérieur de la figure).	Fig. 7—Viscosity of MF-AlF$_3$ molten baths (M = Na, K) simulated from MD at 1305°K and compared with experimental data.[18,48]

Fig. 2 : comparison of figures 3, 5, 6 & 7of Diop's paper 2021 with originals from the PhD thesis of Machado 2017.

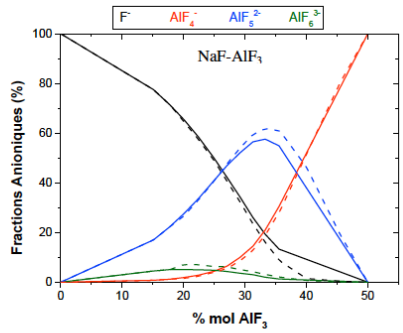
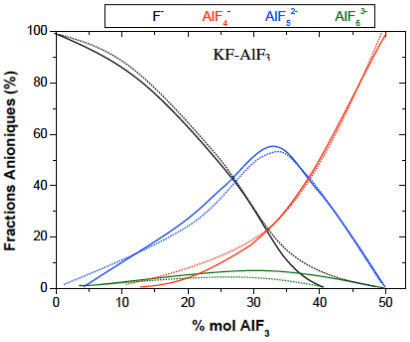
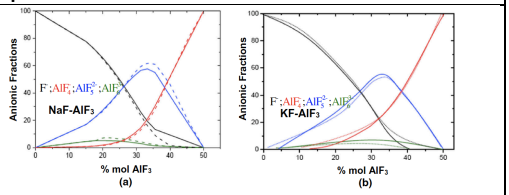
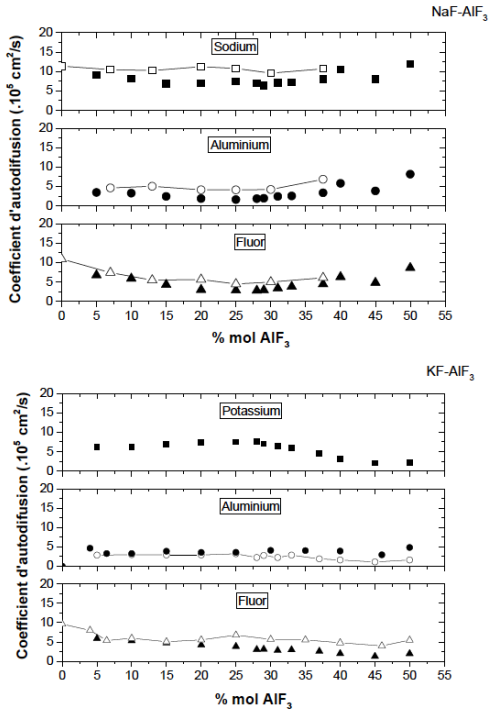
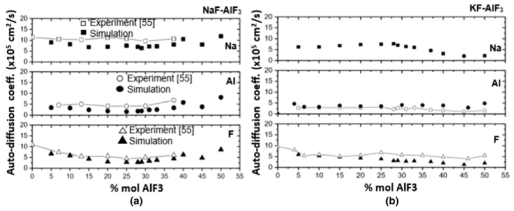
Kelly Machado PhD Thesis 2017	Diop et al. 2021
  **Figure III-4 :** Fractions anioniques des différentes espèces en présence dans les bains NaF-AlF_3 et KF-AlF_3. En traits pleins, les données issues des expériences RMN. En pointillés les données issues des expériences Raman [76].	 Fig. 4—Anionic fractions of the different species present in (*a*)-NaF-AlF_3 baths and (*b*)-KF-AlF_3. In solid lines, the data are from the NMR experiments. Dotted data are from Raman experiments.[40]
	 Fig. 8—Auto-diffusion coefficients of alkali ions, aluminum, and fluorine ions in (*a*) -NaF-AlF_3 and (*b*) -KF-AlF_3 at 1032 °C as a function of mol pct of AlF_3 from MD simulation and experimental data.[58]

Fig. 3 : comparison of figures 4 & 8 of Diop's paper 2021 with originals from the PhD thesis of Machado 2017.

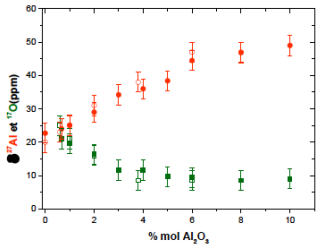
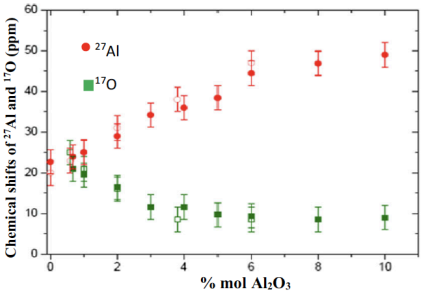
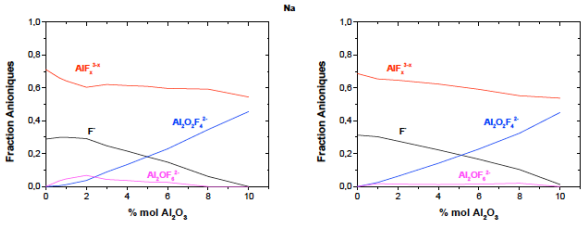
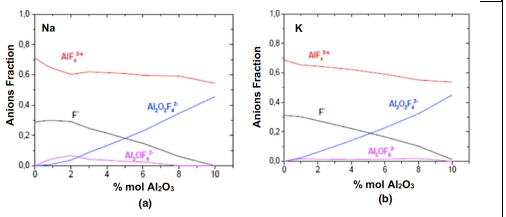
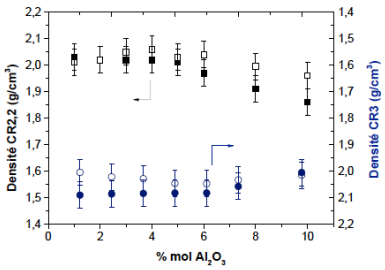
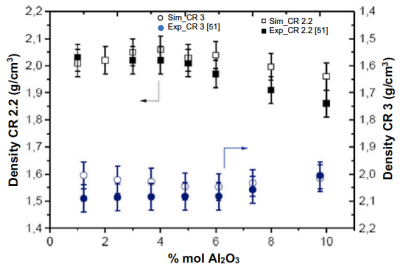
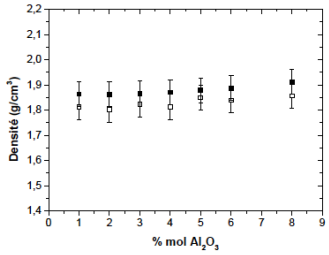
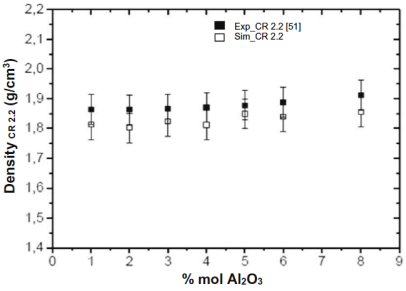
Kelly Machado PhD Thesis 2017	Diop et al. 2021
	
Figure IV-6 : Déplacements chimiques à haute température pour les noyaux ^{27}Al et ^{17}O du système NaF-AlF_3-Al_2O_3 avec un CR 2,2 (marqueurs pleins) et CR 3 (marqueurs vides).	Fig. 9—Chemical shifts at high temperature for the ^{27}Al and ^{17}O nuclei of the system NaF-AlF_3-Al_2O_3 with a cryolite ratio 2.2 (full markers) and cryolite ratio 3 (empty markers).
	
Figure IV-8 : Fractions anioniques déduites des déplacements chimiques de la RMN à haute température pour les systèmes fondus MF-AlF_3-Al_2O_3 (M= Na à gauche et M=K à droite) pour un CR 2,2.	Fig. 10—Anion fractions deduced from the chemical shifts of the NMR at HT for molten MF-AlF3-Al_2O_3 systems ((*a*) M = Na on the left and (*b*) M = K on the right) for a cryolite ratio 2.2.
	
Figure IV-10 : Densités calculées (marqueurs vides) et expérimentales (marqueurs pleins) [5] en fonction du % molaire d'alumine dans le système NaF-AlF_3-Al_2O_3 dans le liquide avec un CR (NaF/AlF_3) de 2,2 (symboles carrés) et CR 3 (symboles cercles).	Fig. 11—Simulated and experimental densities[50] in the function of molar pct of alumina in NaF-AlF3-Al_2O_3 system in liquid with cryolite ratio (NaF/AlF3) 2.2 and 3.
	
Figure IV-11: Densités calculées (marqueurs vides) et expérimentales (marqueurs pleins) [5] en fonction du % molaire d'alumine dans le système KF-AlF_3-Al_2O_3 avec un CR (KF/AlF_3) de 2,2 dans le liquide.	Fig. 12—Numerical and experimental densities[50] in the function of the molar pct of alumina in the KF-AlF_3-Al_2O_3 system with a cryolite ratio (KF/AlF_3) 2.2 in the liquid.
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Fig. 4 : comparison of figures 9, 10, 11 & 12 of Diop's paper 2021 with originals from the PhD thesis of Machado 2017.

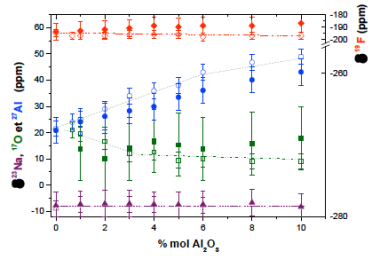
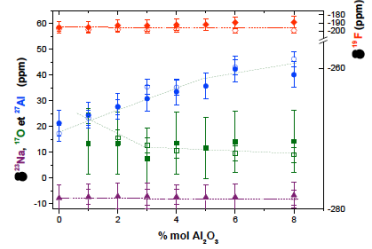
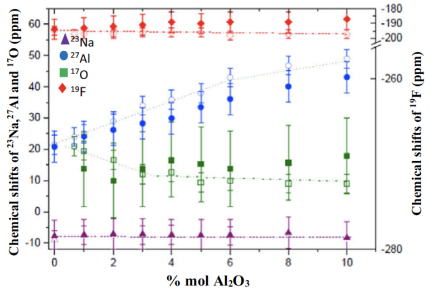
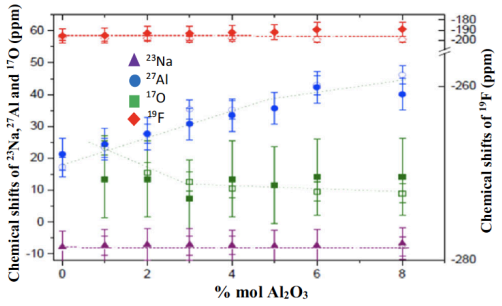
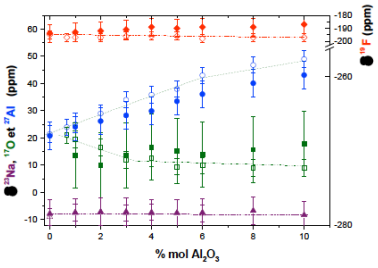
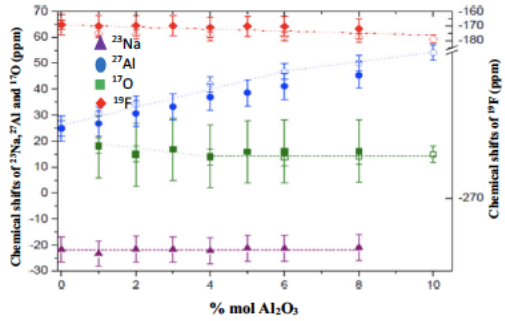
Kelly Machado PhD Thesis 2017	Diop et al. 2021
 **Figure IV-12 :** Déplacements chimiques RMN dans le liquide des noyaux ^{27}Al (●○), ^{17}O (■□), ^{23}Na (▲△) dans l'axe principal et ^{19}F (♦◊) dans l'axe secondaire. Valeurs expérimentales en marqueurs vides et valeurs calculées en marqueurs pleins pour le système $[NaF\text{-}AlF_3]_{CR2,2}\text{-}Al_2O_3$. Afin d'évaluer la capacité du potentiel à décrire convenablement le système pour des rapports cryolithiques NaF/AlF_3 légèrement supérieurs, nous avons effectué les mêmes calculs pour un CR plus basique (CR=3). La Figure IV-13 montre que nous obtenons là encore une bonne concordance avec les valeurs déduites des mesures RMN à haute température.  **Figure IV-13 :** Déplacements chimiques RMN dans le liquide des noyaux ^{27}Al (●○), ^{17}O (■□), ^{23}Na (▲△) dans l'axe principal et ^{19}F (♦◊) dans l'axe secondaire. Valeurs expérimentales en marqueurs vides et valeurs calculées en marqueurs pleins pour le système $[NaF\text{-}AlF_3]_{CR3}\text{-}Al_2O_3$. La même démarche a également été entreprise dans le cas du système $KF\text{-}AlF_3\text{-}Al_2O_3$ avec succès. Outre le bon accord obtenu pour les trois noyaux étudiés (^{19}F, ^{17}O, ^{27}Al) avec les données 148	 Fig. 13—NMR chemical shifts in the liquid of ^{27}Al, ^{17}O,^{23}Na nuclei in the main axis and ^{19}F in the secondary axis. Experimental values in markers empty, and values were calculated in full markers for the $[NaF\text{-}AlF3]_{CR2,2}\text{-}Al_2O_3$ system.  Fig. 14—NMR chemical shifts in the liquid of nuclei ^{27}Al, ^{17}O, ^{23}Na in the main axis, and ^{19}F in the secondary axis. Experimental values in empty markers and values calculated in full markers for the $[NaF\text{-}AlF3]_{CR3}\text{-}Al_2O_3$ system.
 **Figure IV-12 :** Déplacements chimiques RMN dans le liquide des noyaux ^{27}Al (●○), ^{17}O (■□), ^{23}Na (▲△) dans l'axe principal et ^{19}F (♦◊) dans l'axe secondaire. Valeurs expérimentales en marqueurs vides et valeurs calculées en marqueurs pleins pour le système $[NaF\text{-}AlF_3]_{CR2,2}\text{-}Al_2O_3$.	 Fig. 15—NMR chemical shifts in the liquid of nuclei ^{27}Al, ^{17}O, ^{23}Na in the main axis, and ^{19}F in the secondary axis. Experimental values in markers empty and values calculated in full markers for the $[NaF\text{-}AlF3]_{CR2,2}\text{-}Al_2O_3$ system.

Fig. 5 : comparison of figures 13, 14, & 15 of Diop's paper 2021 with originals from the PhD thesis of Machado 2017.

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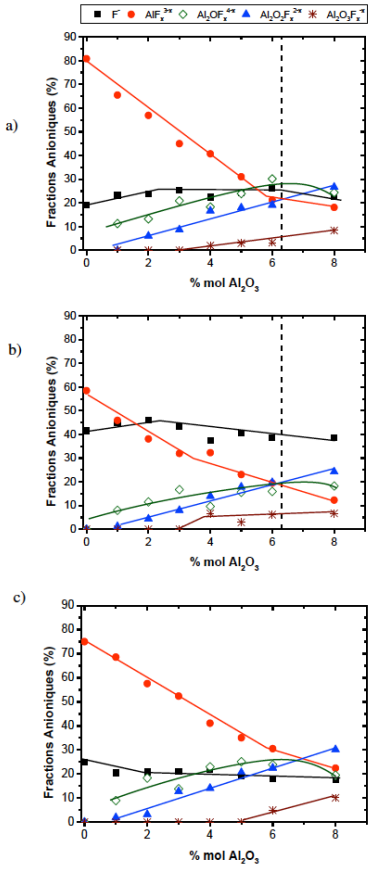


Figure IV-23 : Fractions anioniques en fonction de l'alumine dans le liquide pour les systèmes MF-AlF_3-Al_2O_3 : a) M=Na et CR2,2 ; b) M=Na et CR3 ; c) M=K et CR2,2.

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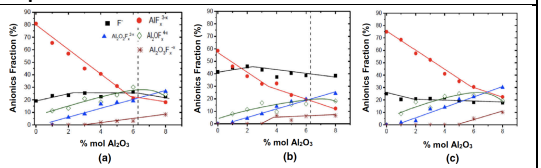


Fig. 16—Anionic fractions as a function of alumina in the liquid for MFAlF$_3$- systems Al_2O_3: (*a*) M = Na and cryolite ratio 2.2; (*b*) M = Na and cryolite ratio 3; (*c*) M = K and cryolite ratio 2.2.

Fig. 6 : comparison of 16 of Diop's paper 2021 with originals from the PhD thesis of Machado 2017.

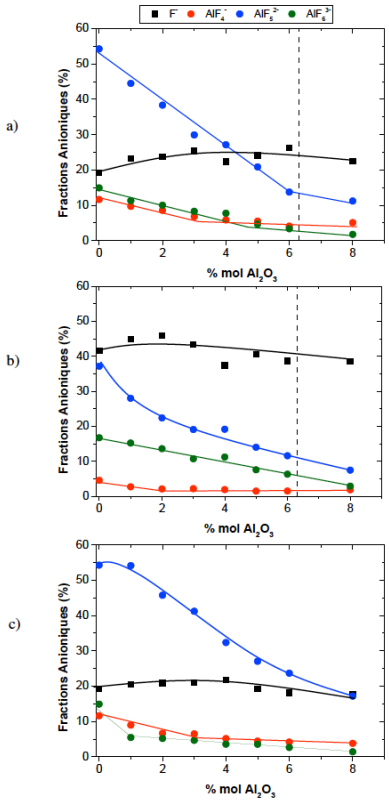
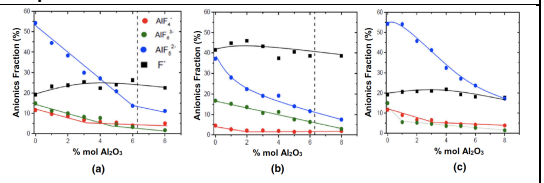
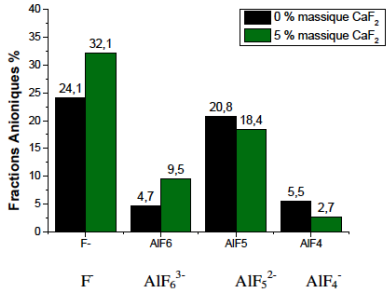
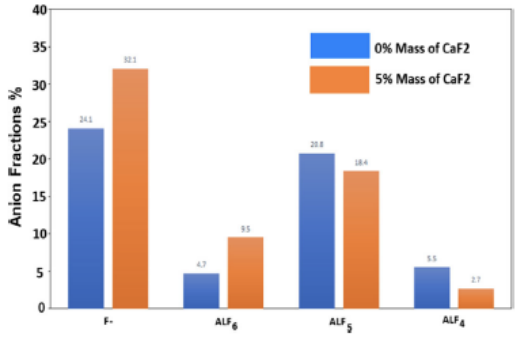
Kelly Machado PhD Thesis 2017	Diop et al. 2021
	
Figure IV-24 : Fractions anioniques des fluoroaluminates et du fluor libre en fonction de la quantité d'alumine à une température de surchauffe de 20°C pour les systèmes MF-AlF_3-Al_2O_3 : a) M=Na et CR2,2 ; b) M=Na et CR3 ; c) M=K et CR2,2.	Fig. 17—Anion fractions of fluoroaluminates and free fluorine as a function of the quantity of alumina at a superheating temperature of 20 °C for the MF-AlF_3-Al_2O_3 systems: (*a*) M = Na and cryolite ratio 2.2; (*b*) M = Na and cryolite ratio 3; (*c*) M = K and cryolite ratio 2.2.
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Figure V-9 : Fractions anioniques des AlF_x^{3-x} et F⁻ dans le système avec (vert) et sans (noir) CaF_2.	Fig. 18—Anion fractions of AlF_x^{3-x} and F⁻ in the system with/ without CaF_2.
	With a remarkable color change

Fig. 7 : comparison of figures 17, & 18 of Diop's paper 2021 with originals from the PhD thesis of Machado 2017.

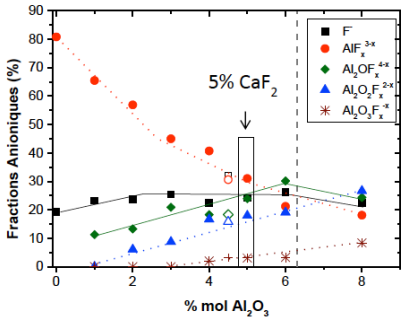
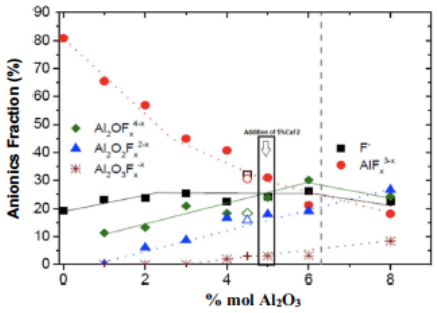
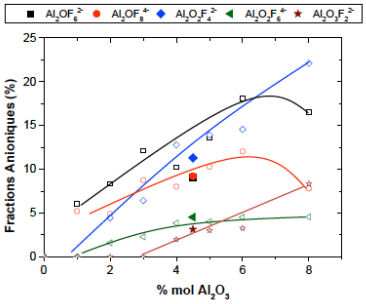
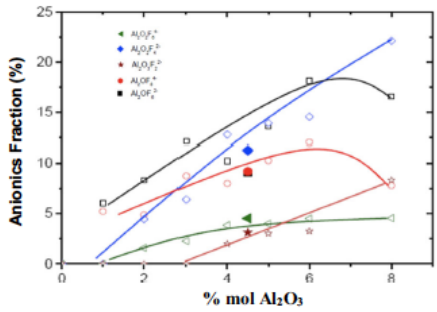
Kelly Machado PhD Thesis 2017	Diop et al. 2021
	
Figure V-10 : Fractions anioniques en fonction du pourcentage molaire d'alumine pour le système fondu NaF-AlF_3-Al_2O_3 à CR2,2. Les marqueurs vides représentent la composition avec 5 % massique de CaF_2.	Fig. 19—Anionic fractions as a function of the molar percentage of alumina for the system molten NaF-AlF_3-Al_2O_3 for a cryolite ratio 2.2. Empty markers represent the composition with 5 pct by mass of CaF_2.
	
Figure V-11 : Fractions anioniques des oxyfluoroaluminates en fonction de l'alumine pour le système fondu NaF-AlF_3-Al_2O_3 à CR2,2 (lignes avec marqueurs vides) et le système avec 5 % massique de CaF_2 (en marqueurs plein).	Fig. 20—Anionic fractions of oxyfluoroaluminates as a function of alumina for the system melted NaF-AlF_3-Al_2O_3 for a cryolite ratio 2.2 (lines with empty markers) and the system with 5 pct by mass of CaF_2 (in full markers).

Fig. 8 : comparison of figures 19 & 20 of Diop's paper 2021 with originals from the PhD thesis of Machado 2017.