NATIONAL HIGH MAGNETIC FIELD LABORATORY

Molecular Characterization of Soluble Organic Material from Meteorites by 21T FT-ICR MS

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Introduction

The most common meteorite type to fall to Earth are stony and of those, carbonaceous chondrites make up a very small percentage, less than five percent.[1] This classification contains the highest concentration of organic carbon in both soluble and insoluble forms.[1,2] A vast majority of studies performed focus on the classification of meteorites and examine characteristics such as petrology, chondrule presence, aqueous alterations, amongst others. Previous work on the organic material extracted from meteorites has concentrated on specific classes of compounds, such as amino acids or carbohydrates, as well as bulk elemental analysis.[3] Broadband analysis of the soluble organic material is rarely performed as the mass resolving power requirements for molecular characterization are quite high. The use of high-field ultra-high-resolution Fourier transform ion cyclotron resonance mass spectrometry provides the resolution requirement, mass accuracy, and dynamic range to resolve each peak for molecular assignment and provides the best analytical performance for untargeted analysis.

Methods

The Murchison and Aguas Zarcas meteorites were chosen for analysis. A sequential extraction method was developed with a range of solvents varying in dipolar moment, from methanol to toluene. Samples were homogenized before aliquots of 30-40 mg of material were subjected to the extraction method shown in **Figure 1**. Each sample was washed with a solvent prior to extraction in a mortar and pestle with 1 mL of extraction solvent. The solvent and material are centrifuged for 15 mins at 4000 rpm, the supernatant is drawn off, and both the supernatant and remaining material are dried down under a gentle stream of nitrogen gas. The remaining material is then washed in the next solvent before the next extraction. All the supernatant material is reconstituted in the extracted solvent and brought to a 50:50 mixture of solvent:methanol at 250 μg mL^{-1}. Extracts are characterized by positive (+) and negative (-) electrospray ionization (ESI) coupled to a 21-tesla Fourier transform ion cyclotron resonance mass spectrometer (21 T FT-ICR MS). Each extract has a spray modifier doped in to aid in ionization (formic acid for (+) ESI and tetramethylammonium hydroxide for (-) ESI). Data processing and elemental composition assignment were facilitated by Predator Analysis and PetroOrg© software. Venn diagrams were produced with Venny 2.1.0.[4]

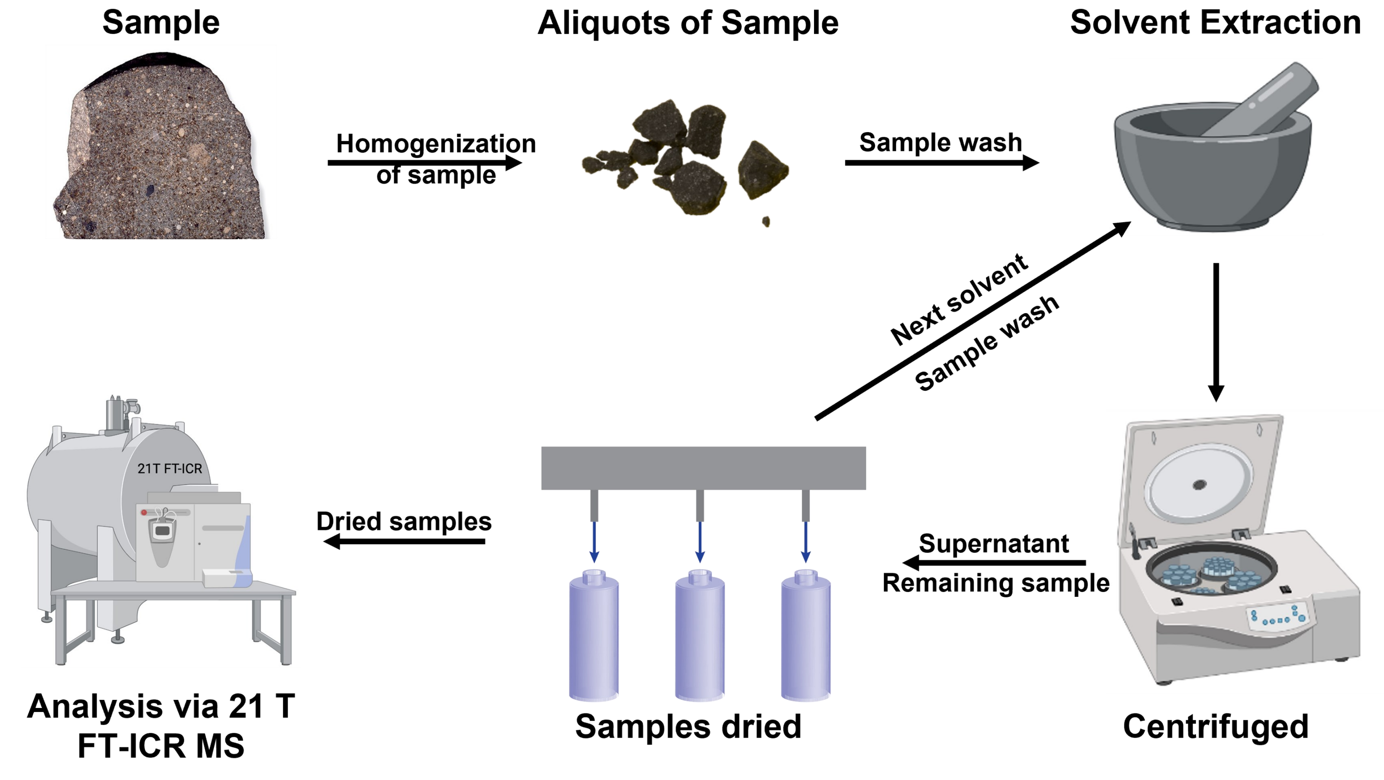

Figure 1. Sequential extraction method for soluble organic material from meteorites. Extraction is performed by starting with methanol and decreasing in dipolar moment to ethanol, chloroform, and ending in toluene.

Results and Discussion

Peaks Assigned from Murchison Extractions

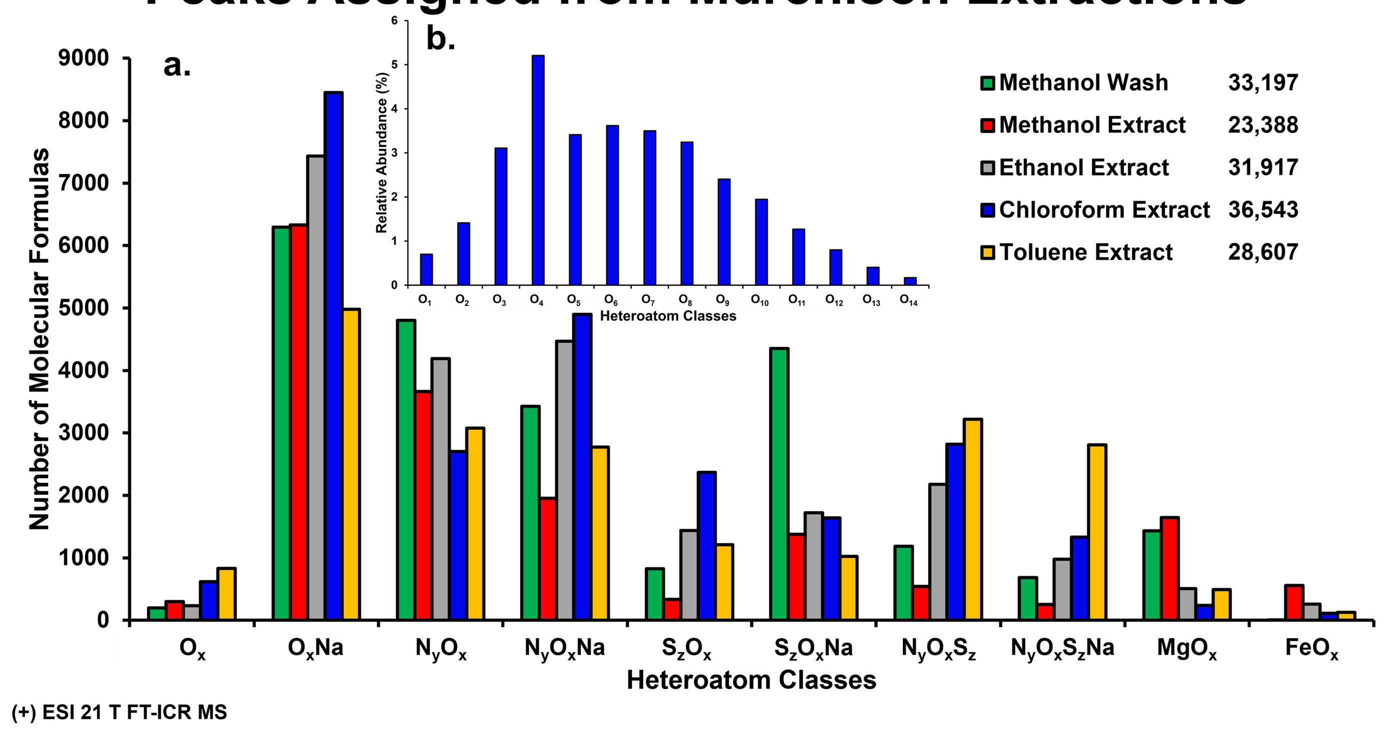

Figure 2. a. Number of molecular formulas assigned and heteroatom class distributions obtained via (+) ESI 21-tesla FT-ICR MS analysis for each solvent extract for Murchison meteorite. The solvent with the most formulas assigned was chloroform, whereas methanol contained the least number of species. The sodiated O_x compounds had the most formulas assigned whereas the FeO_x class contained the least. There was extensive sodiated species with peaks assigned for N_yO_x, S_zO_x, and $N_yO_xS_z$ heteroatom classes. There was also a significant number of peaks assigned for MgO_x class which seems to preferentially extract in methanol. b. Relative abundance for the sodiated O_x class from the chloroform extract, the most assigned class, is also displayed. Here, a mostly Gaussian distribution shows that a majority of the material was formed via abiotic processes.

Unique Formulas for Each Murchison Extraction

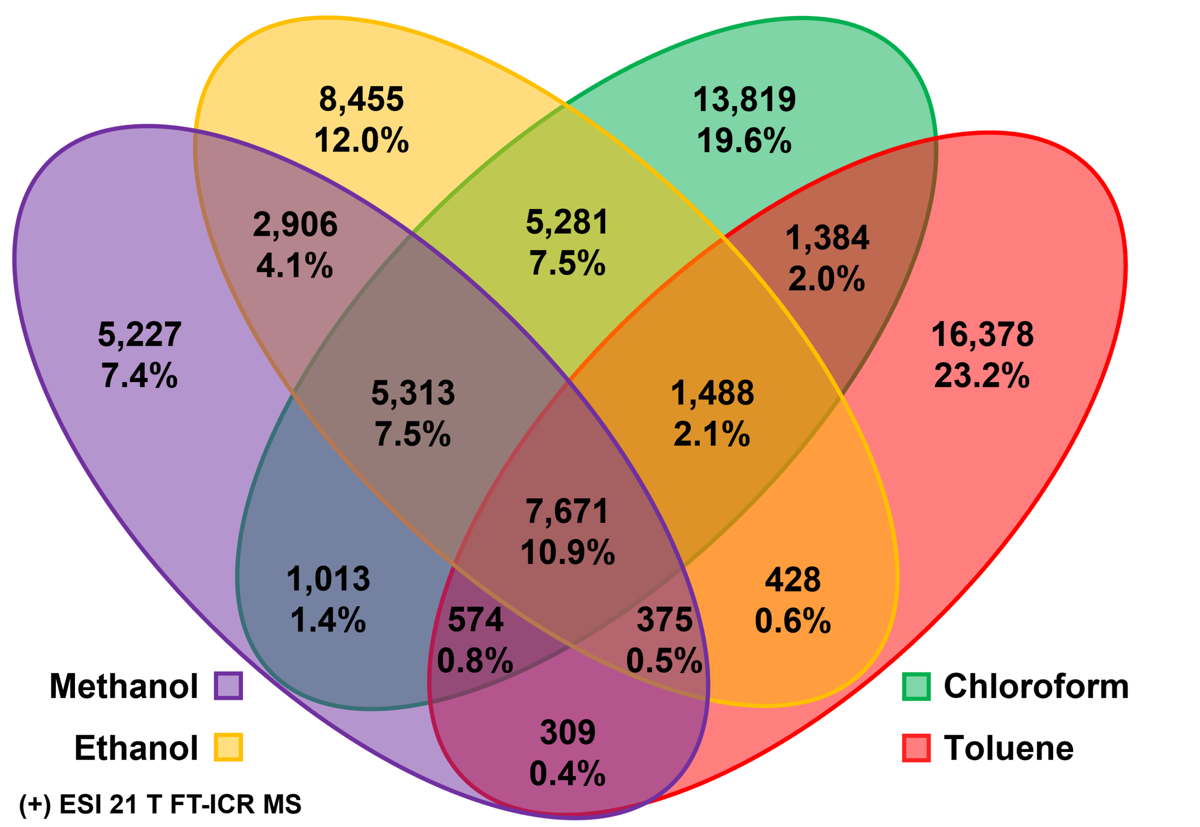

Figure 3. Comparison of molecular formulas assigned for each extraction solvent analyzed with (+) ESI 21-tesla FT-ICR MS. Each successive extract assigns more unique molecular formulas than the previous extract. Overall, only 11% of formulas were shared between all four solvents. Very few formulas were uniquely shared between methanol and toluene, only 0.4%.

Testing Reproducibility with Murchison

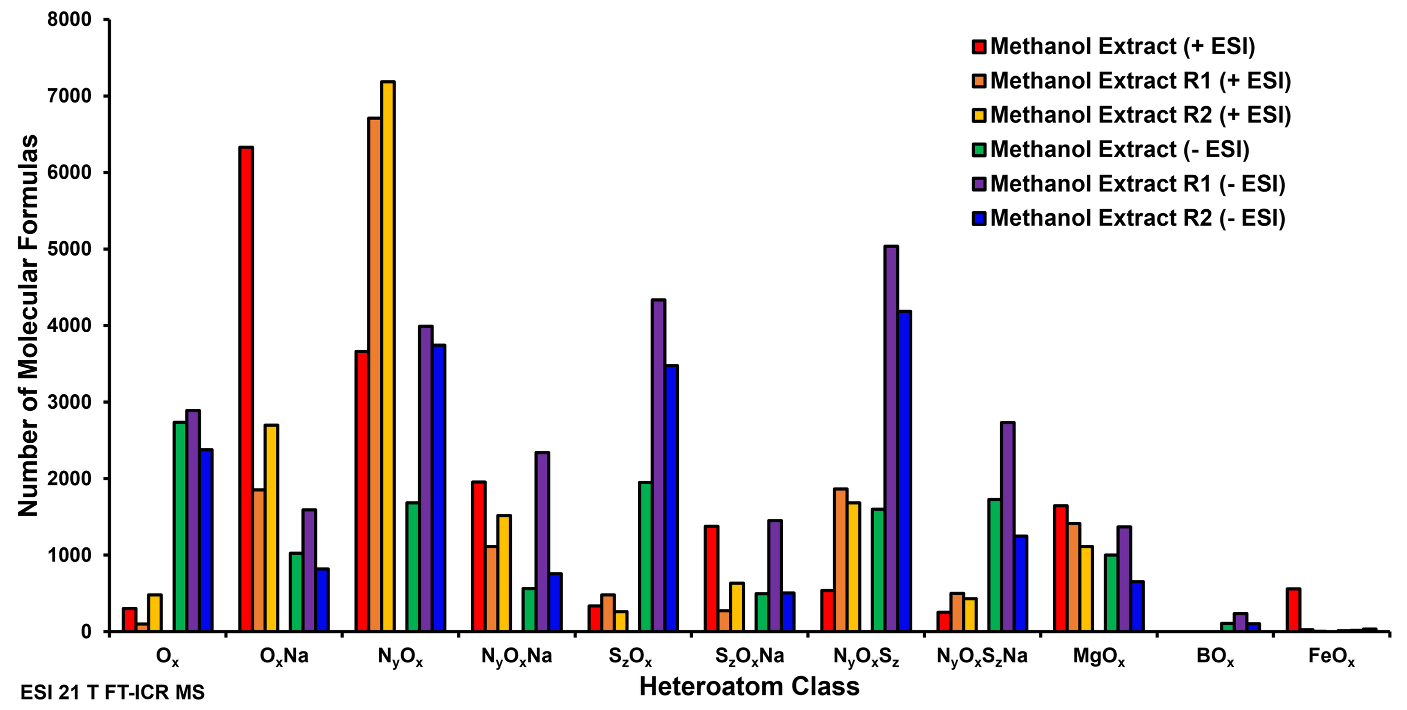

Figure 4. Number of formulas assigned for heteroatom classes after (+) and (-) ESI 21-tesla FT-ICR MS analysis of methanol extracts from the first extraction series and two replicates. Replicates produced with the initial methods used for the first extraction were inconclusive, so the extraction method was modified slightly by homogenizing the fragment prior to beginning the extractions. This improved reproducibility but yielded slightly different results than the initial extract. The replicates assigned more peaks in the N_yO_x class for (+) ESI than the original. In (-) ESI, the replicates also assigned more N_yO_x, S_zO_x, and $N_yO_xS_z$.

Peaks Assigned for Aguas Zarcas

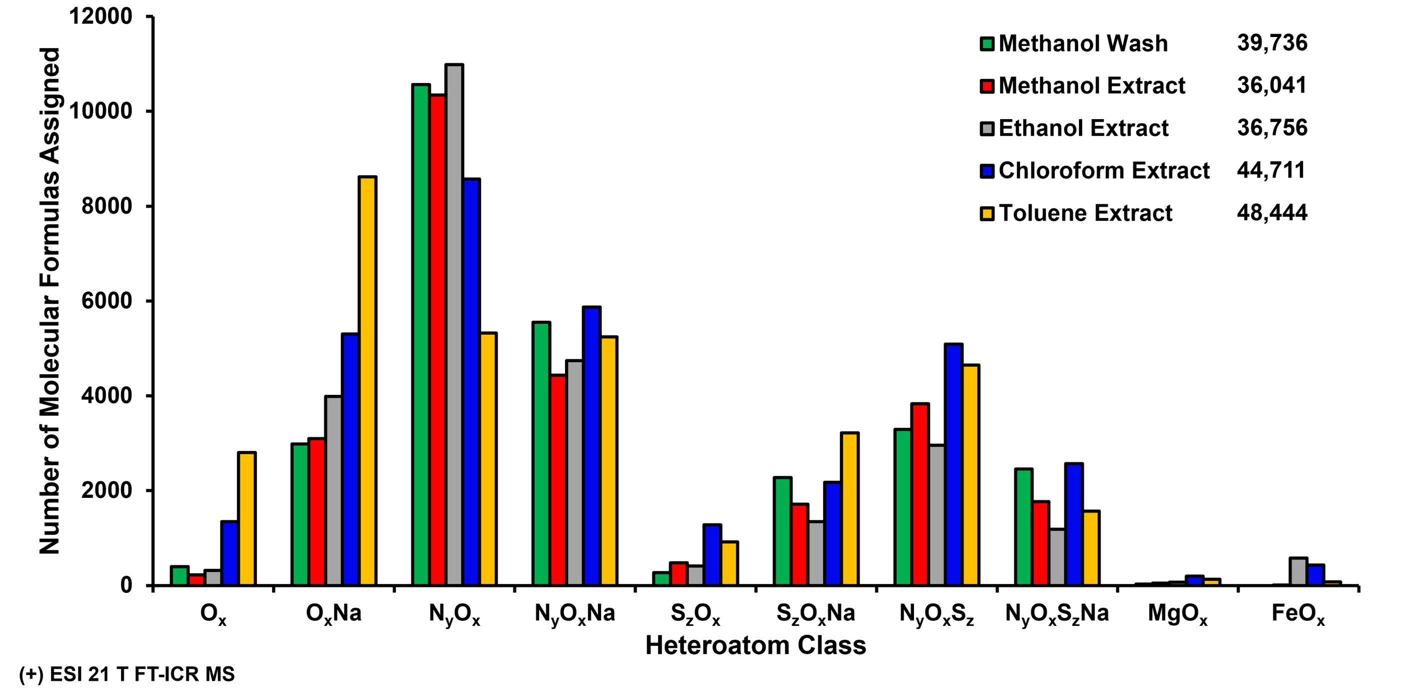

Figure 5. Number of formulas assigned for heteroatom classes after (+) ESI 21-tesla FT-ICR MS for each solvent extract plus the methanol wash of the Aguas Zarcas meteorites. When comparing the number of peaks assigned in Aguas Zarcas between solvents, toluene had the most assigned while methanol had the least. The most abundant class is N_yO_x. Like Murchison, there is extensive sodium-containing species assigned (N_yO_x, S_zO_x, and $N_yO_xS_z$). However, there was very little assigned in the MgO_x, organomagnesium compounds.

Sample	Methanol	Ethanol	Chloroform	Toluene	Unique
Murchison (I)	23,388	31,917	36,543	28,607	43,879
Murchison (R2)	19,860	21,442	35,289	31,146	31,893
Aguas Zarcas	36,041	36,756	44,711	48,444	50,444

Table 1. Peaks assigned for each extract and the total number of unique formulas in the initial Murchison, second replicate of Murchison, and Aguas Zarcas after (+) ESI 21-tesla FT-ICR MS analysis. Overall, Aguas Zarcas had more peaks assigned in each extraction solvent in comparison to either Murchison extractions, indicating that Aguas Zarcas has more complex organic material present.

Compositional Comparison

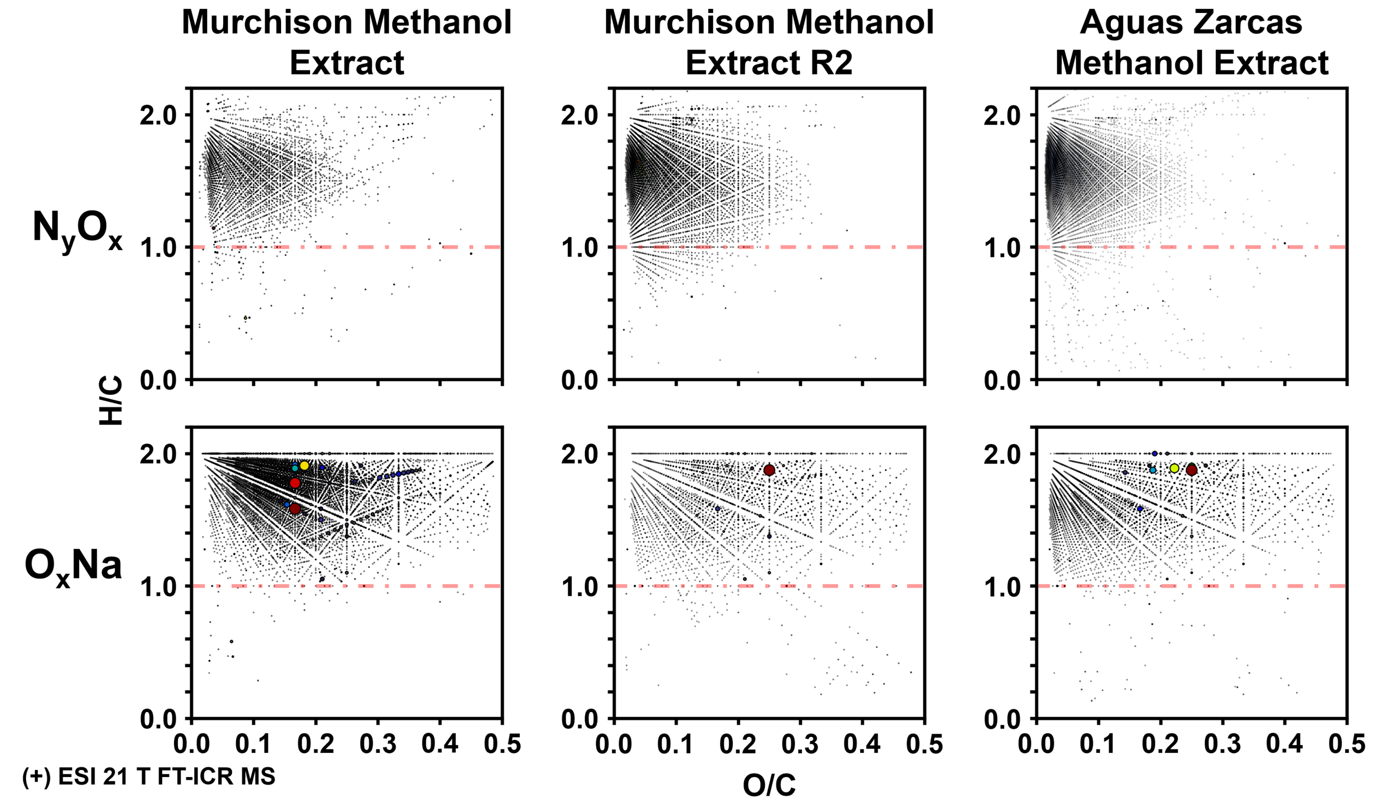

Figure 6. Compositional comparison with van Krevelen plots of Aguas Zarcas methanol extract to the original methanol extract and the second replicate after (+) ES 21-tesla FT-ICR MS analysis. The second replicate and Aguas Zarcas occupy similar compositional space and looks slightly different from the initial extract. Overall, the three extracts have similar compositions but varying concentrations of species present.

Conclusions

- Small changes in extraction methods can make large changes in the composition observed by FT-ICR MS.
- Sequential extractions allow for extensive molecular coverage with each solvent extracting more material than the previous.
- Significant sodiated species are present in all extractions analyzed.
- Aguas Zarcas contained more formulas assigned overall when compared to multiple Murchison extracts.

References

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Acknowledgments

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