**Atmospheric
Chemistry
and Physics
Discussions**

# *Interactive comment on* "Studies of aerosol at a coastal site using two aerosol mass spectrometry instruments and identification of biogenic particle types" *by* M. Dall'Osto et al.

**Anonymous Referee #2**

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ACPD 5, 10799-10838 Dall'Osto et al. Studies of aerosol at a coastal site using two aerosol mass spectrometry instruments and identification of biogenic particle types.

This paper tries to show that a novel type of magnesium-rich biogenic particle was measured with single particle mass spectrometry (ATOFMS) at Mace Head, Ireland. AMS data are used to support this claim. I think that the authors have let their excitement run ahead of them. There are more ordinary explanations for the observations than a new type of particle, and the authors have not fulfilled the burden of proof that biogenic particles are the only or even most likely explanation for the mass spectra.

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No direct evidence is presented in the mass spectra for biogenic processes, and the indirect evidence for biogenic processes also has other explanations. The paper is not suitable for publication in its current form.

The key observation is a series of mass spectra of individual particles with a large Mg peak along with significant peaks due to Cl, K, and Na. The time series shows that these particles were highly correlated with normal sea salt mass spectra that have Na as the largest peak (Figure 3). Both the Mg-rich and normal sea salt mass spectra were present when the winds were off the ocean.

There are at least three possible explanations of the Mg-rich mass spectra:

- The explanation favored by the authors: They represent Mg-rich biogenic particles.

- They could represent non-biogenic Mg-rich particles, produced either at the ocean surface or afterwards by fragmentation of sea salt particles in the atmosphere.

- They could be normal sea salt particles for which ionization biases in the ATOFMS oversampled the natural sea salt Mg. That is, the Mg-rich mass spectra might not represent Mg-rich particles.

I will discuss the last possibility, although there is some literature support for the second.

It is important to realize that the ATOFMS does not produce ions from an entire particle, especially above 1 micrometer where most of the Mg-rich spectra were observed (p. 10812). Instead, only a portion of the particle is ionized with some bias toward the surface. Just how representative a mass spectrum is of the particle composition depends on many factors, including laser power, particle size, particle composition, and the internal structure of the particle. The latter depends on relative humidity: a sea salt particle can exist as anything from a solution droplet to an agglomeration of different salt mineral crystals. If one pictures an electron microscope image of a dried sea salt particle one can easily imagine composition biases from blowing up one side of the

particle.

The relative humidity of the inlet line was estimated at roughly 35% for average temperatures inside and outside the sampling trailer (p. 10811). The efflorescence point of sea salt aerosols is roughly 45% RH. Therefore, the mass spectrometer was probably measuring effloresced particles at least some of the time. As a sea salt particle dries, the first precipitates are calcium carbonate, calcium sulfates, and NaCl. A magnesium and potassium rich brine is left behind, possibly surrounding the crystals. This brine crystallizes at lower relative humidity in a complicated sequence. If the ionization in the mass spectrometer occasionally preferentially sampled this Mg-rich brine or its crystals it would explain the observed mass spectra without invoking a new type of biogenic particle.

Both the effloresence point and crystallization sequence of seawater are sensitive to the degree of chemical aging (e.g. replacement of NaCl by NaSO4), so in a partially crystallized particle the composition of the crystals and brine will be different in clean marine versus mixed marine-aged pollution air. This could make it very difficult to distinguish real effects from ionization biases. If the Mg-rich spectra come and go it could be a real effect or it could be that Mg is changing its chemical form in partially dried particles with subsequent changes in ionization biases. Even in a single air mass, some sea salt particles will have been produced right off the coast and others will have had a few days to pick up non-sea-salt sulfate. Then they will effloresce differently in the sample inlet line.

The first piece of supporting evidence offered for biogenic Mg-rich particles is that the AMS data showed somewhat different sulfate and organic size distributions when Mg-rich spectra were or were not present (Figures 11 and 12). The AMS doesn't measure Mg, so it provides no proof that either the organics or the sulfates were in the same particles as the Mg. Aged pollution can be present even in a "clean" wind sector, so the organics and sulfate would not have had to come from the ocean.

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The second piece of supporting evidence offered is that the Mg-rich spectra time series was correlated with rainfall (Figure 13). Since the Mg-rich mass spectra were correlated with winds from the ocean, does this simply mean that it rained more when the wind was off the ocean? Or perhaps the outside and trailer temperatures were systematically different when it rained, leading to different relative humidities in the sampling line causing different amounts of efflorescence and hence different ionization biases?

Figure notes: In Figure 4, the mass 77 peak that is provisionally identified as $C_6H_5^+$ from aromatic compounds (p. 10812) could also be a cluster ion: $H_2O.MgCl^+$.

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