

First of all we would like to thank Willi Brand for his comments and suggestions which made us rethink our interpretations regarding the broad Kr tail. By incorporating these suggestions we considerably improved the paper.

Note, the original reviewer text is in blue, our response is in black.

This manuscript by Schmitt and coauthors reports on a very important finding affecting carbon stable isotope measurements of methane in air, firn air, and ice bubble samples. During analysis, Kr in these samples is often poorly separated chromatographically from CH₄; it co-elutes with the sample CO₂ generated on-line from the methane peak and therefore can affect the quantitative assessment of the different isotopologues. Such phenomena are not new; they have for instance been encountered for nitrogen isotopes, which can suffer from argon interference (Mariotti, Nature 311; 1984) and for oxygen isotopes, which also suffer from argon (Sarma et al, Anal. Chem. 75; 2003) [1]. In these cases, the underlying causes are not attributable to a direct isobaric interference of a particular peak; the effect is rather some undefined phenomenon, which has to be quantified in order to be correctable. Alternatively, and preferentially, the interfering Ar should be removed.

In this paper, Schmitt and coauthors argue that the observed effect originates from Kr₂⁺, m/z 43, which has a high-mass tail extending over several mass units, thus adding to the CO₂ ion currents. Thus, the effect is attributed to the abundance sensitivity of the respective instrument, which in turn is a function of the mass dispersion and the geometry of the respective Faraday cups. Low mass dispersion instruments like the Isoprime instruments in Bern and Bremerhaven should exhibit a larger effect than the Delta+ XP in Utrecht or the 252 at Penn State, which seems to be the case, roughly (Figure 2). The abundance sensitivity is defined as the contribution from a neighbouring mass ion current to the next. It is illustrated in the manuscript as Figure 7 (I would like to see real data here, not just a formal sketch) [2]. With He in the source, abundance sensitivity usually ranges from 10⁻⁴ for the smaller instruments to <10⁻⁶ for the largest instruments. For m/z 45, the contribution from the large m/z 44 ion current of CO₂ would thus range from 0.01 % (i.e. 1 % of the ¹³C signal) to 0.0001 % (i.e. 0.01 % of the m/z 45 signal). For m/z 46, the corresponding contribution from m/z 44 would be the square of these contributions. These can safely be discarded; the contribution from the m/z 45 signal itself is much larger. In addition, most of the contributions to neighbouring cups arise from collisions in the ion source, generating an energy deficit and thus leading to pronounced low-mass tail. The He⁺ contribution to the m/z 3 current in 2H/1H analyses is a prominent example of this. In this context, it seems rather unlikely that the very minor Kr₂⁺ peak at m/z 43 (less than 1 % of

the major beam of the ^{86}Kr isotope) should be responsible for the observed contribution, unless there are special effects causing an unusual high mass tail. In particular, I cannot see why the effect on the mass 46/44 ratio should be 7 times larger than on the 45/44 ratio, in spite of the different cup width and sensitivity values. I have been looking for special Kr^{2+} effects, which could lead to a broad high-mass tail, so far at no avail. The Kr^{2+} chemistry has been investigated by Adams and Smith (IJMSIP 35, 1980) using a SIFT flow tube. A reaction with CO_2 leads to Kr^+ , CO^+ and O^+ , none of which would cause a highmass tail. The 2nd ionization potential is 24.36 eV, hence one could argue that extra Kr^{2+} is generated from He^+ (1st IP = 24.58 eV). Again, I do not see where a special high-mass tail would arise from in this case. Likewise, Kr^+ could generate extra CO_2^+ via Charge Exchange (14.0 eV ! 13.79 eV). This would generate CO_2^+ in a different energetic state with a different fragmentation pattern, possibly affecting the 44-28 and 44-16 fractionation. I doubt that this would be visible under the given circumstances.

There are two effects which I consider more likely to cause the observed phenomenon. (1) Space charge. When an extra cloud of ions is formed in the ionization region, the extraction conditions for all other ions are affected, including the possibility for mass dependent fractionation at the alpha slit due to pre-dispersion. After all, there are magnet fields present, having a mass-dependent effect on ion motion [3]. (2) New beams which are not focused to a detector hit the walls of the mass spectrometer somewhere along the flight tube. Kr^+ would hit the outer walls inside the magnet. Such collisions generate secondary particles (mostly electrons), which can find their way to some of the detectors along the focal plane. These reflections usually are rather broad features, often small enough to remain undetected by the naked eye [4]. Secondary particles in general have less than full acceleration energy; hence they can be discriminated against with static fields like a deceleration lens or an electrostatic analyzer. Double focusing mass spectrometers should be largely immune against such interferences (another reason to use such instruments for stable isotopes). I think that the strategy to separate CO_2 and Kr chromatographically after the CH_4 -to- CO_2 conversion is the best option to ensure that the effect is not entering the analytical results. The attempts to correct for the effect are too variable to expect them to be under control in daily routine. On the other hand, when strictly adhering to the principle of identical treatment of sample and reference, the effect should cancel for normal air samples, where the Kr/CH_4 ratio is more or less constant. Hence, reference should always be made with air containing the right amount of Kr and CH_4 . For ice bubbles, this is not an option; here the Kr should always be separated chromatographically. These arguments should be considered before final publication (this should also affect the title; replace “ $^{86}\text{Kr}^{2+}$ ” with “ Kr ”) [5].

Response by Schmitt et al.

Your comments and suggestions were very useful and we realised that our observed Kr interference likely consists of two separate phenomena rather than a single one due to an extremely broad $^{86}\text{Kr}^{2+}$ tailing we assumed earlier. To respond to your individual statements, we added numbers in brackets in the review, i.e. [1], and respond to them individually below:

[1] We added both suggested papers (Mariotti, Nature 311; 1984 and Sarma et al, Anal. Chem. 75; 2003) to bring our findings in a broader historic perspective.

[2] Regarding your suggestion to construct the schematic shown in Fig. 7 from real data, we want to explain why we constructed the scheme this way: First, we want to keep a clear line between measured data, shown in the other figures, and a schematic which uses the results from the measurements to construct an idealised signal which can be plotted on a constructed x-axis in the m/z domain. As you convinced us with your argumentation that the contribution in the minor1 and minor2 cups cannot be explained by a very broad m/z 43 tail, but rather results from a separate process, we redraw Fig. 7 and included both effects separately. In the new schematic (Fig. 7b), we illustrate that the Kr contribution of the major cup is due to the m/z 43 tail in the sense of abundance sensitivity, while for minor1 and minor2 this contribution becomes progressively smaller. For these two cups the second Kr effect, in the sense of a broad unspecific scattering effect, is the dominant factor.

[3] The interaction of CO_2 with Kr during the ionisation in the ion source leading to changed ionisation of CO_2 itself was also one of our early favourite explanations, but the experiment using pure Kr in the source ruled out this possibility.

[4] Your suggestion that secondary particles generated by Kr ions hitting the mass spectrometer walls contribute to the signals in minor1 and minor2 is very convincing. It could explain why the signal measured in minor2 is almost flat, i.e., signal intensity does not change significantly when the accelerating voltage is varied (Fig. 6b). Since we observe positive peaks only, electrons as secondary particles seem unlikely as they should lead to negative peaks or dips below the background. Consequently, the secondary particles are either sputtered metal ions from the flight tube or reflected Kr^+ ions. In both cases the observed peaks should not only be produced by Kr isotopes but by other gas species of similar m/z range present in the ion source as well. The only puzzling thing is, that the used mass spectrometers (MAT 252, Delta Plus XP and Isoprime) have very different

geometries of their flight tube and the orientation of the Faraday cups should also differ. Yet, all instruments show Kr effects which are not too different from each other.

[4] We changed the title accordingly and replaced $^{86}\text{Kr}^{2+}$ with Kr, we did the same throughout the main text where we refer to the broad tail extending into the minor1 and minor2 cup.