

Referees Comment on ATONA Charge mode system.  
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This is a timely paper concerning the introduction of the ATONA charge mode collection system to an ISOTOPX NGX.

The challenge of getting the the capacitive feedback system to work has been ongoing for a number of years. Both Cary and Keithley electrometers have had the ability to measure charge accumulation, but getting it to work in a routine analytical setup has been somewhat difficult (see Esat 1995, and Ireland et al. 2014).

The physics behind charge mode and the implications for data collection are interesting, but are not particularly well explained in this paper. Potentially this is because of the patent that is being sought for this system. In any case, the issues concerning the noise floor for a capacitive system effectively relate to a “read” noise in the capacitor system as opposed to the Johnson Noise in a resistive system. Hence, there is a constant noise component in the capacitive read system (see Ireland et al. 2014), and the longer you integrate the better the signal to noise. On the other hand, you continually integrate Johnson Noise and so the signal/noise does not improve as quickly for an increase in integration time. For comparison, we have set up our capacitive system for a 2 s integration and the noise is similar to the  $10e-13$  ohm resistor, pretty much similar to what is achieved here. The 2s integration is appropriate for an ion microprobe because of the continual change in analytical conditions. A longer integration time is fine for a noble gas instrument because the gas is effectively homogenised in the source and there are only longer term fractionation processes to deal with.

The work in the Isotope NGX is based around noble gas analysis, and specifically Ar isotopes. On one hand, this is a good system to look at because there is a good dynamic range in the isotope ratios under consideration. It also has the benefit that the ion beam is only changing at a (slow) steady rate allowing a good description of the progression of the counting statistics. The data show that the system performs well at the level commensurate with the measured ratios. On the other hand, Ar isotopes are not typically measured to high precision (e.g. as might be achieved for TIMS or ICP-MS analysis, or even SIMS analysis). This makes it also more difficult to establish the linearity of the system as well.

It is evident that the noise floor is still an issue for the  $^{36}\text{Ar}$  measurements described here. So as the volume of Ar gas is reduced, the error magnification from measuring the  $^{36}\text{Ar}/^{40}\text{Ar}$  and resulting corrections to  $^{40}\text{Ar}/^{39}\text{Ar}$  are still going to be a limitation and will likely still need to be carried out on an electron multiplier.

The benefit of the capacitive system is that measurements can be carried out on more Faraday cups, and potentially without the need for an electron multiplier (ion counter). The noise floor we have achieved is better than 500 c/s which means that for most isotope ratio measurements Charge mode is adequate and very often superior to an electron multiplier. At the upper level of count rates, 250-1000 x  $10e3$  c/s, the charge mode seamlessly connects with  $10e12$  ohm resistor capability. At the lower end, we have measured isotope ratios down to 10,000 c/s, which is well removed from the gain drift and dead time issues of an electron multiplier. As such charge mode does provide that connection between electron multipliers and the traditional resistor feedback amplifiers. But as demonstrated in this paper, it is a complementary aspect of the measurement of isotope ratios in geochemistry.

#### References

T.M. Esat, Charge collection thermal ionization mass spectrometry of thorium. *International Journal of Mass Spectrometry and Ion Processes* 148 (1995) 159–170.

T.R. Ireland, N. Schram, P. Holden, P. Lanc, J. Ávila, R. Armstrong, Y. Amelin, A. Latimore, D. Corrigan, S. Clement, J.J. Foster, W. Compston, Charge-mode electrometer measurements of S-isotopic compositions on SHRIMP-SI. *International Journal of Mass Spectrometry* 359 (2014) 26–37.