Noblesse *HR*

NOBLE GAS MS

ADVANTAGES FOR ^{40}AR/^{39}AR DATING

In this note we consider the advantages of Noblesse HR for ^{40}Ar/^{39}Ar dating. We will show that

- **all C-based interferences at Ar are resolved**
- **measurement of ^{36}Ar without H^{35}Cl also possible**
- **edge resolution preferable to true resolution for Ar interferences**
- **^{36}Ar frequently the dominant source of uncertainty in ^{40}Ar/^{39}Ar dating**

Mass resolving power — why it matters for Ar

Noblesse HR offers signficantly enhanced mass resolving power (MRP). MRP describes the ability of a mass spectrometer to resolve interferences.
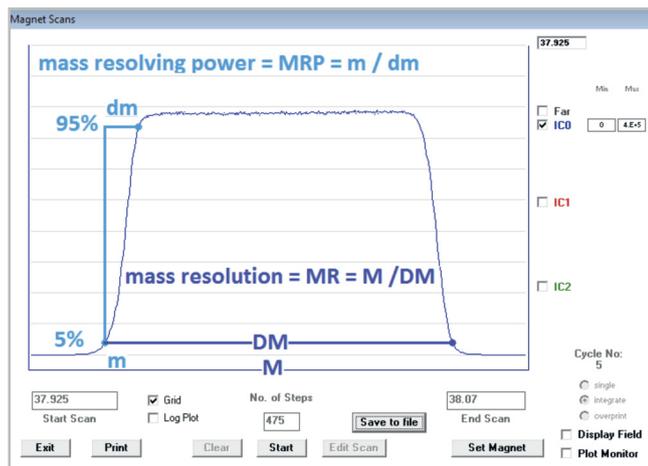

Fig 1: **Mass resolving power (MRP)** describes ion beam width. It corresponds to the width of the side of the peak in the mass scan. If the beam is narrower, the peak sides – formed by sweeping the beam over the edges of the collector slit – will be steeper. **Mass Resolution (=MR)** depends on total width of the peak, and hence on the slit width, as well.

Mass Resolving Power is a more fundamental property than than Mass Resolution. To resolve interferences, a sufficiently high MRP is required. In contrast, it is not always necessay to have a narrow collector slit (i.e. high mass resolution). Resolving interferences using a wide collector slit is often called edge resolution, and works very well for some applications, including Ar isotope measurement.

Resolution of [^{36}Ar+H^{35}Cl] from [^{36}Ar+H^{35}Cl+^{12}C$_3$]

Figure 2 shows the mass 36 peak with an MRP of 3500. C$_3$ is well resolved from the combined ^{36}Ar+H^{35}Cl. The mass difference between (hydro)carbon and Ar increases through the masses 36 to 40; mass 36 is the most difficult to resolve.
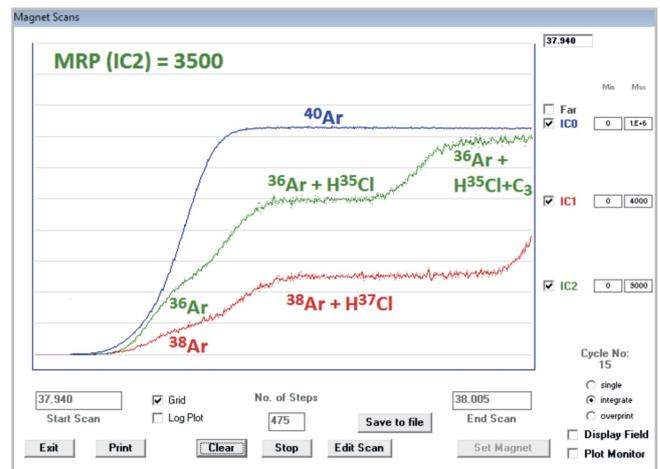

Fig 2: Noblesse mass scan with IC2 MRP=3500. This enables resolution of the C$_3$ interference, and provides sufficient peak flat for easy measurement of the combined ^{36}Ar+H^{35}Cl peak. The source getter was intentionally isolated in order to increase the amounts of interference in this scan.

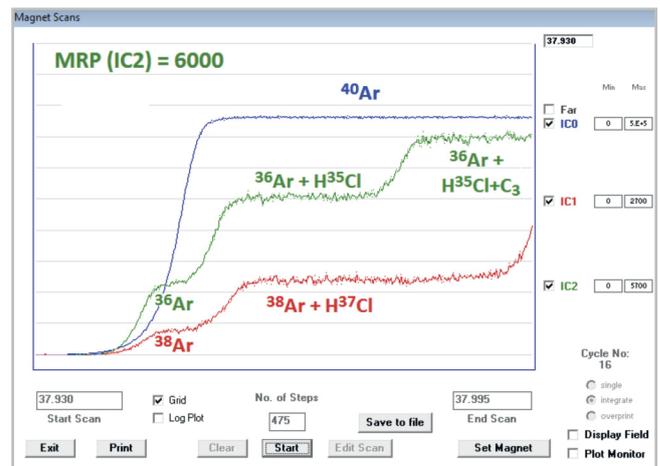The Noblesse source may be tuned to higher MRP; figure 3 was made with MRP (IC2)~6000.

Fig 3: Same instrument as figure 2, but with source tuned to MRP~6000, which permits measurement of Ar without the HCl interferences.

Measurement of ^{36}Ar without $H^{35}Cl$ is more challenging than resolution of the $^{12}C_3$ — owing to the very limited peak flat — but is nevertheless possible. A detailed account of such measurements is given elsewhere, but it is necessary to consider possible tailing from the $H^{35}Cl$, and also possible reduction in efficiency caused by measurement at the extreme edge of the ^{36}Ar peak. Even if the $^{36}Ar/^{40}Ar$ measurements are reproducible, ignorance of these effects can result in systematic errors. These effects can be understood and calibrated by reference to the combined $^{36}Ar+H^{35}Cl$ peak, which exhibits ample peak flat.

Edge resolution versus true resolution

Figure 4 shows a mass scan obtained with a narrow slit fitted to the IC2 detector, which allows higher mass resolution.
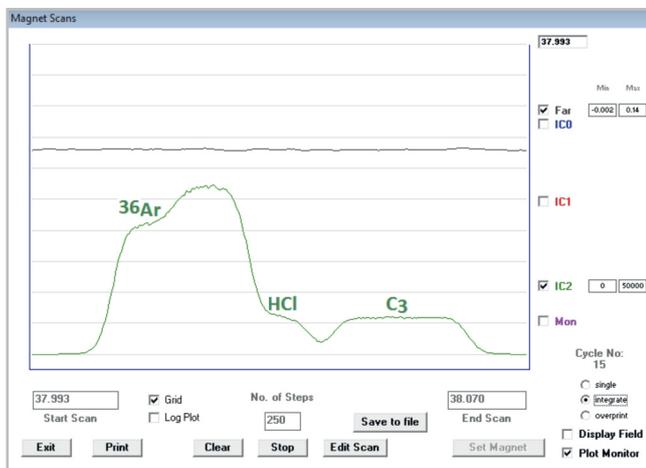

Fig 4: Fitting a narrow slit in front of IC2 allows true resolution of $^{36}Ar+H^{35}Cl$ from the C_3 peak, but does not increase the peak flat available for ^{36}Ar; furthermore, the peak flat on the combined $^{36}Ar+H^{35}Cl$ peak has also disappeared.

We have previously shown that the $^{36}Ar+H^{35}Cl$ peak, which showed significant peak flat using edge resolution, was essential to calibrate (or verify) the difficult ^{36}Ar measurements. Furthermore, in some circumstances it may be satisfactory (and also considerably easier) to measure the combined $^{36}Ar+H^{35}Cl$ peak, and blank subtract the HCl (e.g. if the HCl is small and stable). True resolution makes this previously simple measurement problematic, as the combined peak no longer shows significant peak flat. For these reasons, edge resolution is preferable to true resolution for Ar isotope measurements.

Importance for $^{40}Ar/^{39}Ar$ dating

Mass 36 is important, as it is used to correct for trapped air using $^{40}Ar^* = {}^{40}Ar_{TOTAL} - 296\,{}^{36}Ar$, where $^{40}Ar^*$ is radiogenic ^{40}Ar from ^{40}K decay. Given this equation, and a sample with particular $^{40}Ar/^{39}Ar$ and $^{40}Ar/^{36}Ar$, we can ask: which ion beam (mass 36, 39 or 40) is the

greatest source of uncertainty in the final age? The answer is shown in figure 5. The calculations assume that the ion beam measurements are limited only by 'shot noise' (also known as counting statistics).
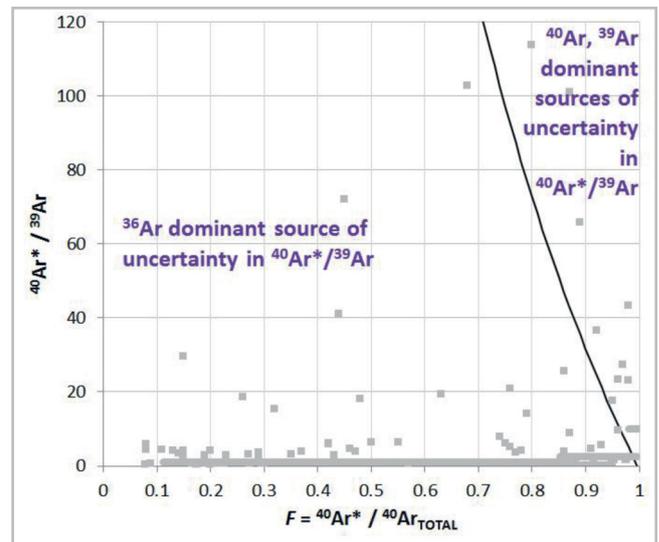

Fig 5: Indicates whether masses 40 and 39, or mass 36, dominate the age uncertainty for samples of different compositions ($^{40}Ar^*/^{40}Ar_{TOTAL}$ and $^{40}Ar^*/^{39}Ar$). In many cases ^{36}Ar is the largest contributor to age uncertainty — especially for samples which are not very radiogenic (low $^{40}Ar^*$). Grey dots represent samples (from a short survey of recent, and mostly Noblesse, papers).

Both HCl and C_3 may interfere with ^{36}Ar. In practice, it appears that C_3 may be the greater problem, as it appears to be unstable, and therefore cannot be blank subtracted. Further details are given in our published paper and references therein. Hydrocarbon interferences are also present at the other Ar masses too (especially 39) and these can also be easily resolved with Noblesse.

Finally, we note the trend in recent years to obtain highly precise ^{40}Ar and ^{39}Ar measurements using Faradays on a high sensitivity instrument at low resolution. Such conditions may achieve shot noise limited precision for ^{40}Ar and ^{39}Ar (if we ignore potential interferences at these masses). However, this precision will be of limited use if ^{36}Ar is the dominant source of uncertainty — and will be even less use if ^{36}Ar is also compromised by interferences. ^{36}Ar must also be measured to high precision, and evidence indicates this requires high resolution (resolution of at least C_3^+ is desirable). To do otherwise risks a systematic error, with no means of detecting it, and of possibly significant magnitude.

Reference:

J M Saxton, Chemical Geology, 309 (2015), 112-117.