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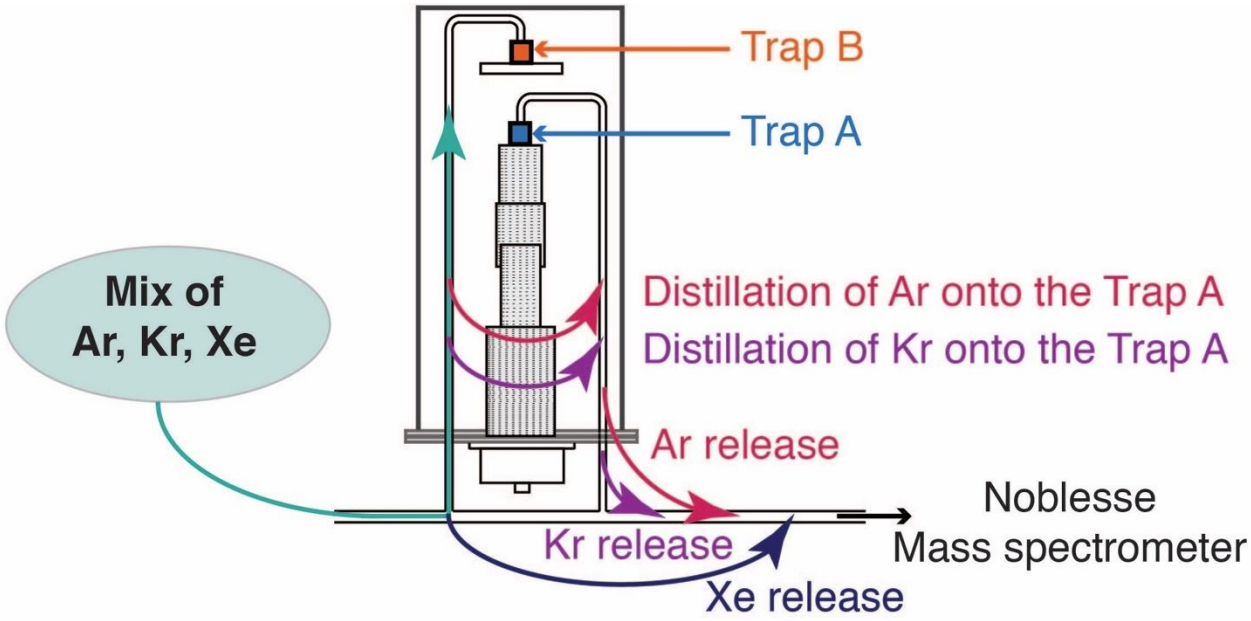

Title: A new dual stainless steel cryogenic trap for efficient separation of krypton from argon and xenon

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Abstract:
The elemental and isotopic abundances of krypton and xenon provide critical insights into processes ranging from stellar nucleosynthesis to volatile accretion and paleotemperatures on Earth. Accurate and precise determination of the krypton and xenon elemental abundance and isotopic ratios requires sample purification and noble gas separation to avoid interferences in the mass spectrometer. However, effective separation of krypton (Kr) from argon (Ar) and xenon (Xe) has remained challenging. Here, we present a new cryogenic instrument associated with a new protocol to achieve an efficient and effective separation of Kr from Ar and Xe. Using two electropolished stainless steel cryogenic traps on a single cold head, distillation of the noble gases from one trap onto the other and temperature cycling of the traps to reduce the effect of cryotrapping allows ≥ 98 % of the Kr in a sample to be recovered with < 0.5 % of the Ar and < 1 % of the Xe abundances of the sample. Likewise, more than 99 % of the Xe fraction can be recovered with < 1 % Kr. No variations in the isotopic ratios of the separated Kr and Xe fractions are observed as a function of the signal size for air standards. Moreover, we find that krypton isotopes can be fractionated during Ar-Kr separation. We suggest that more accurate krypton isotopic compositions can be obtained by maximizing the recovered krypton fraction instead of minimizing the argon fraction within krypton.

Introduction

Noble gases (helium, neon, argon, krypton and xenon) are invaluable tracers due to their inertness and as a consequence are used for a wide range of applications in Earth and planetary sciences including geochronology, hydrology, paleoclimatology, cosmochemistry and mantle geochemistry (1–3). Among the 22 noble gas isotopes, some are primordial in the Earth's mantle (e.g., ^{3}He, ^{20}Ne, ^{38}Ar, ^{124}Xe), some are produced by cosmic rays on planetary surfaces (such as ^{3}He, ^{21}Ne), some are radiogenic (such as ^{40}Ar produced on Earth from the decay of ^{40}K, or ^{129}Xe produced from the decay of now extinct ^{129}I) and others are fissiogenic (as $^{131\text{-}132\text{-}134\text{-}136}$Xe produced by fission of extinct ^{244}Pu and extant ^{238}U). Since noble gases do not react with their environments in near-surface conditions, elemental and isotopic ratios of primordial isotopes are key tracers of volatile sources on terrestrial planets, whereas cosmogenic, radiogenic and fissiogenic isotopes have proved to be useful dating tools for early Solar System processes, terrestrial climatic and tectonic processes, and planetary degassing events (1–5). Noble gases hence offer a powerful way to understand formation of planets and their subsequent evolution.

Noble gas analyses are often challenging due to very low abundances, isobaric interferences (e.g., $^{40}Ar_2^+$ with $^{80}Kr^+$) and varying mass discrimination effects due to changes in partial pressures in the mass spectrometer. As an example, the concentrations of ^{36}Ar, ^{84}Kr and ^{130}Xe in the atmosphere are of 9.58×10^{-13} mol/g, 1.98×10^{-14} mol/g and 1.08×10^{-16} mol/g, respectively,

whereas in the bulk Earth's mantle there are estimated to be of $7.8x10^{-14}$ mol/g, $1.9x10^{-15}$ mol/g and $2.6x10^{-17}$ mol/g, respectively (6). With the exception of resonance ionization mass spectrometry (7,8), isotopic analyses of noble gases mostly involve mass spectrometers equipped with electron bombardment sources and magnetic sector filters (9). This type of ionization source shows strong dependence on partial pressure, as variations in partial pressure can significantly affect the mass spectrometer sensitivity and mass discrimination (9). Therefore, sample purification followed by separation of the five noble gases (He, Ne, Ar, Kr, Xe) from one another before sequentially introducing them into the mass spectrometer are generally considered best practices for reliable noble gas analyses.

Samples are commonly purified through a series of hot and cold getters to remove reactive species (e.g., CO_2, H_2O, N_2, etc) (e.g., 9). After purification, noble gases are cryogenically separated by being adsorbed at very low temperature (as low as 15 K) onto a substrate, usually activated charcoal, and sequentially desorbed in order of mass by increasing the temperature (9–11). The disadvantages of activated charcoal are the significant overlaps between the release curves of argon, krypton and xenon (e.g., 12), rendering the complete separation of Ar-Kr-Xe very difficult, if not impossible. The separation of the heavy noble gases thus often involves two separate traps to partition the gases (13). First, all the heavy noble gases are trapped on one trap. The temperature of this first trap is then set to partially desorb Ar, in order to progressively transfer Ar by distillation onto the second trap, which is kept at liquid nitrogen temperature (i.e., 77 K, temperature to which 100 % of Ar, Kr and Xe are adsorbed on charcoal) or lower. The same procedure is then repeated to separate Kr from Xe (13). Even with this protocol, significant amounts of argon can still be present in the krypton and xenon fractions due to the overlap in the release curves (e.g., 12), making krypton and xenon analyses difficult, krypton and xenon being typically two to five orders of magnitude less abundant than argon. Other variants of this procedure involve for example using two charcoal traps, one operating at 148 K for trapping Kr and Xe and the other operating at 77 K for trapping Ar, the noble gases are separated into three fractions – He/Ne, Ar, Kr/Xe (14,15). Alternatively, Kr and Xe are trapped onto a quartz finger at liquid nitrogen temperature while Ar mostly stays in the gas phase (16,17) although it is not completely clear what fraction of the Ar gets trapped with Kr and Xe. In both these cases, Kr and Xe have to be simultaneously admitted into the mass spectrometer and analyzed together, which can generate lower measurement precisions due to quick consumption by ionization in the mass spectrometer (typically half of the Kr, Xe signals can decrease in 30 minutes given the source parameters).

Some of the limitations of the charcoal trap can be overcome using a polished stainless steel trap (12). This type of trap shows steeper release curves and lower release temperatures compared to charcoal traps, allowing for significantly better separation of the heavy noble gases (12,18,19). However, even with a stainless steel trap, there is still overlap between the Ar, Kr and Xe release curves and the use of a single trap does not allow proper separation of the heavy noble gases (12,18,19). Hence, a new cryogenic system was designed with two stainless steel traps on a single cryogenic head and a technique was developed to effectively separate Ar from Kr from Xe.

Apparatus design and experimental procedure

A new cryogenic system was fabricated by Janis Research Company for the UC Davis Noble Gas Laboratory (Figures 1 and S1 in Supplementary). The system uses a 4 K cold head with 0.5 W cooling power available on the second stage at 4.2 K (Sumitomo Model RDK-205J). There are two electropolished stainless steel traps associated with the cold head, one attached

to the second stage of the cold head with a high temperature stage and the second trap on the radiation shield; the radiation shield provides the thermal link between the trap and the first stage of the cold head (Figure 1). The two traps have independent silicon diode temperature sensors and heaters. For safety, the heaters are interfaced with a temperature sensor on the first stage of the cold head, so that heater power is automatically cut off when the cold head first stage reaches 290 K. The trap on the second stage of the cold head can be cooled down to < 5 K (lowest achieved temperature was 4.7 K), hereafter named Trap A, and can reach a temperature of 500 K for bakeout. The trap on the radiation shield achieves temperatures of < 50 K (lowest achieved temperature was 31 K), hereafter named Trap B, and can reach temperatures of 500 K for bakeout. The temperature on the two traps can be controlled independently, with no observable temperature feedback between them. For example, Trap B can be held at 200 K and the Trap A temperature can be easily controlled between 200 K and 5 K. The two traps are controlled by a Lakeshore Model 335 temperature controller that interfaces with an Omega iSeries temperature controller used for monitoring the temperature of the first stage of the cold head. The Lakeshore controller interfaces with control computer of the vacuum line through a General Purpose Interface Bus.

On Trap A, neon is completely adsorbed at 10 K, allowing a significant temperature buffer to counter the long-term degradation of the cold head. The Trap A can be cooled down from 200 K to 8 K in less than 30 minutes. Likewise, the Trap B can be cooled down from 200 K to 70 K in less than 30 minutes. Additionally, the Trap A can be cooled from 110 K to 6 K in 10 minutes. The rapid cooling times allow for significant shortening of sample processing times. We also note that no pre-cooling time is needed, whereas charcoal cryogenic system often requires 30 minutes to 1 hour before starting the analysis to cool the system from 375 K (Xe release temperature) to about 15 K.

We first obtained the release curves for Ne, Ar, Kr and Xe from a single trap (Figure **2**). These release curves were similar to that previously determined for a stainless steel trap (12,19). For example, neon was completely adsorbed at 10 K, argon at 55 K, krypton at 70 K and xenon at 90 K (Figure 2). The temperatures at which more than 99 % of Ne, Ar, Kr and Xe are released were 22 K, 83 K, 100 K and 135 K (Figure 2, Protocol 1, see below), respectively, in very good agreement with previous observations (12). Helium started to be adsorbed at 7.5 K.

Based on the release curves (Figure 2), three different protocols, described below and in Figure 3, are tested to efficiently separate Ar, Kr and Xe from each other. In the first protocol, an aliquot of an air standard is purified using a series of hot and cold MP10 SAES getters. After the purification, the noble gases are exposed to the Trap B set to 70 K to adsorb Kr and Xe. At 70 K, a small fraction of Ar is also adsorbed (Figure 2). Then, the Trap A, set to 25 K, is opened to adsorb Ar for 10 minutes. During this process, as the Ar partial pressure decreases in the line due to Ar adsorption onto the 5K trap, Ar adsorbed on the 50K trap is progressively released and adsorbed on the Trap A. Both traps are closed and the line is pumped for 5 minutes and then opened again for 10 minutes to finish the transfer of Ar onto the Trap A, so that the total transfer duration of 20 minutes remains the same as for the second protocol (described below). Argon is then progressively released from the Trap A in steps of 2-5 K, inlet into the Noblesse (Nu Instruments) mass spectrometer and measured along with the Kr signal. Between each temperature step, the vacuum line and the mass spectrometer are pumped. After all the Ar is inlet into the mass spectrometer, Kr is distilled from the Trap B to the Trap A by setting the Trap B to 90 K and the Trap A to 70 K. Kr, and then Xe, can be desorbed from the Trap A and the Trap B, respectively, in temperature steps of 2-5 K. The release curves are determined by measuring Kr and Xe by mass spectrometry. While measuring the Kr abundance, Ar and Xe

abundances are also measured, and while measuring the Xe abundances, the Kr abundances are measured as well.

In the second protocol, after Ar is frozen onto the Trap A, both traps are closed and the temperature of the Trap B is increased from 70 K to 120 K, held at 120 K for 5 minutes and then set back to 70 K. This temperature cycling is done to limit the effect of cryotrapping, which is the mechanism of one noble gas being trapped by another one (12,18). The temperature cycling allows the heavier noble gases to be layered beneath the lighter noble gases, making the separation of Ar, Kr, Xe more efficient (18). After this temperature cycle, both traps are opened so that the Ar that is no longer cryotrapped by Kr and Xe in the Trap B can be adsorbed onto the Trap A. After argon has been adsorbed onto the Trap A, the temperature of the Trap A is increased in steps of 2-5 K as per the first protocol, and the Ar abundance, as well as Kr abundance in the Ar fraction, are measured by mass spectrometry.

Krypton is separated from xenon following the same principle. The Trap B is set to 90 K and the Trap A to 70 K. Both traps are opened to distill Kr from the Trap B onto the Trap A and then both traps are closed. The temperature of the Trap B is increased to 150 K, held at 150 K for 5 minutes and cycled back to 90 K to freeze Xe. Both traps are opened again to adsorb Kr initially cryotrapped by Xe onto the Trap A. Kr, and then Xe, can be desorbed from the Trap A and the Trap B, respectively, in temperature steps of 2-5 K in order to determine the release curves as well as Ar and Xe abundances with Kr and Kr abundance in the Xe fraction, as for the first protocol.

In the third protocol, two temperature cyclings of the Trap B are performed to separate krypton from xenon (i.e., cycling the Trap B each time to 150 K and cycling it back to 90 K before opening the two traps for Kr distillation onto the Trap A).

For the three protocols (Figure 3), the quantities of gas being processed in the line were of 3.8×10^{-8} cm^3 of ^{40}Ar, 2.38×10^{-11} cm^3 of ^{84}Kr and 1.30×10^{-13} cm^3 of ^{130}Xe, that is comparable to the quantities of gas analyzed from basaltic glass samples for instance (20,21). The blank of the vacuum line is 5.1×10^{-10} cm^3 of ^{40}Ar, 6.9×10^{-15} cm^3 of ^{84}Kr and 4.4×10^{-16} cm^3 of ^{130}Xe, which is very low in comparison and can therefore be neglected in these experiments.

We note that the release curves for the above experiments were determined by desorption of the gases at several temperature steps and inlet into the mass spectrometer, which corresponds to an effective distillation of the gas into the mass spectrometer. When a single temperature is chosen for desorbing a noble gas of interest, such as Kr or Xe, as is the case for processing most natural samples through the vacuum lines, the efficiency of separation would be expected to decrease. Hence, in another set of experiments, the effectiveness of the second protocol in separating Ar from Kr from Xe for natural samples is tested by desorption of the gases at single temperatures based on the release curves, using an air standard aliquot with 1.7×10^{-8} cm^3 of ^{40}Ar, 1.2×10^{-12} cm^3 of ^{84}Kr and 6.6×10^{-15} cm^3 of ^{130}Xe. Following the temperature cycling and distillation process, argon was desorbed from the Trap A at 120 K, Kr from the Trap A at 140 K and Xe from the Trap B at 160 K (Figure 2). Different distillation temperatures were tested, such as 67 K and 70 K to separate argon from krypton and 92 K and 95 K instead of 90 K to separate krypton from xenon. In the Ar fraction, the Kr abundance is monitored, in the Kr fraction, the Ar, Kr and Xe abundances are measured, while in the Xe fraction Kr and Xe abundances are measured.

In a final set of experiments, we investigated the influence of the argon partial pressure (as measured by the abundance of ^{40}Ar in the mass spectrometer) on krypton isotopic ratios, using air standard aliquots with 1.1×10^{-7} cm^3 of ^{40}Ar, 7.5×10^{-12} cm^3 of ^{84}Kr and 4.1×10^{-14} cm^3 of ^{130}Xe. Krypton isotopic ratios were measured using distillation (second protocol described above and Figure 3) and different Ar-Kr distillation temperatures (from 67 K to 75 K) as well as using a single trap (Trap A) and no distillation. For the experiments with the single Trap A with no temperature cycling, the Ar-Kr separation temperature was varied from 68 K to 75 K. This allowed us to vary the argon partial pressure during krypton measurements by a factor of 22. We also carried out experiments with the same distillation temperature but with two distillations and one temperature cycle (Protocol 2 in Figure 3) as well as with three distillations and two temperature cycles for the separation of Ar from Kr in order to change the Ar partial pressure but not the Kr signal, and thus to further study the influence of the argon partial pressure.

The time to run a sample analysis is globally comparable between the use of a charcoal trap or a stainless steel trap. However, in detail, the time will be less for the dual trap if doing a single distillation without temperature cycle for Ar-Kr and Kr-Xe (~ 3 hours to run a sample), comparable if doing two distillations and one temperature cycle for Ar-Kr and Kr-Xe (~ 4 hours to run a sample), and more if three distillations and two temperature cycles are used (~ 5 hours to run a sample).

For all measurements, Ar abundances were determined through measurement of ^{40}Ar, Kr abundances through ^{84}Kr and Xe abundances through ^{129}Xe using the Nu Noblesse HR mass spectrometer equipped with five faraday cups and five electron multipliers. The mass spectrometer source is operated at 9KV and uses a yttrium coated tungsten filament for ionizing the noble gases. The mass spectrometer is fitted with two NP10 getters, two ion pumps and has an inline UHV all-metal valve that can be used to isolate the mass spectrometer source from the flight tube and detectors.

Abundance of ^{40}Ar was measured with one of the Faraday detectors while ^{84}Kr and ^{129}Xe were measured with an ion counter in pulse counting mode. The krypton isotopic ratios were measured during twelve cycles in three steps on the five electron multipliers. The first step was for determining the baselines of the collectors, the second step consisted of measuring ^{78}Kr, ^{80}Kr, ^{82}Kr, ^{84}Kr and ^{86}Kr and the third step was for measuring ^{83}Kr. The sensitivities of the Noblesse mass spectrometer at 250 μA trap current and a filament voltage of -75 V are typically 1.1×10^{-7} cm^3/V for ^{40}Ar, 4.7×10^{-16} cc/cps for ^{84}Kr and 4.8×10^{-16} cc/cps for ^{130}Xe.

Results and discussion

The results of the three protocols used to separate krypton from argon and xenon in air standards are shown in figure 2 and in table 1. In figure 2, the release curves of Ar and Kr are very similar between the different protocols, as both noble gases are released from Trap A that did not have temperature cycle. For Xe, which is released from Trap B, the release curve obtained with no temperature cycle is shifted to the left compared to the release curve with temperature cycling. Xe appears more easily desorbed from the stainless steel trap when no temperature cycling is applied. Hence, this shift in Xe release highlights the need of carefully choosing a release temperature depending on the protocol applied.

Table 1 lists the proportions of each gas remaining with the other gases with the different protocols. It is important to point out first that using only one stainless steel trap does not allow effective separation of Ar, Kr, Xe due to overlaps in the release curves (Table 1, row 1).

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Using two traps improves the heavy noble gas separation and adding one temperature cycling procedure produces a further improvement in the separation (Table 1, rows 2-3). For example, the recovered Kr fraction (i.e., the percentage of Kr in the fraction primarily analysed for Kr) increases from 81.0 % to 96.2 % of the sample Kr abundance while the Ar in Kr decreases from 2.7 % to 0.2 % of the sample Ar abundance. The Xe in Kr also decreases from 1.7 % to 1.4 % of the sample Xe abundance. Figure 4 shows the corresponding step-release of Ar, Kr and Xe with the respective abundances of other gases obtained for the three protocols (Table 1, rows 2, 3, 4). This figure illustrates the significant improvement in the separation of Ar, Kr and Xe with the protocol with temperature cycling (i.e., the low proportions of other gases when releasing Ar, Kr or Xe).

For the experiments where the Ar, Kr and Xe were desorbed at a single temperature, the effectiveness of the separation compared to observations from the release curves decreased slightly, but is nonetheless high (Table 1, row 3 vs. 5; step-release vs. single release for T1). The separation of krypton from argon and xenon can be even further improved. For example, doing two temperature cycles for Kr-Xe separation allows us to decrease the proportions of Kr in Xe and of Xe in Kr to less than 1 % (Table 1, row 4). Depending on the scientific objective, this second cycle can be important even if it is time-consuming; a full temperature cycle takes about 30 minutes to complete. Changing the release or freeze-down temperatures slightly is also interesting as it can increase the recovered proportion of Ar, Kr or Xe. For example, changing the distillation temperature of Ar from Kr from 70 K to 67 K increases the argon fraction into Kr to 0.5 % but lowers the krypton fraction into Ar to less than 1 % (Table 1, rows 5-6). Setting the distillation temperature of Kr from Xe to 92 K or 95 K instead of 90 K allows the krypton fraction into Xe to be less than 1 % but increases the xenon fraction into Kr (Table 1, rows 5-6). Therefore, ≥ 99 % of Ar, ≥ 98 % of Kr, and ≥ 99 % of Xe can be recovered from a sample with ≤ 1 % contribution from the other noble gases.

We used the single temperature cycling protocol (Protocol 2, Figure 3) with a Ar-Kr distillation temperature of 67 K and a Kr-Xe distillation temperature of 92 K to verify that no mass fractionation effects as a function of signal size were introduced by the distillation process. The results obtained for krypton and xenon for air standards with such a protocol are shown in figures 5 and 6. The analyses are well reproducible and variations in mass discrimination are not observed over of range of Kr and Xe partial pressures. The measurement precision ranged from 0.16 % to 0.54 % for the $^{78}Kr/^{84}Kr$ ratio and from 0.29 % to 1.19 % for the $^{128}Xe/^{130}Xe$ ratio.

Figure 7 shows the evolution of the krypton isotopic ratios depending on the krypton trapping temperature and the argon partial pressure during measurements of air standard aliquots of the same size. For these experiments, the isotopic ratios are plotted normalized to the measured values of the air standard using both traps with a Kr trapping temperature of 68 K. The measured krypton isotopic ratios within uncertainties are consistent for a given krypton trapping temperature between the experiments using one and two traps. For instance, for a krypton trapping temperature of 68 K, the normalized $^{86}Kr/^{84}Kr$ ratio is 1.0013 ± 0.0015 (1σ) using one trap and of 1.0000 ± 0.0016 (1σ) using two traps and a temperature cycling. The argon partial pressure for these two experiments varied by more than a factor of ten in the mass spectrometer (^{40}Ar of 78.8 mV and of 7.50 mV, respectively, Figure 7). Figure 7 shows that about a factor 10 difference in the Ar partial pressure does not influence the measurement of Kr isotopes. This observation is confirmed for experiments with a varying number of distillations but with the same trapping temperature (Figure 8), where the measured Kr isotopic ratios are similar

whereas the Ar partial pressure changes by a factor of 1.8. Therefore, the argon partial pressure at this level does not seem to have an important effect on the measured krypton isotopic ratios, which may be counter-intuitive.

However, the krypton trapping temperature seems to have a non-negligible effect. For example, the normalized $^{86}Kr/^{84}Kr$ ratio is significantly higher for a krypton trapping temperature of 75 K (1.0094 ± 0.0017 with one trap and 1.0041 ± 0.0016 with two traps) than for experiments at 68 K or 70 K (Figure 7). In particular, the isotopic fractionation when using only one trap is significantly larger compared to using the dual trap. Although uncertainties are larger, similar observations can be drawn for the other krypton isotopic ratios (Figure 7).

The increase in $^{86}Kr/^{84}Kr$ is compatible with expectations that as the krypton trapping temperature is increased, more krypton is lost in the argon fraction, with the lost fraction preferentially enriched in the lighter isotopes (lower measured ^{84}Kr abundances, figure 7). As can be seen in figure 2, using a distillation temperature of 75 K for separating Ar from Kr, a small fraction of krypton is lost with argon (Figure 7).

Hence, rather than minimizing the argon fraction in krypton, maximizing the recovered krypton fraction will provide more accurate Kr isotopic data, even if this marginally increases the argon fraction in krypton. Using a distillation temperature below 70 K (between 67 K and 70 K) for separating argon from krypton should provide the best Kr abundance and isotopic data. Therefore, given that variations in Ar partial pressure by over a factor of ten has very limited effect on measured krypton isotopic ratios, we recommend analyzing ≥ 98 % of the Kr aliquot for the most accurate Kr isotopic ratio measurements, especially when using a single stainless steel trap where the krypton isotopic fractionation appears to be larger.

Conclusion

The protocol described in this study using the new cryogenic system, combined with temperature cycling of the trap, allows a clean separation of the heavy noble gases (Ar, Kr, Xe) with less than 1 % of one gas phase in another gas phase. We recommend maximizing the recovered krypton fraction even if this increases the argon fraction in krypton so as not to fractionate krypton isotopes during Ar-Kr separation. The reproducibility of air standards with this protocol is high with precisions on measured isotopic ratios reaching 3-7 ‰ for low abundant isotopes (such as $^{78}Kr/^{84}Kr$ and $^{128}Xe/^{130}Xe$). The protocol should allow for more accurate determinations of the krypton and xenon isotopic compositions of samples with very low krypton and xenon abundances such as oceanic basalts.

Conflicts of interest

The authors declare no conflict of interest.

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Figure 1. Schematic of the dual stainless steel cryogenic trap fabricated by Janis Research Company. The design is considered proprietary by Janis Research, therefore the full schematic is not shown.

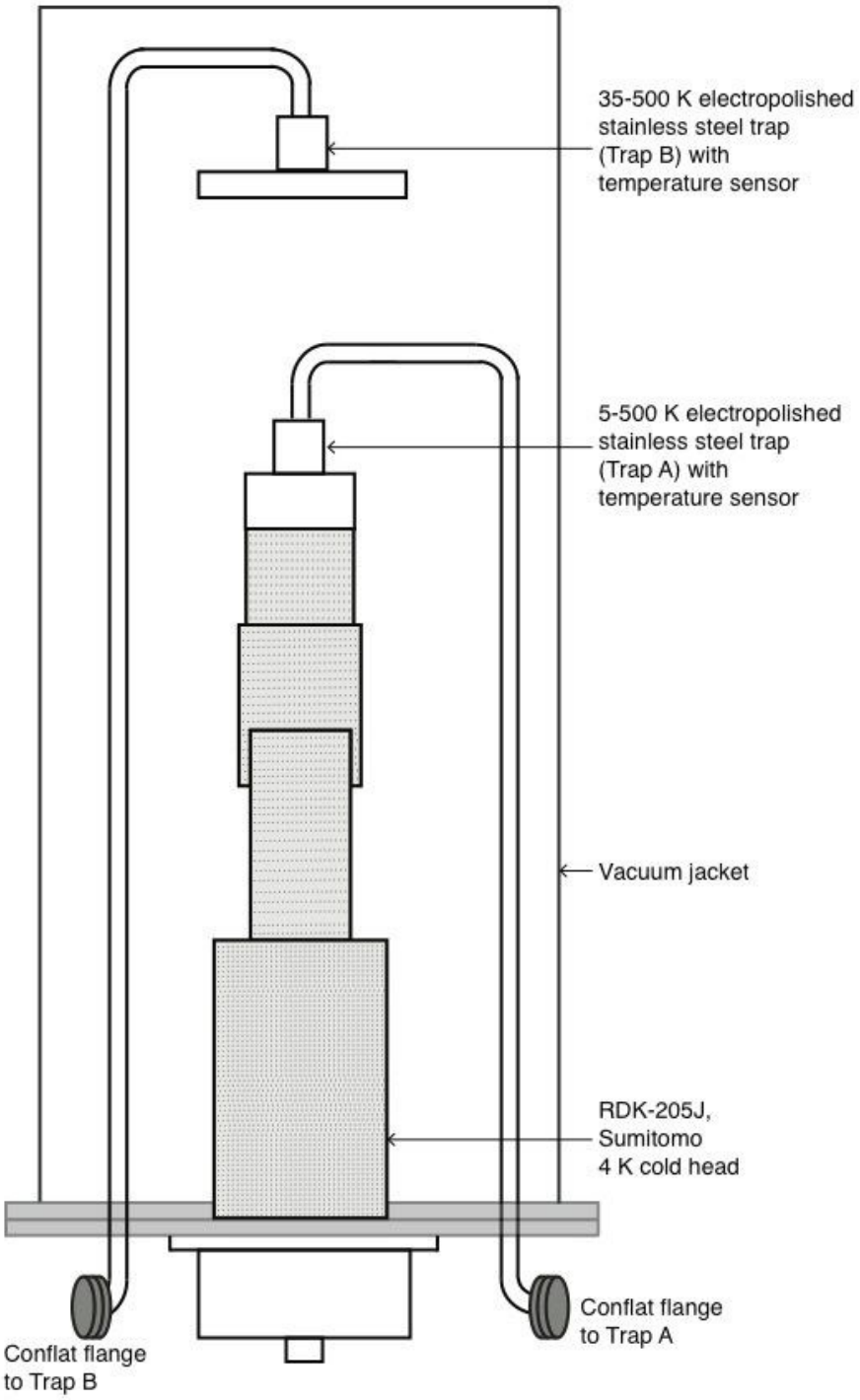

Figure 2. Release curves of Ne, Ar, Kr, Xe from the stainless steel traps. The release curves of Ar, Kr and Xe were determined with different protocols (see the experimental procedure and figure 3). The dashed grey lines highlight the overlap of the release curves at 70 K and 90 K.

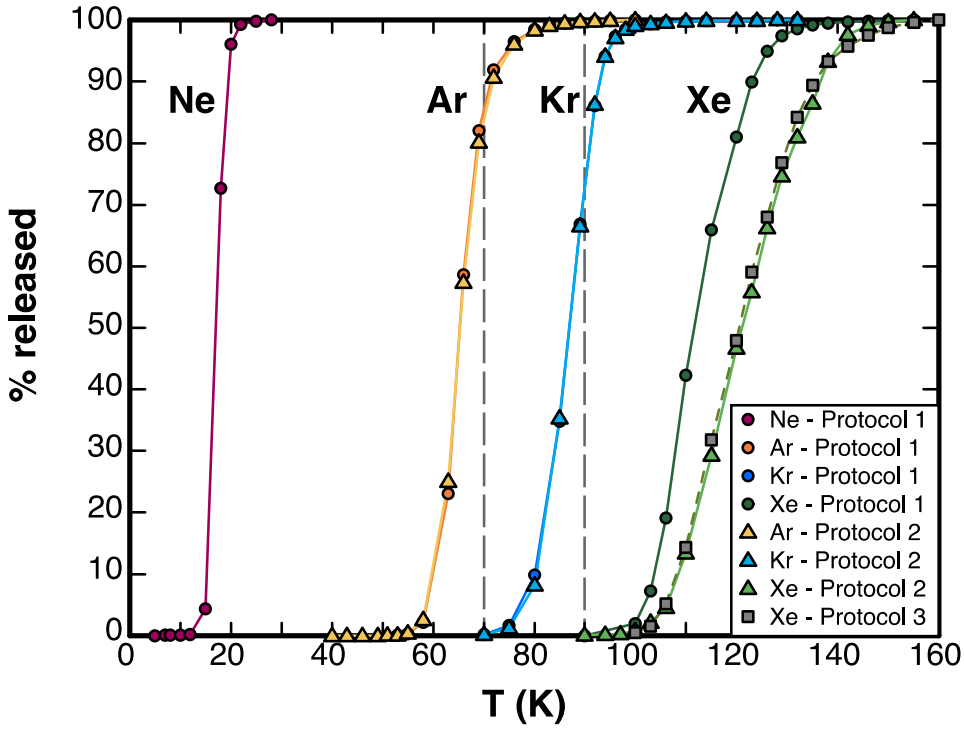

Figure 3. Flow chart describing the sequence of the three protocols. As mentioned in the text, a temperature cycle takes about 30 minutes, the total duration of the protocols (purification and separation) without taking into account the mass spectrometry analysis time is indicated at the top. We note that no time is needed in advance to allow the traps to reach 25 K and 70 K respectively as the system can be cooled down from 200 K to 25 K for Trap A and to 70 K for Trap B in less than 30 minutes (i.e, during the purification).

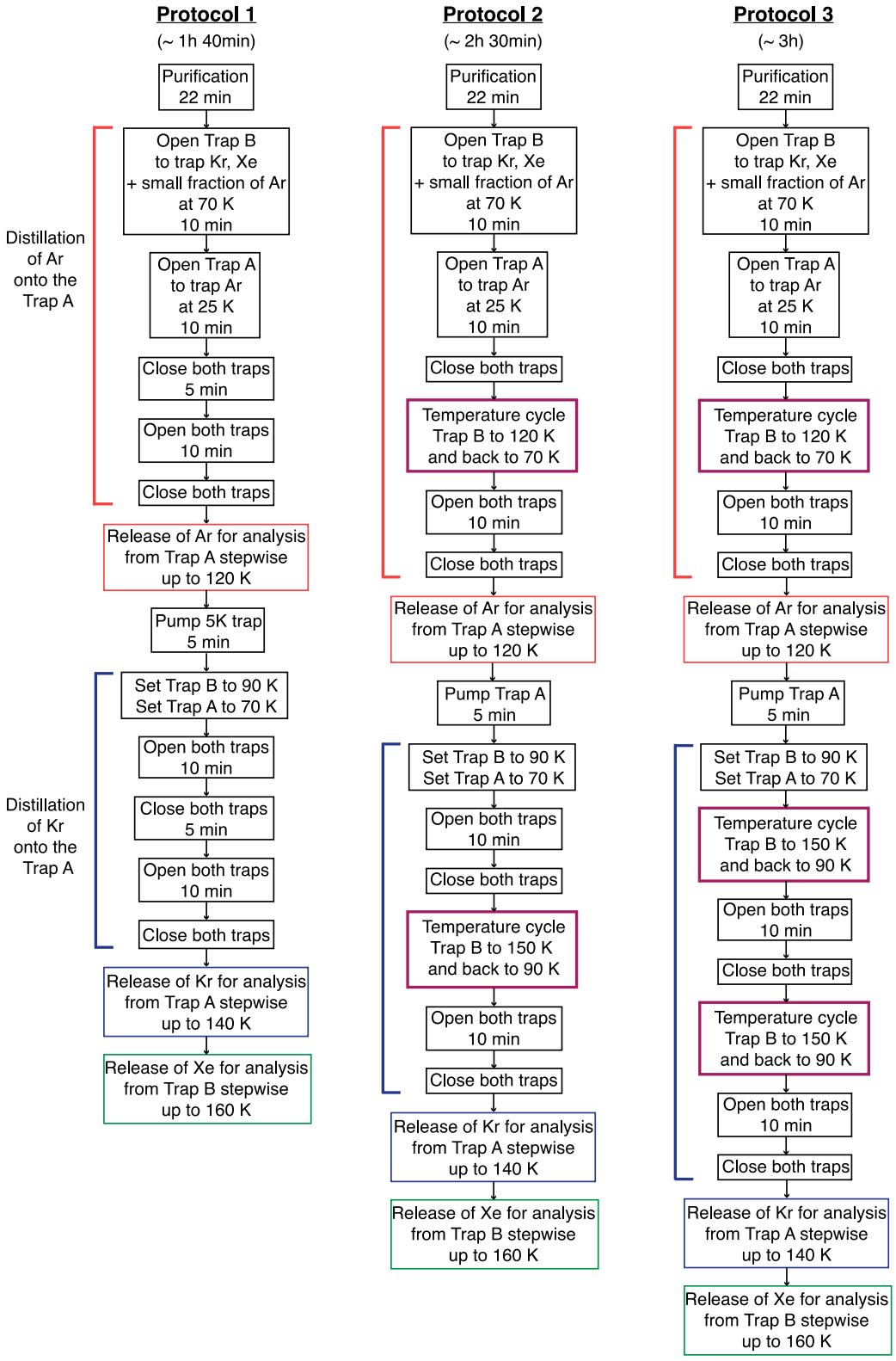

Figure 4. Step-release of the gases with the different protocols (Protocols 1, 2 and 3 in Figure 3). The figures show in row a) the Ar release from Trap A and the proportion of Kr in Ar, in row b) the Kr release from Trap A with the proportions of Ar and Xe in Kr, in row c) the Xe release from Trap B with the proportions of Kr in Xe. The percentage of one gas corresponds to the fraction of its total abundance in the sample (refer to Table 1, rows 2, 3 and 4 for the precise values). The x-axes have different scales on the sub-figures. Note the contrast in the degree of separation of the heavy noble gases compared to figure 2 and between Protocol 1 and Protocol 2.

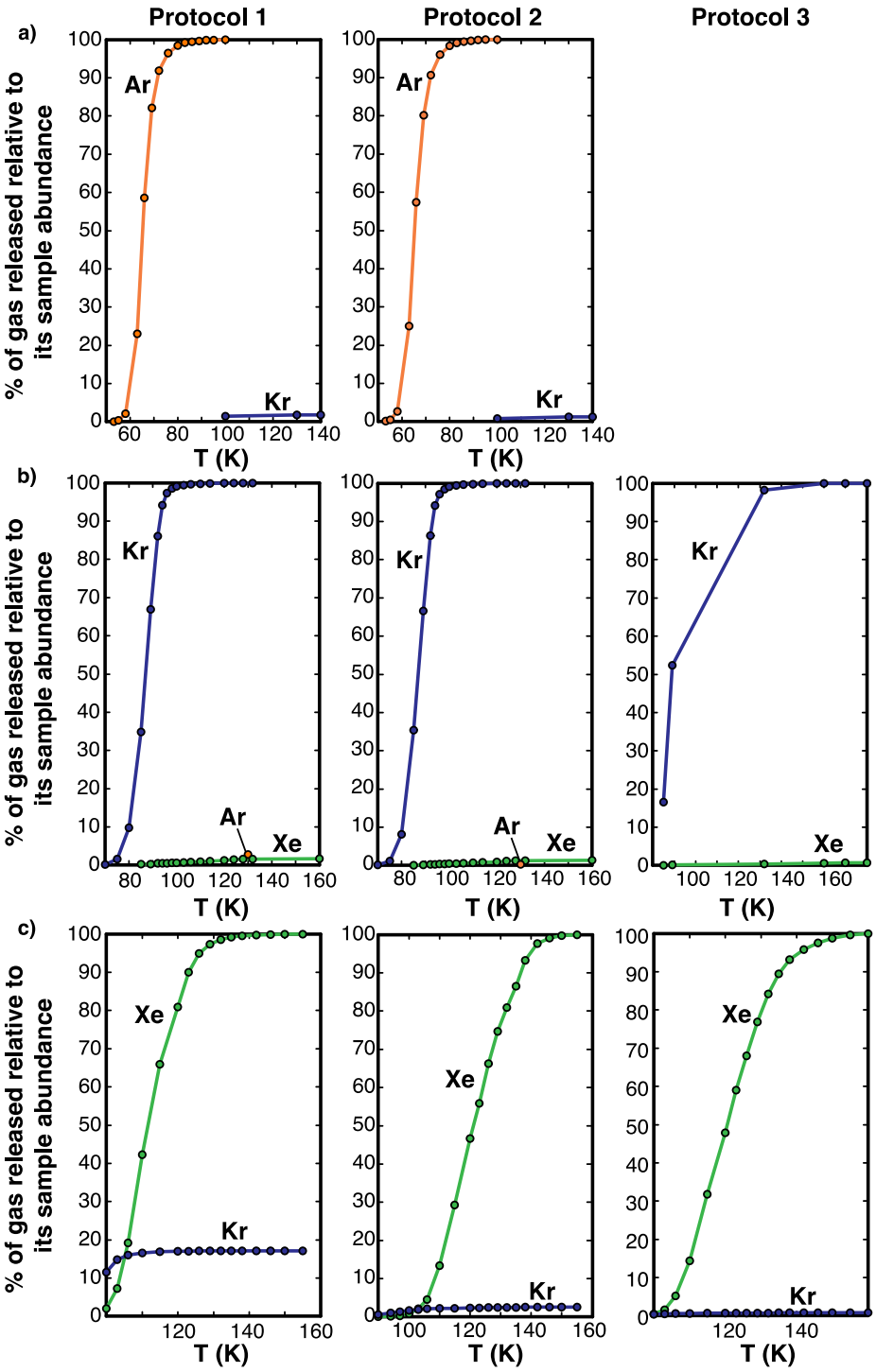

Figure 5. External reproducibility of (a) $^{78}Kr/^{84}Kr$ and (b) $^{128}Xe/^{130}Xe$ ratios obtained for different aliquots of the air standard with the distillation and one temperature cycling protocol. To observe the deviation from linearity, the ratios are normalized to the average of the largest standard. Each dot is the average of *n* analyses and the error shown is the standard deviation.

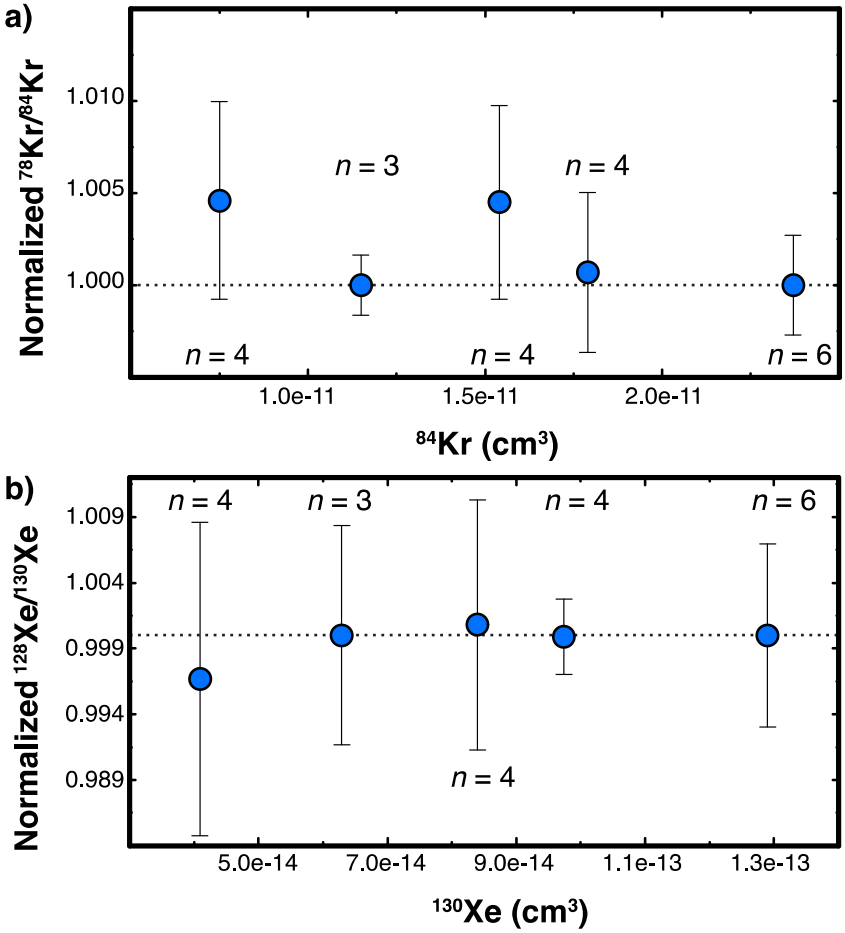

Figure 6. Reproducibility of Kr and Xe isotopic ratios from air standard aliquots of different sizes. a) ^{78}Kr/84Kr, b) ^{80}Kr/^{84}Kr and c) ^{128}Xe/^{130}Xe. This set of standards was measured over 13 days with Protocol 2 and include three standard sizes, ranging from 7.52x10^{-12} cc to 2.37x10^{-11} cc of ^{84}Kr and from 4.1x10^{-14} cc to 1.29x10^{-13} cc of ^{130}Xe.

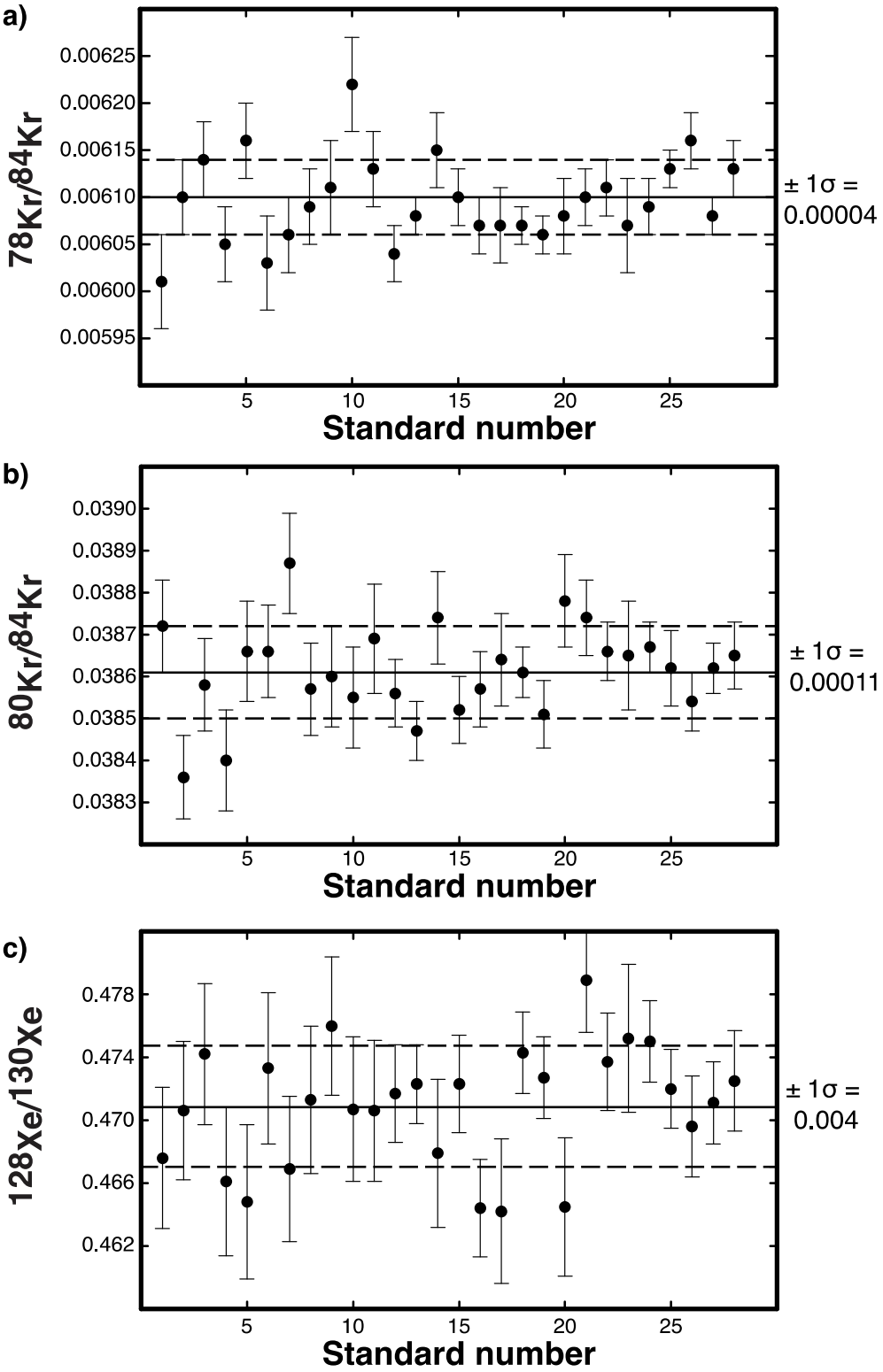

Figure 7. Krypton isotopic ratios depending on the krypton trapping temperature and the argon partial pressure (as determined by the abundance of ^{40}Ar in the mass spectrometer) for air standard aliquots of the same size (aliquots with $1.1x10^{-7}$ cm^3 of ^{40}Ar and $7.5x10^{-12}$ cm^3 of ^{84}Kr). a) $^{80}Kr/^{84}Kr$ and b) $^{86}Kr/^{84}Kr$, each ratio is the average of 4 to 9 analyses, the error bars being the standard deviations on these 4 to 9 analyses. In order to show the fractionation, the ratios are normalized to the one measured at 68 K using the distillation technique. The measured ^{84}Kr signal (in cps) is indicated at the top as well as the amount of ^{40}Ar (in mV) measured after Kr. Experiments using only the Trap A are represented with orange circles and experiments using the two traps with the distillation technique are in purple diamonds. Note that for better comparison of the results, the temperature on the x-axis increase on both sides from a middle point at 67 K.

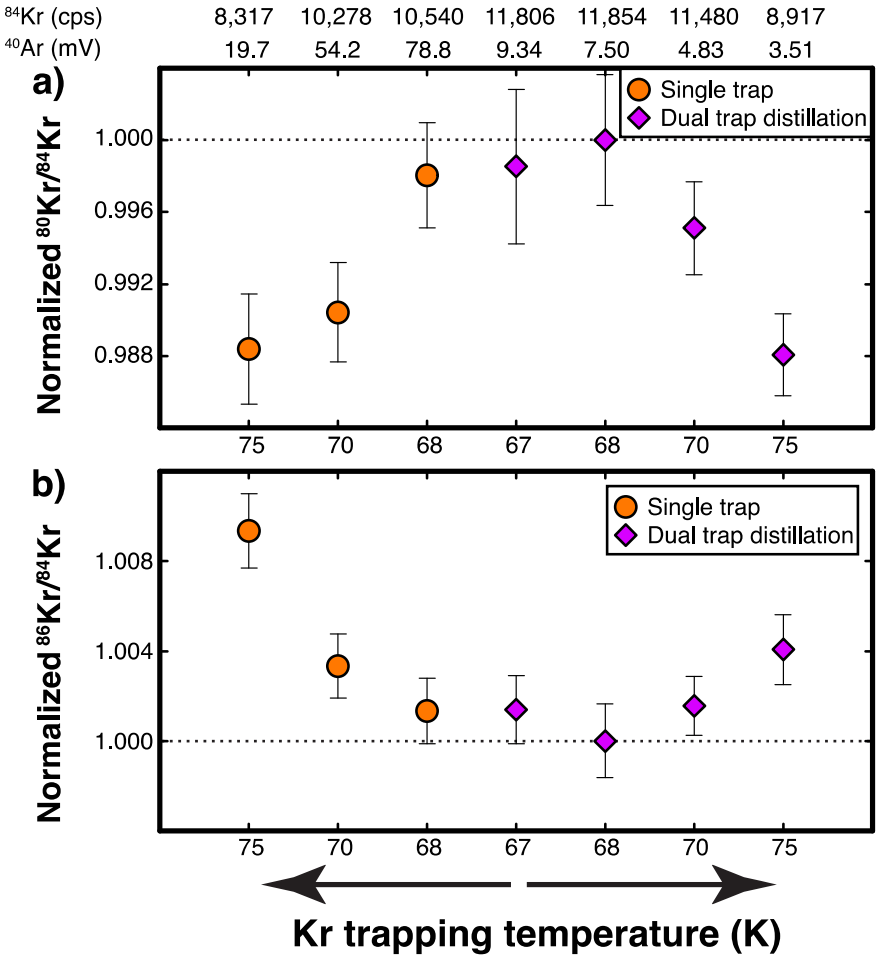

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Figure 8. Krypton isotopic ratios for separation experiments involving two Ar-Kr distillations with one temperature cycle (orange square) and three Ar-Kr distillations with two temperature cycles (blue circle) for air standard aliquots of the same size (aliquots with 1.1×10^{-7} cm^3 of ^{40}Ar and 7.5×10^{-12} cm^3 of ^{84}Kr). a) ^{80}Kr/^{84}Kr and ^{78}Kr/^{84}Kr and b) ^{82}Kr/^{84}Kr vs ^{86}Kr/^{84}Kr. The only difference between the two sets of experiments is the number of Ar-Kr distillation and temperature cycle. The two distillation experiment has been repeated five times, and the three distillation experiment six times. The average for each set of experiment is shown with the bigger open symbol and bold uncertainties. The partial pressure of Ar in the mass spectrometer was 1.8 times lower for the three distillation experiments than for the two distillation experiments. The Kr isotopic ratios are similar for all the analyses.

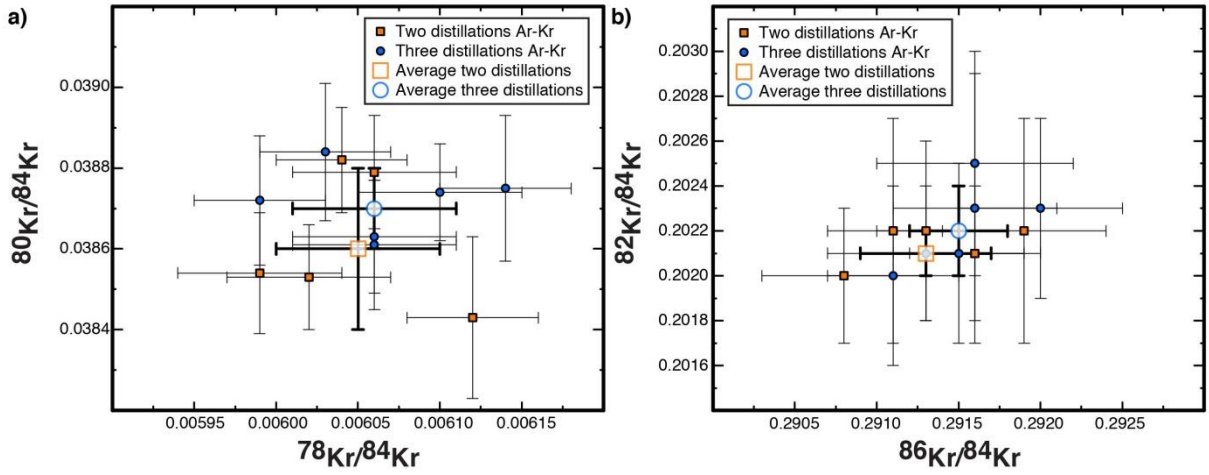

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Table 1. Level of separation of heavy noble gases (Ar, Kr, Xe) with the new cryogenic system. The percentages refer to the percent abundance of one gas relative to its total abundance in the sample. Different protocols have been applied with a varying number of temperature cycling steps and slightly different distillation temperatures (see the experimental procedure) to compare the efficiency of heavy noble gas separation. The temperature T_1 refers to the distillation temperature of Ar from Kr and T_2 to the distillation of Kr from Xe. The results show that one temperature cycling drastically improves Ar, Kr, Xe separation. *n.a.* not analyzed. Uncertainties, estimated from the uncertainties on the measured abundances, are less than 0.2 %.

Protocols	**Protocol number in Figure 3**	**Kr in Ar**	**Ar in Kr**	**Xe in Kr**	**Kr in Xe**
Single trap, no cycling (estimated based on the release curves, T_1 = 70 K, T_2 = 90 K)		< 2 %	14.6 %	< 2 %	26.7 %
Dual trap, no cycling, step-release (T_1 = 70 K, T_2 = 90 K)	Protocol 1	1.8 %	2.7 %	1.7 %	17.2 %
Dual trap, 1 cycling, step-release (T_1 =70 K, T_2 = 90 K)	Protocol 2	1.2 %	0.2 %	1.4 %	2.6 %
Dual trap, 2 cycling (Kr-Xe), step-release (T_1 = 70 K, T_2 = 90 K)	Protocol 3	1.5 %	*n.a.*	0.7 %	0.8 %
Dual trap, 1 cycling, single release (T_1 =70 K, T_2 = 95 K)	Protocol 2	3.7 %	0.2%	3.6 %	0.4 %
Dual trap, 1 cycling, single release (T_1 = 67 K, T_2 = 92 K)	Protocol 2	0.7 %	0.5 %	1.2 %	0.9 %