1 Setting a Limit on Anthropogenic Sources of
2 Atmospheric ^{81}Kr through Atom Trap Trace Analysis

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12 **Abstract**

13 We place a 2.5% limit on the anthropogenic contribution to the modern
14 abundance of $^{81}\text{Kr}/\text{Kr}$ in the atmosphere at the 90% confidence level. Due to
15 its simple production and transport in the terrestrial environment, ^{81}Kr (half-
16 life = 230,000 yr) is an ideal tracer for old water and ice with mean residence
17 times in the range of 10^5 - 10^6 years. In recent years, ^{81}Kr -dating has been
18 made available to the earth science community thanks to the development of
19 Atom Trap Trace Analysis (ATTA), a laser-based atom counting technique.
20 Further upgrades and improvements to the ATTA technique now allow us
21 to demonstrate $^{81}\text{Kr}/\text{Kr}$ measurements with relative uncertainties of 1% and
22 place this new limit on anthropogenic ^{81}Kr . As a result of this limit, we have
23 removed a potential systematic constraint for ^{81}Kr -dating.

24 **keywords:** ^{81}Kr ; groundwater dating; anthropogenic effects; radioiso-
25 tope tracers; noble gas tracers; atom trap trace analysis

1. Introduction

Since the discovery of ^{81}Kr in the atmosphere (*Loosli and Oeschger, 1969*), the geoscience community has sought to apply this noble gas isotope as an environmental tracer. It is predominantly produced by cosmic rays impinging on stable krypton isotopes in the atmosphere and decays by electron capture to ^{81}Br with a half-life of $(2.29 \pm 0.11) \times 10^5$ years (*Baglin, 1993*), resulting in a cosmogenic atmospheric $^{81}\text{Kr}/\text{Kr}$ ratio of 6×10^{-13} (*Collon et al., 2004*). The long half-life, along with its inert chemical nature, makes it an ideal tracer for water and ice in the range of 10^5 - 10^6 years, a range beyond the reach of ^{14}C dating (*Lu et al., 2014*).

The Atom Trap Trace Analysis (ATTA) technique was developed to perform routine ^{81}Kr analysis. ATTA is a laser-based atom counting method, free of interferences from other isotopes, isobars, atomic, or molecular species. Since the completion of the third-generation ATTA-3 system at Argonne National Laboratory (ANL) (*Jiang et al., 2012*) $^{81}\text{Kr}/\text{Kr}$ ratios have been routinely measured in environmental samples with better than 10% precision for a variety of applications using both water (*Aggarwal et al., 2015*) and ice samples (*Buizert et al., 2014*), typically requiring samples sizes of 100 kg of water or 40 kg of ice. As we demonstrate in this paper, recent developments in ATTA have improved the precision of the technique to the 1% level. These advances offer a unique opportunity to probe the effects of human activity on the ^{81}Kr abundance in our atmosphere. Not only does such a measurement better our understanding of anthropogenic impact on isotopes in the atmosphere, but it also addresses the potential systematic effects that such activity could have on dating old groundwater, especially

51 as ATTA measurements are pushed to even higher precision.

52 Since the advent of human nuclear activity, we have potentially been in-
53 jecting anthropogenic ^{81}Kr into the atmosphere. Testing of nuclear devices,
54 nuclear fuel reprocessing, and usage of medical isotopes are all potential an-
55 thropogenic sources of ^{81}Kr . Any anthropogenic contribution of ^{81}Kr from
56 these sources above the precision level of current dating measurements would
57 disturb the atmospheric baseline over the past 100 years thereby adding an
58 unacknowledged systematic error on all ^{81}Kr -dating measurements. When
59 viability of ^{81}Kr as an environmental tracer was initially demonstrated in
60 1999 using accelerator mass spectrometry (AMS), no difference was mea-
61 sured between a sample of krypton from air before human nuclear activity
62 began and another sample from after the end of atmospheric nuclear weapons
63 testing (*Collon et al.*, 1999). This measurement carried a one-sigma, relative
64 uncertainty of $\sim 30\%$. Subsequently, with the development of the second-
65 generation ATTA-2 system, the same experiment was conducted with one-
66 sigma, relative uncertainties around the 8% level (*Du et al.*, 2003). Previous
67 theoretical considerations of anthropogenic ^{81}Kr estimated the effect to be
68 at or below the 0.01% level (*Collon et al.*, 1999).

69 In this paper, we perform 1% one-sigma relative uncertainty measure-
70 ments using ATTA to place a 2.5% experimental limit on anthropogenic
71 ^{81}Kr in the atmosphere at the 90% confidence level. Given the high precision
72 of this limit, we first present a more detailed theoretical model for anthro-
73 pogenic ^{81}Kr production in the atmosphere, which sets a new upper limit
74 of 0.15%. We then briefly describe the technical developments that allow
75 ATTA to measure $^{81}\text{Kr}/\text{Kr}$ ratios at the 1% level. Finally, we perform mea-

76 surements of samples from the modern era and before the nuclear age at this
77 uncertainty level and use them to place a limit on anthropogenic ^{81}Kr .

78 2. Anthropogenic ^{81}Kr Sources

79 Along with the first experimental limit placed on anthropogenic ^{81}Kr pro-
80 duction (*Collon et al.*, 1999), several theoretical calculations were presented
81 to estimate the expected amount of anthropogenic ^{81}Kr in the atmosphere.
82 Those calculations suggested less than 0.01% contribution of anthropogenic
83 ^{81}Kr to the atmosphere. Here we provide an update to those calculations
84 including an in-depth model that removes several assumptions made in the
85 previous calculations. To determine a scale for how many ^{81}Kr atoms would
86 cause a 1% contribution, we use the fact that krypton is 1.1 parts per million
87 by volume (*Aoki et al.*, 2005) in the atmosphere (using an atmospheric mass
88 of 5.1×10^{18} kg (*NASA*, 2016)) and that the isotopic abundance of $^{81}\text{Kr}/\text{Kr}$
89 is 6×10^{-13} (*Collon et al.*, 2004) to determine that there are about 7×10^{25}
90 ^{81}Kr atoms in the atmosphere. Thus we are searching for effects that cu-
91 mulatively produce 7×10^{23} or more ^{81}Kr atoms, i.e. 1% of the cosmogenic
92 inventory.

93 There are three potential anthropogenic sources that can contribute ^{81}Kr
94 to the atmosphere as described by *Collon et al.* (1999): decay of ^{81}Rb pro-
95 duced for medical usage, release of ^{81}Kr during nuclear fuel reprocessing, and
96 direct and neutron-induced production of ^{81}Kr during the period of above-
97 ground nuclear weapons testing.

98 ^{81}Rb , produced for medical applications, decays to the isomer $^{81}\text{Kr}^*$, and
99 the gamma rays emitted during the decay of this excited state to ^{81}Kr are

100 used to image respiratory systems. The resulting ^{81}Kr was determined to
101 be the smallest of the anthropogenic contributions in *Collon et al.* (1999)
102 extrapolating from an inventory based on estimated ^{81}Rb production in the
103 United Kingdom from 1975 - 1996. The expected contribution was on the
104 order of 10^{19} ^{81}Kr atoms. Since there has been no significant expansion of
105 this technique after this inventory was taken, we continue to consider this
106 contribution as negligible for our purposes.

107 Nuclear fuel reprocessing, by which spent nuclear fuel rods are recycled,
108 requires the chemical processing of these fuels rods, causing a release of
109 trapped gaseous decay remnants. For instance, ^{235}U or ^{239}Pu fissions pro-
110 duce ^{85}Kr and other short-lived isotopes which decay to ^{85}Kr . Since ^{85}Kr
111 has a half-life of 10.76 years, the majority of it has not decayed by the time
112 the rods are processed. At that point the trapped ^{85}Kr is released into the
113 atmosphere. Reprocessing has had an enormous effect on the isotopic abun-
114 dance of $^{85}\text{Kr}/\text{Kr}$ in the atmosphere, increasing the ratio over the natural
115 equilibrium in the atmosphere by over four orders of magnitude in the last
116 sixty years (*Ahlsvede et al.*, 2013).

117 ^{81}Kr production due to reprocessing is strongly suppressed versus ^{85}Kr .
118 ^{81}Kr has a substantially lower neutron-induced-fission yield and is shielded
119 from the decay chain of neutron-rich mass 81 isobars by stable ^{81}Br . More-
120 over, the natural equilibrium of $^{81}\text{Kr}/\text{Kr}$ in the atmosphere is also greater
121 than that of $^{85}\text{Kr}/\text{Kr}$ due to the the longer half-life. It nonetheless remains a
122 potential anthropogenic contribution. In *Collon et al.* (1999), ^{85}Kr activity
123 determined in 1985 by *von Hippel et al.* (1985) is doubled to produce an esti-
124 mate of ^{85}Kr atoms produced by nuclear fuel reprocessing up to the present

125 day. Then the ratio of the neutron-induced fission yields between ^{81}Kr and
 126 ^{85}Kr was used to determine the resulting number of ^{81}Kr atoms. We follow
 127 the approach of *Collon et al.* (1999), but consult a more recent and extensive
 128 inventory of ^{85}Kr production in *Ahlsvede et al.* (2013) to determine a cumu-
 129 lative ^{85}Kr emission up until 2002¹ of 11,800 PBq, equivalent to 5.8×10^{27}
 130 ^{85}Kr atoms. Applying the ratio of neutron-induced fission yields from *Eng-*
 131 *land and Rider* (1994) of 6.9×10^{-3} for ^{85}Kr and 2.4×10^{-9} for ^{81}Kr gives
 132 2.0×10^{21} ^{81}Kr atoms. This is equivalent to a $\sim 0.003\%$ anthropogenic signal,
 133 which is much smaller than we expect to detect.

134 The largest and most complex source of anthropogenic ^{81}Kr is the test-
 135 ing of nuclear devices in the atmosphere. When a nuclear device detonates,
 136 products of the fission or fusion processes are released along with cascades
 137 of neutrons. Some of the daughter isotopes from fissions can be ^{81}Kr atoms,
 138 and thus contribute to the anthropogenic signal. However, much more impor-
 139 tantly, the released neutrons can be captured (or scattered to lower energies
 140 and subsequently captured) by ^{80}Kr and ^{82}Kr atoms in the atmosphere re-
 141 sulting in reactions that also produce ^{81}Kr .

142 Calculations in *Collon et al.* (1999) determined ^{81}Kr production from the
 143 $^{80}\text{Kr}(n,\gamma)^{81}\text{Kr}$ reaction by examining the nuclear testing contribution of ^{14}C
 144 from $^{14}\text{N}(n,p)^{14}\text{C}$, which is caused by the same cascade of neutrons, and using
 145 the ratio of the thermal cross-sections between the two reactions. For ^{81}Kr
 146 production from the $^{82}\text{Kr}(n,2n)^{81}\text{Kr}$ reaction, a similar approach was applied,

¹As we will discuss in a later section, the krypton from the modern era used to compare with pre-nuclear krypton was sampled from the atmosphere no later than 2002, and thus this calculation represents the largest possible contribution that we can measure.

147 but by using the anthropogenic contribution of ^{39}Ar from $^{40}\text{Ar}(\text{n},2\text{n})^{39}\text{Ar}$
 148 reactions and assuming the cross-sections for both reactions to be equal.

149 Our theoretical model takes a more direct approach of determining $^{80}\text{Kr}(\text{n},\gamma)^{81}\text{Kr}$
 150 and $^{82}\text{Kr}(\text{n},2\text{n})^{81}\text{Kr}$ reaction rates per neutron released from the different
 151 types of nuclear devices. This approach accounts for the varying cross-
 152 sections over the whole energy range of released neutrons and does not rely
 153 upon calculations made on other elements (i.e. ^{14}N and ^{40}Ar). We calculate
 154 these reaction rates by simulating neutrons from a nuclear weapon source at
 155 the center of a 1km radius sphere in air using the Monte Carlo N-Particle
 156 transport code (MCNP) (*Goorley et al.*, 2013).

157 We define the air in our simulation using the break down by volume given
 158 in *Hubbell and Seltzer* (1996). We also allow for the addition of 0-5% water by
 159 volume, which replaces the other constituents proportionally and represents
 160 the varying moisture in the air given by humidity (*Wallace and Hobbs*, 2006).

161 The spectrum of fission-produced neutrons can be approximated by a
 162 Watt spectrum (*Shultis and Faw*, 1996), defined as

$$f(E) = Ce^{\frac{-E}{a}} \sinh(bE)^{\frac{1}{2}} \quad (1)$$

163 where E is the outgoing neutron energy in MeV; a and b are parameters
 164 that depend on the incident neutrons energy and the isotope undergoing
 165 fission, in units of MeV and MeV^{-1} , respectively; and C is a normalization
 166 constant. For these calculations, we used the MCNP default values of a and
 167 b which represent an average over incident neutron energies and fissioning
 168 nuclei, since the values for specific neutron energies and target nuclei do
 169 not vary the results (nuclide production rates) significantly. MCNP uses
 170 continuous-energy neutron transport to determine the neutron fluence rate

171 as a function of energy down to thermal energies, and computes nuclide
 172 production rates from the energy-dependent fluence rate and the energy-
 173 dependent cross-sections.

174 For fusion sources we also use the MCNP, but must consider a different
 175 neutron spectrum. In fusion weapons the bulk of the thermonuclear energy
 176 is produced by four reactions (*Glasstone and Lovberg*, 1960)

177 where reactions (2) and (3) are chiefly used to breed helium-3 and tritium for
 178 reactions (4) and (5).² In order to reach high enough temperatures for these
 179 reactions to begin, a smaller fission bomb boosted by the presence of deu-
 180 terium and tritium gas is first detonated within the fusion device (*Union of*
 181 *Concern Scientists*, 2009). We will assume that the energies and products of
 182 this smaller fission device are consumed by the fusion fuel and ignore them for
 183 the purposes of our calculation. The fusion fuel is typically lithium deuteride
 184 (*Union of Concern Scientists*, 2009), which provides not only deuterium, but
 185 lithium-6 and lithium-7 that react with neutrons and breed tritium as well
 186 (*Kaye & Laby Online*, 1995). Since we are only interested in situations where
 187 net neutrons are produced we consider only equations (2) and (4), which pro-
 188 duce what we call DD (deuterium-deuterium) and DT (deuterium-tritium)

²There are obviously a number of other reactions, however, given their relatively lower cross-sections (*Soppera et al.*, 2014) we can ignore them for our purposes.

Table 1: Fission yields used for anthropogenic ^{81}Kr production calculations from *England and Rider* (1994)

Fissile Isotope	Direct ^{81}Kr Yields		
	Thermal	Fast (1 MeV)	High (14 MeV)
^{235}U	9.4×10^{-12}	5.5×10^{-12}	3.7×10^{-9}
^{238}U	n/a	1.1×10^{-13}	1.4×10^{-10}
^{239}Pu	2.1×10^{-9}	4.4×10^{-10}	1.8×10^{-8}

neutrons respectively. We consider them to be mono-energetic neutrons³ which have the energies shown in equations (2) and (4).

Using these three source spectra (Watt, DD, DT) and our dry to humid atmosphere, we calculate $^{80}\text{Kr}(\text{n},\gamma)^{81}\text{Kr}$ and $^{82}\text{Kr}(\text{n},2\text{n})^{81}\text{Kr}$ reaction rates for various situations, and then simply multiply by the total number of source neutrons in each situation. From 1945 - 1993, fission tests produced the equivalent energy of 217 Megatons of TNT and fusion tests produced 328 Megatons over 520 atmospheric tests (*United Nations*, 1993). There are additional underground tests equivalent to 90 Megatons of TNT that we neglect due to the comparatively small interaction of neutrons with the atmosphere from such tests. For fission tests, we assume 2.5 neutrons produced per fission and 200 MeV expended per fission to determine the number of neutrons. For fusion, we assume 17.6 MeV per DT neutron and 7.3 MeV per DD neutron⁴

³They have an energy width, but it is calculable and of order ~ 100 keV (*Kaye & Laby Online*, 1995), which is negligible for our purposes given their high mean energies.

⁴The 7.3 MeV energy used is the combined total energy of equations (2) and (3) since they have comparable reaction rates.

Table 2: Calculated ^{81}Kr atom production by source due to nuclear device detonation (1945-1993)

Source	$^{80}\text{Kr}(n,\gamma)^{81}\text{Kr}$	$^{82}\text{Kr}(n,2n)^{81}\text{Kr}$	direct fission	% of cosmogenic ^{81}Kr
Fission	3.5×10^{22}	8.5×10^{17}	2.9×10^{19}	0.050%
Fusion				
DT	4.6×10^{22}	1.8×10^{22}	n/a	0.066%
DD	2.4×10^{21}	n/a	n/a	0.003%
^{238}U	2.6×10^{22}	6.4×10^{17}	3.2×10^{18}	0.037%
Total	1.1×10^{23}	1.8×10^{22}	3.2×10^{19}	0.15%

and treat DT as 100 times more likely than DD, due to the larger cross-section (*Glasstone and Lovberg*, 1960) and the assumption of sufficient tritium availability from lithium reactions. Note that we are considering that the entire explosive yield is generated purely from these fusion reactions, which is an overestimate, but gives a higher upper limit, which we prefer. According to *Union of Concern Scientists* (2009), 50% (or more) of the energy released in a thermonuclear fusion weapon is generally from the high-energy-neutron-induced fission of natural uranium (that we will consider to be purely ^{238}U) which is packed into a shell around the whole fusion weapon, so we include that in our calculations as well. Finally, for each fission (whether from fission weapons, or this uranium shell in fusion weapons), we applied direct fission yields of ^{81}Kr from *England and Rider* (1994) shown in Table 1. The error on the reaction rates is $\pm 5\%$.

We provide the final results of our calculations in Table 2, aiming to achieve the highest-bounding estimate. Thus the results shown are obtained

217 using the dry air variants (since they produce the higher yields by a factor
 218 of 1.2-1.4 against the most humid cases), and applying the ^{239}Pu yields for
 219 neutron-induced fission in Table 1 (which are two orders of magnitude higher
 220 than ^{235}U yields). In total, nuclear weapons testing provides a ^{81}Kr anthro-
 221 pogenic signal of $\leq 0.15\%$, two orders of magnitude higher than the estimate
 222 in *Collon et al.* (1999) due to our accounting for the cross-sections of the
 223 reactions over all energies and applying spectra for different devices.

224 As a check of the validity of our model, particularly in light of our con-
 225 siderable increase over the previous estimate, we also calculated reaction
 226 rates for $^{14}\text{N}(\text{n,p})^{14}\text{C}$ and $^{40}\text{Ar}(\text{n},2\text{n})^{39}\text{Ar}$ in order to compare our model's
 227 calculations for anthropogenic ^{14}C and ^{39}Ar production against those values
 228 reported in *Collon et al.* (1999). We find that, even in this highest bound-
 229 ing limit scenarios, the model agrees with the anthropogenic ^{14}C and ^{39}Ar
 230 abundances cited in *Collon et al.* (1999) within a factor of 2.

231 3. ATTA Technical Developments

232 ATTA measures relative $^{81}\text{Kr}/\text{Kr}$ ratios in a krypton gas sample by laser
 233 cooling and trapping ^{81}Kr and ^{83}Kr (a stable isotope of krypton) atoms
 234 from the sample and comparing the rates at which they are loaded into
 235 the atom trap. The krypton atoms are first excited by a plasma discharge
 236 to a metastable state from which a strong 811 nm cycling transition is avail-
 237 able for cooling and trapping of the atoms. There are four stages of cooling
 238 and trapping that determine the loading rate: (1) transverse cooling, (2)
 239 two-dimensional focusing using a 2D magneto-optical trap (MOT), (3) lon-
 240 gitudinal slowing via a Zeeman slower, and (4) three-dimensional trapping

241 using a 3D MOT. In the 3D MOT the atoms are confined at the minimum of
242 a quadrupole magnetic field gradient and detected via laser-induced fluores-
243 cence using a sensitive CCD camera. To calibrate the efficiency we measure
244 a standard krypton reference gas, which has a $^{81}\text{Kr}/\text{Kr}$ ratio of modern air.
245 The most recent iteration of the ATTA system at ANL, ATTA-3, is described
246 in full detail in *Jiang et al.* (2012).

247 In order to reach the next level of sensitivity and place a more stringent
248 limit on anthropogenic ^{81}Kr , several upgrades have been implemented on
249 the ATTA-3 system. First, we increased the excited fraction of our krypton
250 atoms by installing an additional turbomolecular pump to compress gas into
251 the source volume. The resulting increase in pressure within the plasma
252 discharge produces higher excitation efficiency and increased throughput in
253 our atom beam, without requiring an increase in sample size. Second, for the
254 longitudinal slowing stage, we have implemented power stabilization feedback
255 on our slowing laser after determining that drifts of $\sim 10\%$ in laser power
256 can result in larger than 3% shifts in isotope loading ratios. Third, at the
257 detection stage, we implemented a new, ion-based detection method for the
258 stable krypton isotope ^{83}Kr detailed in *Jiang et al.* (2014). Finally, due to
259 the increased speed of our measurements from the above improvements, we
260 now measure our reference gas daily after each sample measurement, instead
261 of only once every two weeks. This improvement removes long-term drifts in
262 the measured isotope ratios, as large as 5% , that can occur within the two
263 weeks.

264 As a result of the source upgrade we have increased the count rate such
265 that the typical single measurement $^{81}\text{Kr}/\text{Kr}$ error, which is dominated by

⁸¹Kr statistics, has been reduced from $\sim 9\%$ to $\sim 3\%$. All of the upgrades which have improved stabilization and precision have reduced the overall systematic errors from $\sim 5\%$ to $\sim 1\%$.

4. Measurement Systematics & Procedures

To place an improved limit on anthropogenic Kr-81 in the atmosphere, we use ATTA to measure the $^{81}\text{Kr}/\text{Kr}$ isotopic ratios in two different samples: one from air before the advent of human nuclear activity (“PreAnthropogenic”), and one representing the isotopic abundances in modern air (“Modern”). Any difference in the ratio between these two samples would be interpreted as the anthropogenic contribution to our atmosphere. The PreAnthropogenic sample was prepared at the University of Bern from air in 1944 (*Kuzminov and Pomansky*, 1980). LLC performed at the University of Bern shows the ^{85}Kr activity of this sample to be <1.0 decay per minute per cubic centimeter krypton at STP (dpm/cc). The Modern sample is a commercial bottle of krypton gas purchased in June 2002 and filled at the AGA/Linde facility in Maumee, OH. Although these commercial gases are extracted from air, the exact time of separation is unknown. To ensure that this krypton gas is representative of modern air, we performed LLC at the University of Bern in March 2016 to determine the ^{85}Kr activity. We measured an activity of 32.1 ± 1.2 dpm/cc. Using the values from *Ahlsvede et al.* (2013) and extrapolating the activity of our krypton gas backward in time, we find it to be consistent with krypton taken from the air in 2002.

As noted in Section 3, the relative efficiency of our system can slowly drift over timescales on the order of one week. Thus, the $^{81}\text{Kr}/\text{Kr}$ isotopic

ratios of PreAnthropogenic or Modern samples are actually determined by the $^{81}\text{Kr}/^{83}\text{Kr}$ loading rates in the sample compared with those same loading rates in our daily reference gas measurements. This superratio (SR) is defined as

$$^{81}\text{Kr}_{\text{SR}} = \frac{^{81}\text{Kr}_{\text{Sample}}/^{83}\text{Kr}_{\text{Sample}}}{^{81}\text{Kr}_{\text{Reference}}/^{83}\text{Kr}_{\text{Reference}}} \quad (6)$$

and gives us the $^{81}\text{Kr}/\text{Kr}$ isotopic ratio with the systematic effects due to these drifts removed. Our standard reference gas is the same as our Modern sample, but it is crucial to note that there are differences in the way that we measure the reference from how we typically measure a sample. This is due to a cross-sample contamination problem, which we describe below (and which is discussed in *Jiang et al. (2012)*).

The radio-frequency discharge which excites the krypton also ionizes a fraction of the atoms, and gives them high enough energy to implant themselves inside the surfaces of the source chamber. Because ATTA is used to measure very small amounts of krypton gas ($\sim \mu\text{L}$ of krypton at STP), the gas must be recirculated in our vacuum system for several hours. If there are implanted atoms from previous samples present during the measurement of a new sample, they will be knocked out by the new ions and accumulate as a contaminant within the sample gas volume as the gas is continuously recycled. To avoid this problem during our reference measurements, we measure the standard reference gas without recirculation in order to prevent the accumulation of any significant contamination. We can do this because we have a plethora of reference gas in comparison to the amount of gas we typically have in a sample. However, since we have not previously studied the systematics below the 5% level between the “closed mode” where the gas is

314 recirculated, and the “open mode” where it is not, we cannot simply com-
315 pare the PreAnthropogenic $^{81}\text{Kr}/\text{Kr}$ isotopic ratio given by equation (6) to
316 unity just because we use the Modern sample as our reference gas. Instead,
317 we must follow the normal procedures for measuring both samples in closed
318 mode in order to avoid any potential systematics from these two different
319 modes of measurement. Fortunately, by doing so, we will also be probing
320 for these very systematics we wish to avoid since the Modern gas will be
321 measured as both sample and reference to 1% precision.

322 The measurements of the samples are conducted in the following manner.
323 8 μL of krypton at STP of sample gas is injected into the vacuum system
324 and recirculated in the closed mode configuration. The measurement then
325 takes 2.5-4.5 hours. During the measurement, laser frequencies automatically
326 switch between the different krypton isotopes and thus measure their various
327 loading rates in five-minute cycles. 3.5 minutes is spent on ^{81}Kr , 1 minute
328 on ^{85}Kr , and 0.5 minutes on ^{83}Kr before the sequence repeats. We measure
329 ^{85}Kr to determine the cross-sample contamination since the ^{85}Kr isotopic
330 abundances of our samples are known through LLC.

331 Once the sample measurement is complete, the system is opened to turbo-
332 molecular pumps which remove the sample from the system. Then, with the
333 system left open to these pumps, i.e. the open mode configuration, krypton
334 gas from the reference bottle is flowed through the system at a constant pres-
335 sure. The loading rates for the krypton isotopes are then measured for this
336 reference gas (which is the same gas as the Modern sample). This reference
337 measurement requires about 2-3 hours. Once the measurement is complete,
338 argon gas is then flowed through the system in the open mode configuration

Figure 1: Superratios for ^{81}Kr in both “Modern” (blue squares) and “PreAnthropogenic” (red crosses). The consistency of the results over the 75 day period demonstrates the robustness of our long-term systematic control.

339 with the plasma discharge active overnight. The argon discharge removes
 340 the krypton atoms embedded in the source chamber. This argon “washing”
 341 procedure reduces the total amount of contaminant krypton that can outgas
 342 from the chamber walls during a measurement to $<2\%$ of the sample gas
 343 being measured.

344 5. Results

345 Measurements for this experiment were taken in the manner described
 346 in Section 4 over the course of a two-and-a-half-month period. Nine mea-
 347 surements were conducted for each of the two samples to obtain sufficient
 348 statistical precision for a 1% measurement. Major realignment of the laser
 349 system was done at several junctures throughout the period, but never in
 350 between sample and reference measurements. The results of these measure-
 351 ments are presented in Figure 1. Blue squares represent the Modern samples
 352 and red crosses represent the PreAnthropogenic samples. The superratios
 353 for both the Modern and PreAnthropogenic samples are plotted and fit to
 354 a constant function. The reduced chi-squared values of these fits are 0.73
 355 and 1.16 for the Modern and PreAnthropogenic samples, respectively. The
 356 weighted average of the measurements for each sample type, using the single
 357 measurement errors as our weights, gives us

$$\begin{aligned} {}^{81}\text{Kr}_{\text{Modern, SR}} &= 0.990 \pm 0.010 \\ {}^{81}\text{Kr}_{\text{PreAnthropogenic, SR}} &= 0.988 \pm 0.010. \end{aligned}$$

358 The two average values agree within error, meaning that we have no
 359 significant anthropogenic contribution. Consequently, we report a 2.5% up-
 360 per limit at the 90% confidence level on anthropogenic contributions to the
 361 atmospheric abundance of ${}^{81}\text{Kr}$. The Modern value also represents good
 362 agreement between the open mode and closed mode measurements. As a
 363 check on the influence of cross-sample contamination mentioned earlier, we
 364 conduct outgassing tests on the stable isotopes of krypton prior to each run
 365 and determined a limit of 0.5% contamination per hour, primarily due to

366 gas from the reference bottle. Additionally, we have also compared the ^{85}Kr
367 loading rates from each measurement. On average the Modern ^{85}Kr loading
368 rate was 8740 atoms/hour and the PreAnthropogenic ^{85}Kr loading rate was
369 150 atoms/hour. Presuming that all of the activity measured in the PreAn-
370 thropogenic sample was from the Modern gas suggests that we have a 1.8%
371 maximum contamination effect. Given the average runtime of 3.5 hours for
372 the PreAnthropogenic runs, this result agrees with our outgassing test limit
373 of just below 2%.

374 This 2.5% limit on anthropogenic ^{81}Kr in the atmosphere is in good agree-
375 ment with our theoretical model, which expects a $\leq 0.15\%$ anthropogenic
376 contribution. In placing this limit we have demonstrated that the ATTA
377 technique can measure samples down to 1% precision provided sufficient
378 statistics. We have also removed concerns of systematic effects from an-
379 thropogenic contributions when using ^{81}Kr as an environmental tracer at
380 this level of precision.

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