

FRACTIONATION OF Xe, Kr, AND Ar IN THE SOLAR CORPUSCULAR RADIATION DEDUCED BY CLOSED SYSTEM ETCHING OF LUNAR SOILS

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ABSTRACT

We etched lunar soil samples in several steps in a vacuum-tight device and analyzed the evolved solar noble gases on line in a mass spectrometer. This technique avoids diffusive noble gas fractionation during analysis and therefore provides reliable element abundance ratios as a function of depth in the grains. The ratios He/Ar and Ne/Ar strongly increase in the course of the etching and reach present-day solar wind ratios toward the end of the runs. This shows that the solar wind component, residing in the top few hundred angstroms, lost much of its He and Ne, whereas even these mobile light noble gases are retained nearly un-fractionated in the solar energetic particle (SEP) component at larger depths. In contrast to the light gases, the Kr/Xe ratio is constant throughout all runs, and the same is essentially true also for Ar/Kr. This strongly suggests that the relative abundances of the three heavy noble gases in the incoming solar corpuscular radiation are conserved in lunar samples. The Kr/Xe ratio in samples irradiated in the past ~ 100 Myr is about a factor of 2.5 lower than the most probable value in the Sun. The same ratio was another factor of 2 lower 1–3 Gyr ago. Kr/Ar in the solar corpuscular radiation is also slightly fractionated. Xe is overabundant relative to Ar by about the same factor as are elements with a first ionization potential (FIP) of less than ~ 10 eV relative to high-FIP elements. This seems astonishing, since Xe has a FIP above 10 eV. However, Geiss, Gloeckler, & von Steiger showed recently that the Xe overabundance deduced here is expected if actually the first ionization time rather than the FIP governs the fractionation in the solar wind source region.

Subject headings: Moon — solar wind — Sun: abundances — Sun: particle emission

1. INTRODUCTION

Element abundances in the outer solar atmosphere differ from bulk solar values as a function of the first ionization potential (FIP) or a related parameter (Hovestadt 1974; Webber 1975). The fractionation is usually expressed as a step function. Elements with $\text{FIP} \leq 10$ eV are about 4–5 times overabundant in the solar wind and solar energetic particles relative to their known or assumed abundances in the photosphere (Cook, Stone, & Vogt 1980; Veck & Parkinson 1981; Meyer 1981; Geiss 1982; Anders & Grevesse 1989; review by Meyer 1993). The FIP-related fractionation is thought to arise from an ion-neutral separation in the chromosphere (e.g., von Steiger & Geiss 1989).

To learn more about this separation, the abundances of elements whose FIP is close to the step are particularly important (Meyer 1993). The purpose of this paper is to provide abundance values for Xe (FIP = 12.1 eV) relative to Kr (14.0 eV) and Ar (15.8 eV) from studies of solar noble gases trapped in lunar soil. Xe and Kr are not recorded by the present generation of solar particle detectors on space probes and could not be analyzed in the foils exposed during the *Apollo* Solar Wind Composition (SWC) experiment (Geiss et al. 1972). We will argue that Xe is enriched in the solar wind source region by about the same factor as is otherwise common for elements with a FIP below 10 eV.

Our main task will be to show that lunar regolith samples faithfully record the relative Ar, Kr, and Xe abundances in the incoming solar particle stream. This is not trivial at all, because it became clear with the first noble gas studies on lunar soils that the light gases He and Ne are not well retained. He/Ar and Ne/Ar ratios in different minerals are highly variable and sometimes orders of magnitude below the values of the

present-day solar wind determined by the SWC experiment. In those early days, different opinions prevailed on whether the heavy gases were also fractionated in the carrier (e.g., Eberhardt et al. 1972; Bogard et al. 1973). The issue has not been settled since, in part because it was shown that the N/Xe and N/Ar ratios in lunar soils are roughly constant—possibly suggesting a solar origin for lunar nitrogen—but higher than the accepted solar values by factors of about 3 and 10, respectively (DesMarais, Hayes, & Meinschein 1974; Kerridge 1980; Frick, Becker, & Pepin 1988). Therefore, about two-thirds of even the least mobile noble gas, xenon, may have been lost, leading presumably to an elemental fractionation among the heavy noble gases. Here we will use data obtained by stepwise etching of lunar samples to argue that such a fractionation did not happen and that the regolith of the Moon therefore allows us to deduce the relative abundances of the heavy noble gases in the solar wind. We will then discuss earlier data in the light of the new findings and will also touch upon the “nitrogen puzzle.” Finally, we briefly discuss what the results here add to our understanding of fractionation processes in the solar atmosphere.

Closed system stepped etching (CSSE) releases noble gases by progressively dissolving the carrier, unlike the more familiar stepwise pyrolysis, where gases are set free by thermal diffusion. Therefore, CSSE does not—or at least does much less than pyrolysis—fractionate elements during gas release and thus allows us to determine approximate depth profiles of noble gas concentration ratios in carrier grains. We showed earlier with the same technique that solar noble gases in extra-terrestrial samples consist of two isotopically distinct components (Wieler, Baur, & Signer 1986; Benkert et al. 1993; Wieler & Baur 1994a). One is the well-known solar wind (SW),

which has a ratio $^{20}\text{Ne}/^{22}\text{Ne} = 13.8 \pm 0.1$ (Benkert et al. 1993). SW ions have energies in the ~ 1 keV amu^{-1} range and penetrate only a few hundred angstroms. The second component resides at larger depth and must have been implanted with higher energies. We termed this component "SEPs" for "solar energetic particles" (Wieler et al. 1986). Its $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of 11.2 ± 0.2 may indeed be identical to the average value measured for SEPs by space probes (Selesnick et al. 1993). However, SEP noble gases in extraterrestrial samples are orders of magnitude too abundant to be explained as particles in the 10 MeV amu^{-1} range like those measured in space. Lunar samples must therefore contain a "low-energy SEP" component of higher flux than the "high-energy SEPs" detected with spacecraft. The comparison of noble gas abundances of the two solar components in lunar samples will be crucial in our reasoning.

2. NOBLE GAS ABUNDANCES IN THE SUN

2.1. He/Ar and Ne/Ar

Relative noble gas abundances in the Sun are not easy to obtain, because spectroscopic data are scarce. Although we concentrate in this paper on Ar, Kr, and Xe, we will discuss the light noble gases as well, because they will help us to rule on the extent of fractionations of the heavier gases during or after implantation. The top four entries of Table 1 list "solar system" abundance ratios compiled by various authors. The figures for the light elements are mostly compromises between different sources, including spectroscopic data; SW and SEP measurements; information from outside the solar system, such as H II regions or hot stars; and interpolations of abundances of neighboring elements in the periodic table, which can be accurately determined from meteorites. For He/Ar and Ne/Ar the "solar system" ratios are of less interest here than those measured in the solar corpuscular radiation or its source region, because we will compare the lunar data with the latter values to deduce how much the lighter solar noble gases were fractionated on the Moon. Three sets of reference data for the present-day solar corpuscular radiation are shown in the upper part of Table 1. All these values are similar to one another, except for the somewhat low $^{20}\text{Ne}/^{36}\text{Ar}$ ratio measured in an impulsive flare. Notably, the SWC values and those for high-energy SEPs agree closely. We will use these two data sets as references for the lunar data.

2.2. Ar/Kr and Kr/Xe

Ar/Kr and Kr/Xe ratios in solar system abundance compilations are mostly derived by interpolating values of nearby elements. We include in Table 1 the average ratios in the four lunar samples analyzed for this study. The $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios given by Marti, Wilkening, & Suess (1972) are in quite good agreement with those of the two relatively recently irradiated samples 71501 and 67601. Marti and coworkers noted from a similar comparison that "it appears that no major rare-gas fractionation takes place within the solar wind." However, Ar/Kr and Kr/Xe ratios in the three other compilations are all considerably higher than the Marti et al. values. These newer estimates are probably to be preferred, since they are based on more recent concentration values for the neighboring elements in meteorites. We adopt the Ar, Kr, and Xe abundances given by Anders & Grevesse (1989), who note that their Kr and Xe values agree well with estimates from s-process nucleosynthesis. This choice implies

either a loss of Ar and Kr on the Moon or a fractionation between Sun and solar corpuscular radiation.

3. ARGON, KRYPTON, AND XENON ABUNDANCES OF SOLAR GASES IN EXTRATERRESTRIAL SAMPLES

3.1. CSSE Data in This Work

A major task in studies like this one is to separate different noble gas components in the same carrier or to find undisturbed gas reservoirs and analyze them separately from altered ones. Samples are usually degassed by a stepwise increase of temperature, either in vacuum (pyrolysis) or in the presence of a few torrs of oxygen (combustion). Thus, the gases are released mainly by diffusion, in combustion experiments partly also by oxidizing the carrier. This usually leads to large elemental fractionations during the experiment since the lighter gases diffuse faster. We therefore developed a technique to extract noble gases essentially at room temperature (Wieler et al. 1986; Signer, Baur, & Wieler 1993). A sample in a vacuum line is exposed in several steps to an acid like HF, first as vapor and later sometimes as liquid. After thorough cleanup, the noble gases are measured on line in a mass spectrometer. The material dissolved per step can be varied over a wide range by adjusting vapor pressure, acid temperature, and time. The extremely shallowly sited SW gases are released first by very gentle acid attack. The more deeply sited SEP component is released later under much harsher etching. This component separation works best if monomineralic samples are analyzed.

We discuss here profiles of concentration ratios of elements (always light over heavy element, as in Ne/Ar or Kr/Xe) obtained by the etch technique in four lunar soils. Two samples are ilmenite separates. Among the abundant minerals in the lunar regolith, ilmenite best retains the light noble gases. Soil sample 71501 received its solar gases relatively recently, presumably within the last 100 Myr, and is thus said to have a low "antiquity." The loosely consolidated soil breccia 79035 trapped its solar gases at least 1 Gyr ago. More details about these two samples and their complete noble gas data are given by Benkert et al. (1993) and Wieler & Baur (1994a). Sample 14301 is a mildly metamorphosed soil breccia from which we analyzed a pyroxene separate (grain-size range 25–200 μm). This sample contained about 10%–15% reworked particles (agglutinates) adhering to the pyroxene crystals. The antiquity of 14301 is presumably above 3 Gyr (Eugster, Michel, & Niedermann 1992). The breccia belongs thus to the earliest irradiated samples we know of. It also contains xenon from the fission of now extinct ^{244}Pu (half-life 82 Myr) and the β -decay (15.7 Myr) of ^{129}I (Bernatowicz, Hohenberg, & Podosek 1979). Like the solar gases, both of these components reside near the grain surfaces. Solar and fissionogenic/radiogenic noble gases can, however, readily be separated by stepwise etching (Wieler & Baur 1994b), and the Ne isotope data (unpublished) reveal that in the first and last etch steps, respectively, essentially the pure SW and SEP components are released. These two facts show that no major redistribution of noble gases occurred during metamorphism. Sample 67601 is a sieve fraction (25–42 μm) from the bulk soil. It is rich in plagioclase, which easily loses its light noble gases. This sample was measured primarily to test procedures for heavy noble gas analyses by CSSE, but it turned out that the element ratios deserve to be discussed here.

The $^{84}\text{Kr}/^{132}\text{Xe}$ and $^{36}\text{Ar}/^{84}\text{Kr}$ ratios of the solar component and the cumulative fraction of solar ^{36}Ar of all four samples are given in Table 2. These values were obtained by

TABLE 1
NOBLE GAS ELEMENT RATIOS IN VARIOUS RESERVOIRS

reservoir	$\frac{^4\text{He}}{^{36}\text{Ar}}$	$\frac{^{20}\text{Ne}}{^{36}\text{Ar}}$	$\frac{^{36}\text{Ar}}{^{84}\text{Kr}}$	$\frac{^{84}\text{Kr}}{^{132}\text{Xe}}$	data source/remarks
reference data: solar system					
	31500	37	3320	20.6	He-Ar: extrasolar & solar spectra, SEP; Kr,Xe: neighbour. elements ¹
	24800	37	3380	22.5	He, Ne: extrasolar spectra, SWC; Ar-Xe: neighbouring elements ²
	20300	26	3800	15.5	He, Ne: SEP, solar spectra; Ar-Xe: neighbouring elements ³
	16000	40	2500	10	neighbouring elements ⁴
reference data: solar corpuscular radiation					
solar wind	25200 ±6400	45 ±10			Apollo Solar Wind Composition experiment (SWC) ⁵
high energy SEP ⁸	21600 ±4500	47 ±8			spacecraft data ⁷
upper solar atmosphere ⁸	25100	27 ±9			impulsive flare ⁶
this work⁹					
71501 ilmenite			1870	8.98	recently irradiated (<100Ma)
67601 bulk ¹⁰			(1670)	8.39	recently irradiated (<100Ma)
79035 ilmenite			2120	4.68	irradiated ~1Ga ago
14301 pyroxene			2390	5.19	irradiated ~3-4Ga ago
other lunar & meteorite data					
75081 pyrox. ¹¹			2010	7.4	mean, major steps (etch, pyrol.)
68501 metal ¹²			2070	9.64	mean, combustion steps 1-3
Pesyano ¹³				7.5	
Acfer111 ¹⁴			2570		etch analysis, mean (as measured)
71501 ilmenite ¹⁵			2030	8.42	combustion/pyrolysis, mean
79035 ilmenite ¹⁶			2010	4.70	combustion/pyrolysis, mean

NOTES.—(1) Anders & Grevesse 1989. (2) Anders & Ebihara 1982. (3) Cameron 1982. (4) Marti et al. 1972. (5) Cerutti 1974; Bochsler 1987. (6) Feldman 1992; Feldman & Widing 1990 for Ne/Ar. (7) Brenemann & Stone 1985; Stone 1989; He/Ar from compilation by Anders & Grevesse 1989. (8) Element ratios given in original work. Isotopic composition of SW or SEP components (Benkert et al. 1993) used to calculate nuclide abundances. (9) Average of etch steps. (10) Ar loss possible. (11) Rider et al. 1995. (12) Becker & Pepin 1994. (13) Marti 1969; Marti et al. 1972. (14) Pedroni & Begemann 1994. (15) Frick et al. 1988. (16) Becker & Pepin 1989.

correcting the measured data for noble gases produced by cosmic-ray interaction (mostly very minor) and in sample 14301 also for fission Xe. The complete noble gas element and isotope data for the two ilmenites are given by Benkert et al. (1993) and Wieler & Baur (1994a); the complete data for the other two samples are available upon request. Before discussing the heavy noble gas patterns, we will consider the light gases.

3.1.1. He/Ar and Ne/Ar

Since we have independent information on the abundances of He, Ne, and Ar in the solar corpuscular radiation, Figure 1 allows us to rule on element fractionations and noble gas losses. All three mineral separates (samples 71501, 79035, 14301) show similar patterns. Both ratios $^4\text{He}/^{36}\text{Ar}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ increase during the etch sequence from values clearly below those of present-day solar wind (SWC) or high-energy

TABLE 2
ELEMENT RATIOS OF SOLAR NOBLE GASES IN FOUR LUNAR SAMPLES MEASURED BY CLOSED SYSTEM STEPPED ETCHING

sample/ etch step	³⁶ Ar/ ⁸⁴ Kr	⁸⁴ Kr/ ¹³² Xe	³⁶ Ar (cum. rel.)	sample/ etch step	³⁶ Ar/ ⁸⁴ Kr	⁸⁴ Kr/ ¹³² Xe	³⁶ Ar (cum. rel.)	sample/ etch step	³⁶ Ar/ ⁸⁴ Kr	⁸⁴ Kr/ ¹³² Xe	³⁶ Ar (cum. rel.)
71501 ilmenite				79035 ilmenite				67601 bulk			
1	2050	12.4	0.2026	(a)	70	18.2	0.0002	(1)	470	5.20	0.0005
2	2580	12.4	0.3795	(b)	70	16.0	0.0004	2	1740	6.83	0.0044
3	1300	7.72	0.5076	(c)	160	11.5	0.0009	3	2220	8.28	0.0230
4	1440	4.66	0.5295	1	1340	3.56	0.0027	4	2010	8.14	0.0355
5	2110	8.17	0.5454	2	1620	4.41	0.0032	5	2020	8.40	0.0538
6	2080	8.62	0.6514	3	1960	4.39	0.0219	6	1840	8.54	0.1238
7	1990	8.14	0.7258	4	2380	5.02	0.0435	7	1740	8.25	0.2123
8	2070	9.33	0.8016	5	2440	5.22	0.1643	8	1710	8.42	0.3021
9	1720	8.43	0.9227	6	2260	4.87	0.2236	9	1710	8.18	0.4156
10	1600	8.05	0.9544	7	2140	4.77	0.2933	10	1670	8.14	0.4268
11	1480	7.58	0.9734	8	2040	4.38	0.3802	11	2580	13.1	0.5028
12	1640	9.07	0.9821	9	2070	4.33	0.4508	12	1480	8.43	0.7002
13	1310	7.97	0.9947	10	2160	4.68	0.4870	13	1550	8.51	0.7887
14	1370	8.20	0.9986	11	2150	4.72	0.5457	14	1470	7.95	0.9022
(15)	1130	4.71	0.9995	12	2350	4.98	0.6626	15	1590	7.66	0.9393
(16)	1030	7.01	1.0000	13	2090	5.03	0.8584	16	1610	7.60	0.9608
mean 1-14	1870	8.98		14	1930	4.52	0.9518	17	1710	8.09	0.9810
				15	2750	5.22	0.9542	18	1660	7.98	1.0000
				16	1560	3.44	0.9587				
				17	1610	3.51	0.9922	mean 2-18	1670	8.39	
				18	1150	4.14	0.9951				
				19	1450	4.84	0.9986				
				20	1230	4.07	1.0000				
				mean 1-20	2120	4.68					
14301 pyroxene											
1	2750	5.03	0.3026								
2	2830	5.01	0.5902								
3	2270	5.54	0.8777								
4	1880	5.33	0.9605								
5	1060	5.08	0.9960								
6	2080	3.18	1.0000								
mean	2390	5.19									

NOTES.—Total ³⁶Ar concentrations in units of 10¹⁴ atoms g⁻¹: Sample 71501: 15.3; sample 79035: 19.8; sample 67601: 32.2; sample 14301: 0.854. Weighted means are given. Minor gas fractions with step numbers in parentheses are not shown in Figs. 1–3.

SEPs to values only slightly lower or even identical to these references (the ⁴He/³⁶Ar pattern of U-rich sample 14301 is affected by radiogenic He and not considered further). Other ilmenite and pyroxene etch data sets reported by Benkert et al. (1993) all reveal a similar trend. To understand these patterns, it is useful to look first at the isotope ratios. In the initial steps, gas compositions are always close to the modern SW (e.g., ²⁰Ne/²²Ne = 13.8 ± 0.1), whereas toward the end of the runs essentially pure SEP gases are released (e.g., ²⁰Ne/²²Ne = 11.2 ± 0.2; Benkert et al. 1993). Therefore, the low element ratios on the left-hand side of Figure 1 are associated with the SW portion, and the high ratios on the right represent (low-energy) SEP gases. Hence, we conclude that the outermost grain layers lost a large fraction of the light noble gases, particularly He, from the shallowly implanted solar wind. It is remarkable that this loss happened in a way that has not led to appreciable isotope fractionation, as judged by the similar Ne (and He) isotope ratios in the first etch steps and the SWC experiment, respectively. Benkert et al. (1993) discuss several possible explanations e.g., that the gases in the first steps are mixtures from two reservoirs, one having retained all gases completely, and an easily etchable one that lost most of its He and Ne but little or none of the heavier gases. Most importantly, however, ilmenite retains nearly unfractionated He, Ne, and

Ar from (low-energy) SEPs, and also the somewhat less retentive pyroxene shows only little fractionation between SEP-Ne and SEP-Ar.

The patterns of sample 67601 in Figure 1 are very different from those of the mineral separates. The highest ratios are observed first, the lowest ones in the intermediate steps, and no values are close to the SWC reference. It is notoriously difficult to interpret CSSE data of bulk samples, which are mixtures of phases with variable retentivities for light noble gases and variable resistance against acid attack. Presumably, at first plagioclase and glass released noble gases sited near present-day grain surfaces. These gases were less fractionated than those which showed up later because they now reside on interior surfaces of reworked particles. Contributions from pyroxene probably caused the increase of He/Ar and Ne/Ar at the end of the run.

In summary, the He, Ne, and Ar profiles yielded important and unexpected insights. Whereas total fusion analyses and also step heating had just indicated that all constituents of lunar soils lost much of their solar He and Ne, we now see that this loss affected nearly exclusively the SW portion but not the more deeply residing SEP, at least not in such a way as to fractionate this component. With this, we turn to Figures 2 and 3, addressing first the Kr/Xe profiles, then Ar/Kr.

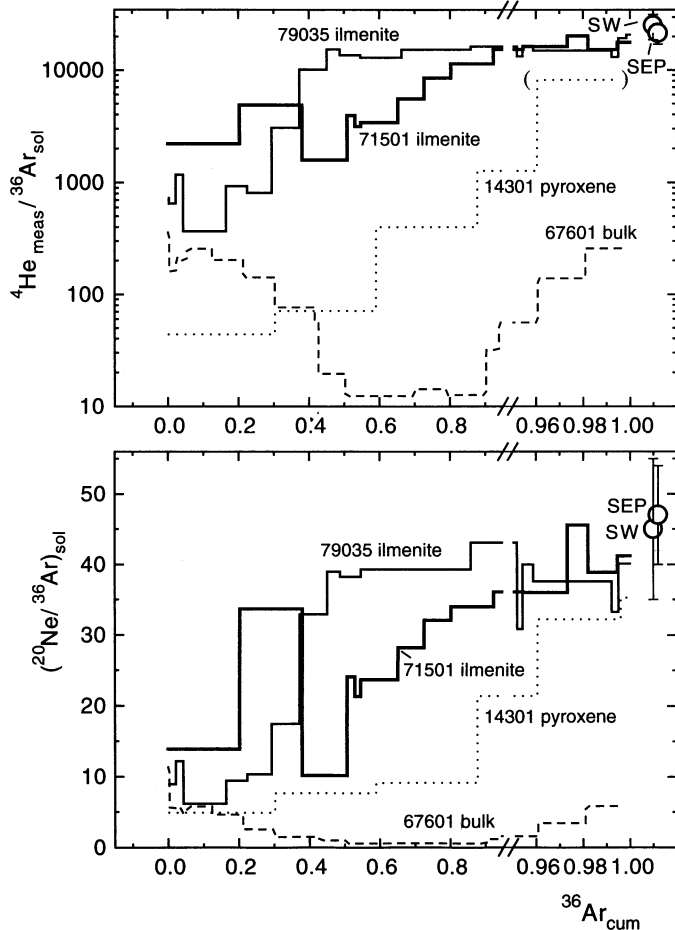


FIG. 1.— ${}^4\text{He}/{}^{36}\text{Ar}$ (top) and ${}^{20}\text{Ne}/{}^{36}\text{Ar}$ (bottom) vs. the cumulative fraction of ${}^{36}\text{Ar}$ for four lunar samples analyzed by closed system stepped etching. Note break in abscissa scales. ${}^{20}\text{Ne}$ and ${}^{36}\text{Ar}$ have been corrected for the cosmic-ray-produced component. ${}^4\text{He}$ has not been corrected for the radiogenic contribution, which is, however, insignificant except perhaps in the last step shown of the pyroxene from sample 14301. The very last step of this sample is severely compromised by ${}^4\text{He}_{\text{rad}}$ and is thus not shown in the upper panel. For comparison, element abundance ratios in the modern solar wind (SW) and high-energy SEPs as reported in Table 1 are shown on the right. Low ratios in the first steps indicate that the light noble gases in the SW portion are severely fractionated. The three mineral separates display, however, values close or identical to the SW and SEP references in later steps, indicating that the low-energy SEP component trapped in these samples retained its light noble gases (nearly) unfractionated.

3.1.2. Kr/Xe

All ${}^{84}\text{Kr}/{}^{132}\text{Xe}$ patterns in Figure 2 are essentially flat, forming a remarkable contrast to Figure 1. This is the most important observation in this work. We will discuss it after a brief digression to examine the few outliers. Some very minor gas fractions at the start or the end of some runs are presumably contaminated with (fractionated) atmospheric noble gases. Most of these data are not shown in the figures but are given in Table 2 with step numbers in parentheses. In addition, the gas-poor step 2 of sample 67601 and the last step of sample 14301 possibly also contain some air. Note that these impurities may shift the Kr/Xe ratio in either direction from the true value, depending on whether the contaminating gases were adsorbed on the sample, dissolved in the acid, hidden as bubbles, etc. The sample 67601 step indicated in parentheses in Figures 2 and 3 cannot be explained by atmospheric contami-

nation, since its ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratio is 500 times lower than the atmospheric value and Ar/Kr moved in the wrong direction. This step is the first after distilling HF onto the sample. An acid droplet in a valve presumably caused element fractionation during gas expansion. In later runs of this work, gas expansion was monitored for each step by follow-up “blank” steps, with the acid kept frozen to prevent further etching. The somewhat variable Kr/Xe ratios in the first part of the sample 71501 run are probably not caused by such an effect. This is the same analysis which also shows considerable scatter in He/Ar and Ne/Ar. Tentatively, this variability may be explained by different implantation depths of light and heavy gases, which might be revealed when etching proceeds very homogeneously, in such a way that a particular step samples gas from a very narrow depth interval. In any case, even the high Kr/Xe ratios in steps 1 and 2 are only some 40% above the sample 71501 average and still clearly below the solar reference value. With this observation, we return to the main discussion of Figure 2.

It is important to note that the Kr/Xe ratio remains constant in each run, while the isotopic composition of the two gases does not. This is most pronounced for the two ilmenites (Wieler & Baur 1994a). Solar Kr and Xe get isotopically heavier in the course of the etching, very much like the three light gases. This indicates that solar Kr and Xe also consist of two components, the light SW being released prior to the heavy SEPs. The isotope data thus show that the constant element ratios are not simply the result of sampling more and more Kr and Xe of the same reservoir. We also note in Figure 2 a grouping according to antiquity. The mean ${}^{84}\text{Kr}/{}^{132}\text{Xe}$ ratios of the recently irradiated soils are nearly twice as high as those of the other two samples. Therefore, the etch data show Kr/Xe ratios similar to the lowest and highest values, respectively, measured in bulk analyses (e.g., Bogard et al. 1973; Hintenberger, Weber, & Schultz 1974). However, the Kr/Xe depth profiles again contain information that was not available from the bulk analyses.

We will now argue that the relative abundances of Kr and Xe in the incoming solar radiation are preserved in the samples. The reasoning is based on the comparison of the Kr/Xe profiles, on the one hand, with the He/Ar and Ne/Ar patterns, on the other. Two observations are remarkable. First, since the fractionation of the lighter gases varies in the course of the etching, we would expect variable Kr/Xe ratios if these two gases were fractionated. It is very notable that sample 67601 shows a flat Kr/Xe pattern just as do the other three analyses, although ${}^4\text{He}/{}^{36}\text{Ar}$ and ${}^{20}\text{Ne}/{}^{36}\text{Ar}$ trends are so different between bulk sample and mineral separates. Second, mineral separates retain (nearly) unfractionated He and Ne in the SEP reservoir, as shown above. If these light gases are retained without fractionation, we would expect even more that the relative abundances of heavy Kr and Xe would remain unaltered. We therefore conclude that the Kr/Xe ratios in the four samples reflect the relative abundance of the two gases in the solar wind and solar energetic particles at the respective time of implantation. Taking the Kr and Xe abundances given by Anders & Grevesse (1989) as solar values, we deduce further that these two elements are fractionated in SW and SEPs relative to the bulk solar composition. The fractionation factor decreased from about 4–4.5 some 1–3 Gyr ago to about 2–2.5 at present.

3.1.3. Ar/Kr

We exclude the same few outliers as above from further consideration. All data plot below the Anders & Grevesse

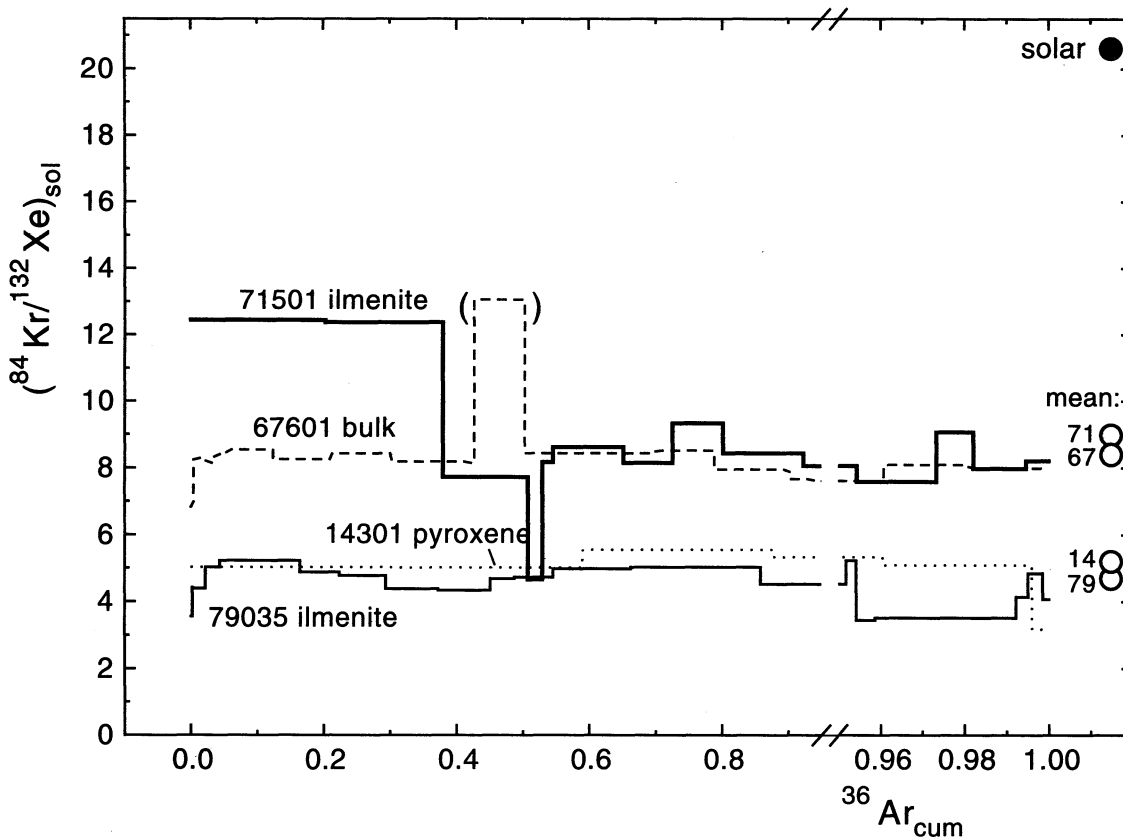


FIG. 2.—Same as Fig. 1, but for $^{84}\text{Kr}/^{132}\text{Xe}$ of the solar component. On the right, the mean of each sample is given, as well as the solar value of Anders & Grevesse (1989). In contrast to Fig. 1, flat patterns are observed throughout the etch runs (the few exceptions are discussed in the text). This is particularly noteworthy for bulk soil sample 67601, which shows very fractionated He/Ar and Ne/Ar patterns. The flat patterns indicate that Kr and Xe are not fractionated relative to the solar corpuscular radiation. The mean Kr/Xe ratios are, however, considerably lower than the solar reference value, indicating a fractionation in the SW/SEP source region. Compared to the last 100 Myr, this fractionation was twice as large some 1–3 Gyr ago, indicated by the differences between early (Nos. 14301 and 79035) and recently (Nos. 71501 and 67601) irradiated samples.

(1989) value, mostly between about 15% and 50% below. Compared with Figure 2, the $^{36}\text{Ar}/^{84}\text{Kr}$ profiles in Figure 3 vary somewhat more within each run, but for the mineral separates this may be due to a tendency toward lower ratios in later steps. If this trend is real, Ar/Kr runs opposite to He/Ar and Ne/Ar. No diffusive loss of SW Ar is therefore indicated. Bulk soil sample 67601 shows a rather flat Ar/Kr pattern, with somewhat lower values in the middle steps. Ar/Kr in this sample thus resembles He/Ar and Ne/Ar, except that the former ratio varies much less. This means that we cannot exclude some diffusive Ar loss from sample 67601. This sample has indeed the lowest average $^{36}\text{Ar}/^{84}\text{Kr}$ ratio, but the difference from the other recently irradiated soil (sample 71501, ilmenite) is only $\sim 10\%$.

Do the Ar/Kr ratios really tend to be lower in later steps in the three mineral analyses? A similar trend has been observed in a CSSE study of the solar-gas-rich meteorite Acfer111 by Pedroni & Begemann (1994). They showed that $^{20}\text{Ne}/^{84}\text{Kr}$ decreases with step number, and from their data we conclude the same for the solar $^{36}\text{Ar}/^{84}\text{Kr}$ ratio. Pedroni & Begemann mention different penetration depths of different elements as the most likely reason. However, we might then expect a similar trend in Kr/Xe. A second possibility is that (low-energy) SEPs have a somewhat lower Ar/Kr ratio than the SW. In this case, one could wonder why no similar differences are observed either for Ne/Ar (Murer et al. 1994; Murer, Baur, & Wieler

1995) nor for Kr/Xe (this work). Therefore, more data are needed to settle this issue.

Additional work is also needed to study a possible temporal variation of the Ar/Kr ratio. Compared to Kr/Xe the slight difference in Ar/Kr between the one low-antiquity sample with reliable Ar data and the two high-antiquity samples has the reverse sign. This marginally significant observation may be supported by bulk analyses. A negative correlation between Kr/Xe and Ar/Kr in ilmenite-rich *Apollo 17* samples may exist (figure not shown), and Ar/Kr ratios in *Apollo 15* drill core samples tend to increase with depth in the core (Bogard et al. 1973). Of particular interest are data reported by Jordan & Heymann (1975) for several *Apollo 17* “trench” soils with a rather high antiquity: Kr/Xe ratios are similar to the values in our two high-antiquity samples, whereas Ar/Kr ratios are close to the “solar” value. However, the scatter in existing data is too large to deduce a secular change of Ar/Kr in the SW. Note also that the low- and high-antiquity ilmenite separates measured by Frick et al. (1988) and Becker & Pepin (1989) have nearly identical Ar/Kr ratios (Table 1).

To summarize, the following conclusions can be drawn from Figure 3: (i) the Ar/Kr ratio is not fractionated due to diffusive Ar loss in the three mineral separates, but presumably is slightly so in the plagioclase-rich bulk sample 67601. (ii) Ar/Kr is lower than the Anders & Grevesse (1989) value, but the difference is less than for Kr/Xe. (iii) With available data no clear

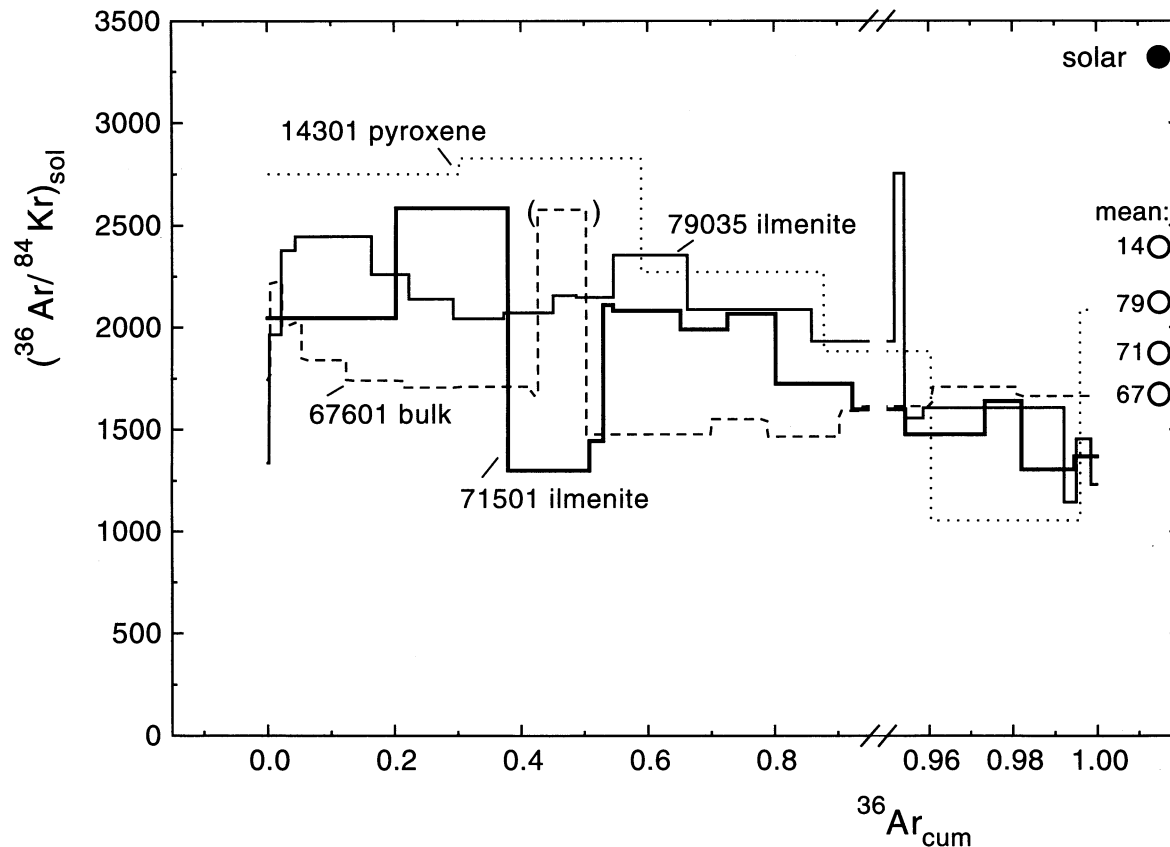


FIG. 3.—Same as Fig. 2, but for $^{36}\text{Ar}/^{84}\text{Kr}$ of the solar component. A possible trend of decreasing ratios toward the right is discussed in the text. As in Fig. 2, no fractionation of Ar/Kr in the carrier grains is observed. This ratio is again somewhat lower than the solar system reference, indicating a fractionation in the SW/SEP source region.

temporal trend can be deduced for Ar/Kr, but, if such a trend existed, it would run opposite to that for Kr/Xe.

3.2. Data of Other Investigators

In this section we compare our CSSE results with other data. We begin mainly with recent studies, some of which used gas release techniques similar to ours. After this, we will examine earlier work in the light of the new studies, particularly discussing reservations expressed about the ability of the lunar regolith to preserve the abundances of implanted heavy noble gases. Rider, Pepin, & Becker (1995) analyzed pyroxene from low-antiquity soil sample 75081 by a combination of stepwise etching and pyrolysis. This is the only other *in vacuo* etch study of a mineral separate that includes Kr and Xe. The major etch and pyrolysis steps both have $^{36}\text{Ar}/^{84}\text{Kr}$ and $^{84}\text{Kr}/^{132}\text{Xe}$ ratios close to those of ilmenite from sample 71501 (Table 1). The same group presented data on a Fe-Ni separate from low-antiquity soil sample 68501 obtained by stepwise combustion, starting at relatively low temperature (Becker & Pepin 1994). The first three steps (less than 410°C) should have released the heavy noble gases by oxidizing the carrier rather than by diffusion. These steps indeed show flat Ar/Kr and Kr/Xe patterns, and the average values are again quite similar to those in ilmenite from recently irradiated sample 71501 (Table 1). Fe-Ni is known as the phase that best retains solar noble gases but, unfortunately, is rare in lunar soils. In our view, the sample 68501 metal data provide further evidence that Ar, Kr, and Xe abundances in the solar wind differ from

bulk solar values, a proposition also considered by Becker & Pepin.

Gas-rich meteorites are compacted samples from asteroidal regoliths which contain solar noble gases like lunar soils. Unfortunately, solar xenon in meteorites is nearly always swamped by primordial xenon retained since the formation of the planetary system. Furthermore, the antiquity of gas-rich meteorites is largely unconstrained. The $^{84}\text{Kr}/^{132}\text{Xe}$ ratio of the solar component has been reported only for one meteorite, the metamorphosed aubrite Pesyanoe (Marti 1969). The measured value of 7.5 (Table 1) is again similar to that of sample 71501.

One on-line etch analysis of a gas-rich meteorite that included solar Kr has been reported (Pedroni & Begemann 1994). This meteorite, Acfer111, is unique, since even bulk samples contain unfractionated light solar noble gases, with $^4\text{He}/^{36}\text{Ar} = 25,000$. The average $^{36}\text{Ar}/^{84}\text{Kr}$ ratio of 2570 (corrected for cosmogenic gases; Table 1) is slightly higher than the highest average of our lunar samples, but still is $\sim 25\%$ lower than the Anders & Grevesse (1989) value. Note that Pedroni & Begemann correct for primordial Kr, by assuming that all measured Xe is primordial, and report an average solar Ne/Kr ratio close to the Anders & Grevesse value. This assumption is doubtful, however, since the $^{136}\text{Xe}/^{132}\text{Xe}$ ratios imply a substantial air-Xe contamination in all steps.

Now we turn to the earlier work. One study that came to an optimistic conclusion was published by Eberhardt et al. (1972),

who showed that bulk samples and ilmenite separates have similar Ar/Kr and Kr/Xe ratios. Therefore, they presumed that bulk soils and ilmenites both should yield reliable SW abundance values for the heavy rare gases. Similarly, Signer et al. (1977) concluded that Ar, and also the heavier gases, are well retained in all major minerals, including plagioclase. On the other hand, it was pointed out that Kr/Xe ratios vary by more than a factor of 2 in different bulk samples (Bogard et al. 1973; Hintenberger et al. 1974). These variations were thought to reflect processes on the Moon. Hintenberger and coworkers attributed systematically lower values in soil breccias to an enhancement in Xe or a depletion in Ar and Kr during brecciation.

Kerridge (1980), noting that the breccias were irradiated much earlier than the soils, showed, however, that the Kr/Xe variations roughly correlate with antiquity. He concluded that lunar samples preserve a record of a secular decrease of the Xe abundance in the SW. Whereas Kerridge did not address the observation that Kr/Xe ratios are always lower than solar values, this problem was again discussed by Frick et al. (1988) and Becker & Pepin (1989). These workers measured noble gases and nitrogen by stepwise combustion/pyrolysis of near aliquots of the two ilmenites studied here by CSSE. The Xe/N ratio was several times below the solar value given by Cameron (1982). They concluded that the samples had lost Xe, since they assumed that nitrogen in lunar soils is predominantly of solar wind origin. However, the total noble gas amounts released up to a certain temperature displayed approximately solar proportions, and the authors inferred the existence of a "low temperature" (LT) noble gas reservoir unfractionated relative to Cameron's solar values, presumably representing the gas trapped most recently. The postulated LT reservoir clearly contradicts the conclusions reached here. We note, however, that in the very first combustion step of sample 79035 at 300° C, Ar/Kr and Kr/Xe ratios are both within 8% of the respective averages of the CSSE run. The temperature in the first step of the ilmenite from sample 71501 was somewhat higher (400° C), but its Kr/Xe and Ar/Kr ratios are still only 25% and 40%, respectively, above the CSSE average. Notably, the data of the first combustion steps of the ilmenites are quite similar to those of the metal from sample 68501 by Becker & Pepin (1994) mentioned above. Note that Becker & Pepin (1989) supported the conclusion by Kerridge (1980) of a secular trend in Kr/Xe, because in the two ilmenite separates this ratio differed by a factor of about 2 not only in the LT reservoir but also in the gas released at higher temperatures.

Ignoring for the moment the high nitrogen concentrations, we conclude that the data by others, recent as well as earlier ones, are well in line with our CSSE results and, hence, with the conclusion that lunar and meteoritic samples correctly reflect the relative Ar, Kr, and Xe abundances in SW and SEP. The differing Kr/Xe ratios have convincingly been shown to reflect a temporal trend, and the existence of an LT reservoir with unfractionated solar abundances according to Cameron (1982) is questionable, since the combustion steps that ought to show the least distorted abundance pattern have Ar/Kr/Xe ratios close to those in etch runs.

What remains is the nitrogen problem. For many years a lively debate has gone on about whether or not nitrogen in lunar soils is mostly of solar origin (e.g., Becker & Pepin 1989, 1994; Kerridge 1993; Geiss & Bochsler 1982, 1991; Bochsler 1994; Brilliant, Franchi, & Pillinger 1994; Becker 1995a). A crucial observation is the large variation of about 30% of the

$^{15}\text{N}/^{14}\text{N}$ ratio in different samples and often even in different release fractions of one sample. Proponents of a solar origin of lunar nitrogen have mostly argued that this reflects a secular change in the N isotopic composition in the solar wind, but no convincing explanation of how to achieve such a large variation has yet been found. This difficulty led to the development of scenarios which invoke other sources, like indigenous lunar nitrogen (Geiss & Bochsler 1982) or terrestrial nitrogen (Geiss & Bochsler 1991; Bochsler 1994). In such models, the nonsolar N is trapped—like the solar noble gases—more or less in proportion to grain surface area and residence time near or at the regolith surface, resulting in a roughly constant N/Ar ratio. It is beyond the scope of this paper to evaluate the arguments of each side in any detail. Therefore, we restrict our discussion to a few points, mostly in response to comments by the reviewer. The N/Ar ratios in lunar bulk soils and mineral separates are consistently about a factor of 10 above the Anders & Grevesse (1989) value, as has been noted many times (e.g., Becker & Pepin 1989; Kerridge 1993). Hence, if most N is of solar origin, our conclusions could be upheld only if Ar, Kr, and Xe were all depleted relative to N by the same factor on the Moon, or if N were enhanced in the solar corpuscular radiation about tenfold relative to Ar. Both possibilities seem unlikely, however. The latter one has been suggested by Becker & Pepin (1994), but Brenemann & Stone (1985) reported a N/ ^{36}Ar ratio in SEPs of 45 ± 8 (recalculated here with a $^{36}\text{Ar}/^{38}\text{Ar}$ ratio in SEPs of 4.9; Benkert et al. 1993), a value within error limits identical to that of 37 given by Anders & Grevesse. As discussed in the next section, a large N/Ar fractionation in the SW source region is also not expected on theoretical grounds. A constant depletion factor of all heavy noble gases on the Moon seems not impossible altogether, but we have not been able to conceive a convincing mechanism that would accomplish this.

Nitrogen and carbon concentrations in lunar bulk samples also correlate roughly (e.g., Petrowski, Kerridge, & Kaplan 1974; Norris et al. 1983), and the average N/C ratio is above the solar value by about a factor of 2 or 3, depending on the choice of the solar ratio. As with N/Ar, a large fractionation between C and N is neither expected nor observed in SEPs: N/C ratios in SEPs fall in between the Anders & Grevesse (1989) and Cameron (1982) values (Stone 1989). Therefore, if solar Ar is well retained, not only would some 90% of the lunar N have to be nonsolar, but also some 70%–80% of the carbon, which may seem unlikely (Becker 1995b). On the other hand, the fact that the N/C ratio in lunar soils is higher than the solar and SEP value suggests that at least some 50% of the lunar N is indeed nonsolar. This fraction could be larger, because it is quite possible that lunar bulk samples contain meteoritic carbon, although it may seem fortuitous that this source and the excess nitrogen would result in a C/N ratio within a factor of 2 or 3 of the solar value. We believe that carbon data on mineral separates are needed to clarify the origin of carbon in lunar soils.

Kerridge et al. (1992) discussed mixing calculations of two N components in lunar soils with different isotopic composition and noted that their particular model cannot explain the lack of a correlation of the $^{15}\text{N}/^{14}\text{N}$ ratio and the N concentration observed in *Apollo 16* soils. In their model, the nonsolar N fraction does not exceed about 40%, however, whereas we argue that 90% or so of the total N is nonsolar (Kerridge and coworkers assume that the nonsolar Ar/Xe ratio indicates loss of solar Ar, whereas we interpret this as a Xe enrichment in the SW source region). If most of the N is contributed by the

nonsolar component, no correlation between isotopic composition and concentration of this element would be expected a priori. The problem, then, is to explain the observed range in the $^{15}\text{N}/^{14}\text{N}$ ratios in lunar samples. Bochsler (1994) suggests that both flux and isotopic composition of terrestrial N accelerated in the magnetosphere and carried to the Moon may be highly variable. It seems to us that to invoke a nonsolar N source with variable isotopic composition does not pose any more severe problems than having to explain a large isotopic variability of solar N.

In summary, we acknowledge that a proper understanding of solar noble gases in lunar samples ultimately requires a solution of the “nitrogen puzzle.” We believe, however, that at this point there are enough reasons—including the data presented here—to doubt that N data offer strong evidence for an (elementally fractionating) loss of solar Ar, Kr, and Xe from lunar samples. We therefore maintain that Ar, Kr, and Xe concentrations in lunar samples correctly reflect the relative abundances of these elements in the solar wind and solar energetic particles, especially if carefully prepared mineral separates are analyzed. In the next section we will discuss some implications of this conclusion with respect to fractionation processes of noble gases in the source region of the solar corpuscular radiation.

4. XENON-KRYPTON-ARGON FRACTIONATION IN THE SOLAR CORPUSCULAR RADIATION

Figure 4 is adapted from Anders & Grevesse (1989). The abundances of about 25 elements in solar energetic particles relative to photospheric values (measured or assumed) are plotted against the first ionization potential. The dashed line is taken from Figure 3 of Anders & Grevesse (1989), but the ordinate scale is shifted by 0.66 units compared to that work. This is to account for new evidence that high FIP elements in SEPs have photospheric abundances relative to hydrogen, which means that low-FIP elements are enhanced in SEPs rather than that high-FIP elements are depleted (Meyer 1993). The Xe/Kr and Kr/Ar ratios from this work (Table 1) are normalized to the values by Anders & Grevesse and anchored to their Ar point. The sample 67601 points are given in parentheses, because this sample has possibly lost some Ar.

The overabundance of xenon relative to argon for all four samples is rather close to the enhancement factors of low-FIP elements. This first gives us yet more confidence that the Xe-Ar (and Xe-Kr) fractionation between SW/SEP and photosphere deduced here is indeed correct. On the other hand, the high Xe abundance is rather astonishing, given the fact that this element has a FIP slightly above the threshold of ~ 11 eV for which commonly no fractionation is expected. Figure 4 also illustrates our two other conclusions: first, that Kr is also somewhat enhanced relative to Ar, although both elements have a FIP clearly above 11 eV, and, second, that the Xe/Kr fractionation decreased about twofold in the past 1–3 Gyr.

The FIP step separating enhanced from nonenhanced elements seems to be quite well defined by the four points Zn, P, S, and C. Xenon plots about 1 eV above this value. The high Xe abundance therefore suggests that the fractionation probably is governed not by the FIP itself but by a related parameter. This fractionation is presumably due to an ion-neutral separation in the chromosphere or transition region (Geiss 1982), possibly across magnetic field lines (von Steiger & Geiss 1989). Geiss & Bochsler (1985) proposed that the time it takes

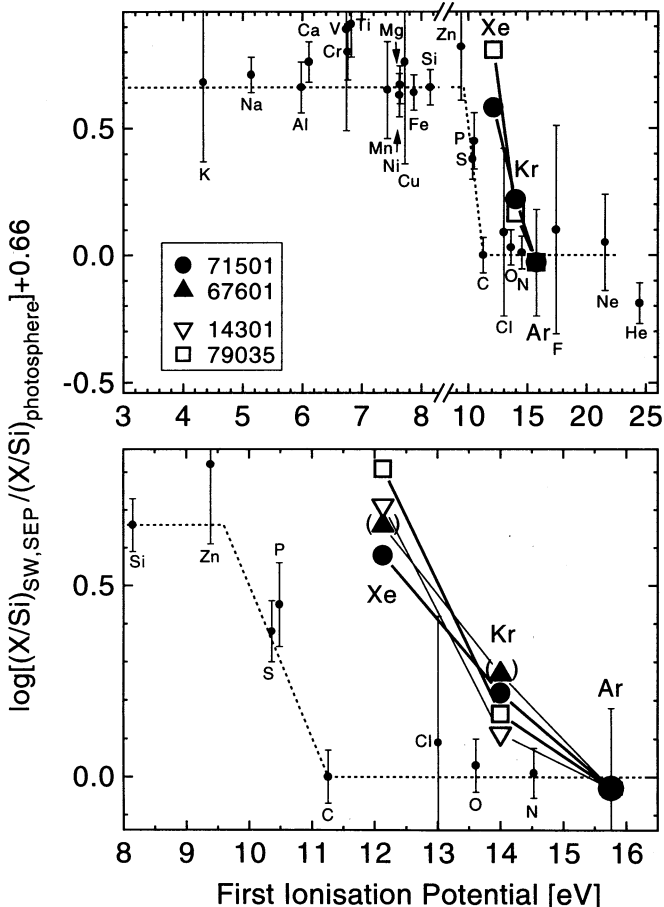


FIG. 4.—Abundances of various elements in the solar corpuscular radiation (normalized to Si) relative to solar photospheric or “solar system” values. The lower panel is an enlarged part of the upper panel. Ar/Kr/Xe ratios in SW and SEPs are from this work and are plotted relative to the solar values of Anders & Grevesse (1989), but the ordinate scale is shifted by 0.66 units compared to that work (see § 4). Only the two ilmenites are plotted in the upper panel. All other data are from the latter reference and represent SEP vs. photospheric abundances. Kr and Xe values are anchored to the Ar point of Anders & Grevesse (1989). The FIP is plotted on the abscissa (note axis break in upper panel). Kr and Xe data from samples with large antiquities (1–3 Gyr) are shown by open symbols, relatively recently exposed samples (less than 100 Myr) by filled symbols. Elements with FIP below about 10–11 eV are enhanced in the solar corpuscular radiation by an approximately constant factor of about 5, indicated by the dashed line. Xenon is also overabundant despite its FIP being slightly above 11 eV. A secular variation of about a factor of 2 in the Kr-Xe fractionation is indicated by the difference between low- and high-antiquity samples.

to ionize atoms is the critical parameter in such a mechanism. Figure 5 shows the element abundances of Figure 4 versus the first ionization time (FIT) as calculated by Marsch, von Steiger, & Bochsler (1995) and Geiss, Gloeckler, & von Steiger (1994). As noted by Geiss and coworkers, the figure shows that the Xe-Ar fractionation observed here supports the concept of separation of ions from neutrals according to ionization times. The same explanation is also in agreement with the partial fractionation between Kr and Ar.

The long-term variability of the Kr/Xe ratio in the solar wind deduced here and in earlier studies is a nice example of the unique potential of lunar and meteoritic samples to record secular variations in the solar atmosphere. This variation is not understood at present. Perhaps the ionization times in the

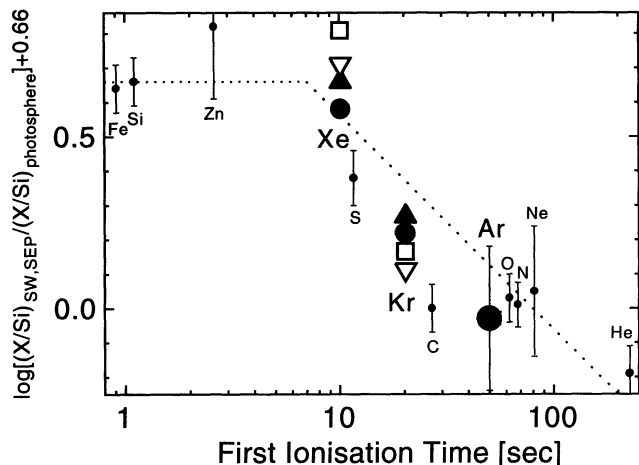


FIG. 5.—Abundance data from Fig. 4 vs. FIT, as calculated by Marsch et al. (1995). The Kr and Xe overabundance deduced here is expected if FIT governs the fractionation in the SW source region.

chromosphere have become larger in the past few billion years. On the other hand, the fractionation factor between low- and high-FIP elements varies in different environments, being about 2 only in solar wind associated with coronal holes (Gloeckler et al. 1989). The secular trend in the Kr/Xe ratio might therefore be related, at least in part, to variable contributions from different SW source regions (Bochsler 1995). The considerable scatter in the correlation between Kr/Xe and the antiquity measure $^{40}\text{Ar}/^{36}\text{Ar}$ (Kerridge 1980) might also indicate short-term variations overlying the long-term trend.

Figures 4 and 5 show that N has a FIP in between those of Kr and Ar and a FIT above that of Ar. An enhancement of N over Ar in the solar corpuscular radiation, as suggested by Becker & Pepin (1994), is thus not expected, the more so because the postulated enhancement factor of about 10 would be higher than those of any low-FIP element.

To learn more about the underlying mechanism of the secular change in Kr/Xe, it would be important to understand several details of Figure 4 better. As pointed out in the previous section, there is some marginal evidence for a secular trend in the Ar/Kr fractionation opposite to the variation in Kr/Xe, and in some bulk samples Ar/Kr is not fractionated at all. If confirmed, the opposite sign of Ar/Kr and Kr/Xe fractionation would certainly be important, though difficult to explain. The samples with solar-like Ar/Kr seem to indicate that under certain conditions these two gases do not get fractionated at the source. A related problem might be the question whether—and why—Ar/Kr in (low-energy) SEPs is lower than in the SW, whereas no such variation is seen in Ne/Ar (Murer et al. 1994, 1995) and Kr/Xe (this work). It would also be important to fix the absolute position of the Xe and Kr points in Figures 4 and 5, by reducing the error of the Ar/Si fractionation. The present uncertainty prevents us from concluding whether Xe is fully enriched today (compared to

low-FIP elements) or was so rather in the ancient SW. The latter view might be preferred, since otherwise in the past Xe would have been enhanced by another factor of 2 or so relative to low-FIP elements. However, we do not know whether these elements were not also enriched more in the past than at present. Future studies of noble gases in extraterrestrial samples—with an emphasis on early irradiated material—combined with investigations of the present-day solar corpuscular radiation are needed to answer such questions.

5. CONCLUSIONS

Analyses of solar noble gases in lunar samples by closed-system stepped etching provide us with new insights about the ability of the lunar regolith to record properties of the solar corpuscular radiation. We conclude that lunar samples conserve the abundances of the heavy noble gases Ar, Kr, and Xe in the solar wind and solar energetic particles, particularly in high-quality separates of the most retentive minerals. This positive conclusion is in contrast to many earlier views. We believe that currently the high N/Ar ratio in lunar samples is not sufficiently well understood to overrule this conclusion. Our argumentation is supported not only by other recent noble gas data but also by earlier work. Of particular importance was the recognition by Kerridge (1980) that the scatter in the relative abundances of the two heaviest noble gases is correlated with the time when the samples were exposed to the Sun.

We conclude that the Xe/Ar ratio in the solar wind source region is enhanced several fold relative to the solar value. Xenon thus behaves like a low-FIP element, although its first ionization potential is slightly above the cutoff value, where commonly no fractionation is expected. This result, surprising at first sight, would be expected if actually the first ionization time governs the fractionation, as has been proposed by Geiss & Bochsler (1985) and Geiss et al. (1994). We confirm the secular change of a factor of 2 in the Kr-Xe fractionation in the past few billion years, whereby earlier data may suggest shorter term variations superimposed upon this secular trend. This result should provide insights into the temporal evolution of the solar atmosphere and details of the fractionation mechanism.

In hindsight, the expectation that the noble gases in the solar wind are unfractionated relative to solar abundances was one of the main reasons to doubt the ability of lunar samples to record the true Ar, Kr, and Xe abundances. Now that this expectation has been shown to be questionable, the lunar—and asteroidal—regoliths have become more important than ever as unique archives of the solar history.

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REFERENCES

- Anders, E., & Ebihara, M. 1982, *Geochim. Cosmochim. Acta*, 46, 2363
 Anders, E., & Grevesse, N. 1989, *Geochim. Cosmochim. Acta*, 53, 197
 Becker, R. H. 1995a, in *Lunar Planet. Sci. XXVI* (Houston: Lunar Planet. Inst.), 89
 ———. 1995b, private communication
 Becker, R. H., & Pepin, R. O. 1989, *Geochim. Cosmochim. Acta*, 53, 1135
 ———. 1994, *Meteoritics*, 29, 724
 Benkert, J.-P., Baur, H., Signer, P., & Wieler, R. 1993, *J. Geophys. Res. (Planets)*, 98, 13,147
 Bernatowicz, T. J., Hohenberg, C. M., & Podosek, F. A. 1979, *Proc. 10th Lunar Planet. Sci. Conf.*, 1587
 Bochsler, P. 1987, *Phys. Scr.*, T18, 55
 ———. 1994, *Adv. Space Res.*, 14 (6), 161
 ———. 1995, private communication

- Bogard, D. D., Nyquist, L. E., Hirsch, W. C., & Moore, D. R. 1973, *Earth Planet. Sci. Lett.*, 21, 52
- Brenemann, H., & Stone, E. C. 1985, *ApJ*, 299, L57
- Brilliant, D. R., Franchi, I. A., & Pillinger, C. T. 1994, *Meteoritics*, 29, 718
- Cameron, A. G. W. 1982, in *Essays in Nuclear Astrophysics*, ed. C. A. Barnes, D. D. Clayton, & D. N. Schramm (Cambridge: Cambridge Univ. Press), 23
- Cerutti, H. 1974, Ph.D. thesis, Univ. Bern
- Cook, W. R., Stone, E. C., & Vogt, R. E. 1980, *ApJ*, 238, L97
- DesMarais, D. J., Hayes, J. M., & Meinschein, W. G. 1974, in *Lunar Sci. V* (Houston: Lunar Sci. Inst.) 168
- Eberhardt, P., et al. 1972, *Proc. Third Lunar Sci. Conf.*, 1821
- Eugster, O., Michel, T., & Niedermann, S. 1992, *Proc. NIPR Symp. Antarctic Meteorites* (Tokyo: Natl. Inst. Polar Res) 5, 23
- Feldman, U. 1992, *Phys. Scr.*, 46, 202
- Feldman, U., & Widing, K. G. 1990, *ApJ*, 363, 292
- Frick, U., Becker, R. H., & Pepin, R. O. 1988, *Proc. 18th Lunar Planet. Sci. Conf.*, 87
- Geiss, J. 1982, *Space Sci. Rev.*, 33, 201
- Geiss, J., & Bochsler, P. 1982, *Geochim. Cosmochim. Acta*, 46, 529
- . 1985, in *Isotopic Ratios in the Solar System* (Paris: Cepadues Editions), 213
- . 1991, in *The Sun in Time*, ed. C. P. Sonett et al. (Tucson: Univ. Arizona Press), 98
- Geiss, J., Bühler, F., Cerutti, H., Eberhardt, P., & Filleux, C. 1972, *Apollo 16 Prelim. Sci. Rep.* (NASA SP-315), 14
- Geiss, J., Gloeckler, G., & von Steiger, R. 1994, *Phil. Trans. R. Soc. London, A*, 349, 213
- Gloeckler, G., Ipavich, F. M., Hamilton, D. C., Wilken, B., & Kremser, G. 1989, *Eos: Trans. AGU*, 70, 424
- Hintenberger, H., Weber, H. W., & Schultz, L. 1974, *Proc. Fifth Lunar Sci. Conf.*, 2005
- Hovestadt, D. 1974, in *Solar Wind III*, ed. C. T. Russell (Los Angeles: UCLA), 2
- Jordan, J. L., & Heymann, D. 1975, *Proc. Sixth Lunar Sci. Conf.* 2201
- Kerridge, J. F. 1980, in *Proc. Conf. Ancient Sun*, ed. R. O. Pepin, J. A. Eddy, & R. B. Merrill (New York: Pergamon), 475
- Kerridge, J. F. 1993, *Rev. Geophys.*, 31, 423
- Kerridge, J. F., Bochsler, P., Eugster, O., & Geiss, J. 1992, *Proc. 22d Lunar Planet. Sci. Conf.*, 239
- Marsch, E., von Steiger, R., & Bochsler, P. 1995, *A&A*, in press
- Marti, K. 1969, *Science*, 166, 1263
- Marti, K., Wilkening, L. L., & Suess, H. E. 1972, *ApJ*, 173, 445
- Meyer, J. P. 1981, *Proc. 17th Int. Cosmic Ray Conf. (Paris)*, 3, 149
- . 1993, in *Origin and Evolution of the Elements*, ed. N. Prantzos, E. Vangioni-Flam, & M. Cassé (Cambridge: Cambridge Univ. Press), 26
- Murer, C., Baur, H., Signer, P., Wieler, R., & Lipschutz, M. E. 1994, *Meteoritics*, 29, 506
- Murer, C., Baur, H., & Wieler, R. 1995, *Meteoritics*, Vol. 30, in press
- Norris, S. J., Swart, P. K., Wright, I. P., Grady, M. M., & Pillinger, C. T. 1983, *Proc. 14th Lunar Planet. Sci. Conf.* B200
- Pedroni, A., & Begemann, F. 1994, *Meteoritics*, 29, 632
- Petrowski, C., Kerridge, J. F., & Kaplan, I. R. 1974, *Proc. Fifth Lunar Sci. Conf.*, 1939
- Rider, P. E., Pepin, R. O., & Becker, R. H. 1995, *Geochim. Cosmochim. Acta*, submitted
- Selesnick, R. S., Cummings, A. C., Cummings, J. R., Leske, R. A., Mewaldt, R. A., & Stone, E. C. 1993, *ApJ*, 418, L45
- Signer, P., Baur, H., Derksen, U., Etique, P., Funk, H., Horn, P., & Wieler, R. 1977, *Proc. Eighth Lunar Sci. Conf.* 3657
- Signer, P., Baur, H., & Wieler, R. 1993, in *Proc. Alfred O. Nier Symp. on Inorganic Mass Spectrometry* (Durango), ed. D. J. Rokop (LA-12522-C; Los Alamos: LANL), 181
- Stone, E. C. 1989, in *AIP Conf. Proc. 183, Cosmic Abundances of Matter*, ed. C. J. Waddington (New York: AIP), 72
- Veck, N. J., & Parkinson, J. H. 1981, *MNRAS*, 197, 41
- von Steiger, R., & Geiss, J. 1989, *A&A*, 225, 222
- Webber, W. R. 1975, *Proc. 14th Int. Cosmic Ray Conf. (Munich)*, 5, 1597
- Wieler, R., & Baur, H. 1994a, *Meteoritics*, 29, 570
- . 1994b, *Meteoritics*, 29, 550
- Wieler, R., Baur, H., & Signer, P. 1986, *Geochim. Cosmochim. Acta*, 50, 1997