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Production rates for cosmogenic krypton and argon isotopes in H-chondrites with known ^{36}Cl-^{36}Ar ages

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Abstract: We present physical model calculations for the production of cosmogenic Kr isotopes in stony meteorites and compare the model results with measured data for bulk samples of 12 H-chondrites which recently had been investigated for their ^{36}Cl-^{36}Ar cosmic-ray exposure ages and light noble gas production rates. The correlation between $P(^{81}\mathrm{Kr})/P(^{83}\mathrm{Kr})$ and $P(^{78}\mathrm{Kr})/P(^{83}\mathrm{Kr})$ modelled here is significantly different from the classical relation commonly used to derive ^{81}Kr-Kr exposure ages. For both relations, the ^{81}Kr ages scatter considerably around the respective ^{36}Cl-^{36}Ar ages, but the new relation on average yields a somewhat better agreement between ^{81}Kr-Kr and ^{36}Cl-^{36}Ar ages. The calculations combined with concentration measurements of the main target elements for the production of cosmogenic Kr (Rb, Sr, Y, Zr, and Nb) show that target element chemistry does hardly influence the isotopic composition of cosmogenic Kr in bulk chondrites. These calculations also confirm earlier conclusions that the isotopic systematics of cosmogenic Kr in lunar samples are applicable for chondrites too.

We derived an average ^{38}Ar production rate at average shielding ($^{22}\mathrm{Ne}/^{21}\mathrm{Ne}=1.11$) of $(0.0431\pm0.0035)\times10^{-8}\,\mathrm{cm^3\,STP/(g\times Myr)}$.

key words: cosmogenic nuclides, cosmic-ray exposure ages, Kr^{81}-ages, Ar^{38} production rates, H-chondrites

1. Introduction

Cosmic-ray produced nuclides in meteorites provide important constraints on meteorite origin, orbital evolution, and parent body histories. However, an accurate interpretation of measured cosmogenic nuclide concentrations requires a good knowledge of the cosmogenic production rates. An elegant way to determine cosmic-ray exposure ages is the ^{81}Kr-Kr method. This technique, which was first proposed by Marti (1967), is based on the assumption that the production rate ratio $P(^{81}\mathrm{Kr})/P(^{83}\mathrm{Kr})$ can be determined from measured ^{78}Kr-^{80}Kr-^{82}Kr-^{83}Kr concentrations by using one of the following equations (Marti, 1967; Marti and Lugmair, 1971):

$$P(^{81}\mathrm{Kr})/P(^{83}\mathrm{Kr}) = 0.95 \times \left(\frac{^{81}\mathrm{Kr} + {}^{82}\mathrm{Kr}}{2 \times {}^{83}\mathrm{Kr}}\right), \tag{1}$$

and

$$P(^{81}\mathrm{Kr})/P(^{83}\mathrm{Kr}) = 1.262 \times \frac{^{78}\mathrm{Kr}}{^{83}\mathrm{Kr}} + 0.381, \tag{2}$$

where all Kr concentrations refer to the spallogenic component. These relations allow the determination of shielding corrected cosmic-ray exposure ages based on a single Kr analysis. The factor of 0.95 in eq. (1) represents the isobaric fraction yield of ^{81}Kr (Marti, 1967). This value has recently been re-determined to 0.92 for chondritic abundances of the relevant target elements (unpublished data from the Bordeaux laboratory). Equation (2) is insensitive to neutron capture production of ^{80}Kr and ^{82}Kr by reactions on Br, which might compromise the analyses of spallogenic Kr in large and/or Br-rich meteorites. Equation (1) is based on nuclear systematics and should therefore be valid for a large variety of samples (Marti, 1967). In contradistinction, eq. (2), which is commonly used to determine ^{81}Kr-Kr exposure ages, was determined from Apollo 12 lunar samples and is therefore strictly valid only for samples that have the same relative abundances of the major target elements as Apollo 12 samples (Marti and Lugmair, 1971). This is not to be expected a priori because the relative abundances of the major target elements in Apollo 12 samples differ substantially from those in chondrites. For example, the Rb/Sr ratio in Apollo 12 samples is about 30 times lower than in H-chondrites. Therefore, Rubidium contributes substantially to the Kr production in chondrites but hardly so in lunar samples. Despite such differences, eqs. (1) and (2) are today widely used for meteorites also, mainly based on work by Finkel *et al.* (1978), who demonstrated that the Kr spallation systematics derived from Apollo 12 samples to first order are also valid for the two chondrites San Juan Capistrano and St.Severin. Furthermore, apart from a few early studies (Eugster *et al.*, 1969; Marti *et al.*, 1969; Finkel *et al.*, 1978), ^{81}Kr-Kr exposure ages of meteorites have never been verified by ages obtained using other cosmogenic nuclide pairs, *e.g.* ^{10}Be-^{21}Ne, ^{26}Al-^{21}Ne, ^{36}Cl-^{36}Ar, measured in the same aliquots. Rare cases where ^{26}Al-^{21}Ne and ^{81}Kr-Kr ages have been determined on *different* samples of the same meteorite (Ochansk, Xingyang, Elenovka, Mocs, Otis, St.Severin) reveal differences of up to 25%, suggesting some inherent problems in either of the two dating systems. In addition, it is not yet clear whether eqs. (1) and (2) hold for the whole range of shielding conditions usually covered by meteorites. Testing the dependence of the Kr production rates and isotopic ratios on shielding, Eugster (1988) presented a correlation between $P(^{81}\mathrm{Kr})$ and $P(^{83}\mathrm{Kr})$ versus ^{22}Ne/^{21}Ne for ordinary chondrites. From these data and from the only available ^{81}Kr depth profile in Knyahinya (Lavielle *et al.*, 1997), it is unclear whether eqs. (1) and (2) hold for the entire range of shielding depths relevant for meteorites.

The goal of this work therefore is to independently test eqs. (1) and (2) using purely physical model calculations for the production of cosmogenic Kr in stony meteorites. The calculations are based on the particle spectra for primary and secondary particles and the excitation functions for the relevant nuclear reactions. For proton-induced reactions these were derived by irradiation experiments using mono-energetic proton beams. The neutron-induced cross sections were derived from numerous Kr analyses of pure element targets exposed within artificial meteorites isotropically irradiated with 1600 MeV protons (Gilabert *et al*., 2002). The model calculations also allow us to test the dependence of the relation between $P(^{81}Kr)/P(^{83}Kr)$ and $P(^{78}Kr)/P(^{83}Kr)$ on the relative concentrations of the main target elements for cosmogenic Kr production, *i.e*. Rb, Sr, Y, and Zr. The calculations performed in this study thereby extend our modelled database for the cosmogenic production of radionuclides and light noble gas isotopes in stony meteorites (Leya *et al*., 2000) and lunar rocks (Leya *et al*., 2001b).

The second purpose of this work has been the determination of ^{81}Kr-Kr exposure ages in 12 H-chondrites, which recently have been analysed for their ^{36}Cl-^{36}Ar cosmic-ray exposure ages (Graf *et al*., 2001), in order to compare the model calculations with independently obtained exposure ages. The ^{36}Cl-^{36}Ar method is particularly reliable because the production rate ratio of cosmogenic $^{36}Cl/^{36}Ar$ in the metal phase of chondrites is independent on shielding (Schaeffer and Heymann, 1965; Lavielle *et al*., 1999; Leya *et al*., 2000). Furthermore, the light noble gas production rates of these chondrites have also been determined recently (Leya *et al*., 2001a), giving additional information on the shielding of the analysed meteorites. These data also allowed us to exclude that any of the meteorites studied obviously had suffered a complex exposure history. Note, that the preatmospheric radius of Uberaba must have been more than a meter, making this meteorite somewhat special for cosmogenic nuclide studies (Leya *et al*., 2001). Note also that Cangas de Onis contains solar gases, which might indicate a complex exposure history. In addition, we analysed a sample of the L/LL5 chondrite Knyahinya, which has been extensively studied for the depth dependency of the production rates (*e.g*., Lavielle *et al*., 1997; Graf *et al*., 1990a).

2. Experimental

The meteorites studied are listed in Table 1. Apart from Knyahinya, all fall around the prominent 7 Myr peak in the exposure age histogram of H-chondrites, since exploring details of this peak was the original purpose of the determination of their ^{36}Cl-^{36}Ar ages (Graf *et al*., 2001). Unfortunately, here the rather low exposure ages lead to very substantial corrections for trapped Kr, limiting the precision of the ^{81}Kr ages, as we will see below.

The samples were prepared by gently crushing ~1 g of bulk meteorite in an agate mortar. The samples were then wrapped in ~60 mg of commercial Al foil and loaded into an all-metal (except for a glass window) noble gas extraction system. The noble gas measurements were performed at the ETH Zürich. In order to reduce atmospheric surface contamination, the samples were preheated for ~20 h at ~80°C. Gases were released in two steps at 600°C and 1700°C (both for 15 min). The 600°C step released almost all remaining atmospheric gases but also up to 10% of the cosmogenic He and Ne. In contrast, cosmogenic Ar, Kr, and Xe were hardly released in the low temperature steps. The 600°C fractions were not analysed routinely because the large concen-

Table 1. Description of meteorites used in this study.

Sample		Mass [mg]	Source
Nassirah	H4	1007.60	Muséum National d'Histoire Naturelle, Paris
Bath	H4	1068.5	Naturhistorisches Museum, Wien
Canellas	H4	1061.50	Muséum National d'Histoire Naturelle, Paris
Ochansk	H4	804.24	The National History Museum, London
Cereseto	H5	1278.60	Naturhistorisches Museum, Wien
Kerilis	H5	1028.30	Muséum National d'Histoire Naturelle, Paris
Epinal	H5	1008.30	Muséum National d'Histoire Naturelle, Paris
Limerick	H5	807.30	The National History Museum, London
Cangas de Onis	H5	711.96	The National History Museum, London
Allegan	H5	1166.70	Muséum National d'Histoire Naturelle, Paris
Uberaba	H5	1000.00	Naturhistorisches Museum, Wien
Merua	H5	792.46	The National History Museum, London
Knyahinya	L/LL5	255.50	ETH Collection

trations of H_2O, CH_4, and CO_2 would increase the memory of the mass spectrometer and therefore compromise further measurements. The $^{84}Kr/^{132}Xe$ ratios in the 1700 °C steps are usually below 1, indicating that non-cosmogenic Kr is mainly of meteoritic origin (see Section 3).

Gases were first cleaned on a Zr-Ti getter at 280°C and then on two Zr-Al getters (SAES®) at 300°C. During the He-Ne analyses Ar, Kr, and Xe were adsorbed on activated charcoal held at the temperature of boiling nitrogen. The Ar fraction was separated from Kr-Xe using a cold trap held at −120°C. Kr and Xe were analysed in the same fraction. Sample gas amounts were determined by peak height comparisons with signals from known amounts of standard gases. Since some cosmogenic He and Ne is already released at 600°C, proper concentrations for cosmogenic He and Ne cannot be given and the He-Ne data are thus not discussed here.

About 100 mg-sized aliquots of the samples were dissolved and Rb, Sr, Y, Zr, Nb (and Ba, not discussed here any further) were separated using standard column chemistry. The element concentrations were measured via Quadrupole ICP-MS using Rh as an external standard. The uncertainties in the element concentrations are about 10%.

3. Results

System blanks were determined by analysing ~60 mg of Al foil with the same heating schedule as used for the samples. Typical blank values are given in Table 2. The blanks usually were below 1.5% of sample gas amounts, adding only negligible uncertainties to the latter. For ^{81}Kr, however, the blanks sometimes reach up to 14% and varied by about a factor of 3, significantly contributing to the uncertainties of the ^{81}Kr-Kr ages.

Cosmogenic $^{36,38}Ar$ and $^{78,80,81,82,83,84}Kr$ concentrations are calculated from mea-

Table 2. Typical noble gas blanks.

^{36}Ar	^{38}Ar	^{40}Ar	^{78}Kr	^{80}Kr	^{81}Kr	^{82}Kr	^{83}Kr	^{84}Kr	^{86}Kr
200	50	78000	8×10^{-3}	0.04	3×10^{-4}	0.2	0.2	1.2	0.3

Noble gas concentrations in 10^{-12} cm^3 STP.

Table 3. Ar in bulk meteorites.

Sample		Gas concentrations in 10^{-8} cm^3STP/g				Cosmogenic fraction	
		Mass	^{36}Ar	^{40}Ar	$^{36}Ar/^{38}Ar$	^{36}Ar	^{38}Ar
Nassirah	H4	1007.60	1.17	4560	2.21	0.228	0.353
Bath	H4	1068.5	*1.00*	*825*	*2.26*	*0.196*	*0.290*
Canellas	H4	1061.50	1.07	3650	2.21	0.207	0.322
Ochansk	H4	804.24	2.16	4975	3.13	0.190	0.292
Cereseto	H5	1278.60	1.14	3002	2.47	0.179	0.282
Kerilis	H5	1028.30	1.52	966	2.73	0.194	0.309
Epinal	H5	1008.30	4.21	1392	3.78	0.223	0.367
Limerick	H5	807.30	1.82	4904	2.84	0.202	0.311
Cangas de Onis	H5	711.96	3.78	4539	4.30	0.142	0.219
Allegan	H5	1166.70	1.25	4882	2.91	0.142	0.222
Uberaba	H5	1000.0	*0.88*	*1192*	*3.15*	*0.088*	*0.130*
Merua	H5	792.46	1.22	3950	2.61	0.176	0.271

The concentrations are in units 10^{-8} cm^3 STP/g. Uncertainties in the absolute amounts are ±4%, in the isotopic ratios ±2%. Cosmogenic ^{36}Ar and ^{38}Ar were calculated using a two component deconvolution with $^{36}Ar/^{38}Ar_{(tr)}=5.32$ and $^{36}Ar/^{38}Ar_{(cos)}=0.63$, respectively. Numbers in italics are lower limits only due to a possible gas release in the 600℃ temperature step.

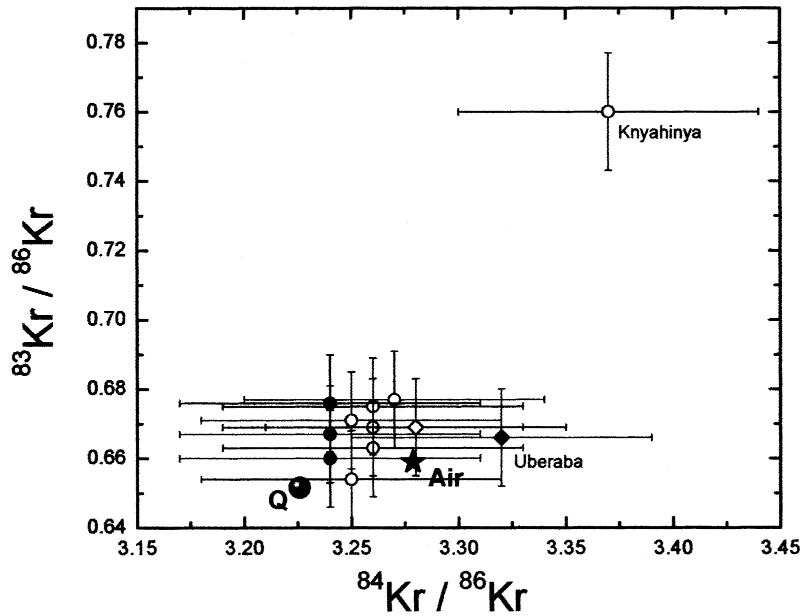

Fig. 1. Measured data for $^{83}Kr/^{86}Kr$ vs. $^{84}Kr/^{86}Kr$ for 12 H-chondrites and the L/LL5-chondrite Knyahinya. The open circles are for Limerick, Cangas de Onis, Canellas, Merua, Kerilis, Bath and Knyahinya. The data for Nassirah, Ochansk, Cereseto, and Epinal are shown as filled circles (Nassirah and Cereseto plotting at identical positions). The data for Allegan and Uberaba are indicated by open and filled diamonds, respectively. Also shown are the isotopic ratios for "phase Q" (Busemann et al., 2000) and air (Basford et al., 1973).

Table 4. Kr concentrations and isotopic compositions in bulk H-chondrites.

Sample		$^{78}Kr/^{86}Kr$	$^{80}Kr/^{86}Kr$	$^{81}Kr/^{86}Kr$	$^{82}Kr/^{86}Kr$	$^{83}Kr/^{86}Kr$	$^{84}Kr/^{86}Kr$	^{86}Kr 1)
Nassirah	H4	$(2.36 \pm 0.05)\times10^{-2}$	0.140 ± 0.003	$(6.28 \pm 0.20)\times10^{-4}$	0.674 ± 0.014	0.676 ± 0.014	3.24 ± 0.07	32.4 ± 1.3
Bath	H4	$(2.28 \pm 0.05)\times10^{-2}$	0.139 ± 0.003	$(3.78 \pm 0.12)\times10^{-4}$	0.666 ± 0.014	0.677 ± 0.014	3.27 ± 0.07	28.9 ± 1.2
Canellas	H4	$(2.53 \pm 0.07)\times10^{-2}$	0.140 ± 0.003	$(4.82 \pm 0.15)\times10^{-4}$	0.669 ± 0.014	0.675 ± 0.014	3.26 ± 0.07	33.1 ± 1.3
Ochansk	H4	$(2.09 \pm 0.05)\times10^{-2}$	0.137 ± 0.003	$(2.78 \pm 0.17)\times10^{-4}$	0.666 ± 0.014	0.667 ± 0.014	3.24 ± 0.07	67.3 ± 2.7
Cereseto	H5	$(2.73 \pm 0.11)\times10^{-2}$	0.138 ± 0.003	$(3.89 \pm 0.13)\times10^{-4}$	0.668 ± 0.014	0.676 ± 0.014	3.24 ± 0.07	38.6 ± 1.6
Kerilis	H5	$(2.29 \pm 0.06)\times10^{-2}$	0.133 ± 0.003	$(2.65 \pm 0.13)\times10^{-4}$	0.662 ± 0.014	0.663 ± 0.014	3.26 ± 0.07	38.6 ± 1.6
Epinal	H5	$(2.31 \pm 0.07)\times10^{-2}$	0.133 ± 0.003	$(2.45 \pm 0.16)\times10^{-4}$	0.664 ± 0.014	0.660 ± 0.014	3.24 ± 0.07	55.6 ± 2.2
Limerick	H5	$(2.28 \pm 0.06)\times10^{-2}$	0.138 ± 0.003	$(3.53 \pm 0.15)\times10^{-4}$	0.670 ± 0.014	0.671 ± 0.014	3.25 ± 0.07	45.4 ± 1.8
Cangas de Onis	H5	$(2.10 \pm 0.05)\times10^{-2}$	0.160 ± 0.004	$(2.94 \pm 0.17)\times10^{-4}$	0.670 ± 0.014	0.654 ± 0.014	3.25 ± 0.07	55.6 ± 2.3
Allegan	H5	$(2.21 \pm 0.05)\times10^{-2}$	0.138 ± 0.003	$(5.08 \pm 0.16)\times10^{-4}$	0.669 ± 0.014	0.669 ± 0.014	3.28 ± 0.07	36.0 ± 1.5
Uberaba	H5	$(3.27 \pm 0.05)\times10^{-2}$	0.143 ± 0.003	$(2.59 \pm 0.31)\times10^{-4}$	0.675 ± 0.014	0.666 ± 0.014	3.32 ± 0.07	27.8 ± 1.1
Merua	H5	$(2.19 \pm 0.05)\times10^{-2}$	0.141 ± 0.003	$(4.36 \pm 0.24)\times10^{-4}$	0.667 ± 0.014	0.669 ± 0.014	3.26 ± 0.07	33.7 ± 1.4
Knyahinya	L/LL5	$(3.70 \pm 0.11)\times10^{-2}$	0.188 ± 0.005	$(4.96 \pm 0.29)\times10^{-4}$	0.736 ± 0.016	0.760 ± 0.017	3.37 ± 0.07	32.3 ± 1.3

		Cosmogenic fraction				
Sample		$^{78}Kr/^{83}Kr$	$^{80}Kr/^{83}Kr$	$^{82}Kr/^{83}Kr$	$^{84}Kr/^{83}Kr$	^{84}Kr 1)
Nassirah	H4	0.172 ± 0.017	0.530 ± 0.031	0.917 ± 0.094	0.42 ± 0.68	0.33 ± 0.53
Bath	H4	0.133 ± 0.012	0.469 ± 0.021	0.563 ± 0.142	1.59 ± 0.49	1.16 ± 0.31
Canellas	H4	0.248 ± 0.011	0.554 ± 0.146	0.727 ± 0.959	1.28 ± 3.71	0.98 ± 2.74
Ochansk	H4	0.094 ± 0.008	0.649 ± 0.061	0.934 ± 0.207	0.64 ± 1.10	0.65 ± 1.12
Cereseto	H5	0.316 ± 0.020	0.448 ± 0.019	0.670 ± 0.152	0.42 ± 0.35	0.39 ± 0.33
Kerilis	H5	0.298 ± 0.203	0.524 ± 0.025	0.910 ± 0.309	2.66 ± 1.06	1.14 ± 0.37
Epinal	H5	0.470 ± 0.104	0.721 ± 0.378	1.496 ± 3.905	1.16 ± 0.60	0.52 ± 4.61
Limerick	H5	0.180 ± 0.020	0.566 ± 0.173	0.935 ± 1.302	1.03 ± 4.48	0.89 ± 3.80
Cangas de Onis	H5	0.657 ± 0.445	25.5 ± 1.7	11.00 ± 8.51	11.6 ± 9.8	0.83 ± 0.44
Allegan	H5	0.157 ± 0.013	0.636 ± 0.033	0.929 ± 0.285	2.86 ± 0.96	1.74 ± 0.47
Uberaba	H5	-	-	-	-	-
Merua	H5	0.145 ± 0.011	0.808 ± 0.042	0.866 ± 0.240	1.72 ± 0.70	0.58 ± 0.36
Knyahinya	L/LL5	0.162 ± 0.003	0.559 ± 0.028	0.780 ± 0.046	1.32 ± 0.07	4.66 ± 0.15

1) The concentrations are in unit 10^{-12} cm^3 STP/g. Cosmogenic ^{78}Kr, ^{80}Kr, ^{82}Kr, ^{83}Kr, and ^{84}Kr were determined using a three-component deconvolution and assuming Kr from "phase Q" and air as the trapped endmembers. The "phase Q" data are from Busemann *et al.* (2000), the data for atmospheric Kr are from Basford *et al.* (1973). For the cosmogenic $^{86}Kr/^{83}Kr_{(cos)}$ a value of 0.0152 (Marti and Lugmair, 1971) is used.

Table 5. ^{36}Cl-^{36}Ar *ages,* $P(^{81}Kr)/P(^{83}Kr)$*, and* ^{81}Kr*-Kr ages.*

Sample		T_{36} [Myr] [1]	$^{81}Kr/^{83}Kr$	$P(^{81}Kr)/P(^{83}Kr)$ [2] (old correlation)	T_{81} [2] (old correlation)	$P(^{81}Kr)/P(^{83}Kr)$ [3] (new correlation)	T_{81} [3] (new correlation)
Nassirah	H4	8.77 ± 0.28	(2.54 ± 0.33)x10^-2	0.579 ± 0.057	7.52 ± 1.23	0.561 ± 0.055	7.29 ± 1.19
Bath	H4	7.62 ± 0.24	(1.41 ± 0.17)x10^-2	0.532 ± 0.048	12.4 ± 1.9	0.518 ± 0.047	12.1 ± 1.8
Canellas	H4	7.79 ± 0.24	(1.99 ± 0.21)x10^-2	0.672 ± 0.030	11.1 ± 1.3	0.646 ± 0.029	10.7 ± 1.2
Ochansk	H4	7.18 ± 0.23	(1.82 ± 0.33)x10^-2	0.484 ± 0.041	8.77 ± 1.76	0.474 ± 0.040	8.59 ± 1.72
Cereseto	H5	6.72 ± 0.21	(1.50 ± 0.20)x10^-2	0.755 ± 0.048	16.6 ± 2.5	0.722 ± 0.046	15.9 ± 2.3
Kerilis	H5	8.19 ± 0.27	(2.17 ± 0.51)x10^-2	0.733 ± 0.499	11.1 ± 8.0	0.702 ± 0.478	10.7 ± 7.7
Epinal	H5	10.20 ± 0.32	(2.98 ± 0.79)x10^-2	0.943 ± 0.209	10.4 ± 3.6	0.894 ± 0.198	9.90 ± 3.42
Limerick	H5	7.41 ± 0.26	(1.84 ± 0.29)x10^-2	0.589 ± 0.065	10.6 ± 2.0	0.570 ± 0.063	10.2 ± 2.0
Cangas de Onis	H5	6.69 ± 0.22	(1.42 ± 0.89)x10^-1	1.172 ± 0.794	3.71 ± 4.05	1.103 ± 0.747	3.49 ± 3.81
Allegan	H5	4.41 ± 0.15	(2.95 ± 0.38)x10^-2	0.561 ± 0.046	6.27 ± 0.96	0.544 ± 0.045	6.09 ± 0.93
Uberaba	H5	6.45 ± 0.21	(1.69 ± 0.13)x10^-2	-	-	-	-
Merua	H5	6.03 ± 0.19	(2.55 ± 0.30)x10^-2	0.546 ± 0.041	7.07 ± 0.99	0.531 ± 0.040	6.87 ± 0.96
Knyahinya	L/LL5		(4.34 ± 0.03)x10^-3	0.567 ± 0.010	43.1 ± 0.85	0.550 ± 0.018	41.8 ± 0.83

[1] The ^{36}Cl-^{36}Ar exposure ages are from Leya *et al.* (2001a), [2] Calculated using the established correlation given by Marti and Lugmair (1971), [3] Calculated using the new modelled correlation (eq. 3).

sured gas amounts by subtracting the trapped components. For the partitioning of the Ar components we assume $^{36}Ar/^{38}Ar_{(tr)}=5.32$ and $^{36}Ar/^{38}Ar_{(cos)}=0.63$. Due to the nearly complete release of atmospheric gases in the 600°C steps, the corrections for non-cosmogenic Ar are only very minor. The Ar data are compiled in Table 3.

Due to the rather low cosmic-ray exposure ages of the studied H-chondrites, subtracting non-cosmogenic Kr is crucial. Figure 1 shows the three-isotope plot $^{83}Kr/^{86}Kr$ *vs*. $^{84}Kr/^{86}Kr$. Also shown are the isotopic ratios for phase "Q" (Busemann *et al.*, 2000) and air (Basford *et al.*, 1973).

For Knyahinya, assuming either "Q" or air as trapped component leads only to a difference of about 6% in the ^{81}Kr-Kr exposure age. In contradistinction, in the 12 H-chondrites Kr is clearly dominated by the trapped component. Four of them, Nassirah, Ochansk, Cereseto, and Epinal (filled circles), have $^{84}Kr/^{86}Kr$ ratios identical to the value of phase "Q" within 1σ. Furthermore, their $^{84}Kr/^{132}Xe$ ratios are between 0.55 and 0.77, clearly indicating that the trapped component is almost purely meteoritic. For the six chondrites Limerick, Cangas de Onis, Canellas, Merua, Kerilis, and Bath (open circles) the $^{84}Kr/^{86}Kr$ ratios plot between "Q" and air. Also the $^{84}Kr/^{132}Xe$ ratios for these chondrites of between 0.6 and 1.07 are on average slightly higher than the ratios for Nassirah, Ochansk, Cereseto and Epinal, again indicating admixture of some atmospheric Kr and Xe. We therefore assume for the meteorites marked by open circles that the trapped component is a mixture of air and phase "Q" with $^{84}Kr/^{132}Xe \approx 0.56$ (the average value given by Nassirah, Cereseto and Ochansk, which show the lowest $^{84}Kr/^{132}Xr$ ratios of all studied meteorites). The mixing ratio is determined for each meteorite by its measured $^{84}Kr/^{132}Xe$ ratio. The $^{84}Kr/^{86}Kr$ ratio for Allegan (open diamond) closely matches the air-value, but its $^{84}Kr/^{132}Xe$ ratio of 0.75 indicates only minor atmospheric contribution. We therefore assume also for Allegan a mixture of atmospheric Kr and Kr-Q as the trapped component. For Uberaba (closed diamond), a reliable correction for trapped Kr is not possible. We will re-analyse this meteorite and not consider the present data here. The cosmogenic ratio $^{86}Kr/^{83}Kr_{(cos)}$ is assumed to be 0.0152 (Marti and Lugmair, 1971). The measured Kr isotopic concentrations and the deduced cosmogenic values for ^{78}Kr, ^{80}Kr, ^{82}Kr, ^{83}Kr, and ^{84}Kr are compiled in Table 4. The $^{81}Kr/^{83}Kr$ ratios together with ^{81}Kr-Kr ages are given in Table 5.

The blank corrections for ^{81}Kr were done by subtracting the average signal on mass 81 detected in various background and blank measurements from the ^{81}Kr sample signals.

4. Production rates of cosmogenic ^{38}Ar

With the cosmogenic ^{38}Ar concentrations (Table 3) and the ^{36}Cl-^{36}Ar cosmic-ray exposure ages (Table 5) we calculated cosmogenic ^{38}Ar production rates. As we already demonstrated in a previous study based on samples from the same meteorites, the ^{38}Ar production rates vary only little with shielding (Leya *et al.*, 2001a) and no clear trend of the ^{38}Ar production rates with $^{22}Ne/^{21}Ne$ was observed for the analysed H-chondrites. Nevertheless, we consider only those meteorites with "average" shielding, *i.e*. with a cosmogenic $^{22}Ne/^{21}Ne$ ratio measured in aliquot samples of 1.11 within

1σ (Table 4 in Leya *et al*., 2001a). These meteorites are Nassirah, Cannellas, Ochansk, Cereseto, Limerick, and Allegan and they yield an average ^{38}Ar production rate $<P38>$ $=(0.0431\pm0.0035)\times10^{-8}$ cm^3 STP/(g$\times$Myr). This value is 16% lower than that of 0.050×10^{-8} cm^3 STP/(g$\times$Myr) reported by Eugster (1988) but is in very good agreement with the values of 0.045×10^{-8} cm^3 STP/(g$\times$Myr) given by Graf *et al*. (1990b) and 0.043×10^{-8} cm^3 STP/(g$\times$Myr) published by Schultz *et al*. (1991). All three literature values also refer to average shielding conditions (^{22}Ne/^{21}Ne$=1.11$). Note that our $<P38>$ would be ~6% lower than the preferred value if all meteorites of this study would be considered (except Uberaba). Note also that the Ar data were obtained from samples with masses of around 1 g. Chemical inhomogeneities, on which earlier ^{38}Ar studies often suffered, should therefore not have compromised the production rates deduced here. We therefore recommend $<P38>=(0.0431\pm0.0035)$ $\times10^{-8}$ cm^3 STP/(g$\times$Myr) as the most likely value for H-chondrites at a mean shielding of ^{22}Ne/^{21}Ne$=1.11$.

5. ^{81}Kr-Kr exposure ages

5.1. *Exposure ages using the classical correlation*

The production rate ratios $P(^{81}\text{Kr})/P(^{83}\text{Kr})$ calculated from ^{78}Kr/^{83}Kr essentially according to eq. (2) are labelled "old correlation" in Table 5. We adopt, however, the new branching ratio of 0.92. The production rate ratios $P(^{81}\text{Kr})/P(^{83}\text{Kr})$ labelled "new correlation" in Table 5 are determined using the physical model calculations presented below. For the determination of ^{81}Kr-Kr exposure ages for both, old and the new correlation, we used the ^{81}Kr mean life of 0.330 ± 0.011 Myr (Baglin, 1993).

The ^{81}Kr-Kr age for Knyahinya of 43.1 ± 0.85 Myr is close to the value of 39.5 ± 1.0 Myr determined earlier by Lavielle *et al*. (1997) also using the ^{81}Kr-Kr method. Furthermore, a systematic study of cosmogenic Kr production in Gold Basin meteorites demonstrates that our ^{81}Kr-Kr ages are reproducible to within a few percent (data not shown). Figure 2a compares the ^{81}Kr-Kr ages (old correlation) with the ^{36}Cl-^{36}Ar ages of the 11 H chondrites considered here (Uberaba is rejected from discussion). For six of the 11 meteorites (Nassirah, Ochansk, Kerilis, Epinal, Cangas de Onis, and Merua), the ^{81}Kr-Kr and ^{36}Cl-^{36}Ar ages agree to within the 1σ uncertainty, although for Kerilis and Cangas de Onis the agreement mainly reflects the large uncertainties of their ^{81}Kr-Kr ages. For Limerick and Allegan the agreement is within 2σ and for Bath and Canellas T_{81} and T_{36} differ between 2 and 3σ. A large discrepancy exists for Cereseto, whose ^{81}Kr-Kr age is higher than the ^{36}Cl-^{36}Ar age by about 4σ. Considering all 11 meteorites gives a mean ratio $<T_{81}/T_{36}>=1.32\pm0.49$; calculating the average without Cereseto and Cangas de Onis results in $<T_{81}/T_{36}>=1.28\pm0.24$. In both cases the stated uncertainty is the error of the mean.

5.2. *Model calculations for cosmogenic Kr production and a new equation for determining ^{81}Kr-Kr exposure ages*

To test relation (2) we determined the rates for the production of cosmogenic Kr isotopes from Rb, Sr, Y, and Zr using a physical model. The model is based on the particle spectra of primary and secondary particles and the excitation functions for the

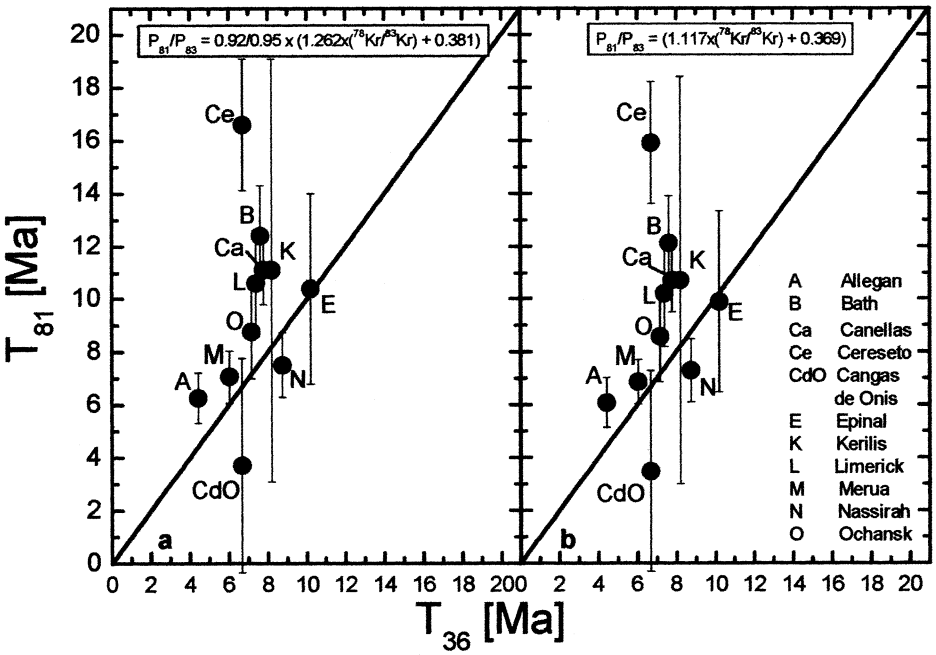

Fig. 2. Comparison of ^{81}Kr-Kr and ^{36}Cl-^{36}Ar cosmic-ray exposure ages of H4- and H5-chondrites. The ^{81}Kr-Kr ages shown in panel (a) are calculated according to Marti and Lugmair (1971) using eq. (2) but adopting the new estimate for the isobaric yield of ^{81}Kr. The ^{81}Kr-Kr ages shown in panel (b) are calculated using the modelled relation between P(^{81}Kr)/P(^{83}Kr) and P(^{78}Kr)/P(^{83}Kr) given in eq. (3). All ^{81}Kr-Kr ages were determined using a ^{81}Kr mean life of $\tau_{81}=0.330\pm0.011$ (Baglin, 1993).

relevant nuclear reactions. The model is described in detail by Leya *et al.* (2000, 2001b). The cross section database for the reactions relevant for the production of Kr isotopes has been compiled by Neumann (1999) and is, for the neutron-induced reactions, based on the Kr analyses of targets irradiated by 1.6 GeV protons within artificial meteoroids (Gilabert *et al.*, 2002). Here we limit ourselves to the discussion of the production rate ratios ^{81}Kr/^{83}Kr and ^{78}Kr/^{83}Kr and their dependence on the target chemistry. The depth- and size-dependent elemental production rates for stony meteoroids will be given in a subsequent paper.

Figure 3 shows the modelled relation between ^{81}Kr/^{83}Kr and ^{78}Kr/^{83}Kr for meteorites with radii between 5 cm and 120 cm and average H-chondrite chemistry. All data representing different meteoroid sizes and shielding depths can well be described by a straight line:

$$P(^{81}\mathrm{Kr})/P(^{83}\mathrm{Kr}) = 1.117 \times \frac{^{78}\mathrm{Kr}}{^{83}\mathrm{Kr}} + 0.369. \quad (3)$$

This relation is also linear but significantly different from eq. (2). $P(^{81}\mathrm{Kr})/P(^{83}\mathrm{Kr})$

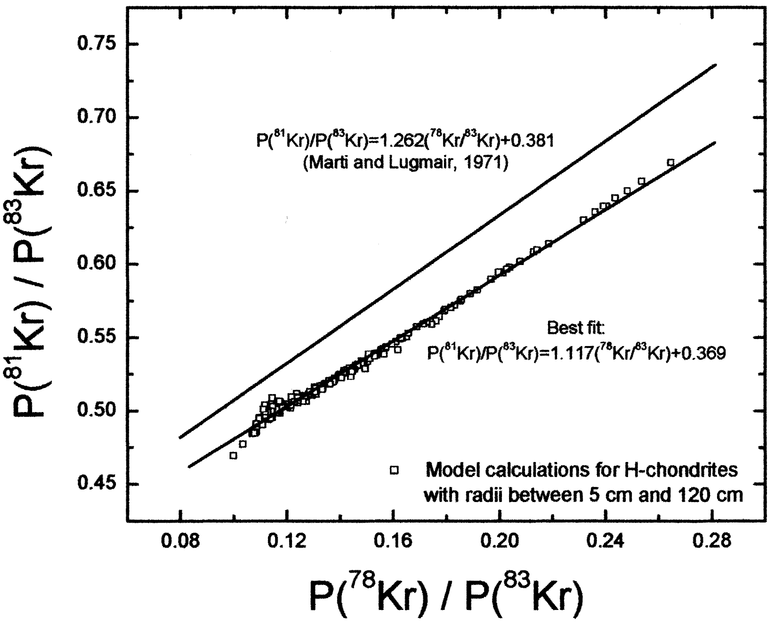

Fig. 3. Modelled isotopic systematics of cosmogenic Kr in H-chondrites with radii between 5 cm and 120 cm. The best-fit line through the modelled data is significantly different from the correlation proposed by Marti and Lugmair (1971) for Apollo 12 rocks.

ratios calculated according to relation (3) are labelled "new correlation" in Table 5. A comparison of the new ^{81}Kr-Kr ages with the ^{36}Cl-^{36}Ar ages is shown in Fig. 2b. Again, for six of 11 meteorites (Nassirah, Ochansk, Kerilis, Epinal, Cangas de Onis, Merua), ^{36}Cl-^{36}Ar ages and ^{81}Kr-Kr ages agree to within 1σ. For Limerick, Allegan, and Canellas agreement is within 2σ, for Bath within 3σ and for Cereseto only within about 4σ. The grand average $<T_{81}/T_{36}>$ ratio for all 11 meteorites is 1.28 ± 0.47; the average without Cereseto and Cangas de Onis results in 1.24 ± 0.23. In each case the stated uncertainty is the error of the mean. Therefore, ^{81}Kr-Kr cosmic-ray exposure ages calculated according to relation (3) agree slightly better with T_{36} than do conventional ^{81}Kr ages. However, using the new correlation does not reduce the scatter in T_{81}/T_{36}. We therefore used the model calculations to check whether $P(^{81}\text{Kr})/P(^{83}\text{Kr})$ and/or $P(^{78}\text{Kr})/P(^{83}\text{Kr})$ might depend on the relative concentrations of the main target elements for cosmogenic Kr production, *i.e.* Rb, Sr, Y, and Zr. If so, the observed scatter between T_{81} and T_{36} might be explained by varying target element concentrations.

Figure 4 shows the modelled correlation of $P(^{81}\text{Kr})/P(^{83}\text{Kr})$ *vs.* $P(^{78}\text{Kr})/P(^{83}\text{Kr})$ for H-chondrites according to eq. (3). The grey area shown in Fig. 4 indicates the range of isotopic ratios modelled for targets having 10 times and 0.1 times the H-chondritic Rb, Sr, Y, and Zr concentrations, respectively. Also shown is the modelled correlation for Apollo 12 lunar samples. It can be seen that the correlation depends only little on the relative target element concentrations. In order to quantify whether the observed scatter between T_{36} and T_{81} might be due to varying target element concentrations, we measured the Rb, Sr, Y, Zr, Nb (and Ba) concentrations in aliquots of the samples. The results are given in Table 6. The Rb, Sr, Y, Zr, and Nb concentrations in the 12 H-chondrites vary between 1.7–3.8 ppm, 9.3–13.6 ppm, 1.7–2.5 ppm, 4.9–8.7 ppm, and 0.2–0.3 ppm, respectively. The results are in good agreement with typical ranges for H-chondrites given by Mason (1979). Furthermore, the range measured for the Ba concentrations of 4.2–6.2 ppm also is in good agreement with the

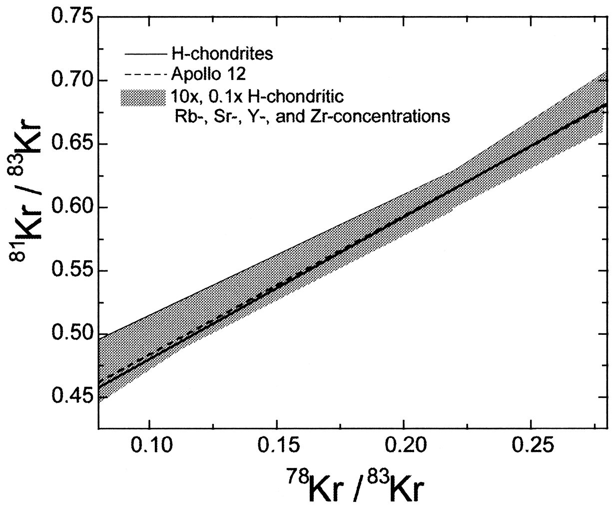

Fig. 4. Modelled isotopic systematics of cosmogenic Kr isotopes. The solid line is the best fit to the modelled data for H-chondrites with radii between 5 cm and 120 cm. The shaded grey area indicates the range of modelled isotopic ratios for samples having 10 and 0.1 times H-chondritic Rb-, Sr-, Y-, and Zr-concentrations, respectively (the three other elements in each case remaining in chondritic proportions). The dashed line indicates the modelled results for Apollo 12 lunar samples. The results clearly indicate that the modelled relation depends only very little on the relative concentrations of the main target elements. Equation (3) is therefore well suited to determine ^{81}Kr-Kr cosmic-ray exposure ages for a wide variety of meteoritic and lunar samples.

Table 6. Rb, Sr, Y, Zr, Nb, and Ba concentrations[1].

Name		Weight [mg]	Rb	Sr	Y	Zr	Nb	Ba
Nassirah	H4	9.94	2.3	11.6	2.4	7.2	0.2	4.5
Bath	H4	10.04	2.7	12.4	2.2	6.7	0.3	5.0
Canellas	H4	9.83	2.6	13.6	2.3	8.7	0.3	4.2
Ochansk	H4	10.45	2.4	12.4	2.5	6.3	0.4	4.2
Cereseto	H5	10.73	2.0	9.3	1.7	4.9	0.2	4.5
Kerilis	H5	10.92	3.8	12.1	2.1	6.3	0.3	6.2
Epinal	H5	10.65	3.7	11.9	2.2	6.3	0.3	5.2
Limerick	H5	14.35	2.3	10.1	1.9	5.2	0.3	4.6
Cangas de Onis	H5	10.60	3.8	12.1	2.4	6.6	0.3	4.5
Allegan	H5	13.50	1.7	9.4	1.6	5.7	0.2	6.4
Uberaba	H5	12.20	2.8	11.2	1.7	6.1	0.3	5.1
Merua	H5	10.07	3.0	12.3	2.1	6.1	0.3	6.2

[1]Element concentration in [ppm]

data for other H-chondrites, 3.2–5.3 ppm, given by Mason (1979).

The observed variations in Rb, Sr, Y, and Zr concentrations (Nb is not discussed due to lack of model calculations) correspond to variations in the ^{81}Kr-Kr exposure ages of less than 2%, 2‰, 3‰, and 1‰, respectively. Therefore, any effects of variable Rb, Sr, Y, and Zr concentrations on the ^{81}Kr-Kr exposure ages in chondrites are much too small to explain the scatter observed in T_{81}/T_{36}.

Since the pioneering days of ^{81}Kr-Kr dating it has been assumed that for meteorites and lunar samples the same relation between $P(^{81}\text{Kr})/P(^{83}\text{Kr})$ and $P(^{78}\text{Kr})/P(^{83}\text{Kr})$ holds (Marti and Lugmair, 1971). This assumption is not trivial because lunar rocks and meteorites differ significantly in their relative Rb, Sr, Y, and Zr concentrations. The modelled relation $P(^{81}\text{Kr})/P(^{83}\text{Kr})$ *vs.* $P(^{78}\text{Kr})/P(^{83}\text{Kr})$ for lunar samples is shown in Fig. 4 (labelled "Apollo 12"). It can be seen that the modelled correlation for Apollo 12 lunar samples is indeed nearly indistinguishable from that for meteorites; the differences between $P(^{81}\text{Kr})/P(^{83}\text{Kr})$ for a given $P(^{78}\text{Kr})/P(^{83}\text{Kr})$ being less than 1%. We therefore conclude that eq. (3) can be used to calculate ^{81}Kr-Kr cosmic-ray exposure ages for H-, L-, and LL-chondrites as well as for lunar samples without further adjustments.

6. Conclusions and outlook

We modelled the production systematics of cosmogenic Kr isotopes with a purely physical approach, based on differential flux densities of primary and secondary particles and the excitation functions of the relevant nuclear reactions. The model results were tested with ^{81}Kr-Kr analyses of a number of H-chondrites with known (shielding-independent) ^{36}Cl-^{36}Ar ages.

The model calculations predict essentially a linear correlation between $P(^{81}\text{Kr})/P(^{83}\text{Kr})$ and $P(^{78}\text{Kr})/P(^{83}\text{Kr})$ over a wide range of isotopic ratios and shielding conditions. Such a linear relationship had already been proposed by Marti and Lugmair (1971), based on data from Apollo 12 lunar samples. Our new correlation differs significantly from this classical correlation, yielding ^{81}Kr-Kr exposure ages being lower by up to 8%. For the samples discussed here the new T81 ages are on average by 3.6% lower compared to values derived by the classical correlation. The new relation yields a slightly better agreement between ^{81}Kr-Kr and ^{36}Cl-^{36}Ar ages for the chondrites analysed here than does the classical relation by Marti and Lugmair (1971). However, the considerable scatter in the data does not allow to firmly conclude which correlation describes the experimental data more accurately.

The model calculations show that the observed scatter between ^{81}Kr-Kr and ^{36}Cl-^{36}Ar ages cannot be the result of variable concentrations of the main target elements for the production of cosmogenic Kr, since the variations in Rb, Sr, Y, and Zr concentrations measured for the 12 H-chondrites hardly affect the cosmogenic Kr isotope systematics. The scatter must therefore (at least partly) be the result of inaccurate corrections for trapped Kr in the analysed meteorites. Therefore, we will expand this work by determining ^{81}Kr-Kr and ^{36}Cl-^{36}Ar ages for chondrites with higher exposure ages and lower concentrations of trapped Kr (*i.e.*, high petrographic types 5 and 6 only).

We also determined production rates for cosmogenic ^{38}Ar in the H-chondrites studied. The mean value at "average shielding" ($^{22}Ne/^{21}Ne = 1.11$) of $<P38> = (0.0431 \pm 0.0035) \times 10^{-8}$ cm^3 STP/(g$\times$Myr) is in good agreement with values given by Graf *et al*. (1990b) and Schultz *et al*. (1991). We consider our value to be very reliable, as it has been determined on gram-sized samples, hence inhomogeneities of target elements should not have been a problem.

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