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Noble gas studies in CAIs from CV3 chondrites: No evidence for primordial noble gases

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Abstract–Calcium-aluminum-rich inclusions (CAIs) were among the first solids in the solar system and were, similar to chondrules, created at very high temperatures. While in chondrules, trapped noble gases have recently been detected, the presence of trapped gases in CAIs is unclear but could have important implications for CAI formation and for early solar system evolution in general. To reassess this question, He, Ne, and Ar isotopes were measured in small, carefully separated and, thus, uncontaminated samples of CAIs from the CV3 chondrites Allende, Axtell, and Efremovka.

The $^{20}Ne/^{22}Ne$ ratios of all CAIs studied here are <0.9, indicating the absence of trapped Ne as, e.g., Ne-HL, Ne-Q, or solar wind Ne. The $^{21}Ne/^{22}Ne$ ratios range from 0.86 to 0.72, with fine-grained, more altered CAIs usually showing lower values than coarse-grained, less altered CAIs. This is attributed to variable amounts of cosmogenic Ne produced from Na-rich alteration phases rather than to the presence of Ne-G or Ne-R (essentially pure ^{22}Ne) in the samples. Our interpretation is supported by model calculations of the isotopic composition of cosmogenic Ne in minerals common in CAIs. The $^{36}Ar/^{38}Ar$ ratios are between 0.7 and 4.8, with fine-grained CAIs within one meteorite showing higher ratios than the coarse-grained ones. This agrees with higher concentrations of cosmogenic ^{36}Ar produced by neutron capture on ^{35}Cl with subsequent β^--decay in finer-grained, more altered, and thus, more Cl-rich CAIs than in coarser-grained, less altered ones.

Although our data do not strictly contradict the presence of small amounts of Ne-G, Ne-R, or trapped Ar in the CAIs, our noble gas signatures are most simply explained by cosmogenic production, mainly from Na-, Ca-, and Cl-rich minerals.

INTRODUCTION

With ages of up to 4.57 Ga (Amelin et al. 2002), calcium-aluminum-rich refractory inclusions (CAIs) are among the first solids formed in the solar system. Despite extensive research, the location and mechanism of CAI formation is still unknown. Direct condensation from a nebular gas as well as CAI formation as a result of intense evaporation are discussed (MacPherson et al. 1988, and references therein). CAIs—like chondrules—were formed at temperatures of up to ~1700 K, but—in contrast to chondrules—cooled much slower at rates of 2–50 K/hr (Jones et al. 2000). Based on this prolonged high temperature processing, primordial trapped noble gases would not be expected to have remained in CAIs. Nevertheless, it might be imagined that small amounts of trapped noble gases in particularly stable carrier phases survived the high temperature processing similar to the small amounts of trapped Ne and Ar that survived chondrule formation (Vogel et al. 2004). Such stable carriers may be presolar diamonds containing Ne-HL, presolar SiC rich in ^{22}Ne, or the carbonaceous phase Q carrying large amounts of heavy primordial noble gases (see Ott [2002] for a summary of meteoritic trapped noble gas components). CAIs might also contain primordial solar noble gases if they were formed close to the young Sun, as proposed by Shu et al. (1997, 2001). This would have profound implications for developing models of CAI formation and for our understanding of nebular evolution in general.

A comprehensive study of noble gases in Allende CAIs was published by Smith et al. (1977). The authors found trapped ^{20}Ne in volatile-rich Allende CAIs but could not ascribe it to a specific component like solar wind (SW) Ne, Ne-Q, or Ne-HL. Enrichments in ^{22}Ne and ^{36}Ar were attributed to cosmogenic production from Na and Cl, respectively.

Göbel et al. (1982) measured noble gases in Allende CAIs along with Na, Cl, and Ca concentrations and, thus, could address the production of cosmogenic Ne and Ar more quantitatively, although, e.g., a correlation of the $^{21}Ne/^{22}Ne$ ratio and the Na content of the samples was difficult to assess. Finally, the authors attributed ^{22}Ne excesses to spallation reactions on Na rather than to the presence of the ^{22}Ne-rich component Ne-G or Ne-R (carried by presolar graphite and presolar SiC; see Ott 2002). Furthermore, they found that excess ^{36}Ar was proportional to the Cl concentration in the CAIs and, consequently, concluded that it was of cosmogenic origin. On the other hand, $^{20}Ne/^{22}Ne$ ratios above the chondritic cosmogenic value point to the presence of trapped Ne-HL, Ne-Q, or SW-Ne in some CAIs.

In contrast, Russell et al. (1998) interpreted a ^{22}Ne overabundance in CAIs from Vigarano as a contribution from nearly pure ^{22}Ne carried by presolar SiC. The associated trapped Ar was described as "planetary," a mixture of noble gases of phase Q and presolar grains (e.g., Busemann 1998).

Murty et al. (1996) reported the Ne composition of two Efremovka CAIs to be in agreement with a trapped $^{20}Ne/^{22}Ne$ ratio of ~10, pointing to the presence of Ne-HL or Ne-Q in the samples. Shukolyukov et al. (2001) interpreted the Ar isotopic composition of an Efremovka CAI as a mixture of cosmogenic, atmospheric, and solar Ar. The Ne isotopic composition was reported to indicate the presence of Ne-HL carried by presolar diamonds.

To reassess the composition and origin of noble gases in CAIs, we measured He-, Ne-, and Ar-isotopes in CAIs of the three unequilibrated CV3 chondrites Allende, Axtell, and Efremovka. Our analytical technique is particularly suited to analyze low gas concentrations (Vogel et al. 2004), thus, only small CAI separates were necessary. This allowed us to avoid the outermost marginal regions of the CAIs during separation, which greatly reduces the risk of contaminating the samples with surrounding matrix with its significantly higher trapped noble gas concentrations (e.g., Vogel et al. 2003). The different exposure ages, pre-atmospheric radii, and degrees of alteration of the meteorites enable the assessment of the effects of these parameters on the noble gas compositions of the CAIs. Also distinguished were macroscopically fine- and coarse-grained CAIs to indirectly address the variable degrees of alteration within one meteorite, since fine-grained CAIs are often more altered than coarse-grained CAIs (e.g., MacPherson and Grossman 1984; Brearley and Jones 1998).

SAMPLES AND METHODS

Small "bulk" samples (see Table 1 for sample masses) of macroscopically visible fine- and coarse-grained Allende and Axtell CAIs and of a fine-grained Efremovka CAI were hand-separated with a steel needle from sawn meteorite chips (Fig. 1) under a binocular microscope. Special attention was paid to avoid cross-contamination of the samples with matrix material surrounding the CAIs, i.e., samples were mostly separated from the interior parts of the CAIs and the third dimension was carefully checked. This generally precluded sampling the outermost margins of CAIs, where the possibility of contamination by matrix material would have been very high and the presence of indigenous trapped gases (e.g., solar wind noble gases) would be very difficult to prove. Additionally, samples from one fine- and one coarse-grained Allende CAI (Al-G and Al-H) were obtained by gentle crushing of a larger piece of Allende and subsequent separation of small clean pieces of CAI material. The sample labels start with the meteorite names (Al = Allende, Ax = Axtell, Ef = Efremovka). Different CAIs are distinguished by capital letters, and several samples of one single CAI taken to address possible heterogeneities within one CAI are distinguished by numbers. The samples Al-D3 (see Fig. 1) and Al-E2 are dominated by material of the Wark-Lovering (WL) rims of the respective CAIs and were taken to elucidate possible differences in the noble gas inventory of CAI cores and rather marginal regions. Small samples of fine-grained matrix (labeled "Ma") were separated from Axtell and Efremovka also. A short description of each CAI sample is given in Table 1. No further mineralogical or chemical analyses were performed due to the scarcity of sample material available, which precluded separating true aliquots of each sample. The weighed samples were mounted into a vacuum extraction system connected to a statically operated noble gas mass spectrometer. Atmospheric noble gases were removed by heating the samples in vacuum for ~24 hr at ~100 °C. For a detailed description of the noble gas extraction technique using a Nd-YAG-laser, the gas purification, spectrometer settings, interference corrections, and the calibration procedure, we refer to Vogel et al. (2003). A detailed description of the blank correction, which is essential for measuring low gas amounts, is given by Vogel et al. (2004). All noble gas results (except for the predominantly radiogenic ^{40}Ar) are given in Table 1.

RESULTS AND DISCUSSION

Helium

The ^{3}He in the CAIs (Table 1) is assumed to be essentially entirely of spallogenic origin; concentrations are similar to those in the respective matrix samples. This is to be expected since the cosmogenic production of ^{3}He shows only minor variations with target chemistry (Wieler 2002). The ^{3}He exposure ages were calculated using an average CAI chemistry and ^{3}He production rates given by Leya et al. (2000), taking into account the different meteoroid radii and assuming average shielding conditions of the samples. The ^{3}He exposure ages from Allende and Axtell CAIs (~4.5 Ma and ~13.6 Ma, respectively) are only slightly lower than the

Table 1. Noble gases in Allende, Axtell, and Efremovka CAIs and Axtell and Efremovka matrix (Ma).[a]

Meteorite, CREA[b], PR[c]	Sample	Type[d]	Sample description	Weight [g] $\times 10^{-4}$	^{3}He[e]	$^{3}He/^{4}He$ $\times 10^{-4}$	22Ne[e]	$^{20}Ne/^{22}Ne$	$^{21}Ne/^{22}Ne$	^{38}Ar[e]	$^{36}Ar/^{38}Ar$
Allende ($CV3_{ox}$)	Al-G1	f	Homogeneously fine-grained white CAI, with delicate light gray streaks. Clear contact between CAI and matrix.	6.289(1)	5.76(7)	20.6(2)	1.93(4)	0.65(2)	0.72(1)	1.117(9)	1.23(2)
CREA: 5.2 Ma	Al-G2	f		11.246(9)	6.21(7)	21.5(1)	1.83(3)	0.64(2)	0.72(1)	1.33(1)	1.30(2)
PR: ≥50 cm	Al-G3	f		4.85(1)	5.68(8)	20.9(4)	2.03(4)	0.68(2)	0.73(1)	1.06(1)	1.38(2)
	Al-A1	f	Fine-grained white CAI with irregular shape.	1.821(5)	6.11(8)	22.1(2)	1.78(9)	0.67(4)	0.72(4)	1.41(2)	2.21(5)
	Al-A2	f		4.690(5)	6.04(8)	23.3(2)	1.81(4)	0.71(2)	0.74(2)	1.38(1)	3.18(5)
	Al-A4	f		2.004(5)	6.3(1)	24.5(3)	1.8(1)	0.75(6)	0.77(5)	1.41(2)	3.24(6)
	Al-B1	f	Fine-grained porous CAI with irregular shape.	1.575(5)	7.0(1)	4.30(6)	2.12(5)	0.75(3)	0.81(3)	0.77(1)	2.96(6)
	Al-B2	f		3.588(5)	6.40(9)	4.50(6)	1.98(5)	0.75(2)	0.85(2)	0.761(8)	2.83(4)
	Al-D1	f	Core of fine-grained irregularly shaped pink CAI surrounded by a pink-greyish banded Wark Lovering (WL) rim that parallels the irregular outer shape of the CAI.	6.089(1)	6.72(8)	18.0(1)	1.98(3)	0.69(2)	0.77(2)	1.07(1)	3.46(3)
	Al-D2	f	Besides the core also a part of the WL-rim was sampled.	3.01(2)	6.15(8)	18.6(2)	1.95(6)	0.66(2)	0.78(3)	0.96(1)	4.75(5)
	Al-D3	f	This sample consists mainly of the WL-rim of A1-D.	2.67(1)	6.74(9)	2.98(3)	1.92(6)	0.79(3)	0.82(3)	1.00(1)	3.76(4)
	Al-E1	f	Fine-grained irregularly shaped pink-grey CAI, also with banded WL rim. In the rim portion small round red minerals visible. The samples contain core and WL rim material. For Al-E1 contamination could not be fully excluded.	5.74(1)	5.79(7)	9.85(6)	1.80(4)	0.73(2)	0.80(2)	0.91(1)	3.96(4)
	Al-E2	f		8.575(3)	6.45(7)	13.60(8)	1.94(4)	0.74(1)	0.80(2)	0.927(9)	3.00(2)
	Al-C1	c	Coarse-grained white sinusoidal CAI with sporadic dark minerals (not matrix) and voids. Contamination with surrounding matrix could not be fully excluded for sample A1-C1.	3.21(3)	7.3(1)	9.87(9)	1.17(5)	0.89(6)	0.83(3)	2.43(3)	1.01(1)
	Al-C2	c		9.48(1)	7.39(9)	8.53(5)	1.27(2)	0.79(2)	0.82(2)	2.42(2)	0.963(8)
	Al-H1	c	Coarse-grained concentric white-grey CAI with sharp contact to surrounding matrix. In interstices between individual large angular minerals fine-grained whitish filling. Sporadic voids. For A1-H3 matrix contamination could not be fully excluded.	7.38(1)	7.47(9)	7.00(4)	1.32(4)	0.75(3)	0.83(2)	2.38(2)	0.722(6)
	Al-H2	c		8.78(2)	7.35(9)	5.19(3)	1.63(3)	0.75(1)	0.77(1)	1.99(2)	1.46(1)
	Al-H3	c		3.06(1)	7.61(9)	4.68(3)	1.49(6)	0.81(4)	0.81(3)	2.13(2)	1.74(3)
	Al-H4	c		3.520(1)	7.2(1)	7.2(1)	1.36(4)	0.76(4)	0.79(3)	2.23(3)	0.92(1)
Axtell ($CV3_{ox}$)	Ax-D	f	Fine-grained irregularly shaped CAI with whitish border region and slightly more grey-greenish core.	1.29(2)	19.7(4)	128(1)	5.8(3)	0.69(4)	0.78(4)	2.20(4)	3.94(4)
CREA: 15.4 Ma	Ax-A	c	Coarse-grained white-greenish concentric CAI with sharp contacts to matrix.	3.35(2)	21.2(2)	21.7(2)	4.13(9)	0.75(2)	0.82(3)	7.58(5)	0.739(7)
PR: ~30 cm	Ax-B	c	Coarse-grained compact white-grey-greenish CAI with irregular shaped outer margins and sharp contacts to matrix.	3.67(2)	18.6(2)	27.3(3)	4.7(1)	0.77(2)	0.83(3)	4.14(3)	1.37(1)
Efremovka ($CV3_{red}$)	Ef-A1	f	Small fine-grained white CAI with irregular shape and 'cloudy' (amoeboid) texture.	1.022(3)	4.9(1)	21.2(5)	3.1(1)	0.76(3)	0.81(3)	4.22(3)	0.76(1)
CREA: 9.4 Ma	Ef-A2	f		1.48(1)	5.02(9)	22.2(3)	2.94(9)	0.75(3)	0.86(3)	4.18(5)	0.698(7)
PR: ~20 cm	Ef-A3	f		0.734(8)	7.0(2)	12.1(3)	3.5(1)	0.72(4)	0.86(4)	3.16(4)	0.76(2)
Axtell ($CV3_{ox}$)	Ax-Ma 1			2.21(1)	19.1(2)	72.2(6)	5.4(1)	2.08(6)	0.75(3)	4.25(3)	4.02(3)
Efremovka ($CV3_{red}$)	Ef-Ma 1			0.62(1)	8.2(2)	24.6(5)	5.8(2)	4.3(1)	0.55(2)	141(2)	5.35(2)

[a]Numbers in parentheses represent 1σ uncertainties in units of the least significant digits. Uncertainties of the gas concentrations include statistical errors, uncertainties in sample weight, blanks, and interference correction. Not included are uncertainties due to short-term variability of the spectrometer sensitivity which are estimated to be <2%. Inter-laboratory comparisons revealed a ~3% uncertainty in the determination of absolute gas concentrations (Wieler et al. 1989). Errors of the isotopic ratios include statistical uncertainties, uncertainties of the mass discrimination, blanks, and interference corrections.

[b]CREA = cosmic ray exposure ages (Scherer and Schultz 2000).

[c]Pre-atmospheric radii: Allende: Vogel et al. (2004); Axtell: estimated according to Alexeev (2003) and supported by ^{60}Co data (Simon et al. 1995); Efremovka: Murty et al. (1996)

[d]Macroscopically fine- or coarse-grained CAI.

[e]Gas concentrations in 10^{-8} cm^3 STP/g.

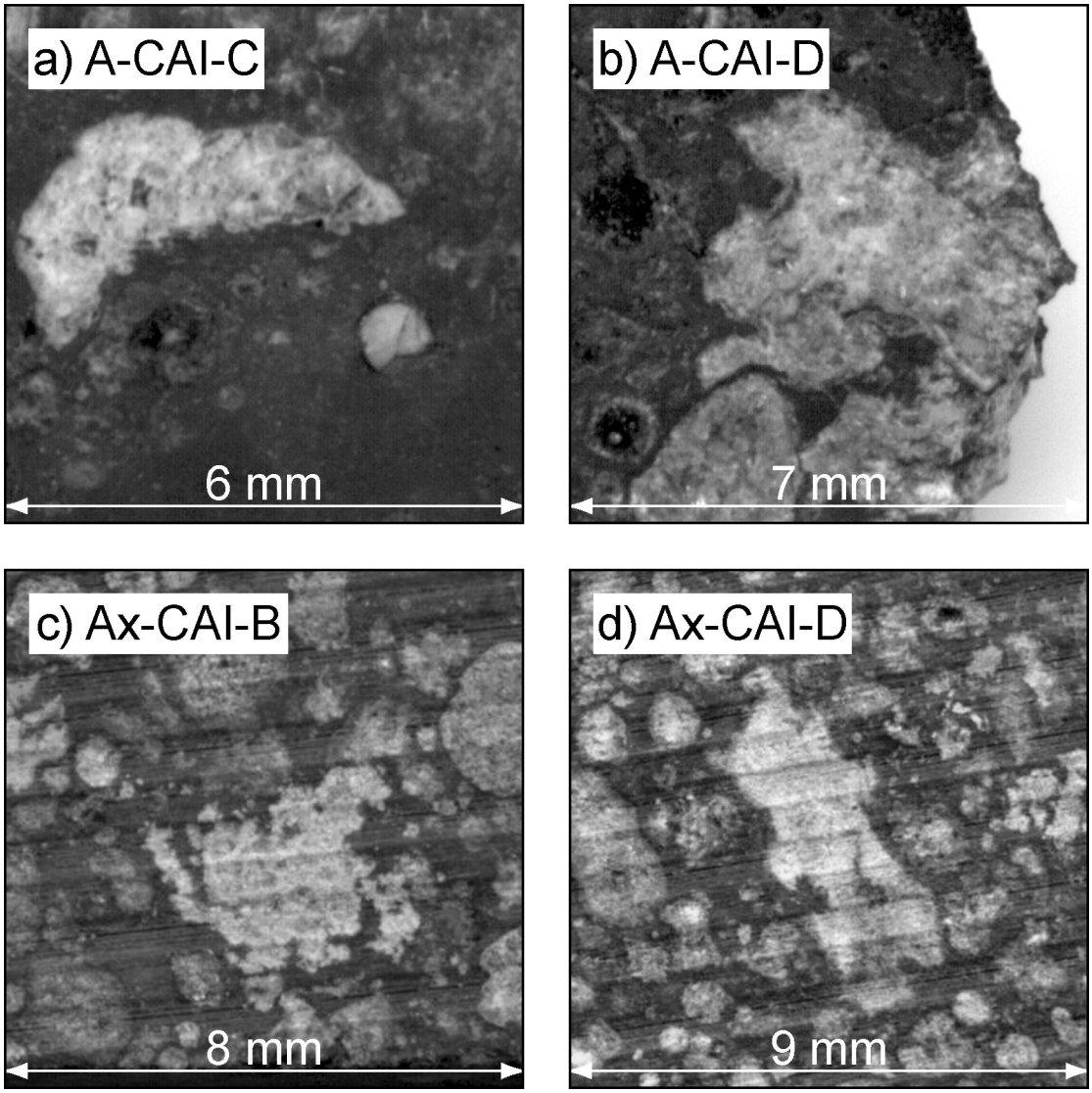

Fig. 1. Two macroscopically coarse-grained (a, c) and fine-grained (b, d) CAIs from Allende and Axtell. For sample description, see Table 1. The streaks across the Axtell images are from sawing.

Ne exposure ages of the bulk meteorites of 5.2 Ma and 15.4 Ma, respectively (Scherer and Schultz 2000; see also Table 1), indicating, at best, minor losses of cosmogenic ^{3}He. In contrast, the ^{3}He exposure age for the Efremovka CAI is ~4.5 Ma, distinctly below the bulk Ne exposure age of 9.4 Ma (Scherer and Schultz 2000). The low ^{3}He concentration is in agreement with the low cosmogenic ^{3}He/^{21}Ne ratio given by Scherer and Schultz (2000) for the bulk meteorite. This indicates a significant loss of ^{3}He, probably due to solar heating of the meteoroid at a small perihelion distance (Hintenberger et al. 1966).

The measured ^{4}He in CAIs is mainly a decay product from $^{235,\ 238}$U, and ^{232}Th with minor contributions of cosmogenic ^{4}He (in our case, generally ~1%). Correcting the measured ^{4}He concentrations for cosmogenic contributions by assuming a cosmogenic ^{4}He production rate ~6 times higher than that for ^{3}He (Alexeev 1998) enables us to infer U and Th concentrations from the radiogenic ^{4}He (^{4}He$_{rad}$) that had been produced over 4.57 Ga. Using a present-day ^{238}U/^{235}U ratio of 137 and a U/Th ratio of 4, we infer an averaged present-day U concentration of ~40 ppb. The average ^{4}He$_{rad}$ concentration for all CAI samples is ~7 × 10^{-5} cm^{3} STP/g. The inferred U concentration compares well with literature values, e.g., 19–36 ppb for bulk Efremovka CAIs (Amelin et al. 2002). Therefore, we exclude any major loss of ^{4}He$_{rad}$ from our samples.

Neon

In Fig. 2, ^{20}Ne/^{22}Ne versus ^{21}Ne/^{22}Ne is plotted for matrix and CAI samples of Allende, Axtell, and Efremovka. The matrix data (for Allende matrix, see Vogel et al. [2003])

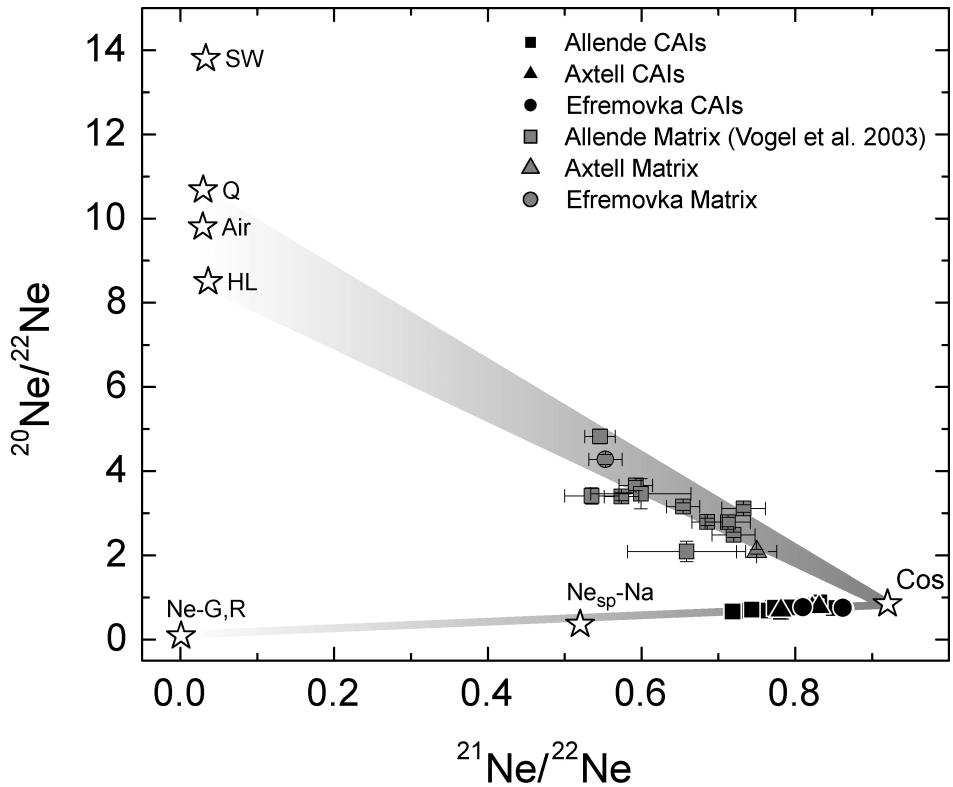

Fig. 2. Neon isotopic composition of matrix samples (grey symbols) and CAIs (black symbols) from Allende, Axtell, and Efremovka. The error bars of the matrix data points represent 1σ uncertainties. The Allende matrix data are published in Vogel et al. (2003). For uncertainties of CAI Ne isotopic compositions, see Fig. 4. The matrix samples represent mixtures of chondritic cosmogenic Ne (Cos) and trapped Ne, mainly carried by presolar diamonds (HL) and possibly with small contributions of Ne-Q (Q) but essentially free of solar wind Ne (SW). The CAIs form an array between chondritic cosmogenic Ne and a component enriched in ^{22}Ne. This could be, e.g., spallation Ne produced from sodium (Ne$_{sp}$-Na), or Ne-G and/or Ne-R carried by presolar SiC and graphite (see Ott [2002] and text for further explanation).

represent mixtures of chondritic cosmogenic Ne and trapped Ne. The latter is dominated by Ne-HL, possibly with small additions of Ne-Q. Unlike the matrix, all CAI data points form a very distinctive array between chondritic cosmogenic Ne and a component rich in ^{22}Ne. The latter could either be Ne-R (former notation Ne-E[L]), being pure ^{22}Ne from the presolar decay of ^{22}Na and brought into the solar system by presolar graphite, or Ne-G (former notation Ne-E[H]), i.e., ^{22}Ne produced directly during stellar nucleosynthesis in AGB stars. The host phases for this component are presolar SiC and graphite (see, e.g., Ott 2002).

In the following, we discuss the possible presence of a "normal" trapped Ne component like Ne-HL, Ne-Q, and solar Ne and/or an "anomalous" component like Ne-R and/or Ne-G for the studied CAIs.

Normal Trapped Ne-HL, Ne-Q, or SW-Ne in CAIs?

A normal trapped Ne component is generally inferred from a shift of the ^{20}Ne/^{22}Ne ratio from a cosmogenic composition toward higher values (compare Fig. 2). All except two of our CAI data points (Fig. 3, black symbols) show ^{20}Ne/^{22}Ne ratios below 0.8, not showing any evidence for the contribution of normal trapped Ne in the CAIs. For the two samples with slightly higher ^{20}Ne/^{22}Ne ratios of 0.81 and 0.89 (Al-H3 and Al-C1, respectively), the possibility of minor additions of gas-rich matrix had been noted during the sample separation, and we ascribe their "elevated" ^{20}Ne/^{22}Ne ratios to contamination.

In our other fine- and coarse-grained samples from Allende, Axtell, and Efremovka, including the two Allende CAI samples rich in WL-rim material, we did not detect any measurable amounts of normal trapped Ne.

This is in contrast to earlier studies, e.g., Smith et al. (1977), who postulated the presence of trapped Ne in volatile-rich Allende CAIs based on ^{20}Ne/^{22}Ne ratios of up to 3.4 in certain temperature steps during step-wise gas release. Also, Göbel et al. (1982) and Shukolyukov et al. (2001) measured ^{20}Ne/^{22}Ne ratios of up to 2.7 (Allende CAIs) and 1.9 (Efremovka CAI), respectively (Fig. 3, small grey symbols), in step-wise release experiments. In most cases, high ratios in single steps are also reflected in the composition of the total Ne in the respective samples, with bulk ^{20}Ne/^{22}Ne ratios being above 0.8 (Fig. 3, large grey symbols). Since the sample amounts used in these earlier studies were, on average, about two orders of magnitude higher than in this work, we believe that the high reported ^{20}Ne/^{22}Ne ratios in single steps as well

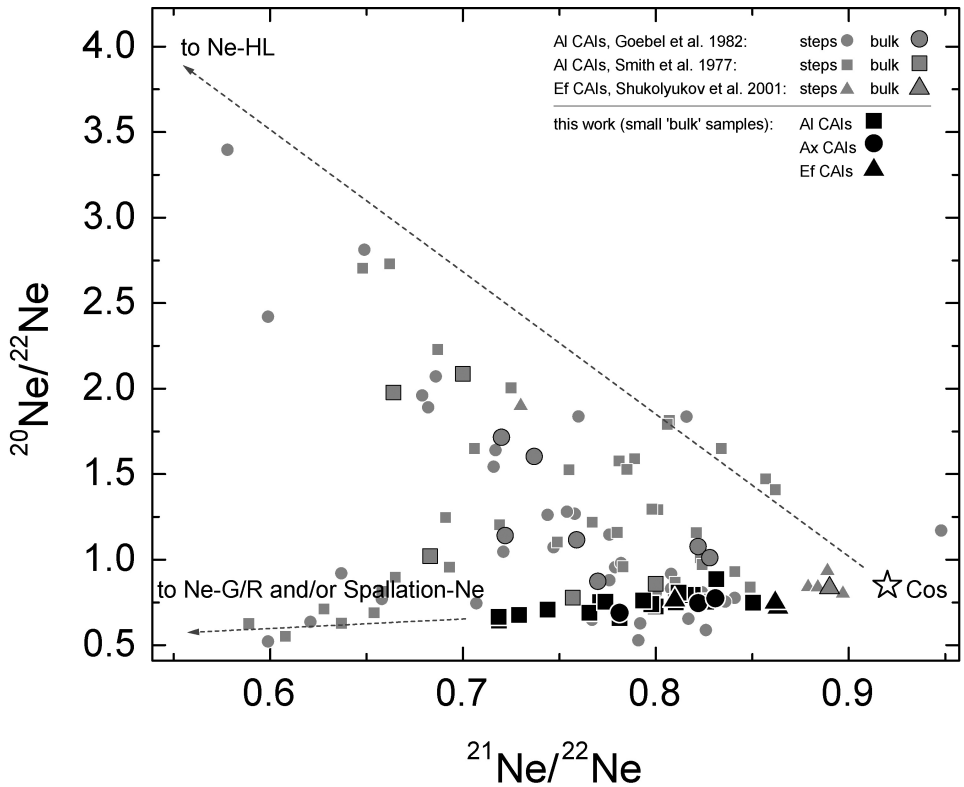

Fig. 3. Comparison of neon isotopic compositions of small CAI samples measured in this work (black symbols) with those determined in earlier studies. The literature data represent individual gas fractions from step-wise heating experiments (small grey symbols) as well as the total gas (bulk) neon isotopic compositions of the respective CAIs (large grey symbols) to compare literature data with our total extraction data. Most literature data (individual steps and bulk) scatter in an area defined by chondritic cosmogenic Ne, Ne-HL, and a component rich in ^{22}Ne. In contrast, the CAIs measured by us always plot below a ^{20}Ne/^{22}Ne ratio of ~0.9. See text for further explanations.

as in the total gas reflect contamination by matrix material rather than bona-fide trapped Ne in CAIs. The many CAIs with irregular outlines (compare Fig. 1b) are particularly prone to contamination if large samples are to be taken. Smith et al. (1977) estimated matrix contamination between 5 and 50% for all but one of their CAI samples. Those values compare well with our own estimates of contamination, using our data as cosmogenic and trapped end member compositions. It is tempting to assume that the studies by Göbel et al. (1982) and Shukolyukov et al. (2001) on similarly large samples as those of Smith et al. (1977) were also compromised by contamination. Using our data as end member compositions, the degree of matrix contamination of those CAI samples can be estimated to be up to ~30%.

Spallation Ne or Anomalous Ne Carried by Presolar SiC or Graphite in CAIs?

At first glance, the ^{21}Ne/^{22}Ne ratios of our CAIs (Figs. 2 and 3) seem to reflect a two component mixture of cosmogenic Ne and Ne-R/Ne-G. However, the chemical composition of CAIs is substantially non-chondritic. Consequently, the isotopic composition of cosmogenic Ne produced in CAIs is also different from that of typical chondritic cosmogenic Ne. To specify the range of cosmogenic Ne that could be expected for CAIs, we calculated the cosmogenic Ne isotopic compositions for minerals common in CAIs (Fig. 4) using the model by Leya et al. (2000) and considering variably shielded samples in meteoroids with radii between 15 and 85 cm. The modeled ratios describe an array from chondritic cosmogenic composition toward the origin of the diagram (Fig. 4, grey boxes). The lowest ratios are due to sodium, which is present in the secondary mineral phases nepheline and sodalite in CAIs. The measured distribution of our CAI data points nicely matches the calculated ranges, in that: 1) all of the measured data points have low ^{20}Ne/^{22}Ne ratios; and 2) there is a large spread in their ^{21}Ne/^{22}Ne ratios (Fig. 4).

Fine-grained Allende CAIs tend to show the lowest ^{21}Ne/^{22}Ne ratios measured here (as low as 0.72), closest to the composition of cosmogenic Ne in the Na-bearing nepheline and sodalite. The Ne composition in coarse-grained Allende CAIs scatters between the values calculated for anorthite, melilite, spinel, and fassaite. This agrees with observations that, within one meteorite, coarse-grained CAIs tend to be less altered and, thus, contain less secondary mineral phases than fine-grained CAIs (MacPherson and Grossman 1984; Brearley and Jones 1998, and references therein). This is further confirmed by a compilation of Na concentration data

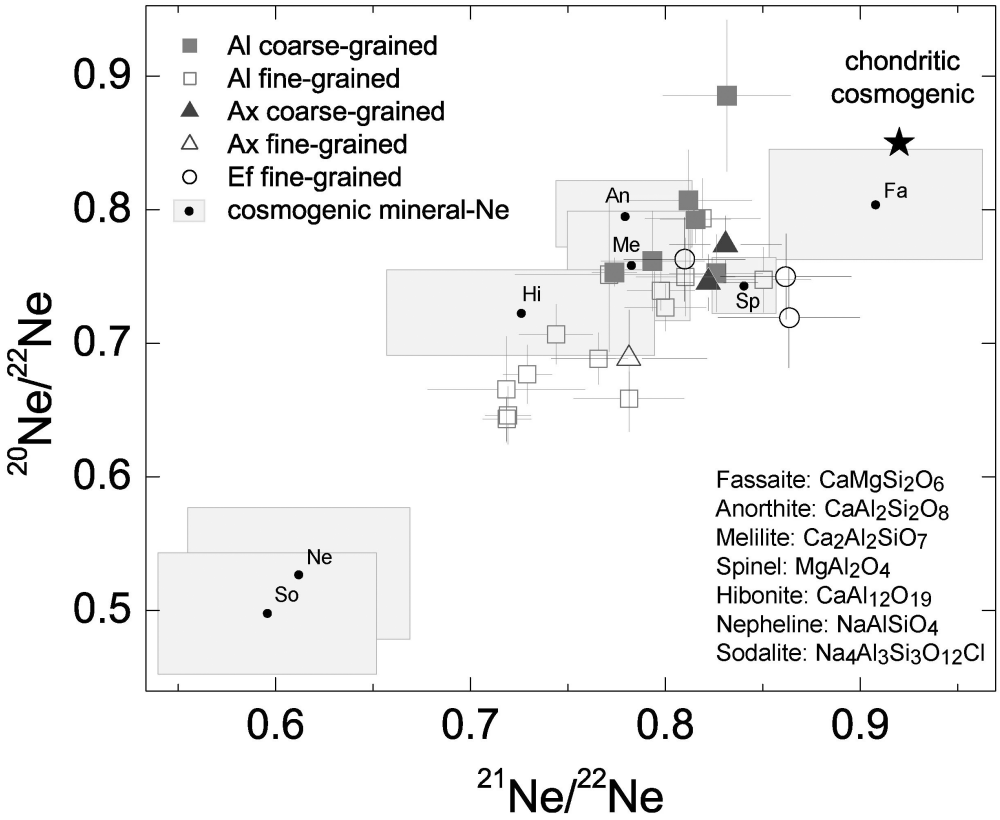

Fig. 4. Comparison of Ne isotopic compositions in fine- and coarse-grained CAIs (open and solid symbols, respectively) measured by us. The grey boxes represent modeled isotopic compositions of cosmogenic Ne from mineral phases common in CAIs. These values are based on the model by Leya et al. (2000) for meteoroid radii between 15 and 85 cm and variable shielding conditions. The listed chemical compositions (in part, simplified) are those used for the calculations. Fa = fassaite, An = anorthite, Me = melilite, H = hibonite, Sp = spinel, Ne = nepheline, and So = sodalite. Pure Na would produce a cosmogenic $^{20}Ne/^{22}Ne$ ratio around 0.35 and a $^{21}Ne/^{22}Ne$ ratio around 0.49. The respective values for Al are ~0.73 and ~0.72. The error bars are 1σ.

in fine- and coarse-grained CAIs of the studied meteorites (Table 2, data sources in table caption): average Na-concentrations decrease from fine- to coarse-grained CAIs within one meteorite. Overall, sodium values also decrease in the order of Allende >Axtell >Efremovka. This trend agrees with decreasing degrees of alteration from Allende to Efremovka reported in the literature (e.g., Brearley and Jones 1998).

Fine- and coarse-grained CAIs in Axtell show a similar pattern as those in Allende (Fig. 4): the fine-grained CAI samples have Ne isotopic compositions closer to sodalite/nepheline-Ne than the coarse-grained samples. Although the data set is small, the higher $^{21}Ne/^{22}Ne$ ratios of the fine-grained Axtell CAI compared to its Allende counter-parts might be due to the slightly lower degree of alteration of Axtell compared to Allende (e.g., Casanova and Simon 1994). Also, the average Na concentration is lower in fine-grained Axtell CAIs than in fine-grained Allende CAIs (Table 2).

The data points of the fine-grained Efremovka CAI in Fig. 4 all plot close to the calculated composition of cosmogenic Ne in melilite, spinel, and fassaite, the major mineral phases in Efremovka CAIs (e.g., Goswami et al. 1994). This is no surprise since CAIs in Efremovka are indeed virtually free of secondary alteration products (Goswami et al. 1994), which is also reflected in their particularly low reported Na concentrations (Table 2). The Efremovka data also argue against the hypothesis that only fine-grained CAIs, but not the possibly (re-) melted coarse-grained CAIs, might have retained Ne-R/Ne-G (or, in fact, any trapped Ne component).

From the above arguments, we infer that the Ne data for the measured CAIs are most simply explained by cosmogenic production from Na-rich secondary minerals and that there is no need to postulate the presence of Ne-R/Ne-G. For Allende CAIs, this has also been the preferred interpretation by Göbel et al. (1982) and Smith et al. (1977).

The fact that Na is sited in secondary alteration phases (e.g., Bischoff and Palme 1987; Sylvester et al. 1993) also rules out another explanation discussed by Göbel et al. (1982). They noted that the observed anti-correlation of the $^{21}Ne/^{22}Ne$ ratios and the Na concentrations in CAIs could also be explained if the trapped component were Ne-R from the in situ decay of ^{22}Na in presolar matter. Also, the authors observed the lowest $^{21}Ne/^{22}Ne$ ratios in the lowest

Table 2. Compilation of literature sodium, calcium, and chlorine concentrations (wt%) in fine- and coarse-grained CAIs.

	Sodium[a]						Calcium						Chlorine[a]	
	Allende	Ref.[b]	Axtell	Ref.[b]	Efremovka	Ref.[b]	Allende	Ref.[b]	Axtell	Ref.[b]	Efremovka	Ref.[b]	Allende	Ref.[b]
Fine-grained	1.500	a	0.350	e	0.247	g	8.5	a			9.7	g	0.86	b
	2.570	a	0.560	e	0.188	g	6.5	a			8.7	g	1.17	b
	2.540	a			0.025	g	11	i			12.3	g	(1.33)[c]	b
	3.230	a					7	i					1.72	b
	1.920	a					(2)[b]	i					0.87	b
	2.300	a					6	i					0.62	b
	1.400	b					8	i					0.33	b
	3.100	b					8	i					0	b
	(5.14)[c]	b					6	i					0	b
	4.230	b					7	i					0.193	a
	2.590	b					12	i					0.4465	a
	1.890	b											0.4241	a
	3.400	b											0.122	a
	3.090	b											0.329	a
	1.440	b											0.17	a
Average	2.514		0.455		0.153		8				10.2		0.52	
Coarse-grained	0.048	c	0.008	f	0.020	h	25.1	d	24.8	f	27.0	h	0	b
	0.028	d	0.017	f	0.034	h	16	k	23.8	f	29.5	h	0	b
	0.129	b	0.021	f	0.026	h	10	k	19.4	f	22.0	h	0	b
	0.062	b	0.030	e	0.008	g	24	k			23.1	g	0	b
	0.137	b	0.040	e	0.025	g	18	k			26.5	g	0	b
	0.152	b	0.060	e	0.050	g	9	k			15.6	g	0	b
	0.164	b	0.060	e	0.088	g	26	k			18.8	g	0	b
	0.027	b	0.100	e	0.004	g	11	k			16.1	g	0	b
	0.833	b	0.100	e			16	k			15.7	l	0	b
	0.090	b	0.130	e			21	k					0	b
	0.471	b	0.130	e			12	k					0.0148	c
	0.057	b	0.200	e									0.0106	d
			0.310	e										
			0.430	e										
Average	0.183		0.117		0.032			22.7		21.6			0.002	

[a]The Na and Cl concentrations might be biased toward upper limits.

[b]a) Göbel et al. (1982); b) Grossman and Ganapathy (1975); c) Bischoff (1989); d) Bischoff and Palme (1987); e) Yoneda et al. (1995); f) Srinivasan et al. (2000); g) Nazarov et al. (1982); h) Sylvester et al. (1993); i) Grossman (1976a); k) Grossman (1976b); l) Shukolyukov et al. (2001).

[c]The Na and Ca values in brackets are not included in the average since the object might be an amoeboid olivine aggregate rather than a CAI.

temperature steps around 400–600 °C, while it is now known that Ne-R is released between 600 and 1000 °C and Ne-G is released at even higher temperatures (Amari et al. 1995).

Summarizing all the arguments above, and agreeing with Göbel et al. (1982) and Smith et al. (1977), we propose that Ne-R or Ne-G be identified in none of our studied CAIs. The Ne isotopic compositions of fine- and coarse-grained CAIs are most consistently explained by cosmogenic production if one takes into account the general chemical trends in CAIs reported in the literature, in particular, the different amounts of Na resulting from variable degrees of alteration.

Argon

In contrast to Ne, Ar has only two isotopes that can be used for deciphering different noble gas components, as ^{40}Ar is predominantly of radiogenic origin. Furthermore, not only do trapped Ar and cosmogenic Ar produced by spallation of Ca (and Fe) (Ar_{sp}) have to be taken into account, but also cosmogenic Ar produced by neutron capture reactions on Cl with subsequent β^--decay (Ar_{Cl}).

Figure 5 shows the ^{36}Ar/^{38}Ar ratios of all CAIs as a function of their ^{38}Ar concentrations. All data points fall between the spallogenic ^{36}Ar/^{38}Ar ratio of ~0.65 and trapped components with ^{36}Ar/^{38}Ar ratios of around 5. At first glance, this might suggest the presence of significant amounts of trapped Ar in some CAIs, as proposed in the literature (Russell et al. 1998; Shukolyukov et al. 2001; Murty et al. 1997). However, we argue that the data can also be explained as two component mixtures of Ar_{sp} and small amounts of Ar_{Cl} with a ^{36}Ar/^{38}Ar ratio of the order of about 300. Similar to the argument for Ne above, we expect larger contributions of Ar_{Cl} in more altered CAI samples, since Cl is mainly carried by the secondary alteration phase sodalite, often going along with nepheline (e.g., Brearley and Jones 1998).

Indeed, our fine-grained Allende CAIs show higher average ^{36}Ar/^{38}Ar ratios and lower ^{38}Ar concentrations than their coarse-grained counterparts. This also agrees with, on average, higher Cl (and thus, $^{36}Ar_{Cl}$) and lower Ca (and thus, $^{38}Ar_{sp}$) concentrations for Allende fine-grained CAIs compared to coarse-grained ones (Table 2). Note that the replacement of primary with secondary mineral phases leads to an increase of Cl and a decrease of the Ca concentration at the same time (commonly, melilite is replaced by nepheline along with sodalite; Brearley and Jones 1998, and references therein). Our noble gas data for Axtell fine- and coarse-grained

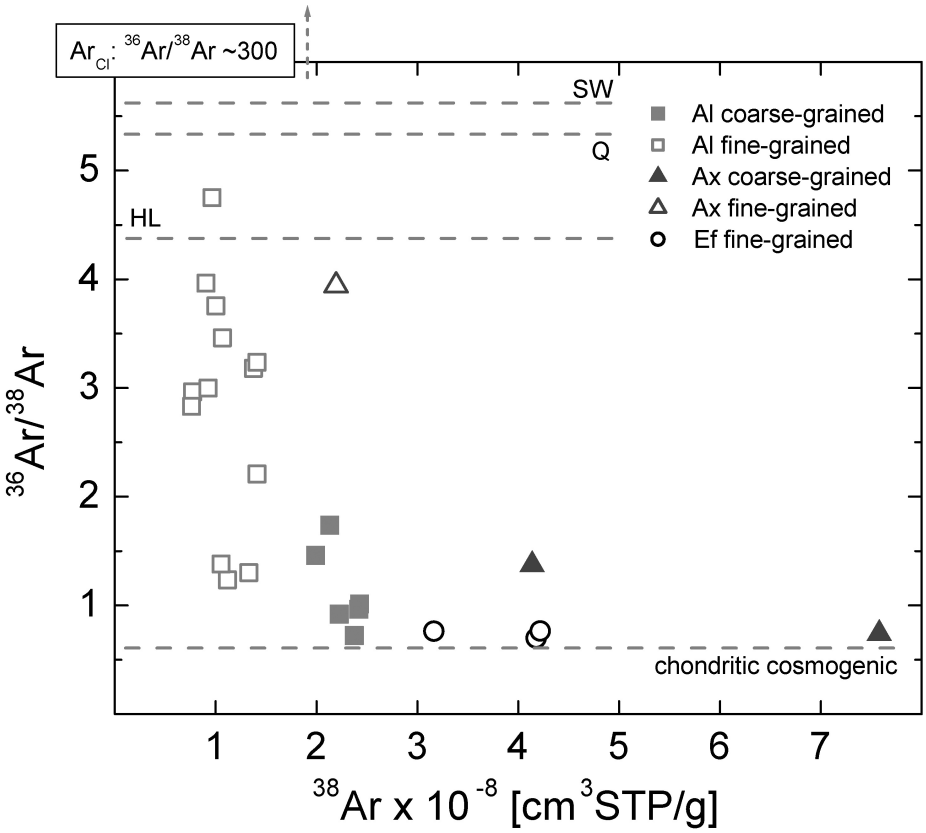

Fig. 5. ^{36}Ar/^{38}Ar ratios versus ^{38}Ar concentrations of fine- and coarse-grained CAIs (open and solid symbols, respectively). The ^{36}Ar/^{38}Ar ratios of chondritic cosmogenic Ar, SW-Ar, Ar-Q, and Ar-HL are ~0.65 (Wieler 2002), ~5.6 (Benkert et al. 1993), ~5.3 (Busemann et al. 2000), and ~4.4 (Huss and Lewis 1994), respectively. Argon produced by neutron capture on Cl with subsequent β^--decay has a ^{36}Ar/^{38}Ar ratio on the order of about 300 (deduced from capture cross sections for thermal neutrons and the natural abundance of ^{35}Cl and ^{37}Cl). See text for further explanation. The 1σ error bars are in the range of symbol sizes.

CAIs show a similar pattern as the Allende CAIs, again suggesting a larger degree of alteration of fine-grained than of coarse-grained CAIs. However, literature Ca and Cl data to support this suggestion are very scarce for this meteorite.

If the elevated $^{36}Ar/^{38}Ar$ ratios of the fine-grained CAIs were due to contributions of trapped Ar, one would—similar to Ne—expect the clearest signal of trapped Ar in the least altered (fine-grained) Efremovka CAI with its small preatmospheric size (Murty et al. 1996) and, thus, minor amounts of $^{36}Ar_{Cl}$. Clearly, this is not the case; in contrast, those samples show particularly low $^{36}Ar/^{38}Ar$ ratios of ~0.7 (Fig. 5). Higher $^{36}Ar/^{38}Ar$ ratios of ~4 for an Efremovka CAI reported earlier (Murty et al. 1997) need to be reassessed due to an inappropriate mass discrimination correction (Rai et al. 2003).

We estimated possible Ar_{sp} and Ar_{Cl} concentrations using the model by Leya et al. (2000) and—as far as available—literature Ca and Cl concentration ranges for fine- and coarse-grained CAIs of the meteorites also studied by us and the exposure times to cosmic radiation for the respective host meteoroids. Using Ca production rates based on those given by Hohenberg et al. (1978) converted to 4π irradiation and our Cl production rates (data not shown), our measured Ar data are reproduced well.

We infer that—in line with Göbel et al. (1982) and Smith et al. (1977)—the Ar signatures in fine- and coarse-grained CAIs of the three different primitive meteorites studied here can consistently be explained as mixtures of the two cosmogenic Ar components produced from Ca and Cl. There is no need to introduce a trapped Ar component, as more recently suggested by Russell et al. (1998) and Shukolyukov et al. (2001). In particular, our Ar data of the fine-grained, least-altered Efremovka CAI strongly argue against the presence of a trapped Ar component like Ar-Q or SW-Ar in the studied CAIs.

CONCLUSIONS

We reassessed the composition and origin of noble gases in CAIs to draw conclusions on possible CAI formation mechanisms. In particular, if CAIs contained primordial solar noble gases, this could support CAI formation close to the young Sun and, thus, have profound implications on early solar system evolution.

In contrast to earlier studies performed by step-wise heating of large bulk samples, in none of our total extractions of small bulk samples of fine- and coarse-grained CAIs from Allende, Axtell, and Efremovka could we detect measurable amounts of trapped Ne. The Ne isotopic composition of the studied CAIs is explained by cosmogenic production from Al- and especially Na-rich secondary minerals: the more altered, fine-grained Allende and Axtell CAIs show lower $^{21}Ne/^{22}Ne$ ratios, probably due to higher Na concentrations than their coarse-grained counterparts. Similarly, $^{36}Ar/^{38}Ar$ ratios are higher in fine-grained Allende and Axtell CAIs than in the coarse-grained ones. This is ascribed to higher production of ^{36}Ar from neutron capture on Cl in fine-grained than in coarse-grained CAIs. This hypothesis is supported by higher literature Na and Cl concentrations in fine-grained Allende CAIs than in their coarse-grained counterparts.

The studied fine-grained Efremovka CAI does not show a significant shift toward lower $^{21}Ne/^{22}Ne$ or elevated $^{36}Ar/^{38}Ar$ ratios caused by the presence of secondary Na- or Cl-rich minerals. This agrees with reports in the literature about the virtual absence of secondary alteration phases in Efremovka CAIs.

Compared to chondrules, in which small remnants of trapped Ne and Ar were detected (Vogel et al. 2004), CAIs experienced high temperatures for a prolonged period since they cooled distinctly more slowly (Jones et al. 2000). This seems to have caused a quantitative release of any trapped Ne and Ar from the studied CAIs that might have been present in the CAI precursor material.

It might be imagined that a formation of CAIs close to the young Sun could have resulted in the uptake of primordial solar noble gases, as was suggested for chondrules of an enstatite chondrite (Okazaki et al. 2001). Although the absence of primordial solar noble gases in the studied CAI samples does not strictly exclude this formation scenario (also taking into account that the outermost microns of the CAIs were not sampled), the noble gas data suggest that the CAIs were formed in high temperature events that did not directly involve the young Sun as the heat source. Such a scenario was also concluded for chondrule formation (Vogel et al. 2004). However, it would certainly be worth studying the noble gas compositions in the more rare CAIs in different chondrite groups, in particular those of enstatite chondrites, in one of which chondrules with high solar-like noble gas concentrations have been reported.

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