

# Origin of Isotopically Light Nitrogen in Meteorites

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**Abstract**—Bulk meteorite samples of various chemical classes and petrologic types (mainly carbonaceous chondrites) were systematically investigated by the stepped combustion method with the simultaneous isotopic analysis of carbon, nitrogen, and noble gases. A correlation was revealed between planetary noble gases associating with the Q phase and isotopically light nitrogen ( $\delta^{15}\text{N}$  up to  $-150\text{‰}$ ). The analysis of this correlation showed that the isotopically light nitrogen (ILN) is carried by Q. In most meteorites, isotopically heavy nitrogen (IHN) of organic compounds (macromolecular material) is dominant. The ILN of presolar grains (diamond and SiC) and Q can be detected after separation from dominant IHN. Such a separation of nitrogen from Q and macromolecular material occurs under natural conditions and during laboratory stepped combustion owing to Q shielding from direct contact with oxygen, which results in Q oxidation at temperatures higher than the temperatures of the release of most IHN. There are arguments that ILN released at high temperature cannot be related to nanodiamond and SiC. The separation effect allowed us to constrain the contents of noble gases in Q, assuming that this phase is carbon-dominated. The directly measured  $^{36}\text{Ar}/\text{C}$  and  $^{132}\text{Xe}/\text{C}$  ratios in ILN-rich temperature fractions are up to 0.1 and  $1 \times 10^{-4} \text{ cm}^3/\text{g}$ , respectively. These are only lower constraints on the contents. The analysis of the obtained data on the three-isotope diagram  $\delta^{15}\text{N}-^{36}\text{Ar}/^{14}\text{N}$  showed that Q noble gases were lost to a large extent from most meteorites during the metamorphism of their parent bodies. Hence, the initial contents of noble gases in Q could be more than an order of magnitude higher than those directly measured. Compared with other carbon phases, Q was predominantly transformed to diamond in ureilites affected by shock metamorphism. The analysis of their Ar–N systematics showed that, similar to carbonaceous chondrites, noble gases were lost from Q probably before its transformation to diamond.

**Keywords:** meteorites, carbonaceous chondrites, ureilites, noble gases, nitrogen, isotopes, stepped combustion

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## INTRODUCTION

The primordial nitrogen of the solar system is isotopically light and shows  $\delta^{15}\text{N}$  values of approximately  $-400\text{‰}$ . This was demonstrated by the analysis of solar wind samples collected by the Genesis mission (Marty et al., 2011). That is, the light nitrogen occurs in the Sun and represents, therefore, the major portion of all nitrogen of the solar system (SS). The isotopic composition of nitrogen in SS objects, meteorites and planets, is very variable, from a solar  $\delta^{15}\text{N}$  value of  $-400\text{‰}$  in the Jovian atmosphere (Owen et al., 2001) and osbornite from Ca–Al inclusions (Maibom et al., 2007) to  $+15000\text{‰}$  in clusters from the Isheyevo meteorite (Briani et al., 2009). In general, nitrogen associating with organic matter in meteorites has a heavy isotopic composition,  $\delta^{15}\text{N} = 0-80\text{‰}$  (Kung and Clayton, 1978; Kerridge, 1985; Grady and Wright, 2003).

It is supposed that IHN was formed from primordial solar nitrogen soon after SS origin. The possible mechanisms of such transformation are self-shielding during nitrogen dissociation induced by the ultraviolet

radiation of the early Sun (Clayton, 2003) and photolysis (Muskatell et al., 2010); the latter process seems to be more realistic. Thus, the materials from which solid bodies were formed in the SS are dominated by isotopically heavy secondary nitrogen. There are some exceptions. First, some iron meteorites show  $\delta^{15}\text{N}$  of approximately  $-100\text{‰}$  (Franchi et al., 1993). Second, enstatite chondrites have  $\delta^{15}\text{N}$  values of approximately  $-40\text{‰}$  (Grady et al., 1986). Iron meteorites are among the earliest objects of the SS formed after refractory inclusions, CAIs (Krot and Bizzarro, 2009). The carriers of light nitrogen in enstatite chondrites are nitrides (Grady et al., 1986), which can also be assigned to refractory inclusions and were probably formed very early. There are some types of achondrites containing nitrides with ILN (Grady and Wright, 2003). Thus, there seems to be a general trend of an increase in ILN content with increasing age of material formation.

The formation of IHN was perhaps a long-term process. Jupiter was formed very early. In addition to ILN, its atmosphere contains He whose isotopic sig-

nature corresponds to the earliest stage of solar evolution, when deuterium had not yet transformed to  $^3\text{He}$  (Owen et al., 2003; Gaiss and Reeves, 1972). The isotopic composition of nitrogen on Jupiter is identical within the analytical error to that of solar nitrogen (Owen et al., 2001). Most likely, the formation of IHN had not began at that time. By the time of refractory inclusion condensation, only a very small amount of such nitrogen was generated, and the  $\delta^{15}\text{N}$  of osbornite (close to  $-350\text{‰}$ ) is not significantly different from the solar value. A higher fraction of IHN ( $\delta^{15}\text{N}$  up to  $-100\text{‰}$ ) is observed in iron meteorites, which were formed later. The refractory minerals of enstatite chondrites were probably formed at a later stage. All other meteorites are even younger, and their nitrogen isotope composition is dominated by IHN. However, ILN with  $\delta^{15}\text{N} \sim -20\text{‰}$  was observed in CO carbonaceous chondrites (Newton, 1997; Wieler et al., 2006). The presence of such nitrogen is most clearly seen during the stepped combustion of bulk meteorite samples of this type (Newton, 1997). It should be noted that ILN has been detected in varying amounts during the stepped combustion of many meteorites, even if its presence could not be established in the bulk composition (Sephton et al., 2003; Grady et al., 2002). The most common interpretation of such observations postulates presolar nanodiamonds as a source of this nitrogen. Indeed, nanodiamonds associating with isotopically anomalous Xe-HL (Huss and Lewis, 1994) produced in supernovae contain ILN with  $\delta^{15}\text{N} \sim -350\text{‰}$  (Russell et al., 1996; Verchovsky et al., 1998). However, in contrast to xenon, this nitrogen is not necessarily of a supernova origin, because nanodiamonds are mixtures of several populations of different nature (Russell et al., 1991, 1996; Verchovsky et al., 1998). This implies that diamonds with ILN could be formed in the SS. This is indicated by the fact that ILN cannot be directly connected with the formation of Xe-HL in supernovae (Clayton et al., 1995). Moreover, the carbon isotope composition of nanodiamonds lies within the range characteristic of the SS (Russell et al., 1996). In any case, the content of nanodiamonds in meteorites is rather high (up to 1400 ppm; Huss, 1990; Hass et al., 2003), and they could be a source of ILN released during the stepped combustion of bulk meteorite samples. Note that nitrogen isotope analysis alone is often insufficient for the identification of nanodiamonds as ILN sources. The analysis of noble gases is required for a more reliable interpretation.

A special case of ILN-bearing meteorites ( $\delta^{15}\text{N} \sim -120\text{‰}$ ) is monomict ureilites, achondrites with high contents of carbon shock-transformed to a large extent to diamond (Vdovykin, 1970; Grady et al., 1985; Rai et al., 2002, 2003; Downes et al., 2015). This diamond contains ILN and planetary noble gases (Gobel et al., 1978), which are very common in carbonaceous chondrites but are almost completely absent in other achon-

drites. There is still no consistent interpretation for all these observations (Goodrich, 1992).

In this study, I attempted to answer the question if there is an unidentified phase in meteorites that could be a source of ILN. The experimental investigation of bulk meteorite samples of various classes and petrologic types by the stepped combustion technique, which has been conducted in cooperation with my colleagues from the Open University over many years, showed that such a source likely exists. It is probably the still enigmatic phase Q, a carrier of planetary gases (Wieler, 2002). It is not yet identified, because all attempts to separate it in a pure form have failed, although its enrichment by factors of tens was attained in certain meteorite fractions by chemical separation methods (Lewis et al., 1975). However, this appears to be insufficient for the determination of the chemical composition of this phase. Most researchers believe that Q is a carbon phase, which is indicated by its oxidation at relatively low temperatures (Ott, 1981; Verchovsky et al., 2003). The isotopic composition of nitrogen in Q can hardly be determined for the same reason, the impossibility of obtaining pure Q phase, although attempts to estimate it were reported (Murty, 1996; Hasizume and Nakaoka, 1998). This means that nitrogen of different origin from other phases is mixed with Q-nitrogen. Our approach is based on the simultaneous measurement of isotope ratios and contents of nitrogen, carbon, and noble gases and determination of the source of ILN through the analysis of correlations in the system of these elements. In addition, we took into account that the helium isotope composition of Q (Ott, 2002) is similar to that of the Jovian atmosphere, which suggests very early formation of Q in the SS and, consequently, the possible similarity of the isotopic signature of its nitrogen to that of solar nitrogen.

## ANALYTICAL METHODS

Bulk meteorite samples were analyzed using a Finesse mass spectrometric complex designed at the Open University. The main feature of this instrument is the possibility to analyze simultaneously the isotopic compositions and contents of several elements (He, Ne, Ar, Xe, N, and C) extracted from a single sample. It consists of two magnetic mass spectrometers with a radius of 12 cm and one quadrupole mass spectrometer connected to a common extraction system. All mass spectrometers are operated in a static vacuum mode. One of the magnetic mass spectrometers is used for the analysis of carbon in the  $\text{CO}_2$  form; the other, for molecular N and Ar; and the quadrupole spectrometer, for He, Ne, and Xe. Gases are released by heating the sample in a double-vacuum furnace with an inner quartz glass tube, an outer corundum tube, and a silicon carbide heater allowing experiments at temperatures up to  $1450^\circ\text{C}$ . Pure oxygen generated by heating  $\text{CuO}$  to  $850^\circ\text{C}$  is used for oxidation, and the unused portion of oxygen is resorbed by cop-

per oxide at 450°C. The oxygen pressure during oxidation is 5–10 mbar, and the combustion time is 0.5 h.

The released gases are separated into the He + Ne, CO<sub>2</sub> + Xe, and Ar + N<sub>2</sub> fractions using cryogenic traps and additionally purified on Al–Ti getters (noble gases) and copper oxide (nitrogen). Each of the CO<sub>2</sub> + Xe and Ar + N<sub>2</sub> fractions is then subdivided into two approximately equal portions and used for the analysis of individual elements after purification. All the volumes of the vacuum system were calibrated; therefore, the fraction of the total amount of a gas comprised in any particular fraction is precisely known. The amount of released CO<sub>2</sub> is determined by pressure measurements using a Baratron with a precision better than 1%. Before introduction into the mass spectrometer, CO<sub>2</sub> is additionally divided depending on its total amount for the reliable measurement of isotopic composition and to avoid exceeding the maximum permissible signal of the amplifier. This is achieved by the calibration of the volumes in which gases are split and the determination of mass spectrometer sensitivity. A similar procedure of nitrogen splitting is based on the preliminary measurement of its small (5%) fraction with the precalibrated quadrupole mass spectrometer. The mass spectrometers for N<sub>2</sub> and CO<sub>2</sub> are equipped with three collectors set for masses of 28, 29, and 30 and 44, 45, and 46, respectively. The measurement itself takes approximately one minute, which yields ~300 counts for each isotope and eventually provides a precision of 0.3–0.5‰. During measurements in a static vacuum mode, CO<sub>2</sub> is rapidly (half-life of ~20 s) transformed to CO; therefore, longer measurements are impracticable. The nitrogen signal also decreases during mass spectrometric measurements, although much slower than that of CO<sub>2</sub>. For the calculation of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , appropriate standards were measured alternately with the samples. To provide identical conditions for both measurements, the amount of the standard must correspond to that of the sample. For this purpose, a sampling system, in which standard gas is continuously bleeding from a reservoir through a capillary, is used. The necessary amount of gas is collected by setting the time of its accumulation in a certain volume. This technique provides highly accurate (<2%) correspondence between the amounts of sample and standard gases during measurements. Since isotope fractionation may occur in gas flow through the capillary, the standards are calibrated using either NBS standards (calcite for CO<sub>2</sub>) or atmospheric nitrogen (for N<sub>2</sub>). The sampling system for noble gas standards is similar and also calibrated in an appropriate manner. In addition, gas flow rate is determined for all sampling systems of standards for the estimation of the sensitivity of mass spectrometers and the amounts of gas (nitrogen and noble gases) using the peak height method.

The measurement system described above is fully automated. For sample measurements, temperature and time of oxidation at each temperature step, the

number of steps, and the list of elements (e.g., C, N, and Ar) are set. A 2–5 mg samples is loaded into a Pt foil (25  $\mu\text{m}$  thick) capsule. The sample is dropped into an extraction furnace through a gate valve and heated at 200°C for at least 0.5 h (the first step of oxidation was always conducted at 200°C to further decrease atmospheric contamination), and the analysis is further conducted in automated mode. Pneumatically controlled valves are used in the vacuum system, and cryotrap are cooled by pumping nitrogen vapor of liquid nitrogen through a small cylinder jacket placed directly adjacent to a cold finger, which has a good thermal contact with it. Regulated thermostats are equipped with a wire heater wound directly around the cold finger between it and the cooling jacket. The duration of the autonomous operation of the instrument during sample analysis depends on the volume of the liquid nitrogen Dewar. A 50-L Dewar is sufficient for continuous operation over 24 h. During this time, 10–15 separate temperature fractions can be analyzed depending on the set of elements analyzed. The system blank was determined by the analysis of empty Pt foil.

## SAMPLES

We investigated samples of carbonaceous chondrites of various classes and petrologic types (number of samples in parentheses): CI (2), CM (4), CO (1), CR (12), and CV (2), and 12 ureilites. Analytical results were mostly published elsewhere (Grady et al., 2002; Sephton et al., 2003; Verchovsky et al., 2002, 2012; Rooke et al., 1988; Greenwood et al., 2007; Jenniskens, 2012). These publications focused mainly on the origin of nitrogen and carbon components. The relation of these components with noble gases was not explored in detail. All the samples were analyzed by the stepped combustion method with a temperature increment of 50–100°C and simultaneous determination of the contents and isotope compositions of N, C, and Ar; He, Ne, and Xe were also analyzed in some samples. The total contents and isotopic compositions of C, N, Ar, and Xe in the temperature fractions are given in the table for most of the samples.

## RESULTS AND DISCUSSION

### *Oxidation Properties of the Q Phase*

The carrier of planetary-type noble gases in meteorites is the so-called Q phase, the identity and origin of which are still poorly understood. The most important known property of Q is that it is susceptible to oxidation by oxidizing acids (for instance, nitric acid) or molecular oxygen (Lewis et al., 1975; Ott et al., 1981; Frick and Pepin, 1981). Oxidation by acid and oxygen occurs at relatively low temperatures of ~200°C and 400–600°C, respectively. It should be noted that Q is not completely oxidized by acid in all samples (Moniot, 1980), which may indicate its heterogeneity. Treatment with molecular oxygen always results in

**Table 1.** Bulk contents of C, N, and noble gases and isotope composition of C and N in the analysed meteorites

Sample	Weight, mg	C, wt %	$\delta^{13}\text{C}$ , ‰	N, ppm	$\delta^{15}\text{N}$ , ‰	SiC, ppm*	Nanodiamond, ppm**	$^{36}\text{Ar}$ , $\text{cm}^3/\text{g} \times 10^{-6}$	$^{132}\text{Xe}$ , $\text{cm}^3/\text{g} \times 10^{-9}$
CR1									
GPO95577	1.455	1.78	12.2	241	180	—	—	0.412	—
Al Rais	4.008	1.86	-6.3	596	143	—	—	0.314	—
CR2									
EET 46259	1.802	0.90	-2.8	637	155	54	124	1.52	5.99
EET 92042	3.712	2.23	-5.7	1260	168	95	224	4.98	17.2
PCA 91082	3.100	0.81	-1.3	791	183	86	194	2.16	8.03
GRA 95229	3.885	0.38	1.8	239	182	33	154	0.466	1.40
EET 87770	5.556	1.27	-7.8	737	159	64	149	1.09	—
MAG 87320	8.478	0.91	-4.9	598	172	41	94	1.28	—
Acfer 59	9.014	0.46	-7.5	160	101	35	82	0.239	—
El Djouf	3.181	0.42	-15.3	174	101	100	244	0.456	—
Acfer 186	2.601	0.56	-9.5	271	137	110	230	1.43	3.74
Acfer 139	3.013	0.53	-13.1	552	58	1100	2600	1.77	1.67
CR3/CV3									
NWA 1152	2.606	1.82	-10.9	165	-4.8	43	785	5.10	—
SAH 00182	4.081	0.23	-14.5	76.0	-2.1	22	56	0.755	—
CO3									
Moss	4.589	0.23	0.7	10.4	-47	17	196	1.77	—
Moss HF/HCl	1.645	1.42	-10.6	48.0	-30	—	520	—	—
CM2									
JBilet	5.190	1.99	-6.5	917	7.0	16	40	1.60	1.06
Murchison	4.867	2.20	-2.7	967	40	7.2	6900	1.69	—
Murchison HF/HCl	1.473	8.20	-19.2	3330	15.8	—	—	9.61	—
Maribo	4.818	2.34	-2.3	1350	40	28	18300	0.525	—
Sutters Mill	6.340	2.2	6.4	559	-0.6	3.0	1320	0.781	1.63
CI2									
Tagish Lake	4.400	5.81	24.4	1220	68	13	3900	1.31	—
Tagish Lake $\text{H}_3\text{PO}_4$	1.327	13.50	-16.0	5370	52	—	—	7.90	24.8
CI1									
Orgueil	2.938	4.50	-16.0	2070	32	—	7800	2.65	—
Orgueil HF/HCl	0.206	9.10	-18.5	1800	21	—	—	9.91	141
Ureilites									
ALHA 77257	5.078	1.35	-4.5	27.8	-3.4	—	—	25.3	—
HH 126	4.715	2.04	-10.2	42.0	-1.2	—	—	29.3	—
HH 064	5.807	1.84	-13.7	36.7	-61	—	—	7.23	—
SAH 99201	13.41	0.90	—	22.0	-25	—	—	10.8	—
Meteoritic presolar grains									
Nanodiamond***	—	100	~-40	3000-10000	-350	—	0-1400	20-40	200-300
SiC****	—	30	~1400	~9000	-600	0-15	—	6	20

\* Calculated from ILN content using data for pure SiC.

\*\* Calculated from ILN content using data for pure nanodiamond.

\*\*\* After Russell et al. (1996), Huss and Lewis (1994), and Huss et al. (2003).

\*\*\*\* After Ash et al. (1989), Russell (1992), and Russell et al. (1997).

complete Q oxidation (Schelhaas et al., 1990; Verchovsky et al., 2002). The decomposition of Q at pyrolysis is observed at much higher temperatures; in particular, noble gases are released only at temperatures of  $\sim 1000^{\circ}\text{C}$  or even higher (Huss et al., 1996). These observations are consistent with the carbonaceous nature of Q. The Q phase can be concentrated by selective dissolution in a mixture of hydrofluoric and hydrochloric acids. This results in the dissolution of all silicates and retention of oxide and carbon phases, including Q (Lewis et al., 1975). The contents of planetary noble gases in the residue increase by a factor of almost 100 compared with the initial sample. However, Q probably accounts for only a very minor fraction of carbon in the residue, because the dissolution of Q in nitric acid changes the total carbon content of the residue by less than 1% (Lewis et al., 1975; Wieler et al., 1991). This is the main difficulty in obtaining pure Q, because it cannot be separated from other carbon phases of the acid-resistant residue. It is important to emphasize that Q may be oxidized in a wide temperature interval during the analysis of bulk meteorite samples (Fig. 1a), which is discussed in detail below, whereas the range of oxidation of acid-resistant residue is always narrow,  $300\text{--}600^{\circ}\text{C}$  (Fig. 1b). This range corresponds to the true temperature of Q oxidation, which is not present in a pure form in these residues but is liberated from the more compact mass of major meteorite materials.

Under natural conditions, in particular, during metamorphism in meteorite parent bodies, Q is also oxidized, which is indicated by a systematic decrease in the content of planetary noble gases in meteorites with increasing degree of metamorphism (Huss et al., 1996). However, this process is slower than the natural oxidation of presolar grains of nanodiamond and SiC. For instance, the latter disappear completely in meteorites of petrologic types higher than 3.8, whereas planetary gases are retained (Huss et al., 1995, 1996). The higher stability of Q is also observed during metamorphism under reducing conditions; for instance, most of organic carbon in enstatite chondrites is graphitized, and its oxidation temperature increases significantly, but the thermal-oxidation properties of Q remain unchanged (Verchovsky et al., 2002). These observations indicate that, although Q is similar in many respects to other meteoritic carbon materials, which strongly hinders their separation from each other, it is nonetheless a distinct carbon phase whose properties are different from those of the main mass of meteorite carbon.

### *Stepped Combustion of Bulk Meteorite Samples*

#### *Oxidation Kinetics*

This section considers the process of Q oxidation in more detail. In particular, we will attempt to explain why Q is oxidized in some samples only at low tem-

perature, whereas other samples exhibit a high-temperature peak of noble gas release with or without low-temperature one.

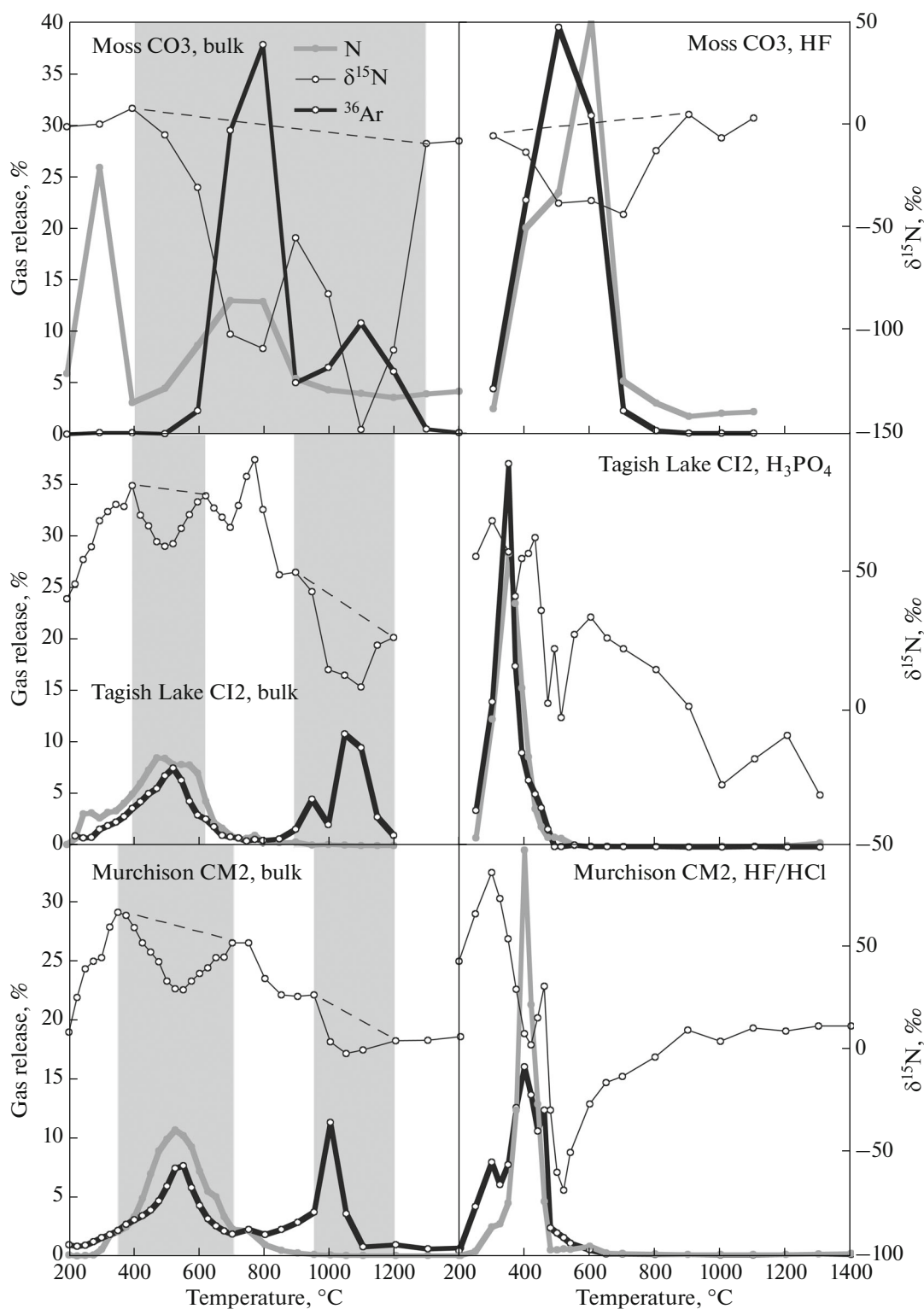
Figure 2 shows examples of different oxidation kinetics. First of all, it should be noted that it is highly improbable that there are several Q forms with different oxidation kinetics. As was discussed in the previous section, the acid-resistant residues always show only one low-temperature peak of noble gas release independently of their release pattern from the initial sample (Fig. 1). Therefore, the most probable reason is the shielding of all or part of Q from direct contact with oxygen during laboratory combustion. It is difficult to say what the reason of shielding is and whether Q can be shielded by a specific phase or by any minerals. It can be suggested that conditions for such shielding had existed during the accretion and/or metamorphism of the parent bodies. It is interesting that, similar to the acid-resistant residues (Fig. 1), only low-temperature release of planetary noble gases was documented for the meteorites significantly affected by aqueous alteration (mainly meteorites of petrologic type 1, such as Orgueil, Al Rais, and Gro 55577; Fig. 2). This allows us to suggest that the effect of aqueous alteration under natural conditions is similar in some aspects to acid treatment in the laboratory: it eliminates shielding and/or prevents its formation during thermal metamorphism. The high-temperature release of noble gases was observed in thermally metamorphosed samples of petrologic types 2 and 3.

In any case, the shielding results in significant separation of Q and the main mass of meteoritic carbon, which could not be achieved using laboratory chemical methods. This resulted in the manifestation of Q properties that could not be detected without stepped combustion. This will be discussed in the following section.

### *Correlation with Isotopically Light Nitrogen*

As can be seen in Fig. 2, in all cases of high-temperature  $^{36}\text{Ar}$  release, it is accompanied by ILN with  $\delta^{15}\text{N}$  up to  $-150\text{‰}$ , and the Ar peak almost exactly coincides the minimum of  $\delta^{15}\text{N}$ . Can this observation be considered as an indicator of a common source for  $^{36}\text{Ar}$  and ILN? The answer appears to be yes. For instance, this source could be meteoritic nanodiamonds mentioned in the Introduction or presolar silicon carbide grains. Both contain ILN ( $\delta^{15}\text{N}$  is  $-350\text{‰}$  in diamonds and up to  $-600\text{‰}$  in SiC) and  $^{36}\text{Ar}$  (Table 1). It can also be supposed the Q phase is the source of these components. This dilemma can be resolved on the basis of the analysis of proportions of Ar, C, and N contents, which are well known for nanodiamonds and SiC.

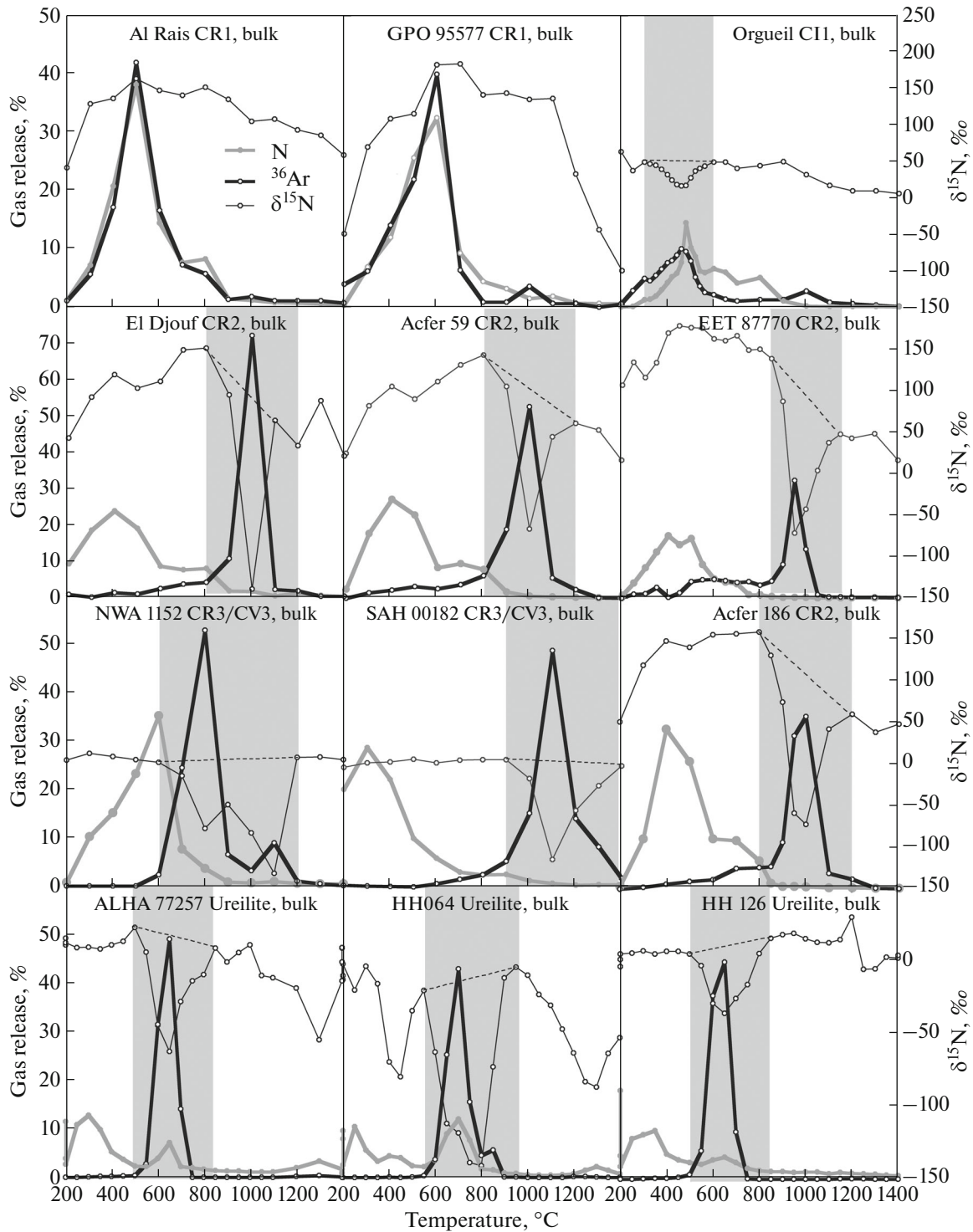
Figure 3a shows  $^{36}\text{Ar}/\text{C}$  variations during the stepped combustion of the samples that exhibit a high-temperature peak of Ar release. For pure carbon phases, such as nanodiamond and, very probably, Q,



**Fig. 1.** Release of nitrogen and  $^{36}\text{Ar}$  and  $\delta^{15}\text{N}$  variations during the stepped combustion of bulk meteorite samples and their acid-resistant residues. Gray shade shows the temperature range of simultaneous release of  $^{36}\text{Ar}$  and isotopically light nitrogen. Dashed lines indicate the  $\delta^{15}\text{N}$  values of isotopically heavy nitrogen.

this ratio is equivalent to Ar content in them. As to SiC, this ratio also gives Ar content after correction for the relative content of C in this compound (i.e., after

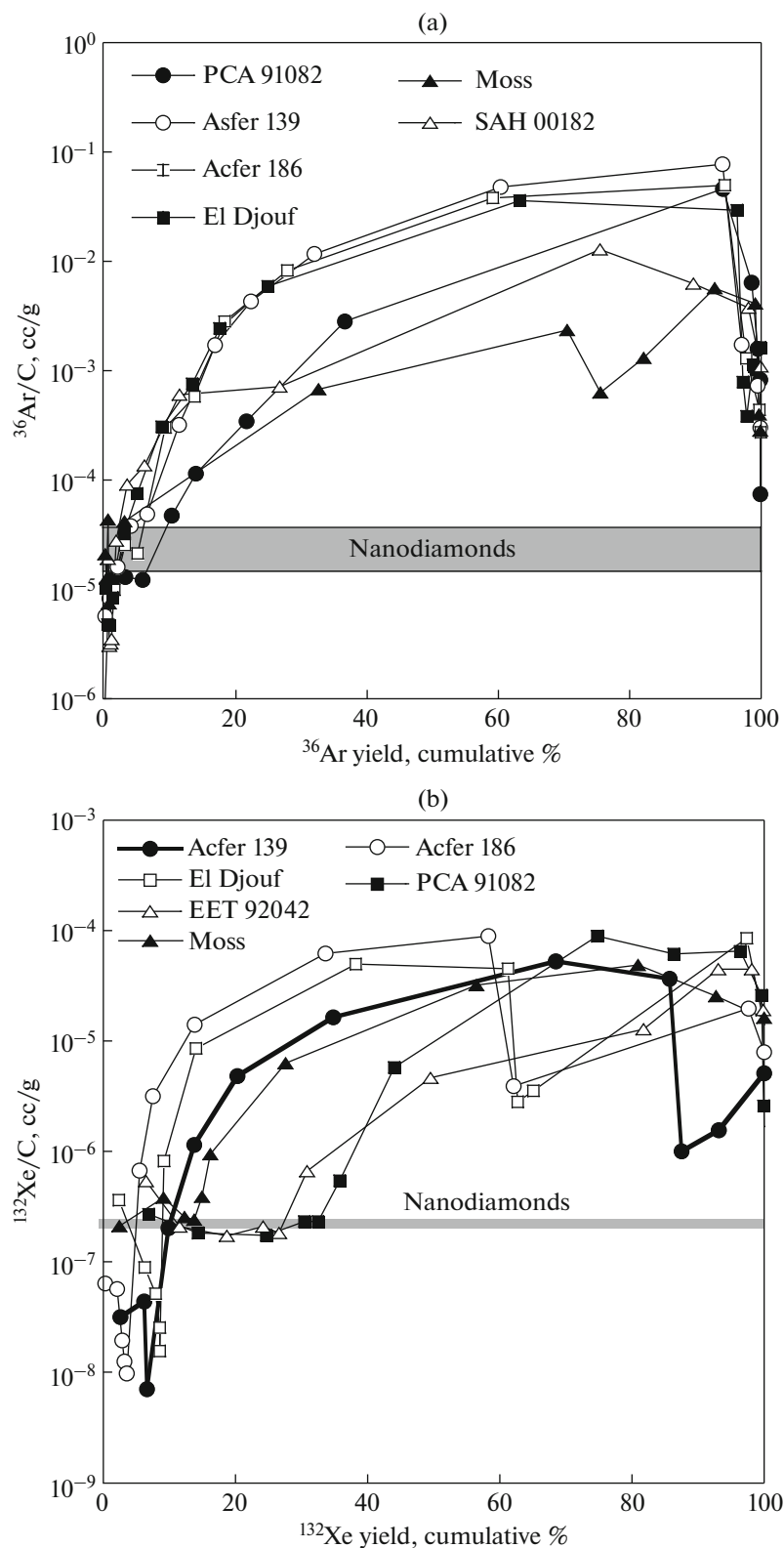
applying a correction factor of 0.3). It should be kept in mind that the measured  $^{36}\text{Ar}/\text{C}$  ratios can be considered only as the lower limits of contents in the



**Fig. 2.** Release of nitrogen and  $^{36}\text{Ar}$  and  $\delta^{15}\text{N}$  variations during the stepped combustion of bulk meteorite samples of various chemical classes and petrologic types. Fields and lines are the same as in Fig. 1.

phases, because the bulk composition of meteorites always includes numerous carbonaceous phases (including carbon of organic origin and disordered graphite-like carbon), which are free of noble gases and can be oxidized over a considerable temperature

range; these phases exert a diluting effect on Ar content. As can be seen in Fig. 3, the possible contribution of nanodiamond is several orders of magnitude lower than the observed contents. The abundance of  $^{36}\text{Ar}$  in presolar SiC normalized to carbon is even lower than



**Fig. 3.** Variations in (a)  $^{36}\text{Ar}/\text{C}$  and (b)  $^{132}\text{Xe}/\text{C}$  during the stepped combustion of meteorites compared with the abundances of respective gases in nanodiamonds.



that in nanodiamond (table). Hence, all  $^{36}\text{Ar}$  owes its origin to the Q phase. The same conclusion is derived from the analysis of  $^{132}\text{Xe}/\text{C}$  values in temperature oxidation steps (Fig. 3b).

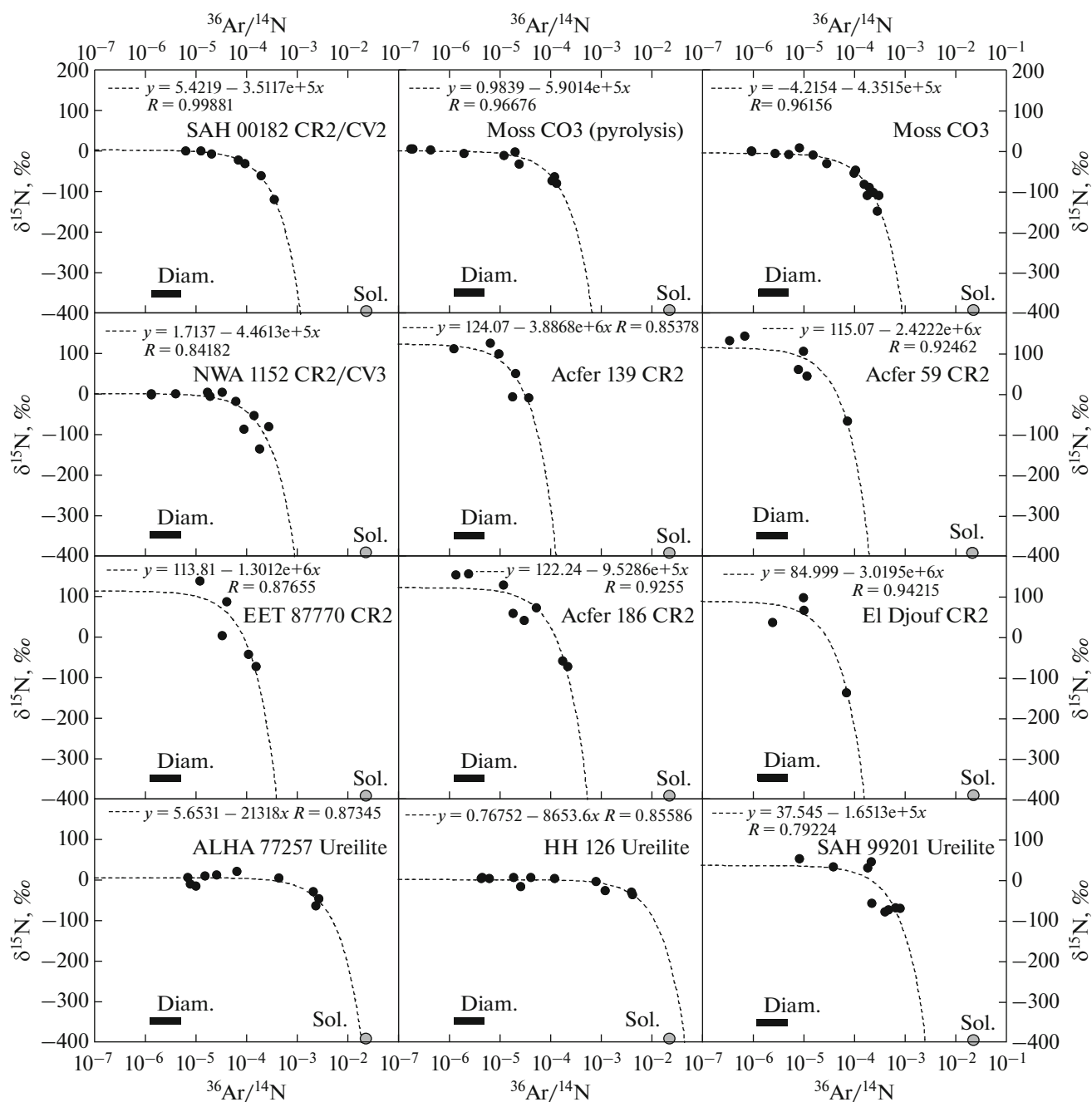
This does not mean that ILN cannot be hosted by nanodiamond or SiC. Assuming that the  $\delta^{15}\text{N}$  variations in the range of  $^{36}\text{Ar}$  release are due to mixing of IHN of macromolecular material and nitrogen from either diamond or SiC, the content of these phases in the bulk composition of meteorites can be estimated. Since the nitrogen isotope composition of macromolecular material varies during stepped combustion, the respective  $\delta^{15}\text{N}$  value in the temperature range of ILN release was determined by linear interpolation between two values corresponding to the beginning and end of ILN release, which is shown by dashed lines in Figs. 1 and 2. Such an interpolation ignores possible variations in the isotopic composition of IHN, which may deviate from the linear relation in either direction. Therefore, the calculated content is associated with an error, which was estimated as  $\pm 50\%$ . The estimated contents of nanodiamond and SiC are given in the Table 1. The content of nanodiamond in the bulk composition of the meteorites determined from the analysis of Xe-HL ranges from 0 to 1400 ppm depending on the chemical class and petrologic type (Huss et al., 2003). The calculated contents appeared to be higher than expected (sometimes orders of magnitude higher) for the CI and CM carbonaceous chondrites, which indicates that the  $\delta^{15}\text{N}$  decrease in the low-temperature fractions of nitrogen was not related to the contribution of ILN contained in nanodiamonds. The nitrogen released in this temperature range is, however, isotopically heavy (10–80‰) despite  $\delta^{15}\text{N}$  variations correlating with the release of Q- $^{36}\text{Ar}$ . A certain contribution to the  $\delta^{15}\text{N}$  variations could be due to variations in the nitrogen isotope composition of various organic substances oxidizing at these temperatures. For all other meteorite types presented in the table, except for one sample (Acfer 139), the calculated nanodiamond contents are within the expected range (200–700 ppm) or even lower, i.e., below the level necessary for the explanation of ILN appearance.

The calculated SiC contents (3–1100 ppm, Table 1) are significantly higher than those estimated from Ne-E analysis in the CR and CO meteorites (<1 ppm) and approximately within the acceptable range for the CI and CM meteorites (10–15 ppm). This means that, in principle, ILN could be derived from nanodiamonds in the meteorites of the CR and CO types, whereas SiC is not an ILN source. However, it has to be assumed in such a case that such different in their chemical nature and origin phases as nanodiamond and Q behave as if they were a single material. This is despite the fact that their only common feature is that they are varieties of carbonaceous substances combustible in molecular oxygen upon heating. Their oxida-

tion temperatures are similar, but not identical. Other chemical properties of these phases are contrasting: Q is soluble in nitric acid, whereas nanodiamond is insoluble; colloidal nanodiamond forms are observed in alkaline media solutions (Lewis et al., 1987), whereas Q does not form colloids; Q is more resistant to metamorphism in meteorite parent bodies compared with nanodiamond (Huss et al., 1996; Verchovsky et al., 2002); and noble gases are released from these phases at different temperatures during pyrolysis (Huss and Lewis, 1994; Huss et al., 1996).

Finally, why is the shielding of Q and nanodiamond from oxygen during laboratory stepped combustion strictly identical despite their different physical (density and grain size) and chemical properties? Of course, as long as the mechanism of shielding remains unknown, it cannot be excluded that both Q and nanodiamonds are affected to the same extent for some as yet unknown reason. However, the linear trends with very high correlation coefficients in the  $\delta^{15}\text{N}$ – $^{36}\text{Ar}/^{14}\text{N}$  three-isotope diagrams (Fig. 4) can hardly be explained by almost perfectly synchronous release at any temperature of noble gases from Q and nitrogen from nanodiamonds. Indeed, if the three-component system is composed of nanodiamond, a source of ILN only (its  $^{36}\text{Ar}$  content is very low compared with Q); Q, a nitrogen-free source of  $^{36}\text{Ar}$  only; and macromolecular material containing IHN and free of  $^{36}\text{Ar}$ , a mixing line away from the nanodiamond composition could appear only if (1) all points in the diagrams (Fig. 4) are uniformly shifted to the right; i.e., all temperature fractions contain identical amounts of  $^{36}\text{Ar}$ ; or (2)  $^{36}\text{Ar}$  release from Q is strictly proportional to nitrogen release from nanodiamonds. The former is inconsistent with the experimental data, and the latter is highly improbable. Mixing lines with very high correlation coefficients (0.95 and higher) are formed independent of the method of gas release, either oxidation or pyrolysis, which was established for the bulk sample of the Moss meteorite (Fig. 4). Therefore, it is much more reasonable to interpret the observed relations as mixing lines between two nitrogen components: isotopically heavy from macromolecular material and isotopically light from Q without any contribution from nanodiamonds. Thus, the source of ILN is Q.

This interpretation of the obtained data is supported by the correlation of ILN with  $^{36}\text{Ar}$  release established for the Saratov meteorite (Verchovsky et al., 2017). It is an ordinary chondrite of petrologic type 4, in which nanodiamond disappeared (was oxidized) completely during parent body metamorphism (Huss and Lewis, 1994). Another argument in favor of our hypothesis is that the acid-resistant residue after treatment of this meteorite with HF/HCl and  $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ , i.e., the fraction that is usually most enriched in nanodiamonds, is free of such a typical component of nanodiamonds as Xe-HL (Matsuda et al., 2016). In addition,



**Fig. 4.** Variations in  $^{36}\text{Ar}/^{14}\text{N}$  and  $\delta^{15}\text{N}$  within the temperature range of simultaneous release of  $^{36}\text{Ar}$  and ILN during the stepped combustion of meteorites of various chemical classes and petrologic types. Experimental points are approximated by linear functions, the equations of which are shown in each diagram together with correlation coefficients,  $R$ . Diam. is the composition of nanodiamonds, and Sol. is the solar composition. Note the semilogarithmic scale of the diagrams.

ILN was found in some individual spots by high-resolution NanoSIMS analysis in the residue obtained by the treatment of a bulk sample of the Saratov meteorite with HF/HCl only (Amari et al., 2015).

It should be noted that the correlation between  $\delta^{15}\text{N}$  and  $^{36}\text{Ar}/^{14}\text{N}$  in other samples may be weaker than that in the SAH 00182 and Moss meteorites (Fig. 4), but the correlation coefficient is almost always higher than

0.8. An increase in the scatter of measurements in these diagrams is obviously related to  $\delta^{15}\text{N}$  variations in IHN of macromolecular material during its stepped combustion; i.e., the scattered correlations (Fig. 4) are produced by mixing with a set of compositions rather than a single IHN component. This is understandable, because the carrier of IHN is a mixture of various organic compounds, the formation of which was

accompanied by variable nitrogen isotope fractionation and which may be oxidized at different temperatures. Perhaps, the high correlation in some diagrams (Fig. 4) is related to the rather homogeneous nitrogen isotopic composition of macromolecular material in the particular samples. As to nanodiamond-hosted nitrogen, it is probably released at low temperatures of 400–500°C characteristic of nanodiamond oxidation. Macromolecular material is mostly oxidized in this temperature interval, and the released nitrogen obscures the signal of nanodiamond-derived ILN.

Thus, since Q is widespread in meteorites in general and in carbonaceous chondrites in particular, ILN is also common in them. The presence of this nitrogen is not always obvious in the bulk composition of meteorites, which depends on the proportion of Q and macromolecular material in the meteorites. ILN can be observed at stepped combustion, if Q is oxidized at high temperature owing to the shielding effect. In such a case, macromolecular material containing IHN, which always dominates over Q-nitrogen, is oxidized, and Q-nitrogen is much better manifested, although not in a pure form, because a certain amount of IHN is mixed with Q-nitrogen even at high temperature. Therefore, the isotopic composition of pure Q-nitrogen cannot be determined. Only the upper limit of  $\delta^{15}\text{N}$  is rigorously constrained by the lowest measured value,  $-150\text{‰}$ . However, assuming the very early formation of Q in the SS, the suggestion of the isotopic similarity of this nitrogen to solar one does not seem unrealistic.

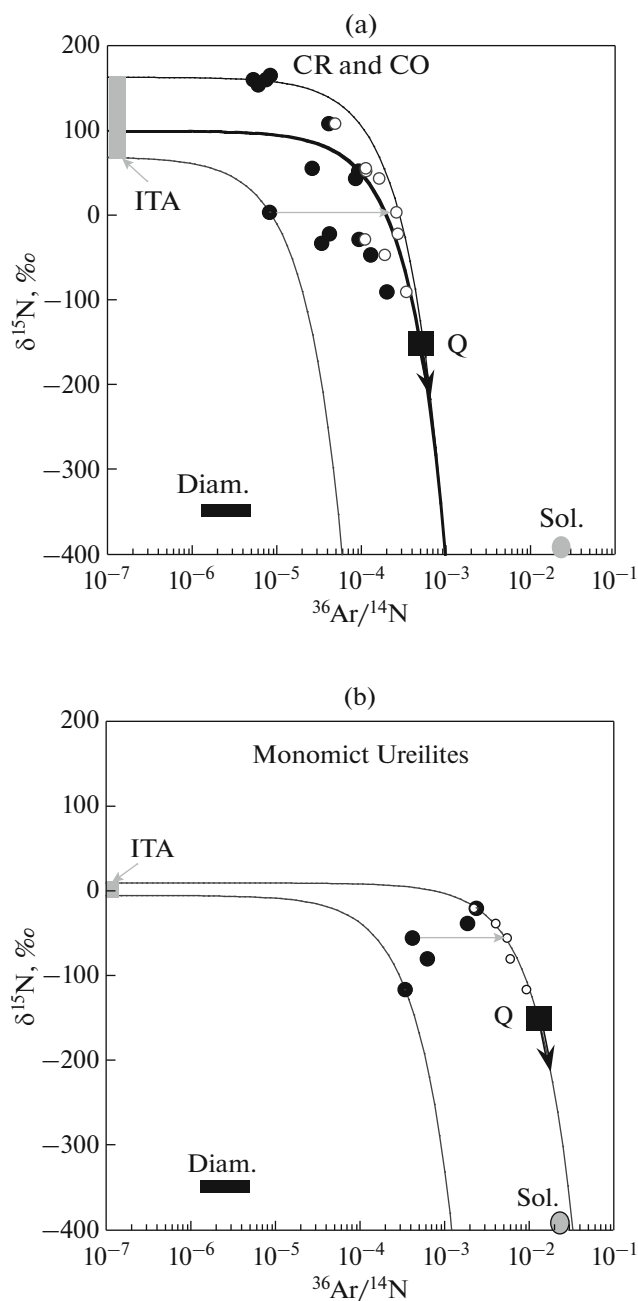
Meteorites of the CR and CO types (Fig. 4) show  $^{36}\text{Ar}/^{14}\text{N}$  variations at the  $\delta^{15}\text{N}$  value supposed for Q ( $-150\text{‰}$  or lower). These variations are within one order of magnitude and can be caused by different  $^{36}\text{Ar}$  losses compared with nitrogen during parent body metamorphism, which is discussed in detail in the following section. Similar  $^{36}\text{Ar}/^{14}\text{N}$  variations are observed in ureilites, although the values are higher than in other meteorites, which indicates a smaller  $^{36}\text{Ar}$  loss compared with nitrogen during the metamorphism of ureilite parent bodies or different efficiency of entrapment in diamond during shock-induced diamond formation (see the section “Q in Ureilites”).

If, owing to an as yet unknown reason and contrary to the arguments presented above, nanodiamond and Q (free of ILN and containing only  $^{36}\text{Ar}$ ) are localized in meteorites at the same sites and in the same environments and are oxidized in an identical manner over a wide temperature range, it should probably be admitted that their connection is genetic rather than merely mechanical. This may open a fundamentally new approach to the investigation of their origin and evolution in the SS. This should be kept in mind, in case new evidence for such a relation will appear in the future. Meanwhile, I favor the hypothesis that nanodiamonds and Q are two independent ILN-bearing carbon phases.

### *Noble Gas Abundances in Q*

As can be seen in Fig. 3, the  $^{36}\text{Ar}/\text{C}$  and  $^{132}\text{Xe}/\text{C}$  ratios of Q, which can be considered as the abundances of these elements, assuming that Q is a carbon phase, may be as high as almost 0.1 and  $10^{-4}$   $\text{cm}^3/\text{g}$ , respectively. It was noted above that these values are only the lower limits for the element concentrations, because the temperature fractions showing the maximum values of these ratios could contain carbon of a different origin. These values are very high and exceed the contents of implanted solar gases in lunar soils. Therefore, it is reasonable to suggest that Q noble gases were also implanted.

In the three-isotope diagram  $\delta^{15}\text{N}-^{36}\text{Ar}/^{14}\text{N}$  (Fig. 5a) for the total of fractions containing simultaneously released  $^{36}\text{Ar}$  and ILN (gray-shaded regions in Figs. 1 and 2), the points of type CR and CO meteorites form a trend of an increase in  $^{36}\text{Ar}/^{14}\text{N}$  with decreasing  $\delta^{15}\text{N}$ . The high scatter of measurements can be readily explained. During accretion and parent body formation, organic matter with IHN and Q with ILN are captured in varying proportions, which is reflected in the bulk nitrogen isotope composition of the parent bodies. Subsequent metamorphic events could result in nitrogen loss from its carriers in different proportions and corresponding changes in the bulk isotopic composition of nitrogen. All these events are also reflected in variations in nitrogen content, such that changes will occur along the mixing lines shown in Fig. 5, which will not increase the scatter. However, the mixing lines for different parent bodies could be different depending on the  $\delta^{15}\text{N}$  of IHN of their macromolecular material, which can cause a scatter in the three-isotope diagram (Fig. 5). However, this factor cannot account for the whole scatter. The mixing lines passing through the composition of IHN and measured values for each sample have different  $^{36}\text{Ar}/^{14}\text{N}$  values at a certain  $\delta^{15}\text{N}$ . This can be caused only by  $^{36}\text{Ar}$  loss. Therefore, considering the rightmost line in the diagram (Fig. 5) as the true mixing line between IHN and Q-ILN, the  $^{36}\text{Ar}/^{14}\text{N}$  value of Q can be determined, assuming a certain  $\delta^{15}\text{N}$  value in it. Any mixing line that does not pass through the Q composition determined in such a way indicates  $^{36}\text{Ar}$  loss. The magnitude of change in the measured  $^{36}\text{Ar}/^{14}\text{N}$  value in such samples required to shift the mixing line to pass through Q is a quantitative characteristic of  $^{36}\text{Ar}$  loss. This loss may be as high as 97% in some samples. The measured  $^{36}\text{Ar}/^{14}\text{N}$  values must be corrected for such losses, which results in higher argon contents in Q reaching, for instance, 3  $\text{cm}^3/\text{g}$  in a sample of the Acfer 139 meteorite, which has lost 97%  $^{36}\text{Ar}$  (Fig. 5a) and showed the maximum measured  $^{36}\text{Ar}/\text{C}$  value of only 0.1  $\text{cm}^3/\text{g}$ .

*Q in Ureilites*

**Fig. 5.** Ar–N isotopic systematics of the total of fractions corresponding to the simultaneous release of  $^{36}\text{Ar}$  and ILN (indicated by gray shading in Figs. 1 and 2) in (a) CO and CR meteorites and (b) ureilites. Also shown are mixing lines between the measured compositions (filled circles) and corresponding ILN determined from dashed lines in Figs. 1 and 2; the shaded gray areas are the ranges of IHN values. Gray arrows connecting filled and unfilled circles show changes in  $^{36}\text{Ar}/^{14}\text{N}$  values related to Ar loss. The arrow in Fig. 5a connects points of the Acfer 139 sample (see text).  $^{36}\text{Ar}/^{14}\text{N}$  values corrected for  $^{36}\text{Ar}$  loss are indicated by unfilled circles. Also shown are the compositions of nanodiamonds (Diam.) and solar wind (Sol.) and the hypothetical composition of Q.

In shocked ureilites (most of the known meteorites of this type are shocked), all noble gases and most nitrogen are incorporated in diamonds, which were produced from organic carbon by the shock metamorphism (Vdovykin, 1970). (There is, however, a hypothesis that ureilite diamonds were formed during condensation from the protoplanetary nebula (Rai et al., 2002)). This is reflected in almost identical kinetics of the release of carbon, nitrogen, and  $^{36}\text{Ar}$  during the stepped combustion of bulk ureilite samples (Rooke et al., 1998). In the temperature range of diamond combustion, 400–600°C, nitrogen is usually isotopically light and shows  $\delta^{15}\text{N}$  values between  $-3$  and  $-80\text{‰}$ , occasionally up to  $-150\text{‰}$  (Fig. 2).

The isotopic signatures and relative abundances of noble gases in ureilites are very similar, if not exactly identical, to the planetary gases of other meteorites (Murty et al., 2010). We leave aside the problem of the origin of planetary noble gases in ureilites, which remains elusive. Thus, there are many grounds to believe that Q and organic matter were transformed in ureilites into diamonds, which retained all the components of the primary material. If CI carbonaceous chondrites are assumed to be the primary material (oxygen isotope composition of ureilites corresponds to that of carbonaceous chondrites), it should be suggested that either part of isotopically heavy organic nitrogen was lost during the transformation of macromolecular material into diamond, whereas Q-nitrogen was more strongly retained, or Q was preferentially transformed to diamond compared with macromolecular material, because ILN similar to that of shocked ureilites was never observed in CI meteorites (Figs. 1, 2) and in diamond-free ureilites (Rai et al., 2002), which were not affected by shock metamorphism.

The argon–nitrogen isotope systematics (Fig. 5b) of monomict ureilites are very similar to those of carbonaceous chondrites (Fig. 5a). One difference is a smaller scatter of measurements related to the lower variations in IHN composition. The loss of  $^{36}\text{Ar}$  provides the major contribution to this scatter. Using the loss correction procedure described in the previous section, we obtained a well-defined mixing line indicating a higher  $^{36}\text{Ar}/^{14}\text{N}$  value at  $\delta^{15}\text{N} = -150\text{‰}$  compared with that for carbonaceous chondrites. The relative loss of  $^{36}\text{Ar}$  from ureilites is also high and similar to that from carbonaceous chondrites.

Although all  $^{36}\text{Ar}$  in monomict ureilites affected by shock metamorphism (table, Fig. 5b) is contained in diamond, such considerable amounts of Ar could hardly be released from diamond, because of the high stability of its structure. These losses occurred most likely from Q before shock metamorphism. If this is the case, the formation of ureilite diamond during the condensation from the protoplanetary nebula is improbable, because such an origin would imply a significant Ar loss from diamond.

## CONCLUSIONS

1. The results of the stepped combustion of bulk meteorite samples of various classes and petrologic types indicate that, in addition to presolar diamond and SiC, there is another common carrier of ILN. The Q phase is such a carrier.

2. The  $\delta^{15}\text{N}$  of Q-nitrogen is  $< -150\%$  and probably similar to the solar value, which is consistent with the very early formation of Q in the SS.

3. The above conclusion was drawn primarily owing to the occurrence of Q in the bulk meteorite samples in a specific surrounding shielding Q from direct contact with oxygen during laboratory combustion. As a result, Q is oxidized only at high temperature, after the combustion of most organic matter enriched in IHN. Therefore, Q-nitrogen released at high temperature is separated to a large extent from nitrogen of other origin, and its isotopic composition can be determined much more accurately.

4. The nature of Q shielding remains unclear. In any case, this is an additional feature of Q distinguishing this phase from other carbon materials of different origin.

5. In carbonaceous chondrites, Q has lost a significant portion of its primary argon (and other noble gases).

6. The content of noble gases in Q is very high: direct determination from the results of stepped combustion yields  $^{36}\text{Ar} > 0.1 \text{ cm}^3/\text{g}$  and  $^{132}\text{Xe} > 1 \times 10^{-4} \text{ cm}^3/\text{g}$ . The noble gas contents of premetamorphic Q were even higher (correction for losses gives up to  $3 \text{ cm}^3/\text{g}$  of  $^{36}\text{Ar}$ ). Such high contents suggest that these gases were implanted.

7. Ureilites probably also contain Q-ILN. It occurs in a more pure form compared with other meteorites owing, most likely, to the preferential transformation of Q to diamond during the shock event compared with carbon of other origin. The formation of ureilite diamond during condensation from the protoplanetary nebula is hardly probable.

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