

THE ACID RESIDUE FROM SARATOV (L4) WITH HIGH Q CONCENTRATION. A. B. Verchovsky¹, A. V. Fisenko², L. F. Semjonova² and A. A. Shiryaev³, ¹SPS, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK, sasha.verchovsky@open.ac.uk; ²Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Kosygin st. 19, Moscow, Russia, anat@chgn.net.ru; ³A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Leninsky pr. 31 korp. 4, Moscow 119071, Russia, a_shiryaev@mail.ru.

Introduction: The planetary noble gas carrier in meteorites - Q, remains an unidentified phase, although all its properties established so far point to a carbonaceous nature of the matter [1, 2]. The problem with the phase identification is that even in the highly Q-enriched residues prepared from different meteorites it is always accompanied by other much more abundant carbonaceous phases such as organic macromolecular material and graphitic carbon with different structures. Further separation of Q from these phases is very problematic because of similarities in their chemical properties. TEM investigations of the Q-enriched residues showed that they often contain nano-sized curved graphite stacks with variable number of layers [3], suggesting that these graphene structure can be a candidate for the Q-phase. Similarity of the thermo-oxidizing graphene stacks' behaviour with kinetics of noble gas release during stepped combustion of Q also supports this assignment [4]. However at present it is difficult to prove unambiguously that Q is graphene-related and therefore it is impossible to exclude that another carbonaceous phase with very low abundance and similar thermo-oxidizing properties serves as a carrier of the planetary noble gases. One of the ways to solve the problem is to investigate the residues extremely enriched with Q.

In the present study we report results of such investigation for a HF/HCl residue prepared from the Saratov (L4) ordinary chondrite.

Preparation of the residue: The choice of Saratov meteorite is determined by two important factors: very low, if any, abundance of nanodiamonds [5], which create additional difficulties for Q identification, and relatively high concentration of Q noble gases [5, 6]. The schematic of Q separation is present in Fig. 1. In contrast to our previous preparations of the Q-enriched fractions, in the present study we applied colloid separation in isopropanol with ammonia directly to the HF/HCl residue after ultrasonic treatment and produced suspension and sediment after centrifugation (~1000g, 30 min). Here we present the results for the suspension fraction SU-2A and suspension, SU-2B, obtained from the SU-2A complementary sediment.

Analysis: The obtained fractions have been analyzed for noble gases, carbon and nitrogen isotopes and amounts on Finesse mass spectrometric complex [7] by combination of pyrolysis and stepped combustion

methods. The sample was first pyrolyzed in three steps (400, 600 and 800°C) and then combusted in a pure oxygen atmosphere from 200 to 1500°C with variable temperature increments.

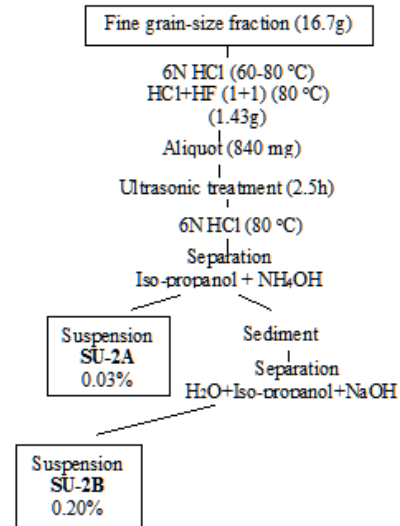


Figure 1. Schematic of the residues preparation.

Results: The concentrations of ^{36}Ar and ^{132}Xe in the sample SU-2A are among the highest for the Saratov HF/HCl residues obtained so far, 6.3×10^{-5} and 4.9×10^{-7} cc/g respectively, and a factor of 6.7 higher for both gases when normalized to carbon. The observed $^{36}\text{Ar}/\text{C}$ and $^{132}\text{Xe}/\text{C}$ ratios are significantly lower (by orders of magnitude) than estimated for the pure Q [8] that suggests a dilution by the carbonaceous matter with no noble gases. The bulk elemental $^4\text{He}/^{36}\text{Ar}=1.9-2.8$ and $^{36}\text{Ar}/^{132}\text{Xe}=70-130$ ratios are similar to those established for Q in the closed-system etching experiments [8]: 5.7 and 90 respectively

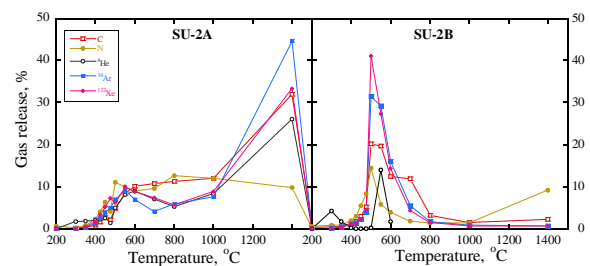


Figure 2. Release patterns of the analyzed species during stepped combustion.

The most interesting result is the release kinetics of the analyzed species from the samples (Fig 2). Whereas for the sample SU-2B most of the volatile species are released in the temperature range from 400 to 700°C, which corresponds to the results obtained earlier for the other bunch of the Saratov residues [4], the sample SU-2A shows a bimodal release (except for N) with a significant fraction of the gases released at $T > 1000^\circ\text{C}$.

Another important result concerns the N isotopic composition: for both samples an excursion to the isotopically light composition at maximum of ^{36}Ar and ^{132}Xe releases (Fig 3) is observed. The minimum $\delta^{15}\text{N}$ equal to -90‰ is observed at the high-temperature release of the sample SU-2A.

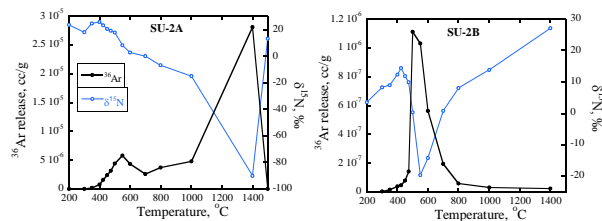


Figure 3. Release pattern of ^{36}Ar and nitrogen isotope profile for the samples analyzed.

Raman spectra of the SU-2A and SU-2B were recorded using 532 and 785 nm lasers. The carbonaceous fraction in these two samples is identical as shown by identical I(D)/I(G) ratio, presence of weak bands due to amorphous carbon, similar second order Raman spectra and identical dispersion of the D-band position. The similarity of the Raman features and significant difference in the noble gas concentrations for SU-2A and SU-2B indicate that Q-gases are present only in a minor fraction of the total carbon.

Besides the carbonaceous phases Raman peaks of chromite (only in the sample SU-2B) and as yet unidentified phase with a single sharp peak at 305 cm^{-1} are observed. The latter phase might correspond to a sulphide, although such an assignment is in conflict with the absence of SO_2 during stepped combustion.

Discussion: In order to explain the high-temperature release observed for the sample SU-2A (Fig. 2) we consider two possibilities. One of them is based on our previous results [4] obtained for the similar Saratov residues, where we argued that few-layer curved graphene stacks observed in the samples by TEM are the most plausible candidate for Q-phase. In this case the high-temperature release can be explained by suggesting that the sample SU-2A contains a significant fraction of multilayer graphenes with noble gases, with oxidation temperature higher than that for bilayer stacks. This suggestion is based on the observation that thermo-oxidizing resistance of graphene depends on

the number layers it consists of [9]. However, at present we do not know whether or not such multilayer graphenes are present in the SU-2A sample and what is their oxidation temperature. Additional investigations are required to clarify these points.

Another possible explanation for the high-temperature release suggests that it occurs due to shielding effect, at which a part of the Q grains was protected from reaction with oxygen during stepped combustion by surroundings – non oxidizable grains, similar to that observed for bulk meteorite samples [7]. Though such shielding effect has not been observed yet for HF/HCl residues, it could be that just for this very fine-grained fraction, nano-sized carbonaceous grains were encaged within surrounding much more abundant non-carbonaceous grains. It is important to note in this connection that judging from the noble gas/C ratios in the temperature steps only a very small fraction of the carbon oxidized in our experiments is associated with Q (see also Raman results). This means that not only Q, but also a fraction of other carbonaceous grains with no noble gases are also shielded. This shielding hypothesis however also requires an independent confirmation.

The isotopic composition of nitrogen observed at maximum of ^{36}Ar release in the analyzed samples (Fig. 3) clearly suggest that Q nitrogen is isotopically light. This is in a good agreement with our earlier investigations of CR, CO and CV meteorite samples where $\delta^{15}\text{N}$ at maximum of ^{36}Ar release reaches to -150‰ [7].

Summary: The most fine-grained colloid fraction, SU-2A, is significantly enriched with C and noble gases compared to SU-2B. The fractions are also different in their chromite content: in SU-2A it is almost absent. A bimodal release of Q noble gases and C is observed for the sample SU-2A: almost equal amounts of them are released before and after 1000°C . We suggest that the high-temperature release of Q gases is either due to their association with multilayer graphene or because Q is shielded by non-carbonaceous grains.

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