PRIMORDIAL NOBLE GASES IN THE UNEQUILIBRATED LL3.2 CHONDRITE KRYMKA ANALYZED BY CLOSED SYSTEM STEP ETCHING.

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Introduction: The Q noble gas component is the most widespread as well as one of the most enigmatic primordial noble gas components in meteoritic material. The Q gases are found in essentially all primitive meteorite classes [1,2] and are dominating the heavy trapped noble gas inventory, but are also contributing to the light noble gases. Phase Q, which is carrying the Q gases, is a carbonaceous phase, defined as the phase which releases Q gases in HF-HCl-resistant residues when treated with an oxidizing acid such as nitric acid [3]. As it is still not possible to separate phase Q from the residues, we analyze the Q noble gases by etching the HF-HCl-resistant residue with nitric acid in an extraction line connected to the mass spectrometer [4]. With this "Closed System Step Etching" technique (CSSE), Q is analyzed by definition. We here use the CSSE gas extraction technique for precise analyses of phase Q noble gases in a HF-HCl-resistant residue of the highly unequilibrated LL3.2 chondrite Krymka.

Sample and Methods: Twenty-nine mg of HF-HCl-resistant residue with a yield of 1.6 % (6.0 g bulk meteorite gave 98.1 mg residue; [5]) was analyzed for elemental and isotopic noble gas compositions. The noble gases were extracted using the CSSE extraction line [2,4], whose acid-exposed parts are made of gold and platinum. The whole run lasted three months, including a break of 6 weeks between steps 8 and 9. The degree of etching was controlled by exposing the sample to nitric acid under different temperatures (25 to 90°C) and for different times (15 min to 96 h). The first 17 steps were extracted using acid vapor, for step 18-28 the gas was released by exposing the sample to the liquid acid under increasing etching-time and temperature. After the gas was released, it was cleaned in a series of getters, separated into three batches (He-Ne, Ar, Kr-Xe) and analyzed in a mass spectrometer built in-house. Step 5 was not analyzed due to too high amounts of reactive gases. The first three steps showed a significant contribution of atmospheric noble gases, the sample was therefore heated to 50°C overnight after step 3 to reduce the effects of atmospheric contamination.

Results: All elemental ratios fall within the range of Q-elemental ratios from previous CSSE analyses [2] (table 1, Fig. 1). Argon, Kr and Xe isotopic ratios are also in good agreement with previously measured values for Q [2]. However, He and Ne isotopic ratios differ from those previously determined for Q by CSSE, and add to the heterogeneity observed earlier for these elements. A significant contribution of cosmogenic ^{3}He results in ^{3}He/^{4}He$\times 10^4$ of around 3.9 (range between 2.2 and 10.2) for steps 3-25, compared to Q isotopic ratios of 1.23 – 1.59 [5, 9]. The last three steps (steps 26-28), which were released using high temperature (90°C) and long etching periods (48-96 h), have high concentrations of cosmogenic He, resulting in a (^{3}He/^{4}He$\times 10^4$)$_{step\ 28}$ of 68.

The Ne isotopic ratios are the most surprising, see Fig. 2. The Ne isotopic ratios in the individual steps can be divided into three groups; the early, vapor etched steps (steps 1-17) which appear to consist mainly of Q noble gases, mixed with small amounts of atmospheric and cosmogenic noble gases; the early post-distillation steps (steps 18-23) which have ^{20}Ne/^{22}Ne ratios that are considerably lower than expected for Q (~8-8.5 rather than a Q value between 10.11 and 10.67), but ^{21}Ne/^{22}Ne ratios that are consistent with Q. The last group consist of the late cosmogenic-Ne-rich steps (steps 24-28). Determining (^{20}Ne/^{22}Ne)$_Q$ for this dataset is not straightforward. Assuming that only the
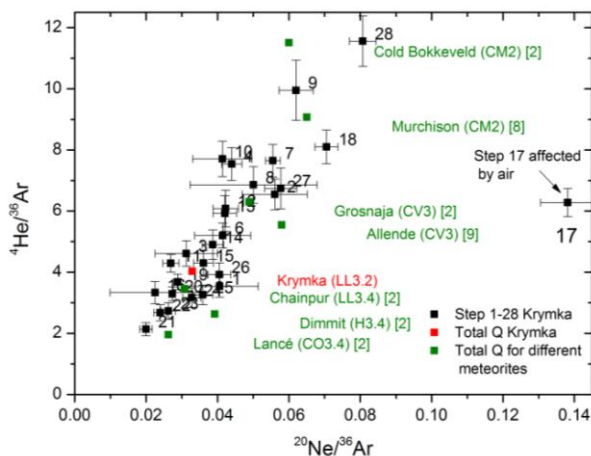

Figure 1. The light elemental ratios for Krymka total Q (in red), as well as the individual etch steps (black), fall on the same trend as total Q light elemental ratios for various meteorites determined by CSSE previously [2,8,9].

Table 1. Elemental ratios of Q in Krymka, and ranges of Q elemental ratios determined by CSSE.

	^{4}He/^{20}Ne	^{4}He/^{36}Ar	^{20}Ne/^{36}Ar	^{4}He/^{132}Xe	^{20}Ne/^{132}Xe	^{36}Ar/^{132}Xe	^{84}Kr/^{132}Xe
Q-Krymka	123±3	4.0±0.1	0.0329±0.0006	220±5	1.83±0.03	56.4±0.4	0.72 ±0.01
Q range [2]	67-162	1.4-11.5	0.012-0.071	133-663	1.2-5.2	53.1-105.2	0.56-1.00

later steps are influenced by trapped components carried by presolar grains, we estimate $(^{20}Ne/^{22}Ne)_Q$ by extrapolation of step 9,12 and 13 through Krymka bulk [6], this gives a ratio of $(^{20}Ne/^{22}Ne)_Q$ of ~10.4.

Discussion: Bulk Q light elemental ratios are correlated: ordinary chondrites and CO3.4 chondrite Lancé have low $(^4He/^{36}Ar)_Q$ and $(^{20}Ne/^{36}Ar)_Q$ ratios, whereas CM2 chondrites have higher $(^4He/^{36}Ar)_Q$ and $(^{20}Ne/^{36}Ar)_Q$ ratios [2], see Fig.1. Busemann et al. interpreted this trend as a preferential loss of helium and neon compared to argon in Q during thermal processing [2]. The bulk Krymka Q elemental ratios are low and fit well into the picture; the elemental ratios are similar to those of other ordinary chondrites and close to, but slightly higher than, the LL3.4 chondrite Lancé, in agreement with less thermal processing experienced by LL3.2 Krymka compared to LL3.4 Lancé. Interestingly, all Krymka CSSE steps (except step 17) fall on the same trend as the bulk Q values and cover the whole range of bulk Q elemental ratios previously measured by CSSE. Both the different meteorite totals and the steps in the Krymka run are consistent with a common pristine Q component of similar $^4He/^{36}Ar$ and $^{20}Ne/^{36}Ar$ ratios which reacts similarly on thermal processing.

Two possible interpretations of the neon isotopic ratios in the later steps will be discussed here; firstly, we look into the possibility that the isotopic ratios reflect a true HL-signal, and secondly, that the apparent HL-signal is caused by a mixture of Q and the presolar graphite component Ne-E or, now Ne-R. HL noble gases are carried by presolar nanodiamonds, which are present in the residue, but not expected to be affected by treatment with nitric acid. Isotopic variations in Xe_Q have previously been attributed to re-trapping of HL

noble gases from presolar nanodiamonds into phase Q [1]. To test whether the late neon steps indeed do contain a true HL signal we estimated the maximum contribution of $^{132}Xe_{HL}$ and calculated the corresponding $^{20}Ne_{HL}$. A maximum $^{132}Xe_{HL}$ concentration in step 18, 19, 22-26 of 3.4^x10^{-10} ccSTP/g (=1% of measured Xe in these steps), which corresponds to 2.3^x10^{-7} ccSTP/g $^{20}Ne_{HL}$, using a $(^{20}Ne/^{132}Xe)_{HL}$ of 485, was derived by two component deconvolution between HL [7] and Q [2]. An apparent $(^{20}Ne/^{22}Ne)_{HL}$ ratio of 8.3 (assuming $(^{21}Ne/^{22}Ne)_{HL}$ to be 0.029) and a $(^{21}Ne/^{22}Ne)_{cos}$ ratio of 0.74 (assuming $(^{20}Ne/^{22}Ne)_{cos}$ to be 0.8) were derived by extrapolating a linear fit through steps 18-28 (except 21). Two component deconvolution between these endmembers resulted in an apparent $^{20}Ne_{HL}$ concentration of 5.7^x10^{-8}, which is considerably lower than the maximum $^{20}Ne_{HL}$ derived from the xenon isotopes. Hence, it cannot be excluded that the apparent Ne_{HL} signal is a true HL-signal by these means.

Secondly, the apparent Ne_{HL} isotopic ratios could be interpreted as a mixing between Q and the pre-solar graphite component Ne-E, which is essentially pure ^{22}Ne. Significant contribution to ^{22}Ne released from Ne-E carried by presolar graphite has been detected in similar experiments, particularly on LL3.4 Chainpur, before, since graphite is not entirely stable against treatment with nitric acid [2]. The low $^{20}Ne/^{22}Ne$ in step 21 (7.5) is most likely a result of mixing with Ne-E, but also the rest of steps 18-28 can be explained by mixing of Q and Ne-E noble gases in relatively constant proportions. None of the two explanations for the neon isotopic ratios can be excluded, we therefore conclude that the apparent $(^{20}Ne/^{22}Ne)_{HL}$ is either a mixture of Q and Ne-E noble gases or a true Ne_{HL} signal, released in small amounts from presolar

Figure 2. Neon three isotope plot. See text for discussion. Ref. $Q_{Murchison}$ [8], $Q_{Lancé}$ [2], Bulk Alaerts [6], HL and Ne-E [7].

nanodiamonds, or, perhaps more likely, re-trapped into phase Q or residual silicates. The cosmogenic neon, released mainly in the last steps, could either have been produced in the silicates in the meteorite, re-trapped in phase Q, or be contributions from a cosmogenic noble gas bearing phase that resides in the residue.

References: [1] Huss G.R. et al. (1996), *GCA, 60*, 3311-3340. [2] Busemann H. et al. (2000), *Meteorit. Planet. Sci., 35*, 949-973. [3] Lewis R.S. et al. (1975), *Science, 190*, 949-973. [4] Wieler R. et al. (1986), *GCA ,50*, 1997-2017. [5] Busemann H. (1998), PhD thesis, ETH Zürich No.12988. [6] Alaerts L. et al. (1979), *GCA, 43*, 1399-1415. [7] Ott U. (2002) *Rev. Mineral. Geochem., 47*, 71-100. [8] Wieler R.et al. (1992), *GCA, 56*, 2907-2921. [9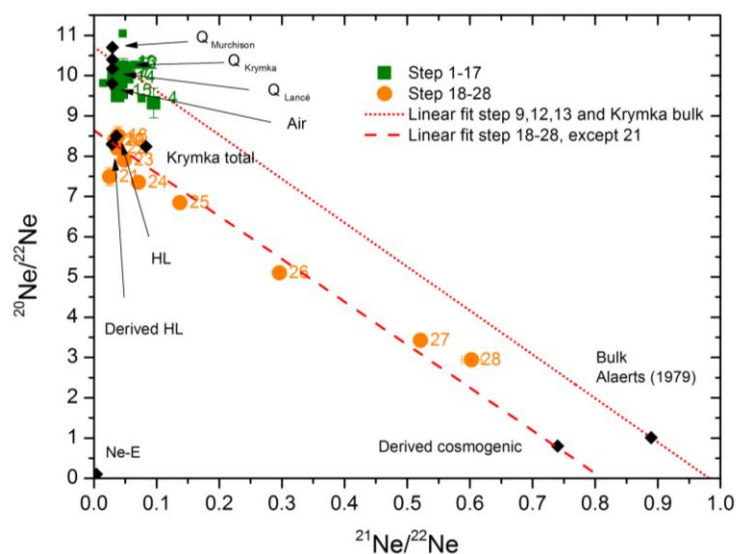] Wieler R. et al. (1991), *GCA, 55*, 1709-1722.