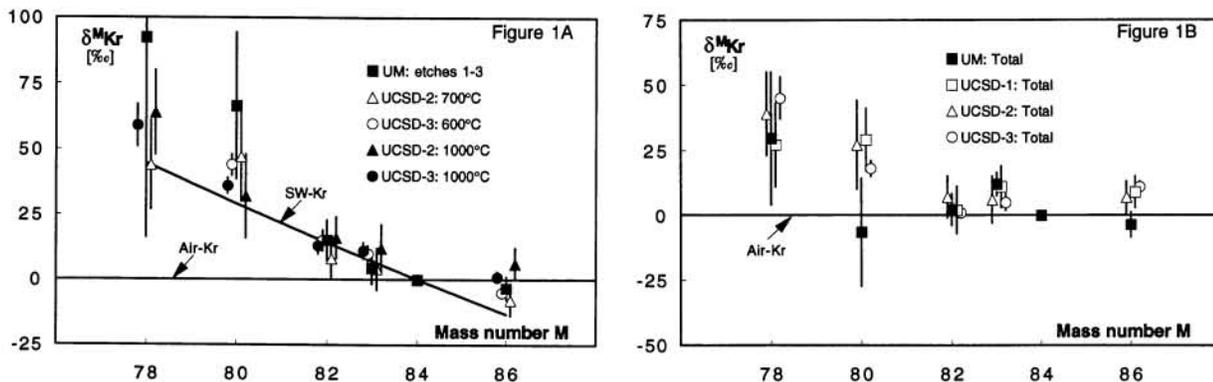


EXAMINATION OF Kr AND Xe ISOTOPES IN PESYANOE BY ACID-ETCHING. R. O. Pepin and P. E. Rider, School of Physics and Astronomy, University of Minnesota, Minneapolis, MN 55455.

Noble gases in the solar-wind-rich Pesyanoe enstatite achondrite have been studied extensively by Marti and co-workers [1-3]. Isotope ratios in low- to intermediate-temperature release fractions of Pesyanoe Kr [2] and Xe [3] were utilized, together with other data from lunar regolith mineral separates, in a recent effort to establish the isotopic compositions of these gases in the solar wind (SW) [4]. However the stepwise-pyrolysis release technique used for the most part by [2,3] is capable, at least in principle, of fractionating gases partially evolved from grain-surface SW reservoirs toward isotopically lighter compositions than those characterizing the implanted reservoir itself. Since Pesyanoe Kr data [2] are important in concluding that SW-Kr is in fact isotopically lighter than air-like Kr [4], and by just about the amount that could be attributable to fractionation in the laboratory, it seemed worthwhile to re-analyze this meteorite by *in-vacuo* acid etching. Noble gas extraction by this technique not only avoids the potential problem of thermal-release fractionation, but also depends on the chemical resistance rather than the thermal retentivity of host phases and thus often provides complementary interpretative perspectives.

Experimental protocol. A 100mg Pesyanoe grain-size separate (~8-250 μ m) was prepared by freeze-thaw disaggregation of a bulk sample, and subjected to six steps of attack by H₂SO₃ of gradually increasing strength followed by four pyrolysis steps at T = 250-1100°C. Additional experimental details are given in [5]. The sample mass available for this analysis turned out to be somewhat marginal for the concentrations of Kr and Xe involved, resulting in relatively imprecise measurement of the two lightest Kr isotopes and no useful data for ¹²⁴Xe and ¹²⁶Xe.

Krypton results. As shown in Fig. 1A, the question of possible thermal release fractionation in the 600-1000°C Kr compositions from [2] (identified as "UCSD" data in this and other Figure legends) appears to be satisfactorily answered. Integration of Kr liberated in acid etches 1-3 from the present ("UM") sample yielded isotope



ratios (plotted as permil [%e] deviations from Air-Kr ratios) that are indistinguishable from the UCSD pyrolysis measurements. They are also in reasonably good accord with the SW-Kr composition deduced from a much more extensive data base [4], but with a couple of deviations. The enrichment above SW-Kr at ⁸⁰Kr suggested by the more accurate pyrolysis data, and attributed by [4] to neutron capture in surface-sited Br, is nominally evident in the etched sample as well. The enhancement at ⁸⁶Kr—which, as seen in the Figure, is a general characteristic of otherwise solar-wind-like Kr in Pesyanoe—is not understood. These anomalies cannot be due to simple mixing of SW-Kr with isotopically heavier SEP-Kr [6] because the correlated variations expected in the other isotopes are absent. This explanation is most rigorously ruled out by the precise UCSD-3:1000°C data [2]: a mixed SW-SEP composition consistent with the measured $\delta^{86}\text{Kr}$ value would lie almost exactly along the Air-Kr line at all isotopes. What these patterns suggest instead is variable mixing of SW-Kr with indigenous Kr highly enriched in ⁸⁶Kr—perhaps a component complementary in ⁸⁶Kr content to the N("Normal")-Kr found in interstellar silicon carbide, which appears to be compositionally similar to Air-Kr (or SW-Kr) except for a striking *deficit* (~65%) in the ⁸⁶Kr/⁸⁴Kr ratio [7].

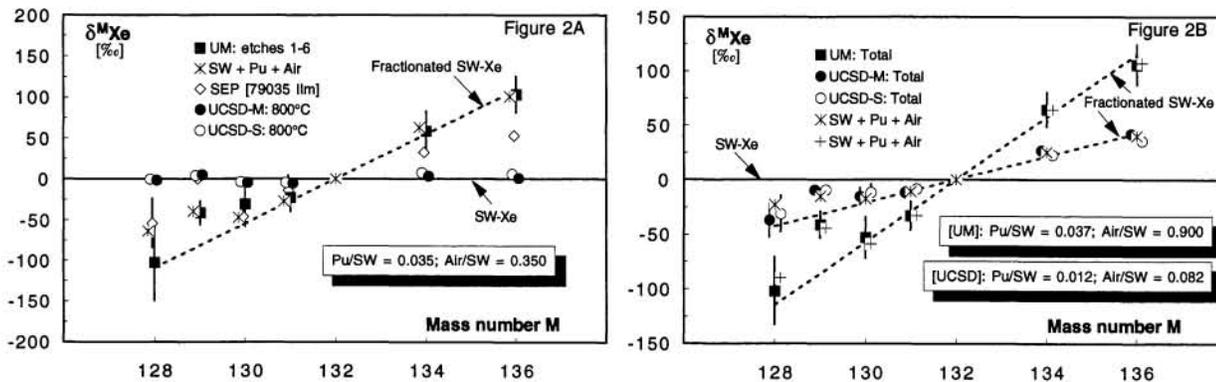
Etches 1-3 released about the same amount of ⁸⁴Kr as pyrolyses of the UCSD samples to 1000°C. The smaller amounts evolved in subsequent etching steps displayed a different compositional pattern, one slightly heavier than Air-Kr and in this case consistent with a mixture of SW and SEP components.

The integrated composition of all the Kr released in the UM experiment is compared in Fig. 1B to those found in the UCSD samples [2]. Total ⁸⁴Kr abundance (~9 x 10⁻¹⁰ ccSTP/g) is somewhat larger than in UCSD-1,2 and identical to that in -3, so Kr degassing appears to be complete or nearly so despite the rather low maximum pyrolysis temperature (1100°C). No spallation corrections have been applied, here or in Fig. 1A. The UM sample is nominally somewhat deficient in ⁸⁰Kr, and is robustly depleted in ⁸⁶Kr (by 14 ± 5%), with respect to the average of the three UCSD measurements. Here the presence of unknown amounts of spallogenic Kr complicates interpretation. Nevertheless the rather good agreement at the three other isotopes suggests the possibility that the lower $\delta^{86}\text{Kr}$ value may again reflect a nearly monoisotopic variation rather than a smaller SEP/SW mixing ratio in the UM sample.

Xenon results. The isotopic compositions of Xe evolved in all six acid etches appeared to be more-or-less uniform within their data scatter, and so were integrated to yield the pattern shown in Fig. 2A, plotted as permil deviations from the SW-Xe isotope ratios reported in [4]. Here, in contrast to the Kr results, there is a remarkably

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large compositional *disagreement* with Xe released at low temperature from the UCSD samples [3]. These latter ratios agree closely with the SW-Xe composition (and were in fact among the many others used to define it [4]). The mass trend of the substantial offsets displayed by the UM sample is fit rather well (and even better in Fig. 2B) by fractionated SW-Xe except at ^{129}Xe , but these isotopic deviations, $\sim 100\%$ for 3% ($4/132$) mass difference, are far too



large to have been produced by credible degrees of diffusive loss from grain-surface SW reservoirs during or after implantation [8,9]. SEP-Xe, even in pure form, likewise cannot account for the discrepancies, as is evident in Fig. 2A where the SEP composition in 79035 ilmenite reported by [6] is seen to plot well below the UM $\delta^{134-136}\text{Xe}$ data. The UM sample pattern is, however, nicely explained by a mixture of SW-Xe, Air-Xe, and ^{244}Pu fission Xe, with the mixing ratios of these three components at ^{132}Xe given in the Fig. 2 legends. Much larger amounts of adsorbed, thermally retentive Air-Xe have been found previously in Pesyanoe grain-size separates [10], and it seems likely that the required abundance of Pu-Xe can be attributed to *in situ* fission (see below).

Fig. 2B is a similar plot of *total* Xe in these samples. Essentially the same anomaly pattern appears in the UM sample—it differs little in the integrated acid-etch and pyrolysis steps. Isotopic correlations analogous to the trend of the UCSD data along the plotted SW fractionation line suggested to [3] that this was indeed the mechanism responsible for deviations from pure SW composition at $>800^\circ\text{C}$ pyrolysis temperatures. It is clear from Fig. 2B, however, that a Pu-Xe component plus a relatively much smaller air contaminant accounts for them equally well. [A minor spallation component has been subtracted from the UCSD compositions, but the three-component mixing fit is just about as good without it—somewhat better at ^{128}Xe . Spallation Xe is not evident in the UM sample, perhaps because comparison of the UM and UCSD degassing vs. temperature profiles indicates that up to $\sim 15\%$ of its Xe, probably highly spallogenic, may have been retained through the 1100°C pyrolysis]. The mystery here, given the present analysis and that by [10], is how the UCSD separates escaped more substantial adsorbed air contamination.

The abundance of (unadulterated) SW-Xe in the UM sample is lower, by a factor of ~ 2.5 , than those in the UCSD separates (yielding a SW $^{84}\text{Kr}/^{132}\text{Xe}$ ratio of ~ 18 , close to the "solar-system" value of ~ 21 [11]); thus the isotopic influences of the air and fission components are correspondingly exaggerated. However the absolute concentrations of Pu- ^{136}Xe differ from their average of $\sim 2 \times 10^{-12}$ ccSTP/g by only $\pm 10\%$. This amount of fission Xe could have been generated by the ^{244}Pu originally associated with a present U concentration of ~ 20 ppb—somewhat high for the average aubrite [12] but perhaps not implausible. Note in Fig. 2 that the three-component mixing interpretations of these isotopic distributions indicate *no* detectable excesses due to radiogenic ^{129}Xe in Pesyanoe.

Finally, it can be argued that the ephemeral [4] SEP-Xe component [6] might itself be an expression of multi-component mixing, in this case of SW-Xe with Air-Xe tightly adsorbed on grain surfaces (and, surprisingly, resistant even to acid attack). As seen in Fig. 3, an Air/SW mixing ratio of 1 at ^{132}Xe reproduces the reported 79035 SEP-Xe composition at least as well as the SEP/SW fractionation relationship ($\propto [M/132]^2$) proposed by [6].

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