

Xe ON SHALES: THE "PLASTIC BAG" EXPERIMENT,
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It is a well-established generalization that the noble gases in undifferentiated meteorites occur in characteristic elemental abundance ratios known as the "planetary pattern." This generalization holds good for atmospheric noble gases as well, except for He, which is not gravitationally bound, and Xe, which is depleted relative to the other heavy noble gases by a factor of 20-25. It has been commonly accepted that Xe is only apparently depleted, and is actually present in a more generalized atmosphere which includes atmophile elements in or on sedimentary rocks, particularly shales (1,2). One potential mechanism for the acquisition of Xe by shales is physical adsorption. This possibility was explored by Fanale and Cannon (2), who with generous input parameters found that about 3 times the atmospheric Xe inventory could be present on shales, or about an order of magnitude less Xe than that requisite for a planetary-type relative Xe abundance. More extensive studies by Podosek *et al.* (3) indicated that at best adsorption could account for an amount of Xe comparable to the atmospheric inventory. Another variant of the shale hypothesis is to assume that the missing Xe is trapped in shale minerals (by whatever mechanism), a possibility which was investigated by Podosek *et al.* (4), who found, however, that the shales which they analyzed could not account for as much Xe as is present in air. More generally, if we consider all of the Xe data obtained for sedimentary rocks (Fig. 1), we find that no sample contains enough Xe to bring the atmosphere inventory up to planetary proportions, and excluding a few scarce and exotic sample types (e.g., thucolite), all but one sample have Xe concentrations lower than that which could account for even an amount of Xe comparable to that in the atmosphere. It is nonetheless possible that both the adsorption and trapped gas measurements could underestimate Xe concentrations in shales, in the former case by possibly insufficient equilibration times (3) and in the latter by removal of Xe during the vacuum exposure prior to analysis (3,5) to which all the samples in Fig. 1 have been subjected.

In the present experiment we have circumvented these ambiguities by sealing shale samples in capsules ("plastic bags") in air, so that the samples are as close to their natural state as possible, and this seal is not broken until the time of analysis. All of the Xe (and other noble gases) associated with the sample are thus collected and analyzed, and questions of the distribution of Xe within the sample or the specific mode of acquisition of the Xe by the shales are irrelevant. Operationally, the encapsulation procedure employs a pyrex container containing the sample which is invaded with Hg and sealed at one end; the Hg is withdrawn to a region of the capsule containing a capillary constriction and the container is then sealed. The gases are released in two stages: The first involves rupturing of the container and collection of the gases released; the second involves melting of the capsule and sample. The two-stage procedure allows a maximum dead or pore space air correction to be made on the basis of the Ne obtained when the container is ruptured. In order to assess the effects of vacuum exposure we have also analyzed (in the usual fashion) pieces of the samples exposed in vacuo for several weeks with and without a week of heating to 100°C in vacuo. The samples analyzed consisted of a Precambrian shale (Fig Tree), a Pleistocene claystone, and three other Paleozoic shales. The Xe concentrations obtained for these samples processed in the three different ways (H = heated; U = unheated; S = sealed) are displayed in Fig. 2.

As shown in Fig. 2, dead space air generally accounts for a small but non-negligible fraction of the Xe; the large contribution to Pleistocene claystone Xe is due to the substantial porosity of this low density (1.75 g/cm³) sample. The data clearly demonstrate that vacuum exposure and/or heating result in loss of Xe from shale samples, apparently about an order of magnitude for the most Xe-rich samples, but a factor of several hundred for Xe-poor Lagonda. The amount of Xe loss from Pleistocene claystone is unclear, since pore space air Xe accounts for practically all of the Xe in the sealed sample, and small errors in the pore air correction here significantly affect the estimation of the trapped Xe abundance. For the purpose of having a reference Xe concentration with which to compare those in shales, we will take the atmospheric ¹³⁶Xe inventory divided by the mass of the earth; the quotient of shale ¹³⁰Xe concentrations with this reference concentration is a convenient "normalized abundance." Assuming that the inventory of shales is 10²⁴ g (6), we thus require that shales have a normalized Xe abundance of about 6000 and 1.3x10⁷ if they are to account for as much Xe as is in air and a planetary-type generalized atmosphere, respectively. Comparison with Fig. 2 shows that, even without dead space air correction, the shale Xe inventory based on our samples would fall an order of magnitude short of even the atmospheric inventory. More important, if we scale the sedimentary rock Xe concentrations in Fig. 1 up by the same differences we observe between our sealed and unsealed samples at similar (unsealed) concentration levels, we find that shales at best contain a Xe inventory equal to that in air. There seems little doubt that the Xe inventory on shales is insufficient to bring atmospheric Xe levels up to the proportion observed in planetary-type noble gases. In our opinion, the shale hypothesis, although simple and compelling, must now be considered incorrect.

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It is possible that some other reservoir than sedimentary rocks contains the "missing Xe," but if so it remains to be shown what this is. It is likewise possible that the Xe might be sequestered in the solid earth, but that it should be selectively and quantitatively retained, unlike the other noble gases, is doubtful. A more fruitful approach would seem to be to abandon the planetary gas analogy, and to consider the origin of the elemental and isotopic differences between terrestrial and meteoritic noble gases as best sought in the pre- rather than the post-accretional history of the earth.

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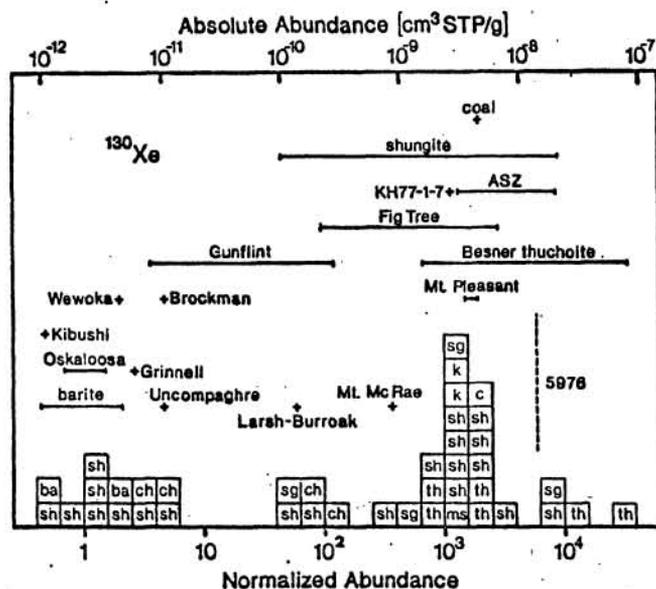


Fig. 1 Summary of all literature data on ^{130}Xe concentrations in sedimentary rocks. Normalized abundance = ^{130}Xe concentration in sample / (atmospheric ^{130}Xe / mass of earth). Line segment at 5976 shows average concentration if 10^{24} g of shale contain as much Xe as air. Codes inside boxes are sh = shale, ch = chert, k = kero-gon, ms = marine sediment, th = thucoilite, c = coal, sg = shungite, ba = barite. From ref. (7).

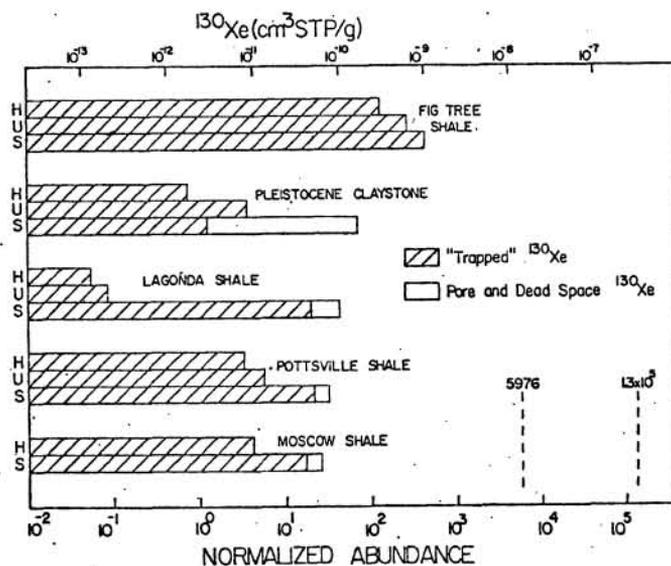


Fig. 2 Xe concentrations in shale samples (cf. Fig. 1). H and U = heated and unheated *in vacuo*, respectively; S = sealed in pyrex capsule. Line segment at 1.3×10^5 shows average concentration if 10^{24} g of shales contain 22 times the atmospheric Xe inventory. See text.