

ISOTOPE COSMOCHEMISTRY II

ISOTOPIC ANOMALIES IN METEORITES

In the previous lecture, we looked at the geochronology of meteorites, both from the perspective of conventional decay systems and from the perspective of extinct radionuclides. The decay of these extinct radionuclides results in anomalous isotopic compositions of the daughter elements. However, there are other isotopic anomalies in meteorites that are not due to the *in situ* decay of radionuclides. Many of these anomalies, like those created by decay of extinct radionuclides, may reflect the injection of newly synthesized material into the cloud of dust and gas from which the solar system ultimately formed. Others, however, may reflect isotopic inhomogeneity within this cloud, and the variable abundance of exotic gas and grains of material synthesized at various times and places in the galaxy. Still other isotopic anomalies may reflect chemical fractionations within this cloud. It is these anomalies we focus on in this lecture.

Neon Alphabet Soup and 'Pre-Solar' Noble Gases in Meteorites

Noble gases were the first group of elements in which isotopic variations were identified, and they occur in virtually all of the carbonaceous chondrites which have not experienced extensive metamorphism. In contrast to the isotopic anomalies of metals mentioned above, most of the isotopically distinct noble gas is contained in the matrix which accreted at low temperature (below 100-200° C), and has recently been shown to be contained in highly unreactive carbon species, including organic carbon, graphite, diamond, and silicon carbide. Noble gases are present in meteorites at concentrations that are often as low as 1 part in 10^{10} . Though they are fairly readily isolated and analyzed at these concentrations, their isotopic compositions are nonetheless partly sensitive to change due to processes such as radioactive decay (for He, Ar, and Xe), spallation and other cosmic-ray induced nuclear processes, and solar wind implantation. In addition, mass fractionation can significantly affect the isotopic compositions of the lighter noble gases (He and Ne). Up to the late 1960's, all isotopic variations in meteoritic noble gases were thought to be related to these processes. For example, Ne isotopic variations could be described as mixtures of three components, "Neon A" or "planetary" (similar in composition to the Earth's atmosphere), "Neon B", or solar, and "Neon S", or spallogenic (cosmogenic) (Figure 24.1). In 1969, evidence of a ^{22}Ne -rich component, named "Neon E" was found in the high temperature (900-1100°C) release fractions of six carbonaceous chondrites. Its release at high temperature indicated it was efficiently trapped in a phase which breaks down only at high temperature.

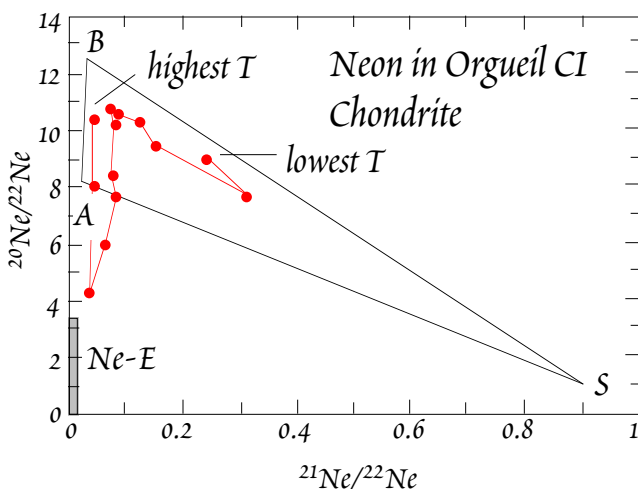


Figure 24.1. Neon isotopic compositions in a step-heating experiment on Orgueil CI chondrite, which produced the first evidence of 'pre-solar' or exotic Ne. The points connected by the line show the changing Ne isotope ratios with increasing temperature. Shaded area was the original estimate of the composition of the pure Ne-E component. Also shown are the compositions of Ne-A ('solar'), Ne-B ('planetary'), and Ne-E ('spallogenic'). After Black and Pepin (1969).

The carrier of Neon-E proved difficult to identify. Many scientists participated in an intensive search over nearly 2 decades for the carrier phase of these components. The search quickly focused on the matrix, particularly that of CM2 meteorites. But the fine-grained nature of the matrix, together

with the abundance of sticky and refractory organic compounds, made work with the groundmass difficult. In the late 1980's, E. Anders and his colleagues at the University of Chicago (e.g., Tang and Anders, 1988) found that Neon-E is associated with fine-grained (<6 μm) graphite and SiC (silicon carbide) of the matrix. Ne-E actually consists of two isotopically distinct components: Ne-E(L), which was found to reside in graphite, and Ne-E(H) which resides in SiC. The $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of Ne-E(H) is less than 0.01, while that of Ne-E(L) is less than 0.2.

The origin of Ne-E, and Ne-E(L), which is almost pure ^{22}Ne , posed something of a mystery. It was originally thought that it was a decay product of ^{22}Na , which has a half-life of 2.6 years, produced in red giants. Na could readily separate from Ne and other noble gases by condensation into grains. However, this hypothesis has now largely been rejected. For one thing, Huss et al. (1997) found that SiC grain in Orgueil (CI), had far too little Na to account for the observed amount of ^{22}Ne . More detailed analytical work (Lewis et al., 1990)

found that the Ne isotopic abundances actually match rather well that expected for nucleosynthesis in the He-burning shells of low mass, carbon-rich thermally pulsing red giants called Asymptotic Giant Branch (AGB) stars. ^{22}Ne is synthesized from ^{14}N , which is synthesized from C, N, and O nuclei during the previous hydrogen burning phase, through the sequence $^{14}\text{N}(\alpha, \gamma)^{18}\text{F}(\beta^+, \nu)^{18}\text{O}(\alpha, \gamma)^{22}\text{Ne}$ (Gallino et al., 1990).

The other key noble gas in this context is xenon. Having 9 isotopes rather than 3 and with contributions from both ^{129}I decay and fission of various heavy elements, isotopic variation in xenon are bound to be much more complex than those of Ne. On the other hand, its high mass minimizes mass fractionation effects, so "solar" (more properly solar wind) and "planetary" Xe are isotopically similar. The first evidence of other isotopic variations in Xe came in the early 1960's, but these variations were thought to be fissogenic (at one time it was argued they were produced by fission of short-lived superheavy elements). Subsequently, several isotopically distinct Xe components were identified. One of these is associated with Ne-E(H) in SiC and is enriched in the s-process only isotopes of Xe (^{128}Xe and ^{130}Xe) and is called, appropriately enough, Xe-S. The isotopic pattern of Xe-S is shown in Figure 24.2. This is most likely synthesized in red giants. Indeed, there is a striking similarity of the isotopic abundances to the calculated production of s-process nuclides in AGB stars. Comparison of the isotopic composition of Kr, which is also anomalous in the SiC, with theoretical calculations further narrows the site of synthesis to low-mass (1-2 solar masses) AGB stars, consistent with the inferences made for ^{22}Ne synthesis. SiC grains are thus apparently condensates from material ejected from red

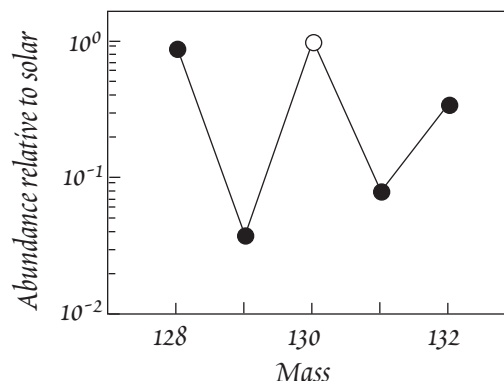


Figure 24.2. Isotopic composition of Xe-S (relative to normal solar Xe with $^{130}\text{Xe}=1$). Xe-S is found in silicon carbide and associated with Ne-E(H). ^{128}Xe and ^{130}Xe are synthesized only in the s-process, hence the most likely site for its synthesis is red giants.

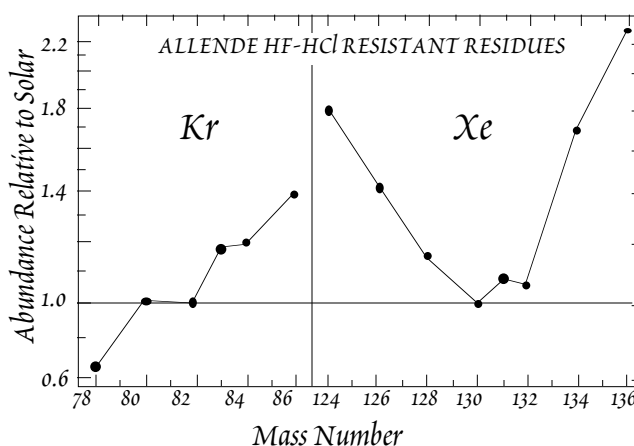


Figure 24.3. The isotopic composition of Kr and Xe of the 'Xe-HL' component in the matrix of the Allende CM-2 carbonaceous chondrite. Xe-HL is characteristically enriched in both the light and heavy isotopes, while the lighter noble gases show enrichment only in the heavy isotopes.

Table 24.1. ISOTOPIC CHARACTERISTICS OF INTERSTELLAR GRAINS

Phase	Diamond	SiC	Graphite
Isotopic Component	Xe-HL	Xe-S, Ne-E(H)	Ne-E(L)
Enriched in Isotopes	$^{124}\text{Xe}, ^{136}\text{Xe}$	$^{128}\text{Xe}, ^{130}\text{Xe}, ^{22}\text{Ne}$	^{22}Ne
Nuclear Process	p, r	s, $^{22}\text{Na}(\beta^+, \nu)^{22}\text{Ne}$	$^{14}\text{N} + 2\alpha \rightarrow ^{22}\text{Ne}$
Grain Size, μ	0.001	0.03-10	0.8-7
Abundance in C2 chondrites, ppm	400	7	<2
$(^{13}\text{C}/^{12}\text{C})/(^{13}\text{C}/^{12}\text{C})_{\odot}$	0.96	0.03 – 50	0.012 – 50
$(^{15}\text{N}/^{14}\text{N})/(^{15}\text{N}/^{14}\text{N})_{\odot}$	0.66	0.015 – 20	0.55 – 6.7

Modified from Anders and Zinner (1993).

giant stars. Noble gases were probably implanted in the grains by the very strong solar winds of these stars.

The Ne in the SiC is a little richer in ^{21}Ne than the predicted products of AGB stars. This is presumably due to cosmogenic production of ^{21}Ne . If so, some 130 Ma of cosmic ray irradiation would be required to produce the observed ^{21}Ne , indicating the grains predate meteorite parent body formation by this amount of time (Lewis et al., 1994). If they had been degassed, however, the grains could be much older.

Another isotopically distinct component, identified in acid-dissolution residues of Allende (CV3) named Xe-HL because it is enriched in both heavy and light Xe isotopes (Figure 24.3) was related in the 700-1000°C temperature step. This particular enrichment pattern can apparently be produced only by a combination of the p- and r-processes. These processes, of course, operate only in supernovae. Unlike Ne-E, Xe-HL is accompanied by the other noble gases, of which Ne, Ar, and Kr all show enrichment in their heavier isotopes. Eventually, Anders group identified the carrier of Xe-HL as microdiamonds. These diamonds are extraordinarily fine, averaging only 10 Å in diameter and containing typically only 10^3 or so atoms. Roughly one in every four atoms is at the surface. As a result, the properties of this material differs significantly from normal diamond, which considerably complicated the effort to isolate it.

Analysis of the noble gases in the SiC, graphite and diamond by step-heating was comparatively easy, since each of these decompose at distinct temperatures. Identifying the carriers proved more difficult. However, once the carrier grains were identified and isolated, it became possible to analyze the isotopic composition of other elements. The isotopic compositions of other elements have also proved to be anomalous to varying degrees. The noble gas, C and N isotopic composition is summarized in Table 24.1. Also shown in the table are the abundance of these phases, which is quite low.

Many of the SiC and graphite grains are large enough so the isotopic compositions of the major elements in individual grains can be analyzed by ion probe. These analyses (e.g., Figure 24.4) reveal a diversity of isotopic compositions as well as correlations between grain size and isotopic composition. Clearly, the SiC grains do not form a single population, but represent a number of populations of grains, each produced in a different astronomical environment. The majority of grains have isotopically heavy C but light N (relative to solar), which are the compositions expected from produc-

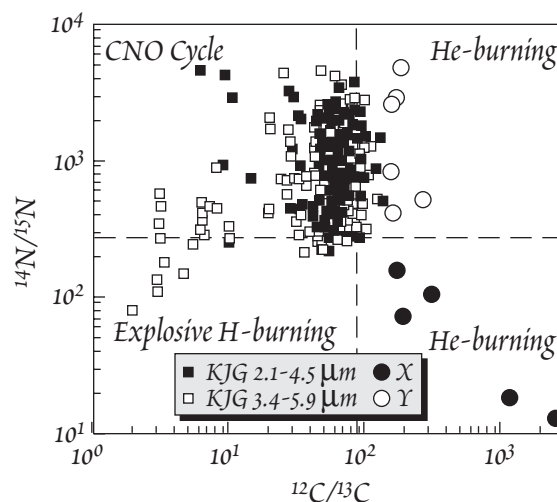


Figure 24.4. Isotopic composition of C and N in SiC from Murchison (CM2) meteorite. Dashed lines show the isotopic composition of normal solar system C and N. Populations X and Y, which are anomalous here, are anomalous in other respects as well. From Anders and Zinner (1993).

tion in the CNO cycle (Lecture 2). However, compositions produced by other mechanisms are also represented. Si isotopic compositions are also anomalous. Anomalies have also been identified in the isotopic compositions of Ti, Sr, and Ba in these grains.

Mg isotopic compositions in both graphite and SiC are also anomalous. A fourth refractory phase more recently identified in the groundmass (but poor in noble gases) is corundum (Al_2O_3). The graphite, SiC, and corundum have inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratios of 5×10^{-5} to 1×10^{-1} . In contrast, we found in the previous lecture that CAI's had inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratios up to 5×10^{-5} , and that most other meteoritic materials showed no excess ^{26}Mg .

Other Exotic Components in Meteorites

Besides isotopic anomalies apparently produced by decay of short-lived radionuclides such as ^{26}Al , ^{129}I , and ^{244}Pu , and those associated with the interstellar grains in the matrix, other isotopic anomalies have been identified in CAI's. Some of these have been observed only in a few CAI's from Allende: Ca, Ba, Sm, Nd, and Sr. They have been termed FUN anomalies: fractionation and unknown nuclear. Other variations are widespread, but appear to be due to fractionation, e.g., Si and Mg. A systematic search by G. Lugmair and colleagues at the University of California at San Diego has revealed that isotopic variations of the iron peak elements (elements clustered around the cosmic abundance peak at Fe), Ca through Zn, are ubiquitous in many CAI's. Variations are up to per mil size relative to terrestrial isotope ratios, and are characterized by overabundance of the most neutron-rich nuclides (^{48}Ca , ^{50}Ti , ^{54}Cr , ^{64}Ni , and ^{66}Zn), often accompanied by underabundance of the most neutron-poor isotopes. In some instances, isotopic variations within single mineral grains have been observed with the ion microprobe. In general, these isotopic variations are most readily explained if the inclusions contain an admixture of neutron-rich e-process material from a supernova.

Ubiquitous Oxygen isotope variations

Another element commonly showing isotopic variations is O. Until 1973, O isotope variations in meteorites were thought to be simply the result of fractionation, as they are on Earth. But when R. Clayton of the Univ. of Chicago went to the trouble of measuring ^{17}O (0.037% of O) as well as ^{18}O and

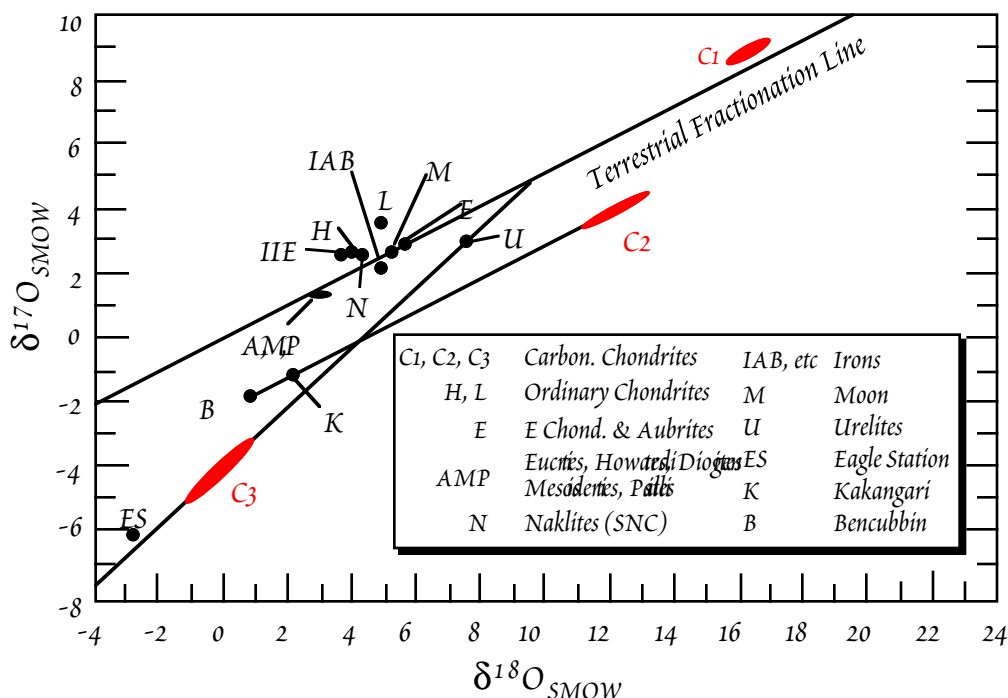


Figure 24.5. Variation of O isotope ratios in meteorites and terrestrial and lunar samples. Most of the data from Allende inclusions is off the plot to the left. From the work of R. N. Clayton.

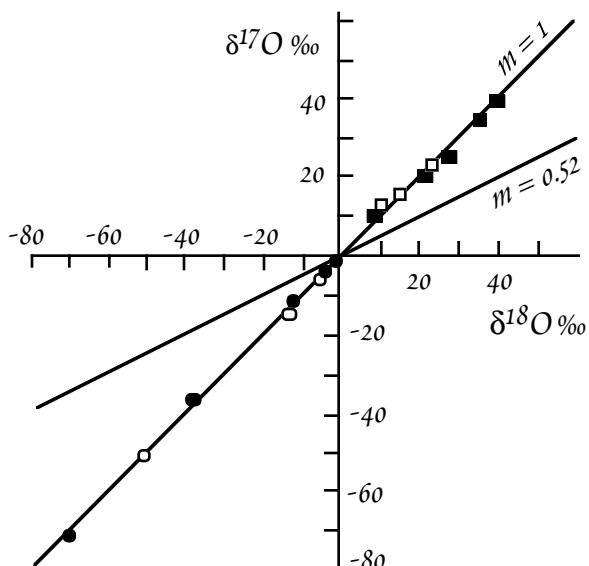


Figure 24.6. Mass independent fractionation during the production of ozone from molecular oxygen. Squares are ozone, dots are oxygen. After Thiemens and Heidenreich (1983).

^{16}O , he found that these variations were not consistent with simple mass-dependent fractionation. This is illustrated in Figure 24.5. On a plot of $^{17}\text{O}/^{16}\text{O}$ vs. $^{18}\text{O}/^{16}\text{O}$, variations created by fractionation should plot along a line with slope of 1/2. Terrestrial and lunar samples do indeed define such a line, but other meteorites or their components fall along a line with slope = 1. One interpretation is that this reflects mixing between a more or less pure ^{16}O component, such as might be created by helium burning, and a component of 'normal' isotopic composition. However, Thiemens and Heidenreich (1983) conducted experiments in which ozone produced by a high frequency electric discharge showed "mass independent fractionation", i.e., where the ozone was equally enriched in ^{17}O and ^{18}O (Figure 24.6) relative to ^{16}O . The experiment demonstrates that a slope of 1 on the $\delta^{17}\text{O} - \delta^{18}\text{O}$ diagram could be produced by chemical processes. Thiemens suggested this kind of fractionation results from a kinetic fractionation mechanism, which arises because non-symmetric (e.g., $^{16}\text{O}^{17}\text{O}$ or $^{18}\text{O}^{16}\text{O}$) molecules

have more available energy levels than symmetric (e.g., $^{16}\text{O}^{16}\text{O}$) molecules (as we will see later in the course, symmetry enters into the calculation of the partition function). However, it is unclear how this mechanism could produce the observed fractionations, and debate still rages as to whether the O isotopic variations are ultimately of chemical or nuclear origin.

Whether the O isotope variations in meteorites are nuclear or fractionation effects, their discovery is one of the most important in the field of cosmochemistry. What we will call 'mass independent' effects, be they nucleosynthetic or chemical fractionation, almost certainly occurred before meteorites accreted. As Figure 24.7 shows, while variations *between* classes are mostly mass-independent, variations *within* groups of meteorites fall along mass-dependent fractionation lines. This strongly suggests that, for the most part, different groups could not have come from the same parent body and that the different groups probably formed in different parts of the presolar nebula. There are a few exceptions: IIE irons fall on a mass-dependent fractionation line (MDFL) with H-chondrites, IVA irons plot on a MDFL with L and LL chondrites, basaltic and hyperstene achondrites plot on a MDFL with IAB irons and some stony-irons, and the moon and the earth plot on a MDFL together with enstatite chondrites and achondrites. This suggests a genetic relationship between these objects, perhaps derivation from a single parent body in some cases.

Oxygen isotope compositions of the minerals of the FUN inclusions of Allende are erratic and do not fall on any line. These are certainly nuclear effects.

Mass-independent effects have not been found among isotopes of other elements such as

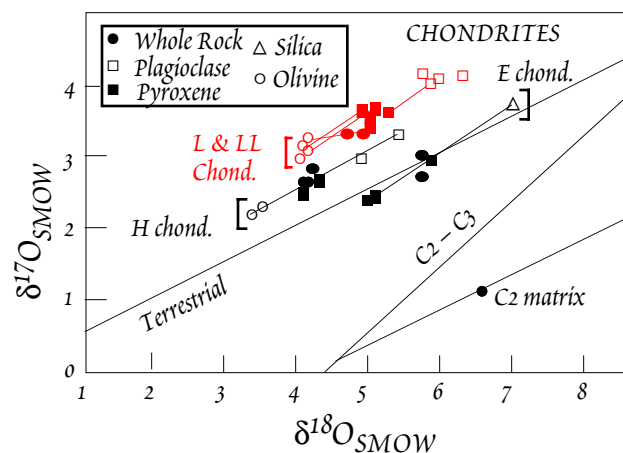


Figure 24.7. O isotope variations among minerals of various meteorite classes (Clayton et al., 1976).

Si, S and Mg (except in some inclusions, groundmass phases, and chondrules as noted above), though large mass-dependent fractionations are ubiquitous. Thus oxygen appears unique. The reason may be related to the partition of oxygen between the gaseous and solid phases of the presolar nebula. Over a large temperature range, only about 17% of oxygen will condense, the remainder being in the gas as H₂O and CO. Isotopic variations could arise by reaction between gas and solid of different isotopic composition. Hydrogen and carbon have only two stable isotopes so mass-dependent and mass-independent effects cannot be distinguished.

EXPOSURE AGES OF METEORITES

Cosmogenic nuclides have been used for many years to determine cosmic-ray exposure ages of meteorites. Meteorites experience a much higher cosmic ray flux because they have no atmospheres to shield them. Unstable and stable nuclides are sometimes used together to determine such ages. The rate of change of abundance of an unstable cosmogenic nuclide is given by:

$$\frac{dN}{dt} = P - \lambda N \quad 24.1$$

where P is the production rate. If we consider the case of the production of a stable nucleus, the number of stable nuclei produced at the surface of the body over some time t is simply given by:

$$N = P t \quad 24.2$$

Combining these equations, we may obtain an expression for t that is independent of variations production rate:

$$N = \frac{N_s(P_s)}{N_u(P_u)\lambda} t \quad 24.3$$

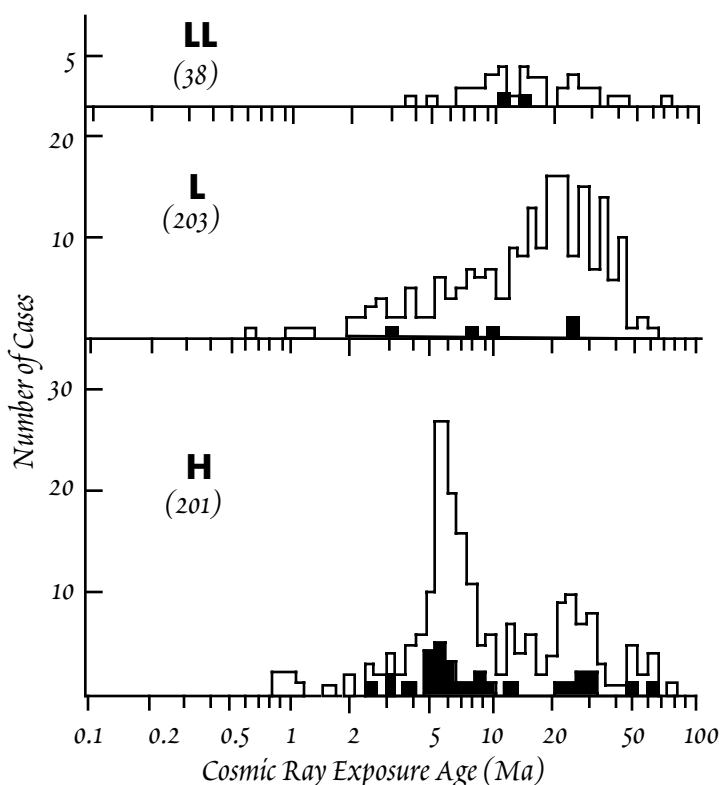


Figure 24.8. Cosmic ray exposure ages for three classes of ordinary chondrites. Filled histogram is for meteorites with regolith histories (i.e., brecciated meteorites). After Crabb and Schultz (1981).

Cosmic ray exposure ages of meteorites have been found to be on the order of millions or tens of millions of years for stony meteorites and hundreds of millions of years for iron meteorites. Ages for the 3 classes of ordinary chondrites are shown in Figure 24.8. These ages are much less than their formation ages as determined by conventional radiometric dating. This implies that through most of their histories, meteorites must have been shielded from cosmic rays. Hence they must have come from much large bodies that were broken up by collisions. The similarity of exposure ages for all meteorites of a given class implies individual meteorite classes are derived from single parent bodies.

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