

Each atomic element (defined by its number of protons) comes in different flavors, depending on the number of neutrons. Most elements in the periodic table exist in more than one isotope. Some are stable and some are radioactive. Scientists have tallied more than 3600 isotopes, the majority are radioactive. The Isotopes Project at Lawrence Berkeley National Lab in California has a web site (<http://ie.lbl.gov/toi.htm>) that gives detailed information about all the isotopes.

Stable and radioactive isotopes are the most useful class of tracers available to geochemists. In almost all cases the distributions of these isotopes have been used to study oceanographic processes controlling the distributions of the elements. Radioactive isotopes are especially useful because they provide a way to put time into geochemical models.

The chemical characteristic of an element is determined by the number of protons in its nucleus. Different elements can have different numbers of neutrons and thus atomic weights (the sum of protons plus neutrons). The atomic weight is equal to the sum of protons plus neutrons. The chart of the nuclides (protons versus neutrons) for elements 1 (Hydrogen) through 12 (Magnesium) is shown in Fig. 16-1. The Valley of Stability represents nuclides stable relative to decay.

Examples:

	Atomic Weight	Protons (Atomic Number)	Neutrons	% Abundance
Carbon	12C	6P	6N	98.89
	13C	6P	7N	1.11
	14C	6P	8N	10^{-10}
Oxygen	16O	8P	8N	99.76
	17O	8P	9N	0.024
	18O	8P	10N	0.20

Several light elements such as H, C, N, O, and S have more than one stable isotope form, which show variable abundances in natural samples. This variability is caused by isotopic fractionation during chemical reactions. Heavier elements like Pb also have several stable isotopic forms but their distributions are controlled more by their different sources than by fractionation.

Fig 16-1

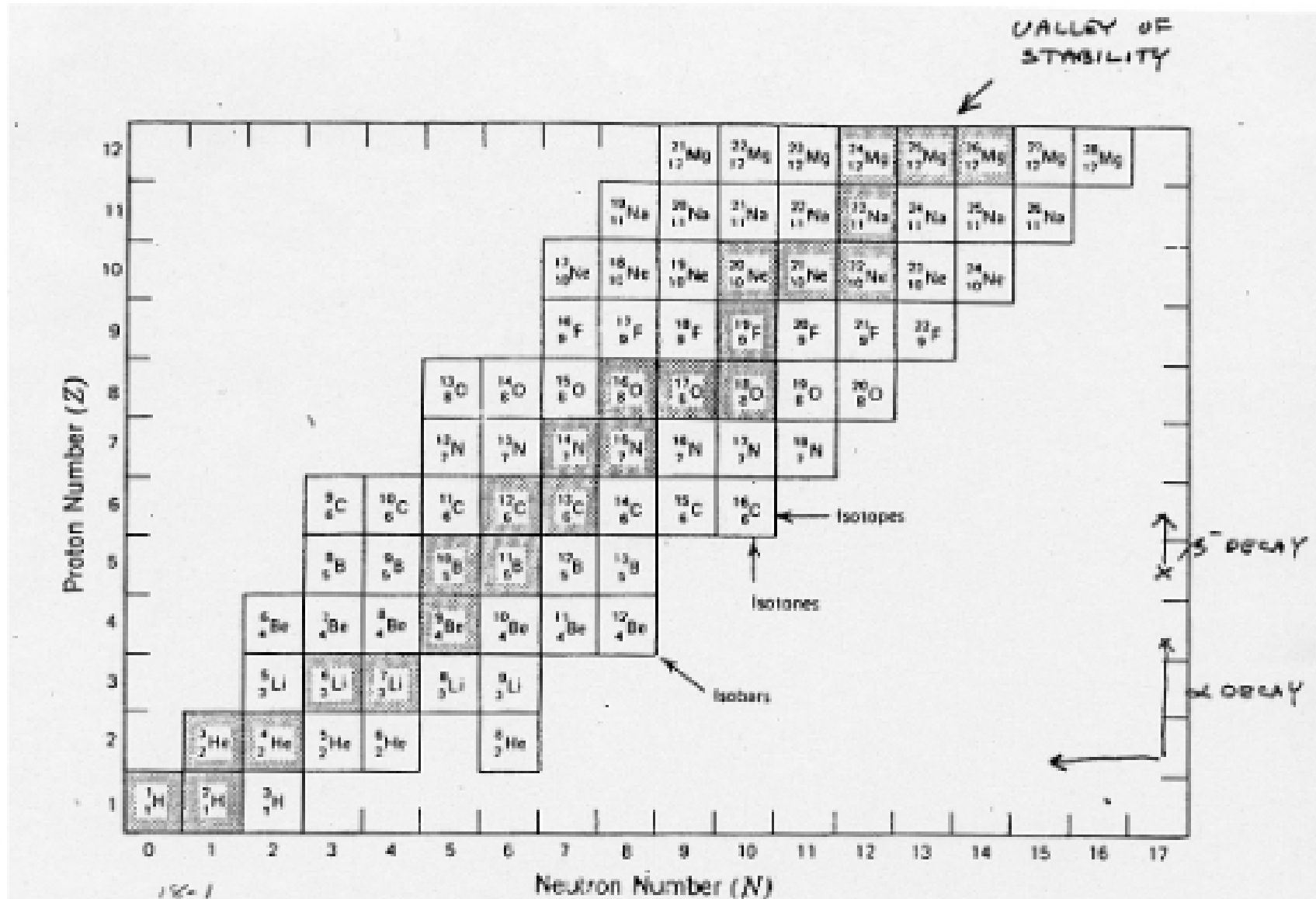


FIGURE Partial chart of the nuclides. Each square represents a particular nuclide which is defined in terms of the number of protons (Z) and neutrons (N) that make up its nucleus. The shaded squares represent stable atoms, while the white squares are the unstable or radioactive nuclides. Isotopes are atoms having the same Z but different values of N . Isotones have the same N but different values of Z . Isobars have the same A but different values of Z and N . Only isotopes are atoms of the same element and therefore have nearly identical chemical properties.

16-I. Stable Isotopes

All isotopes of a given element have the same electronic structure, thus the bonds they form in any given compound are identical. The differences in mass do give rise to differences in energy levels of vibration. As a result different isotopes of the same element have different vibrational frequencies. These differences lead to small **equilibrium fractionations** of isotopes between coexisting phases. During a chemical reaction, molecules bearing the light isotope will, in general, react slightly more rapidly than those with the heavy isotope. In principal, equilibrium fractionation can be calculated from fundamental vibrational frequencies. There may also be **kinetic fractionations**. For example, in a gas the molecules containing the light isotope migrate more rapidly than those with the heavy isotope. This can lead to isotopic fractionation during diffusion. Kinetic fraction can only be measured not calculated.

The concentrations of stable isotopes are usually expressed in delta (δ) notation where the ratio of two isotopes in a sample are compared to a standard adopted by the geochemical community and multiplied by 1000 to avoid using fractional values. The use of a standard material results in much greater precision than a direct analysis of absolute ratios for mass spectrometric analyses. The units for δ are usually per mil or parts per thousand (expressed as ‰). The delta values are defined as:

$$\delta \text{ (in ‰)} = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right] \times 1000$$

or

$$R / R_{\text{std}} = 1 + \delta$$

where R is the isotope ratio with the most abundant isotope in the denominator. When $\delta = 0\text{‰}$ the isotopic composition of the sample is the same as the standard.

16-I.A. Hydrogen/Deuterium

A-1. Rain (to be added)

A-2. Air Temperature (to be added)