Chapter 1

Introduction

1.1 Retrospect and Prospect

In view of their scarcity and failure to form chemical compounds, it is not surprising that noble gases remained unknown until relatively late in the history of chemistry. The first known experimental indication of their existence was a persistent gaseous residue after chemical removal of nitrogen and oxygen from air, as noted by Cavendish in 1784; the residue was small, however, "not more than 1/120th part of the whole," presumably attributed to experimental error, and in any case subsequently ignored. The first definitive identification came when several observers found a previously unknown line in the spectrum of the solar chromosphere during the 1868 eclipse; this was quickly recognized to belong to a new element, not yet known on earth, which was named helium (*ηλιον*: sun); of course, no chemical characterization was possible.

The actual "discovery" of the noble gases came principally from the work of Rayleigh and Ramsay in the late nineteenth century. In 1892 Rayleigh reported that nitrogen prepared from ammonia was consistently less dense (by 0.5%) than "nitrogen" prepared from air (by removal of oxygen, carbon dioxide, and water). Both Rayleigh and Ramsay, working in collaboration, followed up this experimental clue; pursuing the possibility that the density difference reflected admixture of a heavier gas in air, they, like Cavendish, found a residue when chemically reactive species were removed from air. This residue was clearly denser than air and spectroscopic examination (by Crookes) gave a spectrum unlike that of any known element. Rayleigh and Ramsay announced the discovery of a new element in a joint paper in 1895. The discovery attracted interest beyond that due a new element because they

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also found it to be chemically unreactive, an unprecedented property that led to the name argon (*αργον*, negative of *εργον*: not working, idle, inert, lazy). They further found argon to be a monatomic gas of atomic weight 40. This result was puzzling since the concept of the periodic table was then well established, and it was surprising to find an element whose weight was that of calcium, with no apparent place for it in the sequence potassium, calcium, scandium.

Further discoveries proceeded rapidly. In seeking possible compounds of argon, Ramsay suspected that "nitrogen" previously reported to be liberated in acid treatment of a uranium mineral was actually argon rather than nitrogen; he prepared gas in this way (in 1895) and indeed identified argon in its spectrum. He also noted another line in this spectrum; in examining this gas Lockyer and Crookes quickly identified it as the helium line previously found in the solar spectrum. Helium was found to be monatomic, of atomic weight 4, and like argon, chemically inert. By 1897 Ramsay was able to conclude that helium and argon represented a new column in the periodic table and predicted that at least one additional element, of intermediate atomic weight, remained to be found. In 1898 Ramsay and co-workers conducted fractional distillation experiments on liquid air, which led to the identification of three new elements: neon (*νεον*: new), krypton (*κρυπτον*: hidden), and xenon (*ζενον*: alien). The identification included spectroscopic characterization, measurement of atomic weight, and confirmation of chemical inactivity. The noble gas column of the periodic table was completed in 1900–1903 by identification of gaseous emanation of thorium and radium as a noble gas, radon (*ραδιυσ*: ray).

Since their discovery more than a century ago, the unique properties of the noble gases have been the subject of much research in theoretical chemistry and physics. These gases have also found many applications as tools for scientific research and many commercial, industrial, and even medical applications as well. These uses are well known, and our further discussion will focus on the role of noble gases in geochemistry.

The first such application was in geochronology. Even while they were studying the phenomenon of radioactivity of uranium and thorium, Rutherford and Soddy noted its potential value as a geochronometer. The first radiometric age measurement, by the uranium-helium method, was reported by Rutherford at the International Congress of Arts and Science in St. Louis in 1904. Uranium-helium dating was subsequently pursued as a major methodology in geochronology and was later supplemented by (and largely supplanted by) the potassium-argon method (Wasserburg & Hayden, 1955), particularly the ^{40}Ar-^{39}Ar variant (Merrihue & Turner, 1966). Geochronological study of terrestrial, meteoritic, and lunar samples continues to be pursued very actively, and to account for much of the research in noble gas geochemistry.

Appreciation of the relevance of noble gases to broader aspects of geochemistry was somewhat later in developing. A noteworthy step was von Weizäcker's (1937) recognition that atmospheric argon was radiogenic; the corollary inference of gas

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transport from the solid earth to the atmosphere suggests the possibility of the quantitative evaluation of the degassing history of the earth, a subject that has received much attention and in which radiogenic noble gases play the principal role. Subsequently, Brown (1952) used noble gas abundances to argue that the Earth's atmosphere as a whole was secondary rather than primary, that is, the present atmosphere was formed by outgassing the interior (cf. Chapter 6). The discovery of (juvenile) He in sea water (Clarke, Beg & Craig, 1969) showed that this degassing process is incomplete and continues today. Considerable recent work has been done on developing the use of noble gases as geochemical tracers and indices of tectonic activity. More generally, characterization of both primordial and radiogenic noble gas abundances in the mantle is a major present concern in noble gas geochemistry because of the profound implications for both the formation of the Earth and its thermal, tectonic, and chemical evolution. Such developments and prospects are the principal subject of this book.

As with other scientific disciplines, advances in noble gas geochemistry can be seen to follow not only from prior progress in research but also from exploitation of technological and methodological developments. Early work measured gases by volume, using the handling techniques developed by Ramsay and Rayleigh and progressively refined to the point that uranium-helium ages could be determined for ordinary surface rocks rather than only for unusual and scarce uranium and thorium ores (cf. Dubey & Holmes, 1929). The present character of the discipline, however, is set by the research tool which is its sine qua non, the mass spectrometer. The first demonstration of multiple isotopic forms of a stable element (neon!) was made in the "parabolic" mass analyzer by Thomson (1912), and the first focusing mass "spectrographs" suitable for isotopic abundance measurements were constructed by Dempster (1918) and Aston (1919). During the 1930s and 1940s, the basic instrumental configuration for isotope ratio mass spectrometry evolved to the form still most commonly used today: a monoenergetic ion source (with ions of gaseous samples produced by electron bombardment), mass separation by single-focusing magnetic sector analysis, and electrical (rather than photographic) ion detection, usually with an electron multiplier for small samples. A particularly significant development for noble gases was Reynolds' (1956) introduction of techniques and methodologies for static rather than dynamic analysis. This finding permitted the accurate isotopic analysis of very small quantities of gas, which characterizes noble gas geochemistry today and justly may be said to have begun its modern era.

In the early 1980s, an ultra-high-vacuum (pressure below 10^{-10} torr can be maintained in a static condition for hours) mass spectrometer was made commercially available; the machine is capable of analyzing isotopic ratios of an extremely small amount of noble gases. With the introduction of these commercial machines, high-quality noble gas isotopic data on a variety of samples, especially those of mantle-derived materials, are now emerging, widening the scope of noble gas geochemistry and offering a powerful tool to earth science.

1.2 Geochemical Characteristics of the Noble Gases

Although this whole book is about noble gas geochemistry, two important general characteristics should be noted here. These features are commonly known by workers in the field but deserve explicit attention from the nonpractioner.

First, the noble gases are, obviously, noble (i.e., chemically inert). This does not mean that they completely fail to interact with anything (cf. Chapter 2), but that the interactions are of the van der Waals type, much weaker than normal chemical reactions. In practical terms, this means that the interactions are less complicated, and we may be more optimistic that they can be understood in terms of fairly simple ideas. (That the relevant chemistry is still not very well understood reflects more the lack of empirical data than intrinsic complexity.) It also means that the noble gases constitute a reasonably coherent group so that geochemical parameters can often be seen to vary more or less smoothly from light to heavy gases. This coherence is the reason why it makes sense to consider their geochemistry as a group, as well as why, experimentally, they are naturally studied as a group.

Second, the noble gases are scarce, whence their common alias, the rare gases. This feature is a consequence of their inertness. The noble gases are not actually rare in the cosmic sense (Chapter 3) nor in the solar system as a whole (i.e., the sun and presumably the major planets). At some point in its evolution, however, the solar system, or at least that part most familiar to us, passed through a stage in which some of its constituent elements were mostly in solid phases, whereas others, including the most abundant, were in a gas phase. The outstanding chemical characteristic of the terrestrial planets (including meteorites) is that they are made from the solids, to the virtually complete exclusion of the gases. Because of their chemical inertness, the noble gases were overwhelmingly partitioned into the gas phase and so are depleted in the earth and other accessible samples, often to a very striking degree, and in general more than any other elements.

Thus, the noble gases are trace elements par excellence. As an example, a not unreasonable value of Xe concentration in a rock is some 10^{-11} cm^3 STP/g (about 3×10^8 atoms/g), or 0.00006 ppb. It is nevertheless quite feasible to perform an adequate analysis on a 1-g sample of such a rock, in the sense of a sample to blank ratio in excess of 10^2, 5–10% uncertainty in absolute abundance, and 1% or less uncertainty in relative abundances of the major isotopes. Detection limits are much lower than this, and for the scarcer isotopes the blank and thus the quantity necessary for analysis are two to three orders of magnitude lower. It is worth noting that the reason why such an experiment is possible is the same reason why noble gases are so scarce in the first place: their preference for a gas phase and the ease with which they can be separated from more reactive species.

An important corollary of this scarceness is that many effects, which are not intrinsically characteristic of the noble gases, are best studied through them. These are effects in which small amounts of material are added to some reservoir. In many

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cases, such additions are undetectable against the background of material already there, but when the background is low, as it usually is for noble gases, the effects become observable and thereby interesting. An important subclass of such effects is that of nuclear transmutations, many of which are totally unobservable if the daughter nuclide is a "normal" element but which make prominent changes if the daughter is a scarce noble gas. Nuclear chemistry (Section 1.7) is thus a considerable part of noble gas geochemistry.

Many examples of the utility of scarcity will be found in this book, so one will suffice here. The nuclide ^{40}K is naturally radioactive and thus useful for geochronology. Some 90% of the decays produce ^{40}Ca but constitute an imperceptible perturbation on normally present Ca in all but a few highly unusual samples, and K-Ca dating is only marginally useful in geochemistry. The 10% of the decays that produce ^{40}Ar generally overwhelm any Ar initially present and are readily observable experimentally, and K-Ar dating is probably the most extensively practiced form of geochronology. By noble gas standards, the Earth is awash in radiogenic ^{40}Ar. Indeed, on the basis of atmospheric ^{40}Ar overabundance relative to other Ar isotopes, von Weizäcker (1937) predicted the decay of ^{40}K to ^{40}Ar even before K was known to be radioactive.

Finally, we should note that even though Rn is chemically a noble gas, geochemically it might as well not be. Rn has no stable isotopes and is found in nature only because it is part of U and Th decay schemes (Section 1.7). Because of its extremely low abundance even by noble gas standards, it is observed by different techniques (based on its radioactive decay) than the other noble gases. Most important for our purposes, the geochemical factors that determine the distribution of Rn seldom have any close relation to the factors that control the other noble gases. Accordingly, we make no attempt to present a comprehensive description of the geochemistry of Rn.

1.3 Constants and Conventions

A number of physical constants and conversion factors frequently useful in noble gas geochemistry calculations are collected in Table 1.1. These values have been used for all the calculations in this book.

In subsequent data tabulations in this book, primary experimental data are stated with their attendant uncertainties when it is important to do so. Most numerical data are stated without uncertainties, however, because experimental uncertainties are commonly minor in comparison with those originating in the failure of natural systems to conform to simple models or in the fuzziness of quantitative interpretations. In general, numerical values are stated with more significant figures than their precision justifies. This reflects not ignorance but the utility of many such data as starting points for calculations in which the excess figures help alleviate two annoying problems: the accumulation of rounding errors in calculations based only on

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Table 1.1. *Physical constants and conversion factors*

Avogadro's number	N_A	6.02217×10^{23} molecules/mole
Gas constant	R	8.31434 J/K/mole, 82.0578 cm^3-atm/K/mole
Boltzmann's constant	k	1.38062×10^{-16} erg/K
Ice point (0°C)		273.15 K
Electron charge	e	1.60219×10^{-19} C
Planck's constant	h	6.6256×10^{-34} J-s
1 atm (760 torr)		1.01325×10^6 dyns/cm^2 $\equiv 1.01325 \times 10^5$ Pa
1 cm^3 STP		4.465×10^{-5} mole $= 2.688 \times 10^{19}$ molecules
1 cal		4.184 J
1 eV/molecule		23.06 kcal/mole
1 amu ($^{12}C \equiv 12$)		1.66053×10^{-24} g
RT at 0°C		2.24141×10^4 cm^3-atm/mole
RT at 25°C		2.44655×10^4 cm^3-atm/mole

significant figures and the vexation of obtaining different values of the same quantity when calculated by different paths.

Presumably in continuity with early investigations in which gases were actually measured by volume, quantities of noble gases in modern geochemical literature are generally reported in terms of cm^3 STP. This has the advantage that cm^3 STP are proportional to number of atoms, which is the way gases are measured in the mass spectrometers responsible for most of the modern data. Numbers of atoms, rather than, say, weight percent or partial pressures, are fortunately also the units generally most convenient for calculations and interpretations. Reporting of gas quantities in moles, or actual numbers of atoms, would have the same advantage but is not customary. Unfortunately, none of these units (nor others that might be chosen) has the desirable feature of being comparable to a sufficiently extensive set of observed data that its use would permit abundance data to be remembered as integers rather than powers of ten.

A widespread convention in geochemistry, particularly for isotopic data, is use of values in which numerical values are expressed as permil (‰) deviations from some standard:

$$\delta_x = 1000(X/X_0 - 1) \tag{1.1}$$

where X is the quantity of interest and X_0 is the standard value. Other normalizations such as 10^2 for percent (%) deviations or 10^4 for epsilon (ε) deviations are also used (unfortunately, noble gas data cannot yet justify using the epsilon notation), but they do not have as consistent notation as δ for ‰ deviations. This convention has the advantage that small deviations from the standard value are more readily apparent. It has the more important advantage that if the standardization is based on a physical standard measured under the same circumstances as the sample, δ_x can be determined from the ratio of instrumental responses without the uncertainties involved in correcting either X or X_0 for instrumental isotopic discrimination. In high-precision "stable isotope" (O, C, N, S, etc.) geochemistry, δ values are thus the norm as primary experimental data, so variations of isotopic ratios from the standards are known to better precision than are the absolute ratios.

In noble gas mass spectrometry, comparisons using δ values are frequent, but primary experimental isotopic data are generally absolute ratios rather than δ values. To a large extent, the standardization is accomplished by calibrating instrumental performance by analysis of a widely accessible standard (air), but for practical reasons the calibrations are generally less frequent and employ less of a match of sample and standard conditions than is the rule in stable isotope geochemistry. Fortunately, this entails little difficulty in practice, since isotopic effects are frequently so large that minor discrepancies are unimportant or, for all practical purposes, nonexistent. For a few cases of effects near the border of observation, however, a more thorough adoption of δ-value normalization could be of benefit.

1.4 Nomenclature

Most specialized disciplines have their own specialized jargons, each a lexicon and syntax developed partly to make communication more efficient and partly by historical accident. For convenience, this section lists a number of words and phrases used elsewhere in this book and in the pertinent literature that require special attention. Some such terms will be obscure outside the circle of communicants, some have special meanings or connotations beyond their normal dictionary definitions, and some need particular attention because they are not used consistently in the literature.

Component: In isotopic geochemistry, and especially in noble gas geochemistry, this term is widely used to designate any compositionally well-defined and uniform reservoir. It is particularly useful to describe component resolution (i.e., the attempt to interpret analytical data as a superposition of previously known components), the reservoirs of which might have been sampled by the specimen under consideration. A component may have a single and well-understood origin (e.g., the collection of Xe isotopes produced by spontaneous fission of ^{238}U), but it need not. Thus, Xe in air is an ill-understood mixture of Xe contributed by a number of sources; it is nevertheless useful to consider air Xe itself as a component because it is a uniform reservoir that can be and is sampled by materials of interest. The term *component* usually denotes a reservoir of isotopes of a single element. In some cases, it may include more than one element, but it is then less useful. Thus, fission Xe from ^{238}U will be produced in proportion to ^{4}He, and together the Xe and He will constitute a component, but the Xe and He can be very easily separated (much more so than, say, ^{136}Xe and ^{134}Xe), and the notion of U-derived gas is less useful in component resolution than is U-derived Xe.

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Nuclear Component: A nuclear component is one generated by nuclear transmutation. For example, Xe produced by fission of ^{238}U is a nuclear component; air Xe, in contrast, would generally not be considered a nuclear component, even though it contains a contribution from ^{238}U fission. Ultimately, all the isotopes have been produced in processes controlled by their nuclear properties, and so everything is a nuclear component, but it is still useful to make a distinction. In particular, it is common to designate as a primordial component all the nuclides present in the solar system when it was isolated from the rest of the galaxy (cf. Chapter 3), in contrast to a variety of nuclear components generated within the solar system since that time. Subdivision of this category is common (e.g., a radiogenic component is one generated by decay of natural radionuclides).

Trapped Components and In Situ Components: Noble gases in solid samples are grouped into two classes designated trapped and in situ. The *in situ* label designates a nuclear component that is still in the same locations in which it was generated. Gases that are not in situ are trapped. The distinction is operational (although it is sometimes difficult to determine experimentally) and only partly genetic. An in situ component is necessarily a nuclear component, but the origin of a trapped component need not be specified. Usually, we think of a trapped component as originating outside the specimen in question so that the specimen sampled some external reservoir; the gas in the reservoir may itself be primordial, a nuclear component, or a mixture. The origin is not necessarily external, however. As an example, a rock may contain some ^{36}Ar of external origin (trapped) and ^{40}Ar generated by decay of ^{40}K (in situ). If the rock is melted in a closed system and then solidifies again, the subsequently produced radiogenic ^{40}Ar will be an in situ component. The ^{40}Ar produced before the melting will no longer be in the same microscopic locations in which it was produced, so will be a trapped component. As specified, the distinction is operational and rests on the possibility, at least in principle, of separating trapped and in situ components by mechanical or chemical disassembly of the rock or by different diffusional behavior manifested in stepwise heating. (Hence, the distinction between trapped and in situ is not made for liquid or gaseous samples.) Thus, in the example, the first-generation ^{40}Ar, although radiogenic, will have become homogenized with the ^{36}Ar and no longer separable from it by any means short of a Maxwell's demon (or mass-dependent isotopic fractionation). The second-generation ^{40}Ar will be separable from these but not, say, from ^{39}Ar produced by ^{39}K(n, p) in a neutron irradiation: together these will constitute a single in situ component because they are sited in the same place (i.e., wherever the K is). The total ^{40}Ar is thus split between two components, one trapped and one in situ, and these components can be separated. This situation is not hypothetical: "excess ^{40}Ar," not uncommon in rocks, is radiogenic but trapped, not in situ.

Solar and Planetary: In addition to their normal usage in designating the sun and a planet, respectively, the terms *solar* and *planetary* are used to designate specific patterns of noble gas elemental abundances. These are discussed in Chapter 3.

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Atmosphere: Air is the gas phase at the surface of the earth. In this book, as is common in the literature, *atmosphere* will be used in a more general sense to designate all the volatiles in surface reservoirs of the Earth, including air but also water and sedimentary rocks.

Juvenile: It is generally believed that the Earth's atmosphere was formed by degassing of volatiles from the interior. Volatiles that have remained in the Earth's interior, have never been part of the atmosphere, and are observed to be entering the atmosphere for the first time are designated as juvenile. *Atmospheric* is an antonym to juvenile.

Fractionation and Discrimination: Both terms are used in consonance with everyday meaning but also with special connotations. *Fractionation* connotes the process of selecting one element in preference to another or, more commonly in this book, one isotope in preference to another of the same element. For the latter usage in particular, it is supposed that in natural isotopic fractionation processes the only selection criterion is isotopic mass. In nature, isotopic fractionation effects are usually small and measured in per mil (in contrast to elemental fractionation, often measured in powers of ten) and in elements of three or more isotopes can be recognized by their smooth functional (often nearly linear) dependence on differences in isotopic mass. In the technical literature, the term *discrimination* is usually reserved for the specific case of instrumental rather than natural isotopic fractionation (i.e., that which arises as part of the measurement process). In contrast to thermal ionization mass spectrometers, noble gas mass spectrometers usually have rather constant discrimination, and the normal procedure is to calibrate this discrimination by analyzing standards and applying the corresponding correction to sample data. When small fractionation effects are inferred, it is sometimes questionable whether they are actually natural fractionations or perhaps simply artifacts (improper correction for instrumental discrimination). To our knowledge, no geochemical noble gas investigations have used the double-spike technique, which could distinguish between natural fractionation and instrumental discrimination. Even for geochronological applications, the use of a double spike (cf. Macedo et al., 1977) is very rare. However, a single spiking technique is now widely used in paleotemperature application of noble gas geochemistry, in that a high-precision quantitative analysis of noble gas amount is required (e.g., Poole et al., 1997).

Partition (Distribution) Coefficients: In describing the partitioning of a trace element among coexisting phases, we frequently use a partition (distribution) coefficient for a given element, defined as a concentration ratio C_2/C_1. Here C is concentration, and the subscripts identify the phases; often the normalizing phase is some convenient reservoir, such as a silicate melt, with which several other phases may equilibrate. For noble gases, it is often most convenient to normalize to a gas phase. If the concentrations are expressed in the same units, the distribution coefficient is dimensionless. It is conventional to cite noble gas concentrations in condensed phases in cm^3 STP/g, however, and to describe the gas phase by partial pressures, so most of our numerical citations of distribution coefficients will be in cm^3 STP/g/atm.

1.5 Air

Air is a major reservoir for terrestrial noble gases. It is possible that air is *the* major reservoir for the Earth (i.e., that it accounts for most of the terrestrial noble gas inventory, cf. Section 6.9); it is often so assumed, but this assumption should not be made lightly. In any case, air is certainly the most conspicuous and accessible reservoir of noble gases, and its characterization is of fundamental importance in noble gas geochemistry. The geochemical considerations are taken up elsewhere in this book; here we focus on the presentation of basic data. It is noteworthy that these data are important not only in the direct sense of providing information about the Earth and its atmosphere but also in the sense of serving as a standard for noble gas geochemistry. Most data are produced by mass spectrometers whose performance, both sensitivity and mass discrimination, is calibrated by analyzing samples of air or of secondary standards whose parameters are ultimately determined by comparison with air. At least as far as noble gases (other than Rn) are concerned, we generally assume that air is compositionally uniform (not counting high altitudes and nuclear power plants, which are unimportant for total inventory). Actually, studies directed to this point are scarce, but there seems no reason to challenge this assumption (cf. Mamyrin et al., 1970).

Generally accepted data for elemental abundances and isotopic compositions are given in Tables 1.2 and 1.3, respectively. The air "concentrations" in the rightmost column of Table 1.3 are often used as a normalization for observed concentrations in samples. If the atmosphere actually does account for nearly the total terrestrial inventory, then indeed these values are near the average concentration of noble gases in the materials that accreted to from the Earth. Use of these data for normalization does not constitute endorsement of this proposition, however, and whether or not they represent the terrestrial inventory, they are a convenient data set with elemental ratios of air and absolute abundances of the same order of magnitude as many samples.

The primary experimentally determined data in Tables 1.2 and 1.3 are the isotopic ratios and volume fractions in air and the total mass of air; these are tabulated with their reported uncertainties. Quantities derived from these are shown without error limits in Tables 1.2 and 1.3; for reasons cited earlier, they are stated to more significant figures than are justified by the precision of the primary data from which they are calculated.

It seems likely that application of presently available information and technology could result in some improvement in the elemental abundance data (Table 1.2). At least from the geochemical viewpoint, however, relatively little advantage would result. High-precision absolute abundances, as needed, for example, in K-Ar dating or studies of gases dissolved in water, are generally isotopic dilution data calibrated