

Composition and Classification of Magmatic Rocks

FUNDAMENTAL QUESTIONS CONSIDERED IN THIS CHAPTER

1. How are rocks sampled in the field and analyzed in the laboratory to determine their chemical, modal, and mineralogical composition?
2. What do these analyses disclose regarding the composition of magmatic rocks?
3. How can analytical data be presented to reveal petrogenetically significant similarities, patterns, and contrasts?
4. How are magmatic rocks classified so as to convey meaningful petrogenetic information concerning the origin and evolution of the magmas from which they solidified?
5. What special petrogenetic information do the trace element and isotopic compositions of magmatic rocks provide?

INTRODUCTION

Magmatic rocks possess a seemingly endless variety of chemical, modal, and mineralogical compositions from which the petrologist must extract information about how rocks form. Samples can be collected, laboratory analyses made, similarities and contrasts in composition sought through graphed data and classification, compositional patterns found, and interpretive models hypothesized.

Compositions of magmatic rocks, together with their fabrics and field relations (Chapters 7, 9, and 10), are the essential “nuts and bolts” from which interpretive models (Chapters 11–13) can be constructed. After a

brief introduction to sampling and analytical techniques for obtaining compositional data on rocks the chapter focuses on three compositional attributes of rocks:

1. Mineralogical, modal, and major element compositions that are the bases for different classifications of magmatic rocks
2. Trace element compositions
3. Isotope ratios

All of these compositions provide crucial information regarding the sources and evolutionary paths of magmas.

*2.1 ANALYTICAL PROCEDURES

Modern petrology relies heavily on quantitative, or numerical, data on rock and mineral compositions obtained by a variety of analytical devices and techniques. Data can be stored and processed and interpretive models created by using computers.

2.1.1 Sampling

The validity and usefulness of any compositional data are crucially dependent upon the quality of the sample collected in the field. “Garbage” samples collected in the field are liable to yield “garbage” analytical results. The importance of this crucial first step cannot be ignored or minimized. If the analysis of the sample is to be truly representative of the body of rock, the sample should be as free as possible of overprinting effects of alteration and weathering. This is especially important for chemical and isotopic analyses. Virtually all primary, high-temperature (high- T) minerals and glasses are metastable near-atmospheric conditions. Except for quartz, they are subject to replacement by secondary minerals more stable at near atmospheric temperatures such as carbonates, clays, and ferric oxides. This **weath-**

ering is especially common in warm, wet climates and in subaqueous environments. The chemical composition of the rock also changes during these secondary replacement processes, including but not restricted to the addition of water and oxidation of ferrous iron. It is difficult to know to what extent mobile chemical elements in the original rock have experienced gains or losses in their concentration. Hence, the sample must be as fresh and unweathered as possible. Silicate minerals should have vitreous luster with distinct grain boundaries and well-defined cleavage or fracture surfaces. The rock sample should be free of patchy discoloration due to films of secondary manganese or iron oxide, or a whitish clouding of feldspar caused by conversion to clay minerals. Secondary carbonate and silica (e.g., chalcidony) should be absent. Pervasively weathered samples crumble from the outcrop, whereas unweathered rock breaks with difficulty under the hammer and yields sharp-edged pieces. At an outcrop, a hammer may be unable to break far enough into the rock through a weathered rind to obtain a fresh sample. A portable diamond core drill may be required. As a final test for the quality of a sample, a thin section should be examined with a petrographic microscope.

Many rocks have also experienced **alteration** by hot gases around volcanic vents and by hot aqueous (hydrothermal) solutions farther beneath the surface. Alteration can create many of the same secondary minerals as does weathering but also includes conversion of primary magmatic minerals to somewhat higher T zeolites, chlorite, serpentine, epidote, and others.

If a fresh sample can be obtained, the petrologist must next determine how large it should be and where it should be taken from a heterogeneous rock body. Different sampling plans must be adopted to solve different problems. In most plans, the size of the sample should be representative of the outcrop; therefore, it must be many times larger than the dimensions of the coarsest grains. Obviously, a representative sample of a coarse phaneritic granite containing phenocrysts of alkali feldspar 3 cm in length must be considerably larger than a representative sample of an aphanitic, nonporphyritic basalt.

For chemical analyses, samples should be pulverized to at least 200 mesh to ensure homogeneity of the powder. Rock powders are contaminated by pulverizing machines. Alloy steel pulverizers add contaminating Fe as well as possible Cr, Co, Ni, and Mn. Ceramic pulverizers add Al. Agate adds Si. Corrections may be applied to analytical results for such contaminants.

2.1.2 Analyses

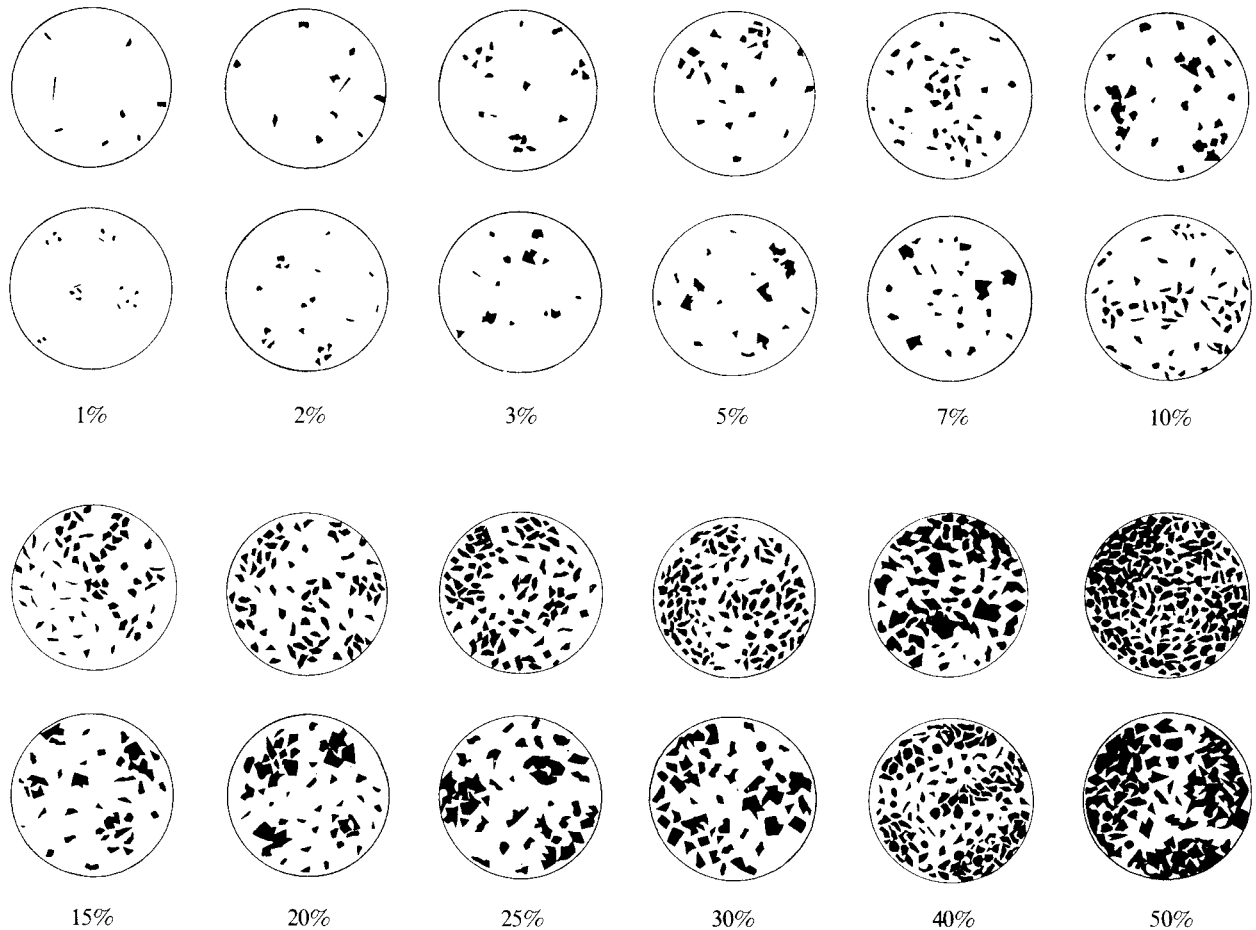
Accuracy and Precision. Any measured value should be accompanied by a statement of accuracy and precision indicating the reliability of the value; otherwise, it has little meaning.

Precision, or reproducibility, is a number that indicates how much statistical variation from the average or mean value occurs in replicate determinations (see, for example, Le Maitre, 1982). The greater the number of determinations of a particular quantity in a sample the smaller is the precision and the more reliable is the average value. Suppose, for example, the precision of analysis of, say, CaO in basalt samples is ± 0.25 wt.%. If analysis of one sample yields an average value of 8.45 wt.% and of another yields 8.75 wt.% it might be supposed that these two values are significantly different. However, if the \pm uncertainties are taken into consideration the first analysis actually lies between $8.45 + 0.25 = 8.70$ and $8.45 - 0.25 = 8.20$ wt.% and the second lies between $8.75 + 0.25 = 9.00$ and $8.75 - 0.25 = 8.50$ wt.%. Hence, the two analyses actually overlap in the range of 8.50 to 8.70 wt.% and it is possible the two samples have the same CaO concentration in that range. Additional replicating analyses to reduce the precision would be necessary to resolve the question whether or not the two samples have the same CaO value.

Accuracy is less easily determined; it is an indication of how close the measurement is to the “true” value. But what is the true value? For chemical analyses, accuracy is an expression of how the result for a standard sample analyzed in a petrologist’s laboratory compares with the “accepted” value (Govindaraju, 1989) for the standard sample.

Modal Analyses. Determination of the volumetric proportions of the minerals that make up a rock—its modal composition or mode—can be done by various techniques, yielding different degrees of precision and accuracy (van der Plas and Tobi, 1965). The quickest, but least accurate technique, adequate for preliminary work, is a visual estimate of mineral proportions in a hand sample or thin section (Figure 2.1). Greater accuracy and precision can be obtained on sawn, polished slabs on which a transparent overlying grid is placed. The proportion (or percentage) of grid intersections falling on a particular mineral indicates its proportion in the rock. The same concept underlies commercially available electromechanical point counters used on thin sections of rocks. Sometimes troublesome distinctions between alkali feldspar, plagioclase, and quartz can be overcome by selective staining (e.g., Bailey and Stevens, 1960).

Because the volumetric proportions of minerals in a rock are based on their proportions on a surface area, the modal composition of a rock having a preferred orientation of inequant mineral grains that is based only on one surface generally will be inaccurate. For example, the mode of a rock in which biotite flakes are strongly oriented in planar fashion would yield, on a surface parallel to that plane, an apparent overabun-



2.1 Charts to aid the visual estimation of modal proportions of minerals in rocks. (From Terry RD, Chilingar GV.)

dance of biotite at the expense of the other minerals. In rocks that contain oriented tablets of plagioclase, an examination in hand sample of a rock surface parallel to their {010} direction would reveal little if any polysynthetic twinning, thus possibly leading to an erroneous modal determination for plagioclase. (This twinning is the surest criterion for recognition of plagioclase in hand sample.) To overcome biasing the mode in anisotropic rocks, it is necessary to average the analysis on three mutually perpendicular surfaces, generally oriented parallel and perpendicular to the planar and/or linear fabric elements.

Modal analyses can also be performed by analyses of digital images on a computer. Digital images of rocks can be produced from backscattered electron intensities that portray the average atomic number of minerals or by element mapping under the beam of an electron microprobe (discussed later). The Rietveld X-ray diffraction method provides modes of wholly crystalline (nonglassy) rocks. However, because the sample is pulverized, this method ignores textures of mineral grains, which might be important in the case of secondary mineral overgrowths and replacements.

Chemical Analyses. Since the 1960s, rapid instrumental methods of chemical analyses of rocks and minerals have taken the place of tedious wet methods requiring skilled chemical analysts. All of these instrumental methods are comparative, based upon a comparison of the intensity of some measured quantity in an unknown sample with the intensity in a standard sample of known composition. Some instrumental methods have very low detection limits that are measured in parts per million (**ppm**) or even in parts per billion (**ppb**) by weight. The detection limit, specific for an element, is what the method can measure in a sample above the background of instrumental "noise." Although *element* concentrations are determined in all of these methods, major elements are nonetheless reported as *oxides*, following the traditional presentation of the results of wet methods of analysis.

Some methods, such as atomic absorption spectrophotometry (AA), flame photometry, emission spectroscopy, and inductively coupled plasma spectrometry (ICP), depend upon detection of shifts in outer electrons in the atom as the sample is heated to extreme temperatures. In X-ray fluorescence spectrometry (XRF), atoms in the sample are bombarded with X rays of sufficient energy to eject an inner orbital electron. As

an outer electron drops into its place, energy is released as fluorescent X rays whose wavelength is characteristic of the atom, whether Ca, Si, Al, etc. The intensity of the wavelength-specific X ray is proportional to the concentration of the chemical element in the sample. Other methods utilize the radioactivity of atomic nuclei. For example, in gamma-ray spectrometry, the intensities of gamma rays of different energies are a measure of the amount of naturally decaying K, Th, and U isotopes. In neutron activation analysis (NAA), artificial radioactive isotopes are induced by reaction with neutrons in a reactor and the energies of decaying radiation monitored. Ratios of isotopes of the elements are determined by a mass spectrometer, an instrument that distinguishes among nuclei of differing masses accelerated through a magnetic field.

Chemical analysis of minerals has been revolutionized by the electron microprobe, which is essentially an electron microscope fitted with XRF spectrometers that has the capability of analyzing a 1- to 10-micrometer-diameter volume of a mineral in situ in a polished thin section of a rock. Thus, spatial variations in composition within a mineral grain can be determined.

An example of an unusually complete whole-rock chemical analysis is shown in Table 2.1. Oxides > 0.1 wt.% (weight percent; in a 100-gram sample) are said to be **major elements**, whereas **trace elements** contain <0.1 wt.% of the element, or more conventionally, <1000 ppm. This limit is rather arbitrary. Some elements are not consistently major or trace elements. For example, Ti is a major element in basalts because of abundant Fe-Ti oxides and Ti-bearing pyroxenes, but it is a trace element in dunites, which are made of more

than 90 modal % olivine that contains virtually no Ti. About 99% of most rocks are made of 11 major-element oxides: SiO₂, TiO₂, Al₂O₃, Fe₂O₃, FeO, MnO, MgO, CaO, Na₂O, K₂O, and P₂O₅. Iron typically occurs in two oxidation states (ferric, Fe₂O₃, and ferrous, FeO) in rocks and minerals, but most instrumental methods cannot distinguish between them and so total Fe is expressed as either Fe₂O_{3,t} or as FeOt.

Most silicate rocks contain **volatiles** such as water, carbon dioxide, sulfur, fluorine, and chlorine. H₂O⁺ is structural or combined water in the form of the hydroxyl ion, (OH⁻) in amphiboles and micas and in secondary limonite and clays and as molecular H₂O in glasses. H₂O⁻ is “dampness,” or water absorbed on grain surfaces and in pore spaces that can be driven off by heating to 110°C. Significant amounts of CO₂ are present if secondary carbonate, usually calcite, has been introduced during weathering or alteration. Total volatiles in a rock can be determined by weighing an aliquot of rock powder, heating it to 1000°C, and weighing again to determine the **loss on ignition (LOI)**. To facilitate comparisons, many rock analyses are recalculated to a volatile-free basis totaling 100.00 wt.%.

Because analyses of rocks and minerals always involve human and instrumental errors and because not all elements are analyzed, the total of major and trace constituents is never exactly 100.00 wt.%. Generally speaking, if an analysis lists all major oxides, including H₂O, and the total lies between 98.8 wt.% and 100.8 wt.% it is considered to be acceptable.

Chemical analyses of average common rock types are listed in Table 2.2.

Table 2.1 Whole-Rock Chemical Composition of Basalt from the Columbia River Plateau, Sample BCR-1^a

SiO ₂	54.06	Ag	27*	Er	3.63	Nd	28.8	Tb	1.05
TiO ₂	2.24	As	650	Eu	1.95	Ni	(13)	Te	(4.9*)
Al ₂ O ₃	13.64	Au	(0.66*)	F	490	Pb	(13.6)	Th	5.98
Fe ₂ O ₃	3.59	Ba	681	Ga	22	Pr	6.8	Tl	0.3
FeO	8.88	Be	(1.6)	Gd	6.68	Rb	47.2	Tm	0.56
MnO	0.18	Bi	47*	Ge	1.5	Re	0.84	U	1.75
MgO	3.48	Br	(72*)	Hf	4.95	Rh	(0.23*)	V	407
CaO	6.95	Cd	130*	Hg	(7.9*)	S	410	W	(0.44)
Na ₂ O	3.27	Ce	53.7	Ho	1.26	Sb	0.62	Y	38
K ₂ O	1.69	Cl	59	In	92*	Sc	32.6	Yb	3.38
P ₂ O ₅	0.36	Co	37	La	24.9	Se	(88*)	Zn	129.5
H ₂ O ⁺	0.75	Cr	(16)	Li	12.9	Sm	6.59	Zr	190
H ₂ O ⁻	0.81	Cs	0.96	Lu	0.51	Sn	(2.7)		
CO ₂	0.03	Cu	(19)	Mo	(1.6)	Sr	330		
LOI	1.67	Dy	6.34	Nb	(14)	Ta	0.81		
Total	99.93								

^aMajor element oxides in wt.%. Less certain values in parentheses. *, Trace element concentration in parts per billion (ppb); all other trace elements in parts per million (ppm).

Data from Govindaraju (1989).

Table 2.2 Average Chemical Compositions of Some Common Rock Types (Recalculated Volatile-Free to Total 100%) and Their Normative Compositions^a

	PHONOLITE	SYENITE	TRACHYTE	GRANITE	RHYOLITE	GRANODIORITE	DACITE	DIORITE	ANDESITE
<i>n</i>	340	517	534	2485	670	885	651	872	2600
SiO ₂	57.43	59.63	62.31	71.84	73.95	66.91	65.98	58.34	58.70
TiO ₂	0.63	0.86	0.71	0.31	0.28	0.55	0.59	0.96	0.88
Al ₂ O ₃	19.46	16.94	17.27	14.43	13.48	15.92	16.15	16.92	17.24
Fe ₂ O ₃	2.85	3.09	3.04	1.22	1.50	1.40	2.47	2.54	3.31
FeO	2.07	3.18	2.33	1.65	1.13	2.76	2.33	4.99	4.09
MnO	0.17	0.13	0.15	0.05	0.06	0.08	0.09	0.12	0.14
MgO	1.09	1.90	0.94	0.72	0.40	1.76	1.81	3.77	3.37
CaO	2.78	3.59	2.38	1.85	1.16	3.88	4.38	6.68	6.88
Na ₂ O	7.96	5.33	5.57	3.71	3.61	3.80	3.85	3.59	3.53
K ₂ O	5.36	5.04	5.07	4.10	4.37	2.76	2.20	1.79	1.64
P ₂ O ₅	0.18	0.30	0.21	0.12	0.07	0.18	0.15	0.29	0.21
<i>Q</i>		0.83	5.00	29.06	32.87	22.36	22.73	10.28	12.37
<i>C</i>				0.92	1.02	0.26			
<i>Or</i>	30.96	29.29	29.41	24.50	25.44	16.11	12.82	10.42	9.60
<i>Ab</i>	35.48	44.34	46.26	31.13	30.07	31.73	32.07	29.96	29.44
<i>An</i>	1.50	7.24	7.05	8.04	4.76	17.34	20.01	24.40	26.02
<i>Lc</i>									
<i>Ne</i>	16.50								
<i>Di</i>	6.89	5.35	2.14				0.11	4.67	4.84
<i>Wo</i>	0.73								
<i>Hy</i>		4.16	2.06	3.37	1.34	7.40	5.73	12.56	9.49
<i>Ol</i>									
<i>Mt</i>	4.05	4.41	4.33	1.75	2.14	2.00	3.53	3.63	4.74
<i>Il</i>	1.18	1.60	1.34	0.58	0.54	1.03	1.09	1.80	1.65
<i>Ap</i>	0.41	0.70	0.49	0.28	0.17	0.42	0.34	0.68	0.50

	TRACHYANDESITE	TRACHYBASALT	BASALT	BASANITE	NEPHELINE	ANORTHOSITE	LHERZOLITE	HARZBURGITE	DUNITE
<i>n</i>	232	161	3594	165	176	104	179	206	93
SiO ₂	59.30	49.99	49.97	45.16	41.81	51.12	45.43	43.73	41.04
TiO ₂	1.10	2.44	1.87	2.56	2.74	0.65	0.45	0.28	0.10
Al ₂ O ₃	17.03	16.89	15.99	14.99	14.76	26.29	4.39	2.57	1.95
Fe ₂ O ₃	3.32	3.75	3.85	4.02	5.64	0.98	5.15	6.00	3.85
FeO	3.27	6.28	7.24	7.65	6.35	2.10	7.44	7.09	10.05
MnO	0.16	0.16	0.20	0.16	0.27	0.05	0.17	0.16	0.76
MgO	2.62	5.25	6.84	8.71	6.58	2.16	30.31	36.34	40.66
CaO	5.06	8.03	9.62	10.39	12.25	12.69	5.68	3.18	1.08
N ₂ O	4.44	4.02	2.96	3.62	4.93	3.20	0.59	0.34	0.21
K ₂ O	3.27	2.59	1.12	2.00	3.56	0.66	0.27	0.15	0.09
P ₂ O ₅	0.42	0.60	0.35	0.75	1.10	0.09	0.12	0.14	0.21
<i>Q</i>	7.80								
<i>C</i>									
<i>Or</i>	19.00	15.06	6.52	11.61	3.16	3.86	1.50	0.83	0.80
<i>Ab</i>	36.80	29.39	24.66	12.42		23.16	4.66	2.60	0.47
<i>An</i>	16.58	20.10	26.62	18.38	7.39	49.71	7.99	4.17	1.69
<i>Lc</i>					13.57				1.17
<i>Ne</i>	3.95	2.23	14.02	9.55	21.95	1.89	13.54	6.93	
<i>Di</i>		11.85		21.03	32.36	8.61			
<i>Wo</i>									
<i>Hy</i>	6.06		15.20				21.48	21.13	14.48
<i>Ol</i>		8.28	1.50	12.38	2.32	2.01	36.31	46.22	67.38
<i>Mt</i>	4.73	5.36	5.49	5.72	7.95	1.40	7.00	7.94	5.20
<i>Il</i>	2.07	4.55	3.49	4.77	5.05	1.22	0.79	0.50	0.18
<i>Ap</i>	0.97	1.38	0.82	1.74	2.51	0.21	0.26	0.30	0.47

^aThe number of analyses averaged is represented by *n*. The rock-type names are those used by the author of the report in which the analyses were published; that is, the names are not based on the IUGS classification. In most instances there is little discrepancy between the original rock-type name and the IUGS name.
Data from Le Maitre (1976).

*2.2 MINERAL COMPOSITION OF MAGMATIC ROCKS

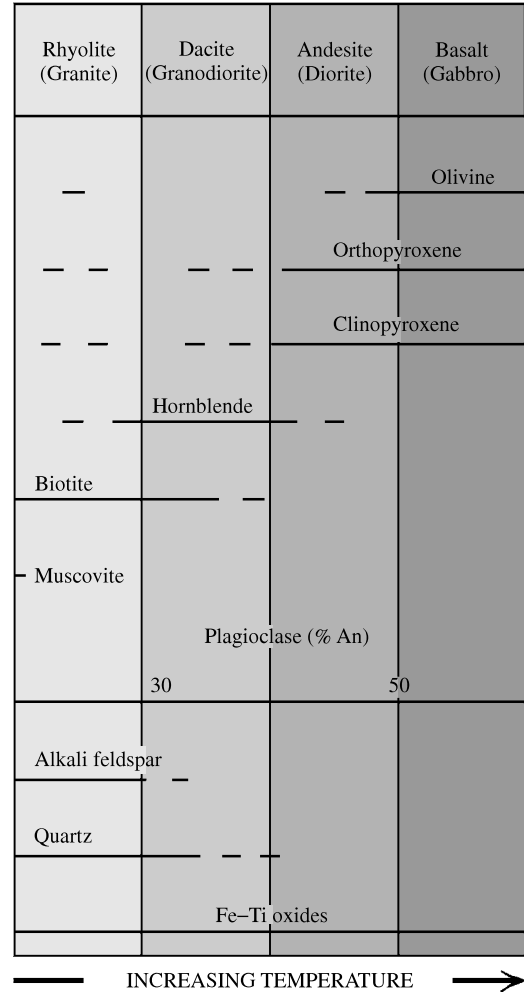
The minerals that crystallize from most magmas include only a very small number of the thousands of known mineral species. Major **rock-forming minerals** include only olivine, pyroxene, amphibole, mica, feldspars, quartz, feldspathoids, and Fe-Ti oxides (chiefly magnetite and ilmenite). All of these are solid solutions, except quartz, although it, too, contains variable concentrations in the ppm range of $Al^{3+} + Li^{+}$ substituting for Si^{4+} and $(OH)^{-}$ for O^{2-} . Very rare magmatic carbonate rocks are composed chiefly of carbonate minerals.

Because of the limited number of major minerals, their identification is relatively straightforward in hand sample with the aid of a hand lens and in thin section with a petrographic polarizing microscope. X-ray diffraction analysis can be useful for mineral identification in very fine-grained rocks, but the electron microprobe is the ultimate tool. In addition to the standard mineral properties such as cleavage, hardness, and habit, the petrologist can use **mineral associations** as a means of mineral identification in hand samples. For example, Figure 2.2 shows highly generalized mineral associations in common subalkaline rocks. (In less common alkaline rocks mineral associations are more complex.) Most magmatic rocks contain feldspar; of the two feldspar solid-solution series—alkali feldspar and plagioclase—the latter is more widespread. One of the most easily identified minerals in rocks is biotite; once recognized, its presence suggests the probable coexistence of quartz, alkali feldspar, plagioclase, and amphibole but not magnesian olivine and perhaps not pyroxene. More reliably, quartz cannot coexist with pale green magnesian olivine, so once one mineral is recognized for certain the other cannot be present, at least under equilibrium conditions. Other “forbidden” associations are feldspathoids (leucite and nepheline) with quartz or orthopyroxene.

Appendix A tabulates chemical compositions of select major rock-forming solid solutions occurring in magmatic rocks. Such tabulations are generally more useful for the petrologist than mineral formulas because they are readily compared to whole-rock chemical compositions presented in the same tabular format.

The standard references for rock-forming minerals are the five-volume work by Deer, Howie, and Zussman (1962) and their abridged, single-volume paperback (1997).

Minerals that occur in small modal proportions of no more than a few percent and do not influence the naming of a rock are sometimes referred to as **accessory minerals**. Some crystalline phases occur only as accessory minerals, such as apatite and zircon, rarely as



2.2 Generalized **mineral associations** of common subalkaline rocks plotted according to relative temperature of equilibration. Rock types listed across top (rhyolite, dacite, etc.) are aphanitic or glassy, usually volcanic. Corresponding phaneritic, usually plutonic, rock types (granite, diorite, etc.) are in parentheses. An andesite (diorite), for example, commonly contains intermediate composition plagioclase (An_{40-50} , or andesine), clinopyroxene, orthopyroxene, hornblende, and Fe-Ti oxides; possible minor constituents are biotite, quartz, and olivine. Greater Mg/Fe ratio in mafic solid-solution minerals and greater Ca/Na and K/Na ratios in plagioclase and alkali feldspar solid solutions, respectively, correlate with increasing temperature.

major rock-forming minerals. Although seemingly insignificant, these minerals can be petrologically important because they contain large concentrations of trace elements (discussed later) and some can be used for age determinations. Common accessory minerals are listed in Table 2.3.

2.2.1 Glass

Glass, not a mineral, originates from magmas that lose heat so rapidly that atoms in the silicate melt have insufficient opportunity to organize into the regular geometric arrays of crystals. Instead, the melt solidifies into

Table 2.3 Generally Compatible Trace Elements and the Minerals in Which They Occur

MAJOR MINERAL	SIMPLE FORMULA	COMPATIBLE TRACE ELEMENTS
Olivine	(Mg, Fe) ₂ SiO ₄	Ni, Cr, Co
Orthopyroxene	(Mg, Fe)SiO ₃	Ni, Cr, Co
Clinopyroxene	(Ca, Mg, Fe) ₂ (Si, Al) ₂ O ₆	Ni, Cr, Co, Sc
Hornblende	(Ca, Na) ₂₋₃ (Mg, Fe, Al) ₅ (Si, Al) ₈ O ₂₂ (OH, F) ₂	Ni, Cr, Co, Sc
Biotite	K ₂ (Mg, Fe, Al, Ti) ₆ (Si, Al) ₈ O ₂₀ (OH, F) ₄	Ni, Cr, Co, Sc, Ba, Rb
Muscovite	K ₂ Al ₄ (Si, Al) ₈ O ₂₀ (OH, F) ₄	Rb, Ba
Plagioclase	(Na, Ca)(Si, Al) ₄ O ₈	Sr, Eu
K-feldspar	KAlSi ₃ O ₈	Ba, Sr, Eu
ACCESSORY MINERALS ^a		
Magnetite	Fe ₃ O ₄	V, Sc
Ilmenite	FeTiO ₃	V, Sc
Sulfides		Cu, Au, Ag, Ni, PGE ^b
Zircon	ZrSiO ₄	Hf, U, Th, heavy REEs
Apatite	Ca ₅ (PO) ₃ (OH, F, Cl)	U, middle REEs
Allanite	Ca ₂ (Fe, Ti, Al) ₃ (O, OH) (Si ₂ O ₇)(SiO ₄)	Light REEs, Y, U, Th
Xenotime	YPO ₄	Heavy REEs
Monazite	(Ce, La, Th)PO ₄	Y, light REEs
Titanite (sphene)	CaTiSiO ₅	U, Th, Nb, Ta, middle REEs

^aAccessory minerals constitute only a small fraction of rock but their very high partition coefficients create a disproportionate influence on bulk distribution coefficients.

^b**Platinum group elements:** Ru, Rh, Pd, Os, Ir, Pt.

a very viscous amorphous glass—a supercooled liquid solution of O, Si, Al, Ca, K, and so on. It is, therefore, common in extruded lavas but is also found along margins of thin dikes emplaced in the shallow cool crust. Rarely, glass is produced locally by frictional processes in fault zones (creating pseudotachylite), by impact of large meteorites, by some lightning strikes (creating “fulgurite”), and by burning of underground coal. No sharp transition appears between the liquid solution and amorphous solid upon heating or cooling (Bouška, 1993). Rhyolitic glass is particularly widespread because the relatively high viscosity of the silicate melt from which it forms hinders crystallization during rapid cooling, particularly of extruded magmas. Rhyolitic glass is colorless in thin section but gray, black, or dark red-brown in hand samples of massive obsidian because of minute crystals of dark colored minerals. Increasing concentrations of Fe, generally accompanied by increasing Ca, Mg, and decreasing Si and K, produce increasingly darker brown colors so that basaltic glass in thin section is honey- to cinnamon-brown and jet black in hand sample.

All glass is metastable at near-surface conditions and is susceptible to replacement by more stable minerals (Section 7.1.1). Geologically older glasses are more rare; most are Cenozoic. Glasses are also susceptible to loss of relatively mobile Na and K.

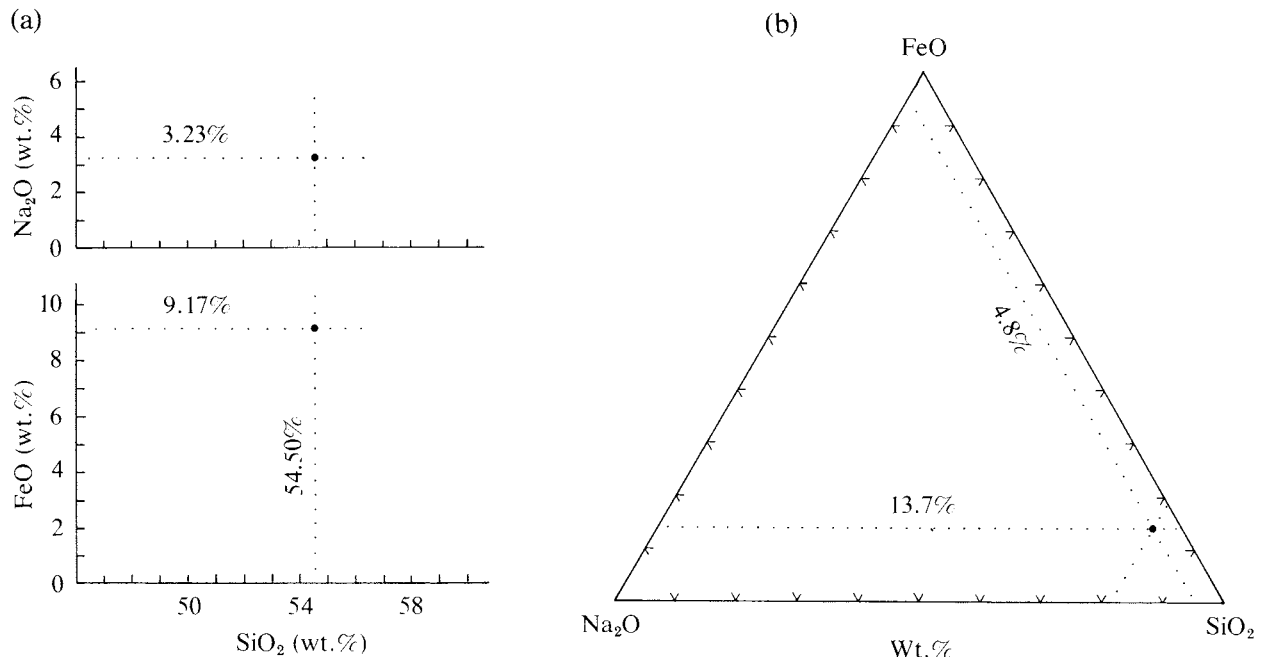
✱2.3 CHEMICAL COMPOSITION OF MAGMATIC ROCKS

2.3.1 Variation Diagrams

Chemical compositions of rocks and minerals are conventionally presented by petrologists in two formats: tables of oxide and/or element concentrations—as in Tables 2.1 and 2.2 and Appendix A—and graphs where points represent the concentrations of chemical constituents. These graphs, called **variation diagrams**, show trends or patterns in the chemical data. Modal data can also be presented in variation diagrams. Three common types of diagrams are used by petrologists:

1. Cartesian graph of two variables (x and y)
2. Triangular diagram
3. Normalized diagrams (see Section 2.5)

The Cartesian diagram (Figure 2.3) best portrays the absolute concentrations of any compositional parameter and is amenable to quantitative interpretations; however, in order to represent all n constituents in a rock, $(n - 1)$ plots are required. The triangular plot presents one more constituent than can be represented in one Cartesian graph but cannot show absolute concentrations of the three variables, only their ratios; it is most useful in portraying trends in variation in suites of rocks but cannot be used to extract any quantitative in-



2.3 Plotting compositional data on **variation diagrams**. A sample contains 9.17 wt.% FeO, 3.23 wt.% Na₂O, and 54.50 wt.% SiO₂. In the Cartesian diagram (a), FeO and Na₂O are plotted against SiO₂ (all in wt.%). To plot SiO₂, Na₂O, and FeO on the triangular diagram (b), they must be recalculated to total 100.00. First, they are summed, $54.50 + 9.17 + 3.23 = 66.90$ and a recalculation multiplier found, $100.00/66.90 = 1.495$. Second, the wt.% of each constituent is recalculated; Si₂O is $54.50 \times 1.495 = 81.48$, FeO = 13.71, and Na₂O = 4.83. The total of the three recalculated oxides is now $81.5 + 13.7 + 4.8 = 100.0$. These recalculated values can then be plotted so that each apex represents 100 wt.% of a constituent and the leg of the triangle opposite the apex is the locus of points representing 0 wt.% of that constituent. A line parallel to the leg of the triangle opposite the FeO apex and 13.7% of the way toward that apex is the locus of points representing 13.7 wt.% FeO. Similarly, the line labeled 4.8% is the locus of points representing 4.8 wt.% Na₂O. The intersection of these two lines is a point that represents the relative SiO₂, FeO, and Na₂O wt.% in the sample. Note that it is only necessary to draw lines for any two of the three constituents represented in the diagram because the third variable is the difference from 100% of the other two.

formation. In either type of diagram, two or more constituents may be combined into one variable or ratios of elements may be represented by a variable.

2.3.2 Continuous Spectrum of Rock Compositions

One of the most frequently used Cartesian diagrams, especially for chemical classification of volcanic rocks (discussed later), is the total alkalis (Na₂O + K₂O) versus silica (SiO₂) diagram. Figure 2.4 is such a TAS diagram, in which are plotted over 41,000 published whole-rock analyses of silicate magmatic rocks of all compositions of all ages from all over the world. (Rare carbonatites are excluded.) This plot has two especially significant attributes:

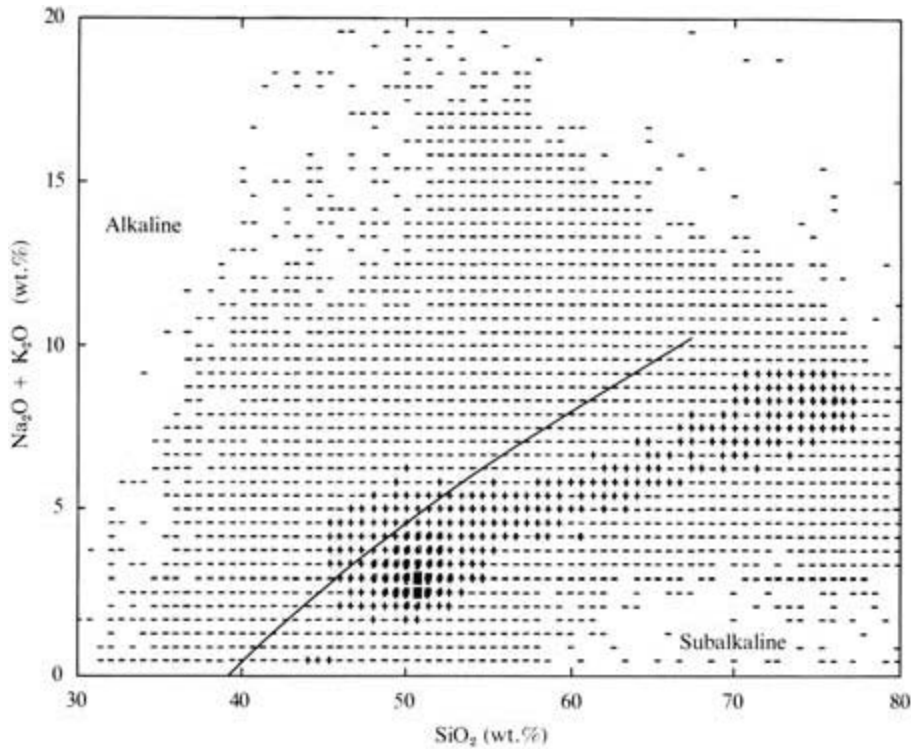
1. Magmatic rocks constitute a continuous spectrum of compositions, lacking natural breaks or discontinuities. Variation diagrams plotting any other combination of elements show the same continuity. This continuous spectrum introduces an arbitrariness into chemical classification of rocks, as discussed later. More importantly, the spectrum poses some of the most fundamental questions in igneous petrology: How is such a large and continuous compositional

range of rocks created? Is there a corresponding range in magma compositions? If so, what processes of generation of magmas from solid source rock could yield such a range? Or, are magmas generated from solid rock more restricted in composition but subsequently diversified in some manner?

2. Variations in silica (about 30–80 wt.%) and total alkalis (0–20 wt.%) occupy only a part of a possible range of 100% in each variable. This attribute of the worldwide compositional spectrum begs the question, What petrologic factors dictate this restricted range? Why, for example, are there no magmatic rocks that contain 95 wt.% SiO₂, or 50 wt.% total alkalis?

These fundamental questions are addressed in later chapters, especially Chapters 11–13.

It is interesting to note that the major rock-forming minerals that make up magmatic rocks form a polygonal envelope surrounding the global rock spectrum (Figure 2.5). Variations in the modal proportions of major minerals can produce any rock within the envelope, whose corners are represented by Fa (Fe-olivine



	Upper limit of analyses	Total analyses	Analyses as %
-	41	19,207	46.73
•	116	15,626	38.02
•	330	5,449	13.25
■	462	820	2.00
Total		41,102	100.00

2.4 Chemical analyses of over 41,000 igneous rocks from around the world of all ages. Each symbolized plotted point represents a particular number of analyses falling within the indicated range (0–41, 42–116, etc.). Nearly half (46.7%) of all igneous rocks are widely scattered over the diagram (dash symbol), whereas slightly more than half (53.3%) are tightly clustered in a central band. Note the still higher concentration of analyses near 2.5 wt.% (Na₂O + K₂O) and 50 wt.% SiO₂, corresponding roughly to basalt, the dominant magmatic rock type on Earth. (Compiled by and furnished courtesy of R. W. Le Maitre, University of Melbourne, Australia.)

end member); Ne, Lct (two of the most common feldspathoids); Kfs; and Qtz. Some accessory minerals, such as magnetite and ilmenite, plot well outside this envelope but, because of their small concentrations, do not disperse whole-rock chemical compositions very far toward them in the diagram.

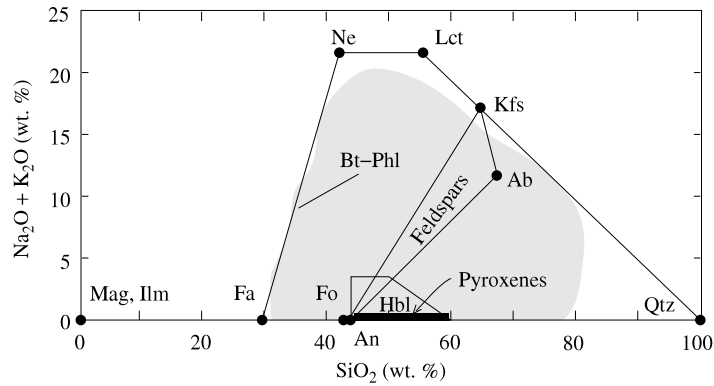
Variation diagrams of modal compositions of rocks are also continuous spectra, such as Figure 2.6.

*2.4 CLASSIFICATION OF MAGMATIC ROCKS

Scientists have traditionally sought regularity, order, and predictability in their investigations of the natural world.

However, for the petrologist, the continuity of rock compositions revealed in Figures 2.4 and 2.6, the seemingly endless variety of fabric, and the wide range of geologic environments in which rocks form pose formidable obstacles to erecting a well ordered, simple, single rock classification. Unlike in the plant and animal kingdoms, which have discrete species, no such natural divisions exist in rocks. Rocks are more like complex, highly variable biological ecosystems; minerals constituting a rock are like the plant and animal species constituting an ecosystem.

Despite the obstacles, a consistent classification of rocks is essential for communication with other petrologists, who should all speak the same language of clas-



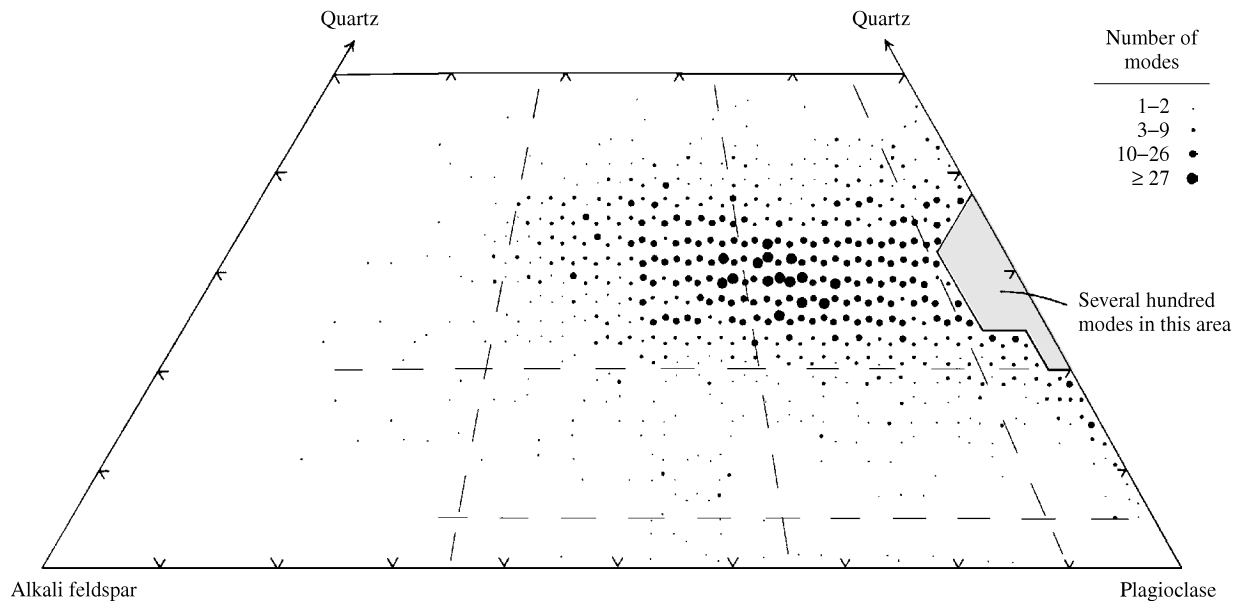
Ab	Albite	Ilm	Ilmenite
An	Anorthite	Kfs	K-feldspar
Bt	Biotite	Lct	Leucite
Fa	Fayalite	Mag	Magnetite
Fo	Forsterite	Ne	Nepheline
Hbl	Hornblende	Phl	Phlogopite
		Qtz	Quartz

2.5 End-member compositions of major magmatic rock-forming minerals compared with the field of worldwide magmatic rocks (shaded) from Figure 2.4. Triangular field of feldspar solid solution is outlined by the K-feldspar-albite-anorthite end members. Trapezohedral field is hornblende solid solutions.

sification; a particular rock name should convey the same meaning to every petrologist, regardless of his or her native tongue. In addition, classification serves as an important means of systematizing information. Through appropriate and relevant classification, meaningful patterns in composition, fabric, field relations, and, therefore, origin can be perceived. As all classifi-

cations of rocks are the fruits of the human mind attempting to erect discrete subdivisions where none exists in the natural, uninterrupted continuum of rock properties, every classification is, to some degree, arbitrary and imperfect.

There are many different criteria for classification; consequently, many different labels exist for the very



2.6 Modal composition of 4368 samples from 102 Late Triassic to Late Cretaceous plutons in the central part of the Sierra Nevada batholith, California. The number of sample modes plotting within a triangular area 2% on a side is coded by the indicated symbol; the greatest number of modes in any such triangle is 35. Note the continuity of modal variation across dashed-line boundaries between rock-type compartments from Figure 2.8. (Data from Bateman, 1992.)

same rock. Each has its own benefit and use; none can combine the merits of all. “A rock may be given one name on the ground of field occurrence and from hand lens examination, only to require another when it is studied in thin section, and perhaps a third when it is chemically analyzed. . . . Different schemes have different objects in view” (Williams et al., 1982, p. 68; see the following pages in this classic text for an extended discussion of igneous rock classification).

2.4.1 Classification Based on Fabric

We review here only the most fundamental rock terminology based on fabric as it is generally introduced in a beginning geology course. Magmatic fabric (Chapter 7) is essentially governed by time-dependent (kinetic) processes in the solidifying magma, such as its rate of heat loss, or cooling.

Four principal types of fabric occur in magmatic rocks: phaneritic, aphanitic, glassy, and volcaniclastic. The first two refer to the dominant crystal grain size, which ranges over several orders of magnitude, from $<10^{-6}$ to 10 m.

Phaneritic applies to rocks that have mineral grains sufficiently large to be identifiable by eye (minute accessory minerals excepted). This texture is typical of rocks crystallized from slowly cooled intrusions of magma. **Aphanitic** rocks have mineral grains too small to be identifiable by eye and require a microscope or some other laboratory device for accurate identification. Aphanitic texture is most common in rapidly solidified extruded magma but can also be found in marginal parts of magma intrusions emplaced in the cool shallow crust. Some magmatic rocks contain essentially two grain-size populations and few of intermediate size; such texture is said to be **porphyritic**. The larger grains are **phenocrysts**, and the smaller constitute the **groundmass**, or **matrix**. Porphyritic aphanitic rocks are far more common than porphyritic phaneritic rocks. **Glassy**, or vitric, rocks contain variable proportions of glass, in contrast to **holocrystalline** rocks made entirely of crystals. A **vitrophyre** is a porphyritic rock that contains scattered phenocrysts in a glassy matrix.

The fabric of **volcaniclastic** rocks is produced by any fragmenting process that creates broken pieces of volcanic rock and/or mineral grains. Classification of volcaniclasts parallels that of sedimentary clasts according to their particle size, as follows:

	$< 2\text{ mm}$	$2\text{--}64\text{ mm}$	$> 64\text{ mm}$
volcaniclasts	ash	lapilli	block, bomb
sedimentary clasts	{	clay,	granule,
		silt,	pebble
		sand	cobble,
			boulder

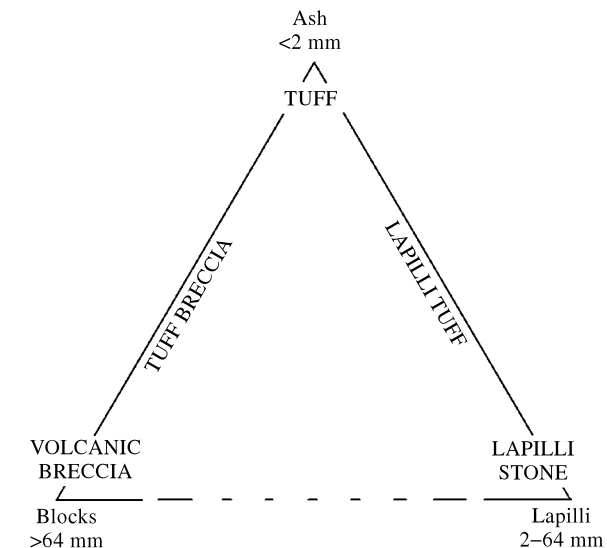
Consolidation of volcaniclasts produces volcaniclastic rock types that are classified according to their particle size (Figure 2.7).

2.4.2 Classification Based on Field Relations

The location where magma was emplaced provides a basis for rock classification. Some petrologists recognize three categories for rocks solidified from magmas emplaced onto the surface of the Earth (volcanic or extrusive), into the shallow crust (intrusive hypabyssal), and into the deep crust (intrusive plutonic). The first and the last categories are readily distinguished on the basis of their field relations but less directly on the basis of their grain size, **degree of crystallinity** (proportion of crystals to glass), and mineralogical composition.

Magmas emplaced onto the surface of the Earth as coherent lava flows or as fragmental deposits form **extrusive**, or **volcanic rocks**. These rocks are typically aphanitic and glassy. Many are porphyritic. Some have fragmental (volcaniclastic) fabric. High-*T* disordered feldspars are common, so that alkali feldspar, where present, is a clear sanidine. Other minerals that occur only at high-*T* and low-*P* in volcanic environments—including leucite, tridymite, and cristobalite—are found in some volcanic rocks. Amphiboles and biotite, especially where they occur as phenocrysts, are commonly partially altered to fine-grained anhydrous aggregates of Fe oxides, pyroxenes, and feldspars. Phenocrysts of feldspar and quartz commonly contain inclusions of glass.

Intrusive, or **plutonic, rocks** form where magma was intruded into preexisting rock beneath the surface of the Earth as **intrusions**, or **plutons**. Plutonic rocks are typically phaneritic. Monomineralic rocks composed



2.7 Classification of volcaniclastic rock types (capital letters) based on size of clasts.

only of plagioclase, or olivine, or pyroxene are well known but rare. Amphiboles and biotite are commonly partially altered, usually to chlorite. Some granites contain muscovite, which is exceedingly rare in volcanic rocks. Perthite—an intergrowth of sodic and potassic feldspar—is widespread and reflects slow cooling and exsolution in initially homogeneous alkali feldspar.

Characteristics of intermediate-depth **hypabyssal rocks** are not clearly distinct from those of volcanic and plutonic rocks. Many occur in shallow crustal dikes, sills, and plugs that represent feeding conduits for surface extrusions of magma. But dikes and sills are also intruded deep in the crust. Hypabyssal rocks can have fabric similar to that of plutonic and volcanic rocks. Because of these ambiguities, many petrologists tend to categorize magmatic rocks in the field simply as plutonic or volcanic.

2.4.3 Classification Based on Mineralogical and Modal Composition

Mineralogical Mnemonics. **Felsic** is a mnemonic adjective derived from the words *feldspar* and *silica*. It is a useful appellation for rocks that contain large proportions of feldspar with or without quartz and/or its polymorphs, tridymite and cristobalite. Granite and rhyolite made mostly of feldspar and quartz are examples of felsic rocks. The term *felsic* also applies to rocks containing abundant feldspathoids, such as nepheline, and to these rock-forming minerals as well. **Mafic** is a mnemonic adjective derived from the words *magnesium* and *ferrous/ferric*. *Mafic* is a less cumbersome term than the synonymous *ferromagnesian*. It refers to major rock-forming biotite, amphibole, pyroxene, olivine, and Fe-Ti oxide solid solutions as well as rocks that contain large proportions of them, such as basalt. **Ultramafic** rocks are especially rich in Mg and Fe and generally have little or no feldspar; an example is the olivine-pyroxene rock called peridotite. **Silicic** rocks contain large concentrations of silica, manifested by an abundance of alkali feldspar, quartz, or glass rich in SiO₂. Examples are rhyolite and granite. The term **sialic** is used less frequently for rocks rich in Si and Al that contain abundant feldspar and is used especially with reference to the continental crust.

Color is usually the first rock property noticed by the novice. However, a particular rock type can possess a wide range of colors; granites, as just one example, can be nearly white, shades of gray, green, red, and brown. These widely ranging colors reflect equally widely variable colors of the dominant rock-forming feldspars, whose pigmentation is a complex function of minute mineral inclusions, exsolution, and small concentrations of elements such as Fe in solid solution; none of these factors may be petrologically very significant and in any case may be difficult to determine.

Color is not a valid basis of rock classification and can, in fact, be highly misleading. **Color index** has been defined as the modal proportion of dark-colored minerals in a rock. But, in view of the fact that dominant rock-forming feldspars can be light- to dark-colored, a more accurate index should be defined on the basis of the proportion of mafic minerals. **Leucocratic** and **melanocratic** rocks can be defined as having 0–30% and 60–100% modal mafic minerals, respectively.

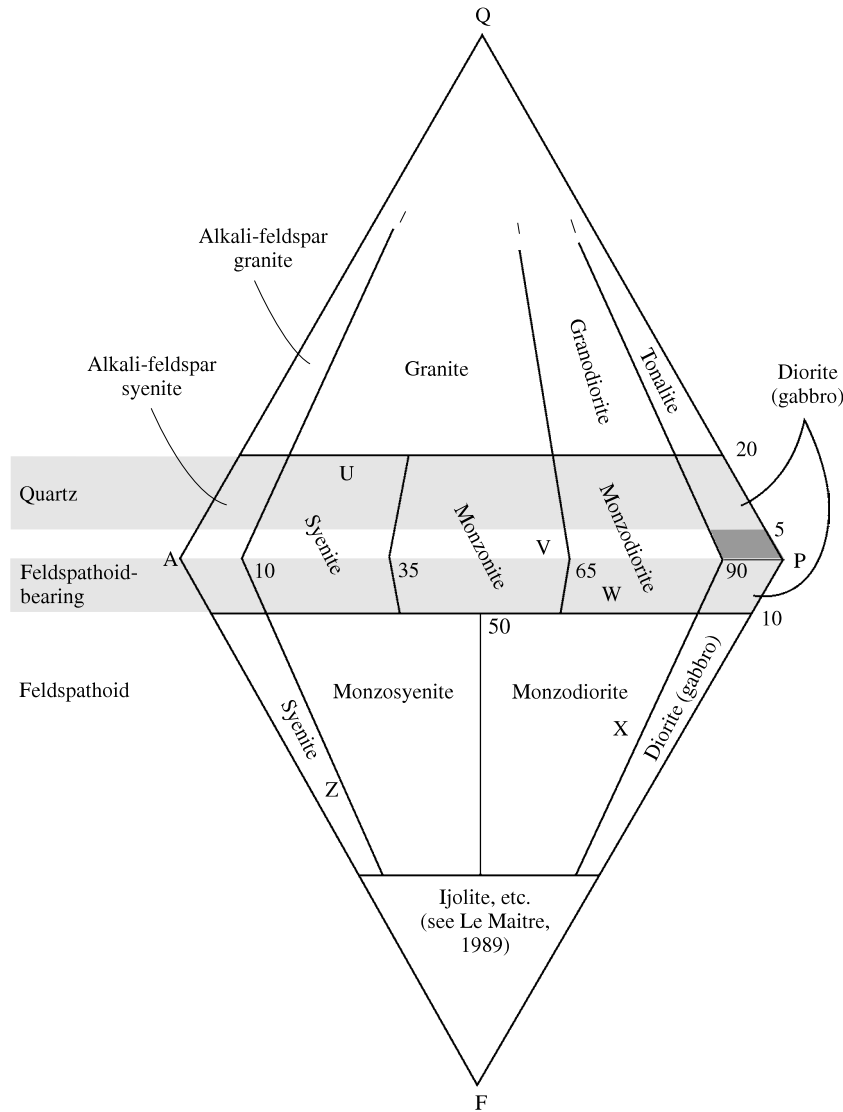
Rock Types. The classification of magmatic rocks most familiar to the beginning geology student is that of rock types. In contrast to the broadly defined compositional labels just described, a **rock type** has a narrowly defined composition and a particular fabric. Familiar rock types include rhyolite, andesite, and basalt (all aphanitic) and granite and diorite (both phaneritic). Many rock-type labels have a long and obscure history stemming from miners' jargon (Mitchell, 1985); many are coined from geographic locales, such as andesite from the Andes Mountains of western South America. About 800 igneous rock-type names are listed in the classic four-volume work of Johannsen (1931–1938), written toward the end of an era when petrology was mostly descriptive petrography and the coining of new rock names was in vogue. Today, most of these names have, fortunately, been abandoned and petrologists need have only a working knowledge of a few dozen major igneous rock-type names (Le Maitre, 1989).

Regrettably, however, few of these major names have had consistent usage among petrologists. One petrologist's andesite has been another's basalt. Personal biases and backgrounds have been strong factors in schemes of classification. If rock compositions were clustered into isolated clumps on any variation diagram it would be a simple matter to draw a line around each cluster and append a rock-type name to it. However, as Figures 2.4 and 2.6 show, compositions are not clustered but consist of a continuum. There are at least two approaches to nomenclature within this continuum:

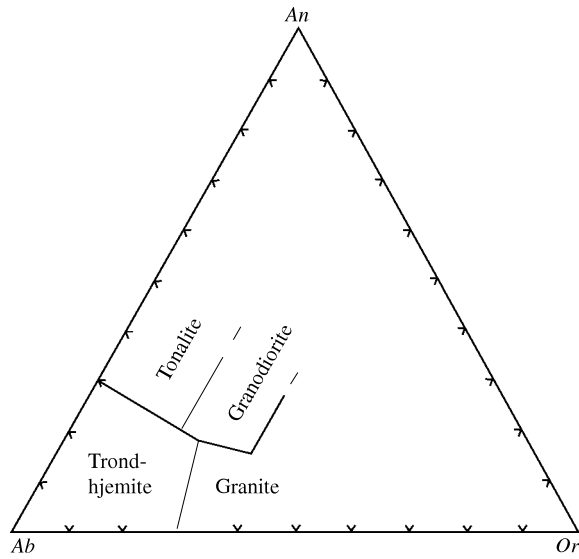
1. Flexible, loosely defined limits could be defined, leaving the details to the individual petrologist guided by the circumstances and need at hand. However, this approach has over the decades resulted in considerable confusion in the geologic literature.
2. The continuous spectrum could be subdivided along specific, well-defined limits that follow as closely as possible a usage agreed upon by as many petrologists as possible. This is the approach of the International Union of Geological Sciences Subcommittee on the Systematics of Igneous Rocks, hereafter referred to as the IUGS. The IUGS system of classification (Le Maitre, 1989) is a *universal standard* that can eliminate individual biases and contradictions among petrologists.

The IUGS rock-type classification for phaneritic (generally plutonic) rocks, which consist mostly (>10 modal % but usually more) of felsic minerals is set out in Figure 2.8. Quartz-rich felsic rocks are also classified in Figure 2.9; these are collectively referred to as **granitic rocks** or **granitoids**. Three special fabric categories of granitic rocks are not shown in these figures. A porphyritic aphanitic to finely phaneritic rock having abundant phenocrysts and occurring in a pluton (in-

trusion) is called **porphyry**; depending on its modal composition it may be a granite porphyry, granodiorite porphyry, or other. Uniformly fine-grained phaneritic, very leucocratic granites composed almost entirely of feldspar and quartz that typically occur in thin dikes within a coarser-grained, somewhat more mafic granitic pluton are **aplite**. Commonly associated with aplite are equally leucocratic rocks called **pegmatite**; these are phaneritic rocks of highly variable grain size in which



2.8 Slightly modified IUGS classification of felsic, phaneritic, magmatic rock types that contain >10 modal % Q (quartz) + A (alkali feldspar) + P (plagioclase) + F (feldspathoids). Coordinates of critical field corners along the A-P join (10, 35, 65, 90) refer to modal percentages of P. Numbers on right side of diagram are modal percentages of Q (5, 20) and of F (10). Mineralogical prefixes on left side of diagram are modifiers to be appended to rock-type names in associated lightly shaded or unshaded fields. For example, a rock whose mode in terms of QAPF plots at U is a quartz syenite, V is a monzonite, W is a feldspathoid-bearing monzodiorite, X is a feldspathoid monzodiorite, and Z is a feldspathoid syenite. Rocks plotting in the small darkly shaded parallelogram near the P apex are **anorthosite** if containing <10% mafic minerals, or, if containing >10% mafic minerals, are gabbro or diorite. **Gabbro** contains plagioclase more calcic than An₅₀ and is further classified according to Figure 2.10a. **Diorite** has plagioclase less calcic than An₅₀. The composition of plagioclase can be approximated in a thin section by optical techniques. In the lower part of the diagram, **ijolite** is a rock composed of nepheline and clinopyroxene; it is essentially a phaneritic equivalent of aphanitic to glassy nephelinite (Figure 2.12). For a supplementary classification of phaneritic felsic rocks (granitoids) containing abundant plagioclase and >20% quartz see Figure 2.9. (Redrawn from Le Maitre, 1989, Figure B.4.)



2.9 Classification of phaneritic felsic rock types (granitoids) containing abundant plagioclase and >20% quartz based on proportions of normative feldspars. (Redrawn from Barker, 1979.)

individual crystals are several centimeters to several meters.

Gabbros—phaneritic rocks made of plagioclase, pyroxene, and olivine—are classified in Figure 2.10a and phaneritic ultramafic rocks that contain <10 modal % felsic minerals in Figure 2.10b.

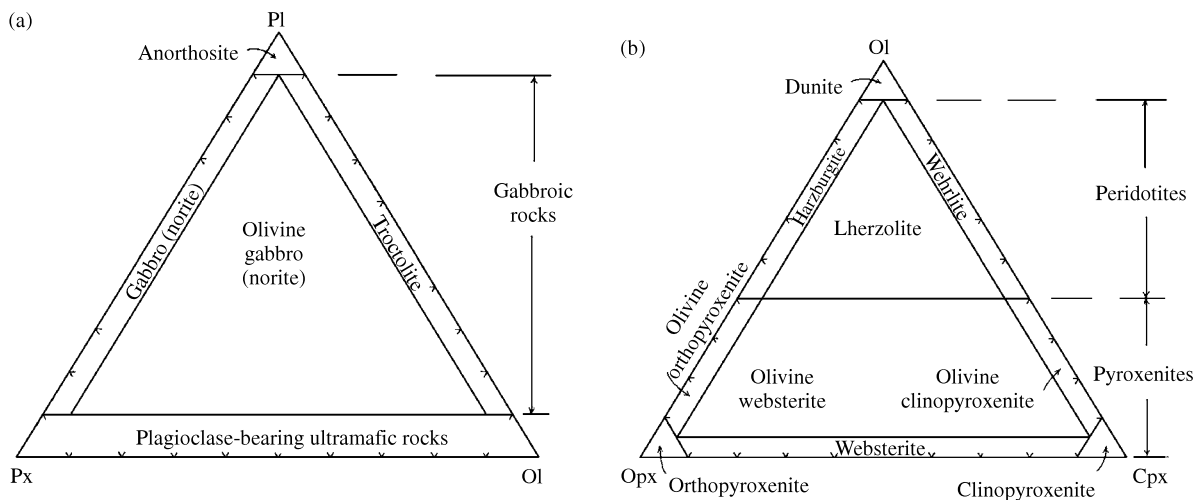
2.4.4 Classification Based on Whole-Rock Chemical Composition

There are many advantages of a numerical chemical classification. Insights are provided regarding the na-

ture, origin, and evolution of magmas. Rigorous comparisons can be made between members of suites of rocks and petrotectonic associations. The advantages of chemical classifications are obvious for very fine-grained rocks, whose mineralogical compositions may be difficult to determine, and certainly for glassy rocks (but beware of loss of Na and other possibly mobile elements). Aphanitic and glassy volcanic rocks can correspond more closely to the composition of the magma from which they formed than do porphyritic and phaneritic rocks, which may have been derived from magmas that experienced crystal accumulation during their evolution. Magmatic rocks whose characterizing minerals have been obliterated by alteration or metamorphism can be analyzed to reveal their original nature, provided diagnostic chemical elements have not been significantly mobilized during recrystallization.

However, an inherent weakness of purely chemical classifications is they have little or nothing to say regarding the effects of geologic processes on fabric and of different *P–T* conditions that govern mineralogical composition.

Aphanitic and Glassy Rock Types. A rigorously quantitative chemical classification of aphanitic and glassy, usually volcanic, rocks must be tempered by the fact that most rock-type names were established decades, and in some instances centuries, ago, when few if any chemical analyses were available and names were based upon mineralogical and modal compositions. Linking chemically based names to mineralogical/modal names was accomplished as follows.



2.10 IUGS classification of phaneritic mafic and ultramafic rock types. (a) Classification of mafic rocks (see gabbro in Figure 2.8 and its caption) based on the proportions of plagioclase, pyroxene, and olivine. **Norite** has more orthopyroxene than clinopyroxene (see Le Maitre, 1989, p. 17, for details). (b) Classification of **ultramafic** rocks that are composed of orthopyroxene, clinopyroxene, and olivine. For hornblende-bearing ultramafic rocks see Le Maitre, 1989, Figure B.8. (Redrawn from Le Maitre, 1989.)

Le Maitre (1976) compiled 26,373 published rock analyses given a rock-type name by the original author(s). All analyses were sorted as to rock-type label, such as “andesite” and “dacite,” irrespective of the classification scheme used. These compiled analyses are shown on a total alkalis-silica diagram in Figure 2.11. Overlap between the two fields of andesite and dacite reflects inherent variability in their composition—an attribute of all rock types no matter how defined. Nonetheless, averages of these two rock types are quite different. Average compositions of common magmatic rock types, which represent the opinions of thousands of petrologists over many decades, are listed in Table 2.2. All of the common volcanic rock-type names were so examined and bounding lines drawn on a total alkalis-silica diagram in such a way as to recognize a “consensus” composition (Le Bas et al., 1992). The resulting IUGS rock-type classification of aphanitic and glassy volcanic rocks is shown in Figure 2.12. Rock samples to be classified should be as fresh as possible

(unweathered and unaltered). Analyses must be recalculated to 100% volatile-free before plotting.

A rock of basaltic composition in which the grain size is marginally phaneritic and transitional into gabbro is **diabase** (alternatively called **dolerite** by United Kingdom geologists). Diabase commonly occurs in dikes and sills but also constitutes local lava flows. An olivine-rich basalt or microbasalt having $\text{MgO} > 18$ wt.% is called **picrite** if $(\text{Na}_2\text{O} + \text{K}_2\text{O}) = 1\text{--}3$ wt.% and **komatiite** if $(\text{Na}_2\text{O} + \text{K}_2\text{O}) < 1$ wt.% and TiO_2 is low, generally < 1 wt.%. Komatiites are commonly ultramafic and composed essentially of olivine and pyroxene so that they are chemically a peridotite, but their glassy to aphanitic texture precludes use of this phaneritic name.

The chemical classification can be appended to fabric **heteromorphs** that solidified from chemically similar magmas but have different fabrics. For example, chemically defined rhyolite can be, depending on fabric, rhyolite tuff, rhyolite breccia, rhyolite obsidian (wholly glass), rhyolite vitrophyre, and rhyolite pumice (vesicular glass).

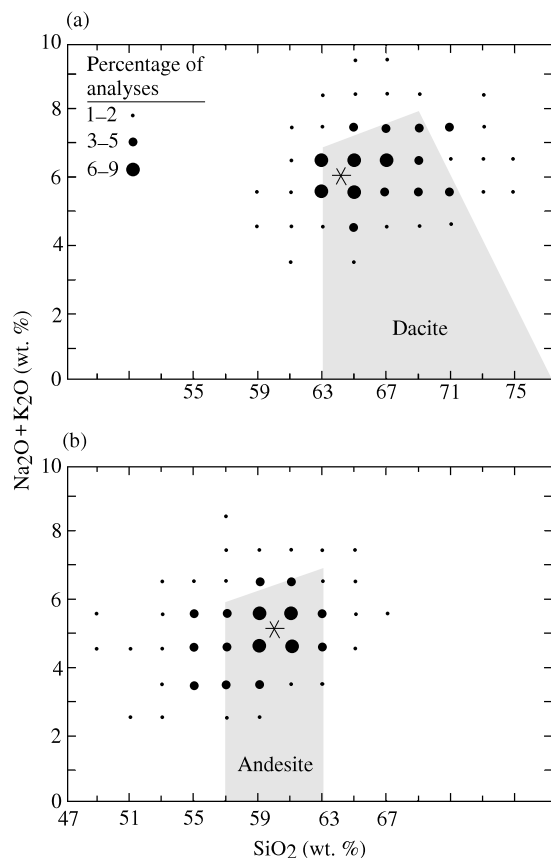
A preliminary IUGS classification for volcanic rocks based upon modal proportions of phenocrysts (Figure 2.13) may be used in the field and before chemical analyses are available. This classification should never be final because the groundmass of porphyritic aphanitic or glassy rocks will always be poorer in plagioclase than the assemblage of phenocrysts because of the way magmas crystallize (Chapter 5). A rock containing sparse plagioclase as the dominant or sole phenocryst could be a dacite, rhyolite, or trachyte in terms of Figure 2.12.

Absolute Concentration of Silica. Except for the very rare carbonatites, silica (SiO_2) is the principal oxide constituent of magmatic rocks and serves as a basis for broadly defined classifications.

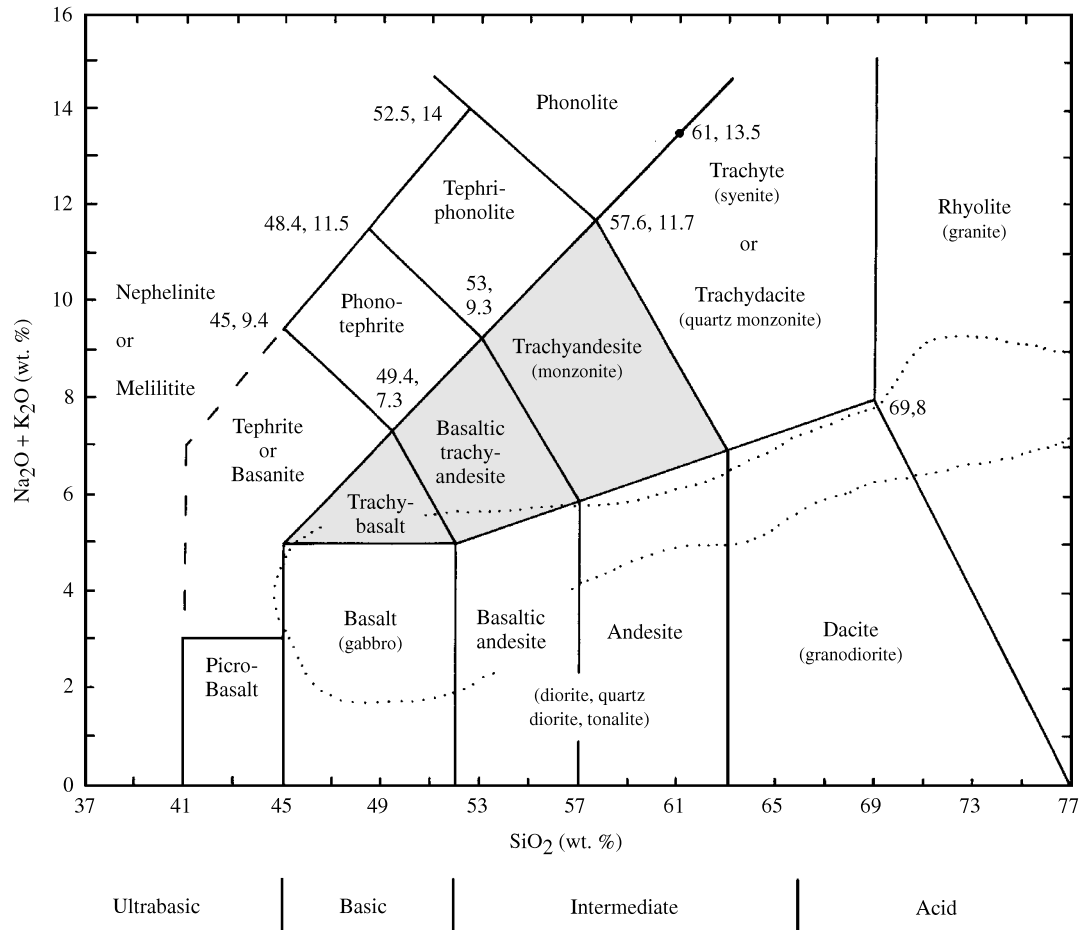
Some petrologists use a classification based on silica concentration in the rock analysis, as follows (Figure 2.12):

Silica concentration (wt.%)	Name
> 66	acid
52 to 66	intermediate
45 to 52	basic
45 or less	ultrabasic

As defined here, acid and basic have no reference whatsoever to hydrogen ion content, or pH, as used in chemistry. (Long ago it was erroneously believed that SiO_2 occurred as silicic acid and metallic oxide components, such as CaO and FeO , as bases in magmas.) These four categories have no direct correlation with modal quantity of quartz in the rock, although as a general rule, acid rocks do contain quartz and ultrabasic ones do not. Two rocks having identical concentrations



2.11 Total alkalis versus silica plots of analyzed rocks. In a worldwide database 727 analyses are designated as dacite (a) and 2864 analyses as andesite (b). Symbols indicate percentage of analyses falling within cells whose sides are 2% SiO_2 by 1% $(\text{Na}_2\text{O} + \text{K}_2\text{O})$. Shaded fields of dacite and andesite from Figure 2.12. Asterisk is average of analyses. (Redrawn from Le Bas et al., 1992.)



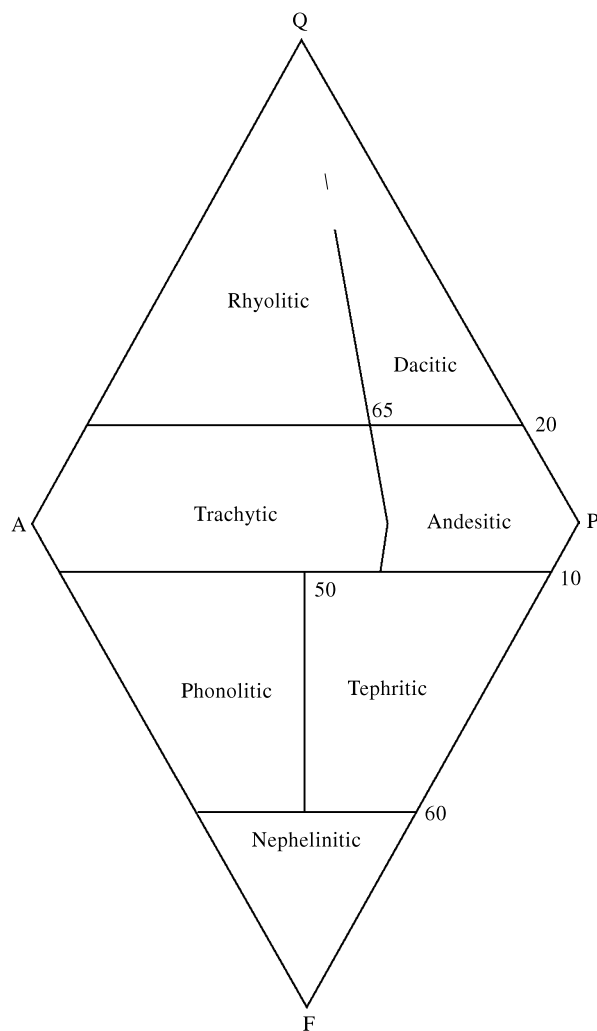
Further subdivisions of shaded fields	Trachybasalt	Basaltic trachyandesite	Trachyandesite
$Na_2O - 2.0 \geq K_2O$	Hawaiite	Mugearite	Benmoreite
$Na_2O - 2.0 \leq K_2O$	Potassic trachybasalt	Shoshonite	Latite

2.12 IUGS classification of aphanitic and glassy volcanic rock types. Coordinates of critical points are indicated as, for example, SiO_2 wt.% = 69 and $(Na_2O + K_2O)$ wt.% = 8 at the common corner of the fields of trachyte, rhyolite, and dacite. Rocks plotting in the shaded area may be further subdivided into sodic and potassic rock types as shown in the box below the main part of the diagram. Figure 2.18 shows an alternate classification based on K_2O versus SiO_2 . The distinction between trachyte ($Q < 20\%$) and trachydacite ($Q > 20\%$) is based on the amount of normative quartz, Q , from a recalculation in which $Q + An + Ab + Or = 100$. The amount of normative olivine, Ol , in the rock distinguishes tephrite ($< 10\%$) from basanite ($> 10\%$). Rock-type names for more or less corresponding common phaneritic rocks are indicated in parentheses. Dotted line encloses 53% of the rocks plotted in Figure 2.4. (Redrawn from Le Maitre, 1989.)

of silica may have widely different quantities of quartz, and two rocks of similar quartz content may have different silica concentrations, depending upon the composition and quantity of other minerals in the rock. Roughly speaking, acid rocks are silicic, basic are mafic, and ultrabasic are ultramafic.

The CIPW Normative Composition. Near the beginning of the 20th century, three petrologists (W. Cross, J. P. Iddings, and L. V. Pirsson) and a geochemist (H. S. Washington) devised an elegant procedure

(from whose surnames the acronym CIPW is formed) for calculating the chemical composition of a rock into a *hypothetical* assemblage of water-free, standard minerals. These standard **normative minerals** (Appendix B) are designated in italics, such as Q , An , Ol , to distinguish them from the actual rock-forming minerals in the rock. Normative minerals are some of the simple end members of the complex solid solutions the actual minerals in the rock comprise. A complex solid solution, such as hornblende, is represented by several simpler normative minerals. The assemblage of normative



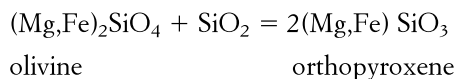
2.13 Preliminary classification of aphanitic and glassy rock types for use in cases in which an accurate chemical analysis is not available. This is a useful classification of rocks in the field or in thin section based upon the proportions of phenocrysts. Some rocks that are chemically rhyolite or dacite (Figure 2.12) contain quartz as the only phenocryst. **Basaltic rocks** plot at the P apex. (Redrawn from Le Maitre, 1989.)

minerals constitutes the **CIPW normative composition**, or simply, the **norm**, of the rock, which can be calculated according to the rules in Appendix B.

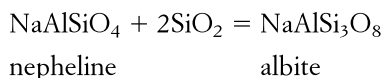
What are the benefits of the normative calculation? Because of extensive solid solution in the major rock-forming minerals, substantial variations in whole-rock chemical composition may not be evident in any obvious variations in mineralogical or modal composition. Basaltic rocks are an example. Much the same assemblage of plagioclase, clinopyroxene, olivine, and Fe-Ti oxides can constitute basalt, trachybasalt, and basanite (Figure 2.12). The norm facilitates comparisons between these basaltic rocks as well as others in which solid-solution minerals conceal whole-rock chemical variations. Aphanitic and, especially, glassy rocks are

readily compared. Mica- and amphibole-bearing rocks that crystallized from hydrous magmas can be compared with rocks lacking hydrous minerals that crystallized from dry magmas of otherwise similar chemical composition. Moreover, rock compositions cast as norms can be easier to relate to the results of experimental laboratory studies of simplified, or model, rock systems (Chapter 5).

Silica Saturation. In its allocation of silica first to normative feldspars and then to pyroxenes and finally to quartz, the normative calculation (Appendix B) emphasizes the concentration of SiO_2 relative to oxides of K, Na, Ca, Mg, and Fe in the rock. The relative amounts of these oxides are compared on a molecular, rather than weight, basis. If there is insufficient silica in the rock to make normative pyroxenes from the amounts of these other oxides, then some FeO and MgO is instead allocated to normative olivine, which requires relatively less silica than Fe-Mg pyroxene; the silica deficiency is thus compensated. This chemical balance may be seen in the reaction

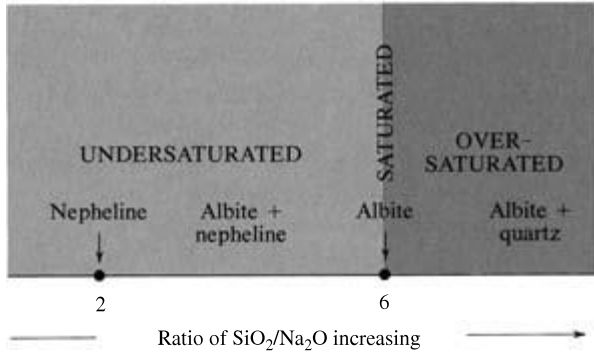


Note that there are equal molar proportions (1:1) of SiO_2 and $(\text{Mg,Fe})\text{O}$ in orthopyroxene, but half as much SiO_2 as $(\text{Mg,Fe})\text{O}$ in olivine, or $\text{SiO}_2:(\text{Mg,Fe})\text{O} = 1:2$. (In the norm, orthopyroxene is represented by the normative mineral hypersthene, *Hy*.) In rocks that still have a deficiency of silica after eliminating all of the orthopyroxene, some silica must be reassigned from albite to nepheline, a silica-poor mineral. This chemical balance may be seen in the reaction



Once again, note the difference in relative molar proportion of $\text{SiO}_2:\text{Na}_2\text{O} = 6:1$ in albite and $2:1$ in nepheline. Creating one mole of nepheline from one mole of albite liberates more silica than does conversion of one mole of orthopyroxene to one mole of olivine. Hence, modest silica deficiencies in rocks are manifest by olivine in lieu of orthopyroxene, whereas greater deficiencies are manifest by nepheline in lieu of sodic plagioclase.

The normative calculation serves as a model for a crystallizing magma and illustrates the concept of the **degree of silica saturation**. Consider a simple hypothetical magma consisting only of O, Si, Al, and Na (Figure 2.14). If there is an excess of molar SiO_2 relative to that needed to make albite from Na_2O , that is, $\text{SiO}_2/\text{Na}_2\text{O} > 6$, then the magma can crystallize quartz in addition to albite. (In a natural magma, the albite would be in solid solution in plagioclase and/or alkali feldspar.) This magma and the corresponding rock are



2.14 Degree of silica saturation in a model system consisting only of Si_2O , Al_2O_3 , and Na_2O .

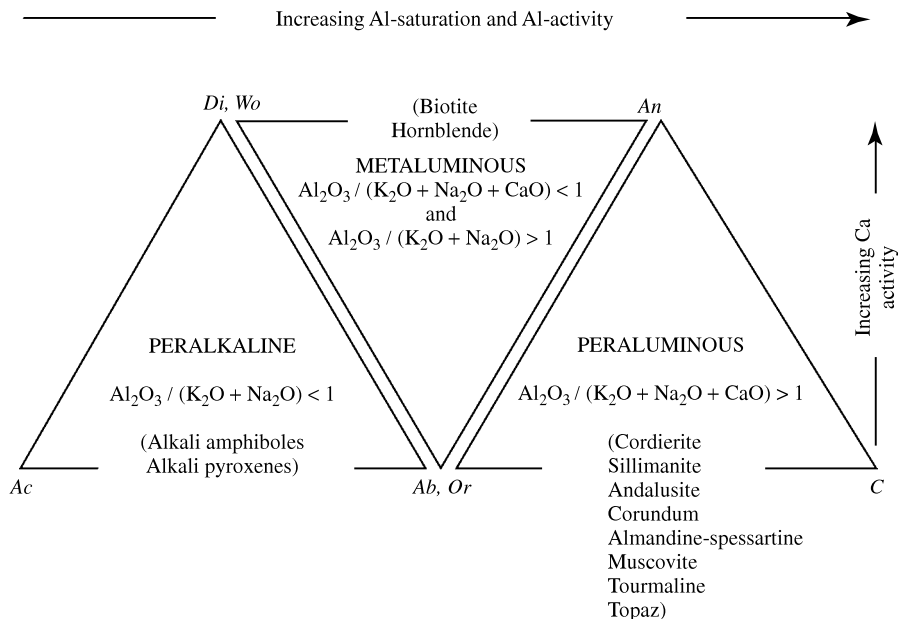
silica-oversaturated. If the magma contains SiO_2 and Na_2O in the exact ratio of 6, then these two constituents can only combine into albite; the magma and rock are silica-saturated. If the molar ratio $\text{SiO}_2/\text{Na}_2\text{O} < 6$ but > 2 in the magma, then there is insufficient SiO_2 to combine with all of the Na_2O into albite and some nepheline is created instead; the magma and rock are silica-undersaturated. If the molar ratio $\text{SiO}_2/\text{Na}_2\text{O} = 2$ in the magma, then there is insufficient SiO_2 to combine with the Na_2O to create any albite at all and only nepheline can be produced; the magma and rock still qualify as silica-undersaturated.

In real magmas and corresponding rocks that contain Mg, Fe, Ca, K, Ti, and so on, in addition to O, Si, Na, and Al, the concept of silica saturation still applies. In the classification that follows, the degree of satura-

tion is manifested in normative minerals (shown in italic letters) and with less accuracy by real minerals (in parentheses).

1. **Silica-oversaturated** rocks contain *Q* (quartz or its polymorphs—cristobalite and tridymite), such as granite.
2. **Silica-saturated** rocks contain *Hy*, but no *Q*, *Ne*, or *Ol* (no quartz, feldspathoids, or olivine), such as diorite and andesite.
3. **Silica-undersaturated** rocks contain *Ol* and possibly *Ne* (Mg-olivine and possibly feldspathoids, analcime, perovskite, melanite garnet, and melilite), such as nepheline syenite.

Alumina Saturation. Al_2O_3 is the second most abundant constituent in most magmatic rocks and provides another means of classification, especially for felsic rocks, such as granitic ones (Figure 2.15). The **alumina saturation index** is defined as the *molecular* ratio $\text{Al}_2\text{O}_3/(\text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO})$, which equals 1 in feldspars and feldspathoids. In magmas crystallizing feldspars and/or feldspathoids, any excess (ratio > 1) or deficiency (< 1), respectively, of Al_2O_3 must be accommodated in mafic or accessory minerals. In alumina-oversaturated, or **peraluminous**, rocks, excess alumina is accommodated in micas, especially muscovite, in addition to Al-rich biotite, and in aluminous accessory minerals such as cordierite, sillimanite, or andalusite, corundum, tourmaline (requires boron), topaz (fluorine), and almandine-spessartine garnet. (But beware: The latter three minerals also occur as vapor-phase precipitates in some metaluminous rocks.) After alloca-



2.15 Classification of felsic rocks on the basis of degree of aluminum saturation. Ratios are molar. Apices of triangles are normative minerals. Diagnostic real minerals are listed in parentheses (muscovite, cordierite, etc.) for each of the three saturation categories.

tion of CaO for apatite, peraluminous rocks contain normative corundum, *C*. In alumina-undersaturated, or **metaluminous**, rocks, deficiency in alumina is accommodated in hornblende, Al-poor biotite, and titanite (but its stability also depends on other compositional properties of the magma including oxidation state). After allocation of CaO for apatite, metaluminous rocks contain normative anorthite, *An*, and diopside, *Di* (or wollastonite, *Wo*). A further constraint on metaluminous rocks is that they have $Al_2O_3/(K_2O + Na_2O) > 1$, whereas **peralkaline** rocks have $Al_2O_3/(K_2O + Na_2O) < 1$. In peralkaline rhyolites and granites the alumina deficiency (alkali excess) is accommodated in alkali mafic minerals such as aegirine end-member pyroxene ($NaFe^{3+}Si_2O_6$) and the alkali amphiboles riebeckite richterite (Appendix A), and aenigmatite in which Fe_2O_3 and TiO_2 substitute for Al_2O_3 . Peralkaline rocks contain normative acmite or sodium metasilicate (*Ac* or *Ns*) and lack normative *An*. Real feldspars in peralkaline rocks contain little of the anorthite end member. Peralkaline rhyolites can be further subdivided into **comendites** in which $Al_2O_3 > 1.33 FeO + 4.4$ (on a wt.% basis), and **pantellerites**, in which $Al_2O_3 < 1.33 FeO + 4.4$. Peralkaline rocks can be silica-oversaturated, -saturated, or -undersaturated, as in, for example, comenditic and pantelleritic trachytes.

An inherent weakness of classifications depending on the ratios of alumina or silica to alkalis is that Na and K can be mobilized and transferred out of a magma by a separate fluid phase. For example, escaping steam from cooling hot lava flows carries dissolved Si, Na, and K. However, Al tends to be less mobile. Initially metaluminous magma can, therefore, become peraluminous after alkali loss. Glasses can also lose alkalis relative to Al during high-*T* alteration or during weathering. A clue to preferential alkali loss is the presence of metaluminous minerals as phenocrysts, formed prior to extrusion, in a glassy matrix.

2.4.5 Rock Suites

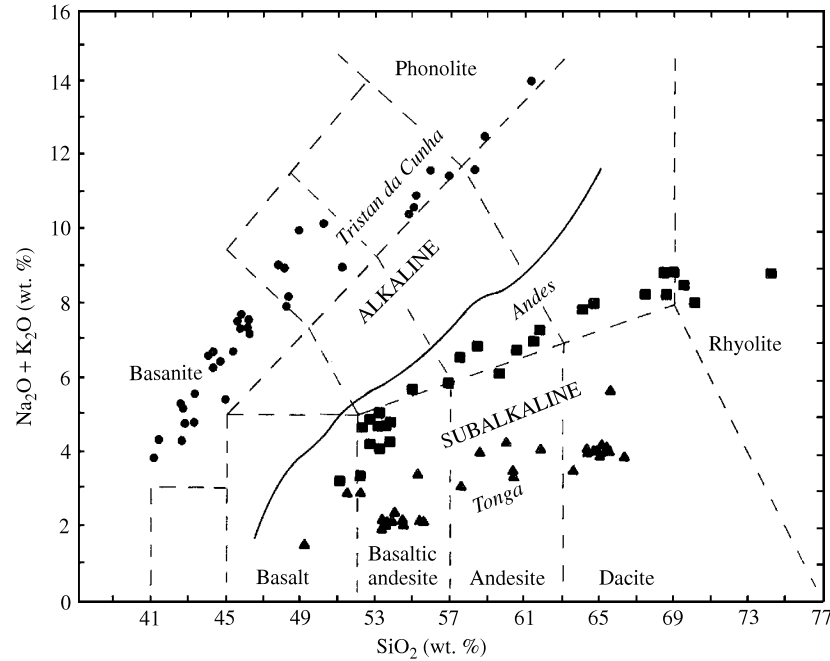
Each of the chemical categories just described may embrace several rock types that share a common chemical attribute. Thus, silica-undersaturated rocks include the phonolite, tephrite, basanite, nephelinite, and melilitite rock types in Figure 2.12 and metaluminous rocks include the more common rhyolite, dacite, andesite, and their phaneritic plutonic counterparts. Peralkaline rocks include rhyolites and trachytes. These and other compositionally related or kindred groups of rock types are called **rock suites**.

Since the beginning of the 20th century, petrologists have recognized that suites of kindred magmatic rock types occur in particular geographic areas. Thus, the volcanic rocks in islands of the Atlantic Ocean were found to be more highly concentrated in alkalis relative to silica than rock types around the margin of the Pacific Ocean. This simple twofold division of mag-

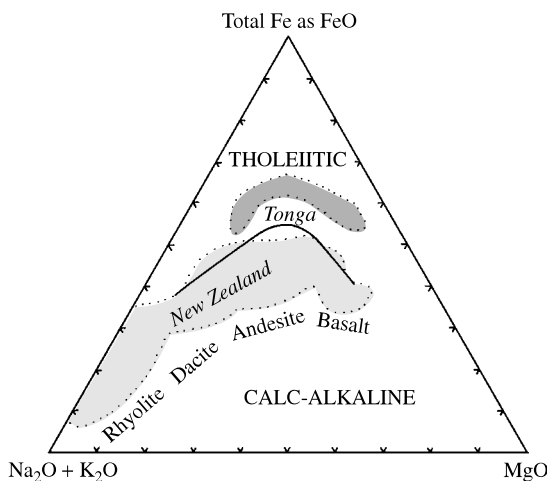
matic rocks into alkaline (Atlantic) and subalkaline (Pacific) rock suites persists today, though it is now realized to be an overly simplistic characterization of these two oceanic regions. For example, the major part of the huge Hawaiian shield volcanoes in the Pacific are made of subalkaline basalt, but alkaline rocks form late capping lava sequences. Both alkaline and subalkaline lavas occur in western Mexico near the Pacific rim.

Despite their relatively small volume worldwide, **alkaline** rocks account for most of the hundreds of rock-type names in the geologic literature because of unusually great variation in chemical, mineralogical, and modal composition. Regrettably, there is no consensus among petrologists as to the precise definition of alkaline rocks, and their classification continues to be challenging (Mitchell, 1996). Alkaline rocks have a relative excess of alkalis over silica (Figure 2.16) but the exact ratio of these constituents has not been established. Most are silica-undersaturated and contain normative nepheline and real feldspathoids (nepheline, leucite). Alkaline rocks commonly include one or more of analcime, alkali feldspar, alkali-rich amphiboles; Na-Ti-Al-rich clinopyroxenes, biotite-phlogopite solid solutions; olivine; and no orthopyroxene or quartz. However, some very rare rocks known as lamproites contain significant modal proportions of leucite yet are quartz normative by virtue of their very low concentration of Al_2O_3 . Alumina deficient peralkaline rocks are also sometimes considered to be alkaline, even though they may be silica-oversaturated. Because Na and K are relatively abundant in alkaline rocks, a twofold subdivision into sodic and potassic series is used (bottom of Figure 2.12).

More common **subalkaline** rocks are usually silica-saturated or silica-oversaturated and lack normative nepheline. Real minerals include combinations of feldspars, hornblende, augite clinopyroxene, orthopyroxene, biotite, quartz in more silica-rich rocks, and olivine in less silica-rich rocks. Subalkaline rocks have been subdivided into the **tholeiitic** and **calc-alkaline** suites. (These two terms emerged from a tangled history spanning many decades. The calc-alkaline label originated in a now virtually abandoned classification scheme of M. A. Peacock proposed in 1931. Tholeiitic originated in the mid-1800s when it was applied to basalts from near Tholey, Saarland, western Germany.) As the term is used today, tholeiitic rocks show stronger enrichment in Fe relative to Mg than do calc-alkaline rocks and generally have less variation in silica, whereas the calc-alkaline suite shows enrichment in silica and alkalis (Figure 2.17; see also Miyashiro, 1974). Tholeiitic and calc-alkaline rocks typify subduction zones, where their composition correlates in a general way with the nature of the crust in the overriding plate. The tholeiitic suite of relatively Fe-enriched basalt, andesite, and dacite develops chiefly in island arcs where two oceanic plates converge. The calc-alkaline suite of



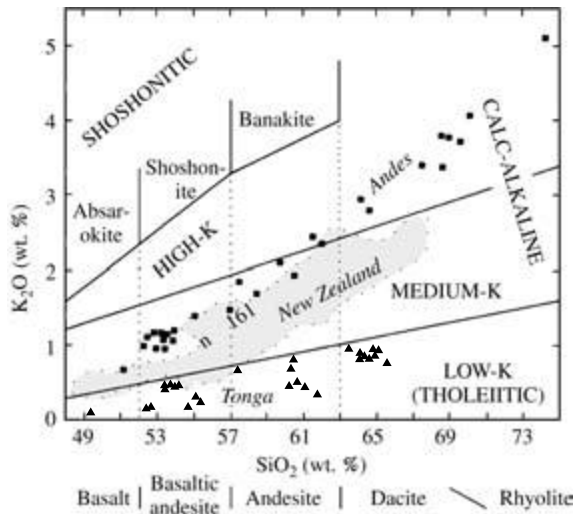
2.16 Total alkalis-silica diagram showing fields and examples of **subalkaline** and **alkaline rock suites**. Irregular solid line separates the field of nepheline-normative rocks from rocks having no normative nepheline in the 15,164-sample database of Le Bas et al., (1992). Light dashed lines delineate the IUGS volcanic rock-type classification from Figure 2.12. Note that a single rock type, such as basalt, can be either alkaline (*Ne*-normative) or subalkaline (*Hy*-normative). The alkaline volcanic suite of basanite, phonotephrite, tephriphonolite, and phonolite (filled circles) is from Tristan da Cunha, a volcanic oceanic island near the intersection of the Mid-Atlantic and Walvis Ridges in the South Atlantic Ocean (Le Roex et al., 1990). The subalkaline volcanic suite from the oceanic island arc of Tonga (filled triangles) is mostly basaltic andesite, andesite, and dacite (Cole, 1982). Subalkaline-suite rocks from Volcan Descabezado Grande and Cerro Azul in the southern volcanic zone of the Andes in central Chile (filled squares) are mostly basaltic andesite, trachyandesite, trachydacite, and rhyolite (Hildreth and Moorbath, 1988).



2.17 Subalkaline rocks can be subdivided into **tholeiitic** and **calc-alkaline rock suites**. **AFM diagram** in terms of alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$), total Fe as FeO, and MgO. Solid line separates fields of tholeiitic rocks, exemplified by volcanic rocks from the Tonga island arc in the Pacific Ocean (Figure 2.16), from calc-alkaline rocks, exemplified by most of the volcanic rocks from the North Island of New Zealand. Approximate range of rhyolite, dacite, andesite, and basalt rock types in New Zealand is indicated. Data from Cole (1982).

less Fe-enriched basalt, andesite, dacite, and rhyolite develops on thicker continental crust above subducting lithosphere. A plot of K_2O versus SiO_2 (Figure 2.18) reveals that subalkaline rocks of increasing concentration of K_2O correspond to increasing thickness of the continental crust. **Low-K rocks**, which are essentially equivalent to the tholeiitic suite, occur where the crust is oceanic and relatively mafic or where the continental crust is thin. **Medium-K** and **high-K** calc-alkaline rocks develop on increasingly thicker continental crust. The **absarokite-shoshonite-banakite** association is found in some subduction zones overlain by thick crust but also in some island arcs.

A Brief Note on Petrotectonic Associations. One reason petrologists plot whole-rock chemical compositions on diagrams such as Figures 2.16–2.18 is to focus attention on the petrogenesis of different rock suites in contrasting global tectonic settings, that is, petrotectonic associations. Such variation diagrams prompt many questions: How do the thickness and nature of the crust influence magma composition? Can one parental magma, such as of basaltic composition created in the mantle, evolve into different daughter compositions depending on the



2.18 Subdivision of subalkaline rocks according to K_2O versus SiO_2 . (Redrawn from Ewart, 1982.) Volcanic rocks from the oceanic island arc of Tonga (filled triangles; see also Figures 2.16 and 2.17), where the crust is only about 12 km thick, define the **low-K**, or **tholeiitic**, series consisting of basalt, basaltic andesite, andesite, and dacite rock types. These rock-type names are from Figures 2.12 and 2.16. The same rock types in the North Island of New Zealand (continental sialic crust about 35 km thick; 161 rock analyses in shaded area) are mostly of the **medium-K** series. (Analyses for Tongan and New Zealand rocks from Cole, 1982.) Basalt, basaltic andesite, andesite, dacite, and rhyolite (filled squares) from Volcan Descabezado Grande and Cerro Azul in the southern volcanic zone of the Andes in central Chile (Hildreth and Moorbath, 1988), where the continental crust is about 45 km thick, belong to the medium- to **high-K** series. Note that all three of these rock suites diverge from basalt in the lower left corner of the diagram. The **shoshonitic** series of still more K-enriched rocks is found in a few subduction zones in thick continental crust and some island arcs.

crust through which it ascends to the surface? Or do magmas moving up from a mantle source differ in composition? Does the oxidation state of Fe somehow influence the evolution of contrasting magma suites? Why should magmas forming the Atlantic Ocean island of Tristan da Cunha differ so distinctly from magmas forming the Tongan island arc in the Pacific (Figure 2.16)? These and many other questions concerning petrotectonic associations are considered further in Chapter 13.

2.4.6 Classification of Basalt

Because basalts are by far the most abundant rock type on Earth (and possibly in the inner planets) and are found in virtually all global tectonic settings, their classification deserves special consideration. Basalts, like all magmatic rocks, define a continuous compositional spectrum (Figures 2.12 and 2.19b). Any classification must artificially divide this continuum.

Yoder and Tilley (1962) used the normative tetrahedron (Figure 2.19a) to portray the wide range of basalt compositions. Because of the difficulty of plotting and visualizing composition points within a three-dimensional tetrahedron, data points can be projected onto the triangular base of the tetrahedron in Figure 2.19b. Three *basalt rock types* can be recognized according to their degree of silica saturation:

1. Quartz-hypersthene normative ($Q + Hy$) **quartz tholeiite**
2. Olivine-hypersthene normative ($Ol + Hy$) **olivine tholeiite**
3. Nepheline-normative (Ne) **alkaline basalt**

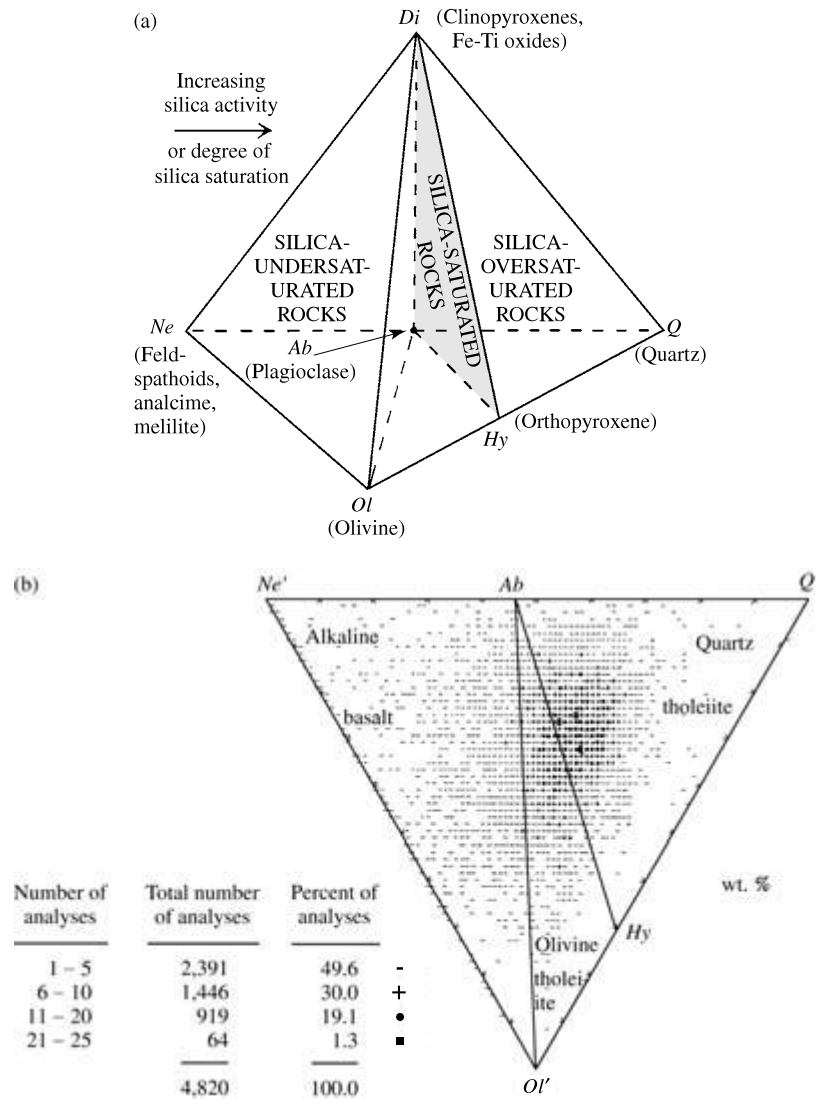
Tholeiitic basalts make up the oceanic crust and, on continents, large flood basalt plateaus and some large intrusions. Alkaline basalt is the most common rock type in the alkaline rock suite and occurs in oceanic islands, such as Hawaii, and in some continental settings.

Different parental basalt magmas evolve into contrasting daughter suites of less mafic, more silica-rich rocks in different global tectonic settings. This is one facet of petrotectonic associations. In Figure 2.16, some basalts are silica-undersaturated and are associated with more felsic rocks of the alkaline suite, whereas others are silica-saturated and are associated with more felsic rocks of the subalkaline suite. In Figure 2.18, subalkaline basalt is either tholeiitic (low-K) or calc-alkaline (medium- and high-K).

*2.5 TRACE ELEMENTS

Previous sections of this chapter have emphasized the great, but limited diversity in major element and mineralogical compositions of magmatic rocks as well as systematic patterns in these parameters. The remainder of this chapter is an introduction to the behavior of trace elements and isotopes in magmas, showing how they serve as powerful **petrogenetic indicators** of magmatic processes. As just one example, the trace element and isotopic composition of basalts is at least as variable as their major element concentrations and provides significant petrogenetic information on the origin and evolution of basalt magmas in different tectonic settings.

About 90 of the known chemical elements occur in rocks and minerals in trace concentrations, arbitrarily set at <0.1 wt.% = 1000 ppm. Concentrations as low as 1 ppb can be detected for some elements. These low concentrations are insufficient to stabilize any major rock-forming mineral but in many cases do stabilize accessory minerals such as zircon. Unlike major elements (Si, Al, Ca, etc.), whose variations are mostly limited to a factor of <100 , trace element concentrations can vary by as much as a factor of 1000 (three orders of magnitude). This fact, together with the way trace elements



2.19 Classification of basaltic rocks according to degree of silica saturation. (a) Tetrahedron of Yoder and Tilley (1962) showing variable degree of silica saturation in basaltic rocks. *Italicized normative minerals* define the degree of saturation. Real minerals (in parentheses) can be used as guides in the absence of normative data. The shaded plane represents **silica-saturated** basaltic rocks separating the volume on the left of **silica-undersaturated** basaltic rocks that contain normative olivine (*Ol*) and possibly normative nepheline (*Ne*), and modal feldspathoids from **silica-oversaturated** basaltic rocks on the right that contain normative quartz (*Q*). (b) Base of tetrahedron. Compositions of over 4800 basalts lying within the tetrahedron have been projected onto its base from the *Di* apex and are thus *Di*-bearing. Apices of triangle are adjusted normative minerals: $Ol' = Ol + [0.714 - (Fe/(Fe + Mg))0.067]Hy$; $Ne' = Ne + 0.542 Ab$; $Q' = Q + 0.4 Ab + 0.25 Hy$. (Data compiled and plotted through the courtesy of Roger W. Le Maitre, University of Melbourne, Australia.)

are distributed between coexisting minerals and liquids in geologic systems, qualify them as highly significant indicators of petrologic processes.

2.5.1 Partition Coefficients and Trace Element Compatibility

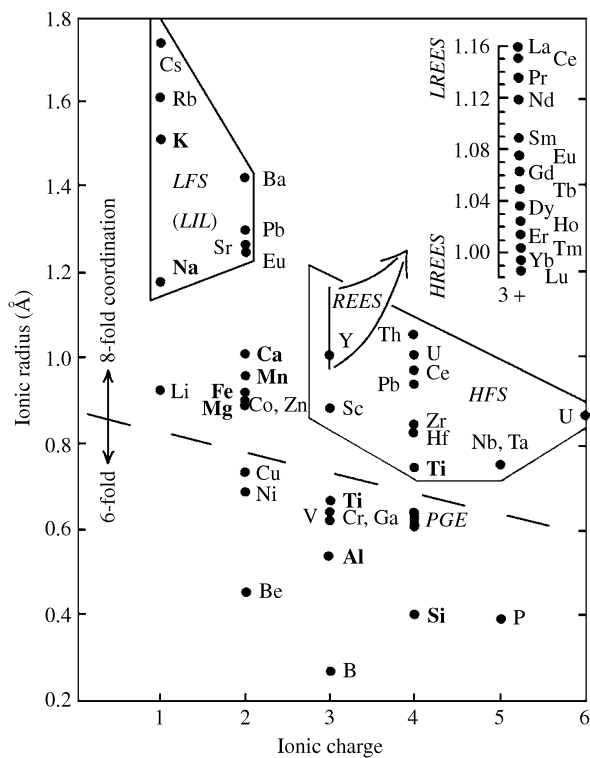
Generation of magma from solid rock in the Earth involves only *partial* melting. Where upper mantle peridotite is partially melted, the resulting magma consists of crystals of pyroxenes and olivines in equilibrium with a liquid solution of ions of O, Si, Al, Mg, Na, and so on, called a **melt**. In this magma, ions of **incompati-**

ble trace elements prefer to be dispersed in the loosely structured (on the atomic scale) melt and are *excluded* from the more restrictive, less tolerant crystalline structure of the coexisting pyroxenes and olivine. On the other hand, ions of **compatible trace elements** are tolerated and largely remain *included* in the crystalline phases. The contrast between these two categories of trace elements is formalized by a simple concentration ratio called the **partition coefficient**, *D*.

$$2.1 \quad D_{melt}^{crystal} = \frac{\text{(Concentration in mineral)}}{\text{(Concentration in melt)}}$$

Thus, compatible trace elements have $D > 1$. For example, Sr, Ba, and Eu are compatible elements that partition strongly into feldspars in silicic magmas. Cr, Ni, and Co are compatible in olivine and orthopyroxenes in basaltic magmas. On the other hand, incompatible elements, such as Rb, Li, Nb, and rare earth elements, have $D \ll 1$ and partition only weakly into the major minerals found in basaltic magmas.

Incompatible trace elements cannot readily substitute for major elements in crystalline phases because of dissimilar ionic charge and/or radius (Figure 2.20; Table 2.4). Thus, Be^{2+} is typically incompatible because its small size (0.45 Å in sixfold coordination) pre-



2.20 Radii and classification of positively charged ions of major (bold letters) and trace elements. Radii based on eightfold coordination in upper part of diagram and on sixfold in lower part. Rare earth elements (REEs) in center of diagram are plotted on an expanded scale in upper right. On the basis of **ionic potential** (charge/radius), most elements can be subdivided into two categories surrounded by polygons, namely, (1) Low field strength (LFS) elements, more commonly called **large-ion lithophile (LIL) elements**, in upper left; (2) **high-field-strength (HFS) elements** in right center. The lithophile designation arises from an affinity for silicate rocks, as contrasted with elements having an affinity for metallic phases (siderophile) containing Fe, Co, Ni, and so on, as in the core of the Earth, or for sulfide phases (chalcophile) containing S, Cu, Zn, and so on. Ionic potential also serves as a rough index of the **mobility** of cations of the elements, that is, their solubility in aqueous solutions; elements with low (<3) and high (>12) potential tend to be more soluble and mobile than elements in midrange. PGE, **platinum group elements** (Ru, Rh, Pd, Os, Ir, Pt). (Data from Shannon, 1976.)

Table 2.4 Trace Elements Substituting for Major Elements of Similar Ionic Size and Charge (see Figure 2.20)

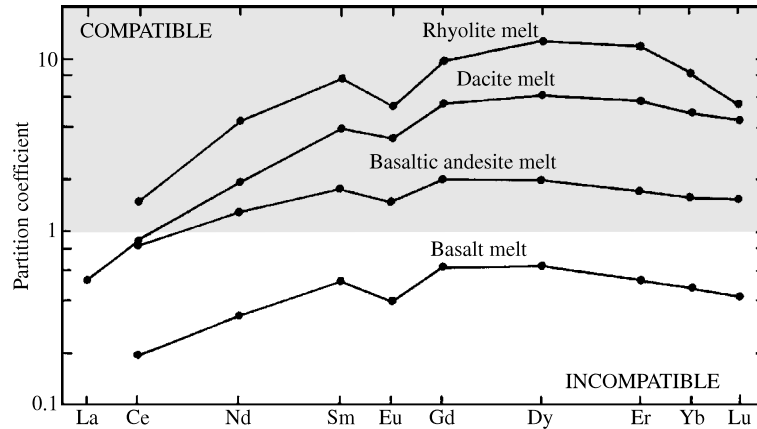
MAJOR ELEMENT	SUBSTITUTING TRACE ELEMENT(S)
Si	Ge, P
Ti	V
Al	Ga
Fe	Cr, Co, Ni
Mg	Cr, Co, Ni
Ca	Sr, Eu, REEs
Na	Eu
K	Rb, Ba, Sr, Eu

cludes substitution for divalent ions and its low charge precludes substitution for similarly sized Si^{4+} . Another typically incompatible element in most major minerals is U^{4+} because it has both a large ionic charge and a large radius (1.0 Å in eightfold coordination). However, compatibility depends on what minerals exist in the magma. Hence, in a silicic magma in which zircon (ZrSiO_4) is crystallizing, U^{4+} is compatible because it substitutes for Zr^{4+} , whose radius is 0.85 Å. (This substitution, incidentally, makes possible isotopic dating of zircon.)

No single partition coefficient describes the behavior of a particular trace element in all magmas. The composition of the magma and that of the mineral both affect the value of D . Coefficients for the same element in the same mineral generally increase as the magma becomes more silicic; variations of a factor of 10 are common (Figure 2.21). Decreasing magma temperature (T) also corresponds with increasing coefficients. Cooler, more silicic melts are more tightly structured, causing trace elements to be rejected and forced into coexisting crystals. The effect of pressure (P) on partition coefficients is apparently small and in the opposite direction of T ; thus, the effect on coefficients of increasing P and T with depth in the Earth might more or less cancel out. The oxidation state of the magma affects the partition coefficient of europium, Eu. In reduced magmas, europium exists mostly as Eu^{2+} , rather than the usual Eu^{3+} of other rare earth elements, and is a compatible element in plagioclase, as is Sr. Obviously, selection of a partition coefficient depends on many factors (e.g., Rollinson, 1993); only a few representative coefficients are presented in Table 2.5. The behavior of important trace elements in magma systems is summarized in Table 2.6.

Because a particular trace element has different affinities for different minerals in a magma, a **bulk partition coefficient**, D_{bulk} , for the behavior of a particular element in the whole magma must be formulated, as follows:

$$2.2 \quad D_{\text{bulk}} = X_1 D_1 + X_2 D_2 + X_3 D_3 \dots$$



2.21 Partition coefficients for REEs between amphibole and indicated melts. REEs are more compatible in more silicic and lower- T melts. (Redrawn from Rollinson, 1993.)

where X_1 , X_2 , and so on, represent the weight fraction, expressed in decimal format (e.g., 0.25) of each mineral, and D_1 , D_2 , are their respective partition coefficients for the particular element.

Simple mathematical equations can be used to construct models of trace element behavior in petrologic processes (Haskins, 1983; Hanson, 1978). These theoretical models are based on idealized assumptions that approximate a particular process in a natural geologic system. Because of the uncertainties in what partition coefficient actually applies to a particular magma system, the petrologist seeks *patterns in trace element behavior* rather than specific details. Trace element models are most appropriately used to evaluate a hypothesized process conceived from other information, such as the fabric, major element, and modal compositional variations and field relations. Applications of the models are discussed in Chapters 11–13.

2.5.2 Rare Earth Elements

Rare earth elements (REEs) are a mostly coherent group of elements that can be especially useful in testing petrogenetic hypotheses. REEs comprise atomic numbers 57 (La) to 71 (Lu) (Figure 2.20). Promethium (61) is not found naturally. Yttrium (Y, 39) has an ionic charge of $3+$, like that of REEs, and a radius (1.019 Å) similar to that of holmium (1.015 Å) and is, therefore, sometimes included as a REE. The existence of a divalent ion of Eu in magmas has been noted; also, Ce^{4+} may exist in some very oxidized magmas. Two properties of REEs make them especially useful as petrogenetic indicators:

1. They are generally insoluble in aqueous fluids; hence, they are useful in altered or weathered rocks.
2. Trivalent ions of REEs have decreasing radii with respect to increasing atomic number, from La (1.160 Å) to Lu (0.977 Å) (Figure 2.20). This small

but systematic variation from light REEs to heavy REEs causes significant differences in their behavior and partition coefficients (Figure 2.22). Because of their slightly larger sizes, light REEs are generally more incompatible in common silicate minerals than are the heavy REEs. Plagioclase, because of the similarity of Eu^{2+} to Ca^{2+} , will accommodate much more of this trace element than immediately adjacent lighter and heavier trivalent REEs, creating a positive **Eu anomaly** (Figure 2.22). The behavior of REEs in garnet-bearing basaltic magmas is striking because of a 1000-fold difference in partition coefficients between La and Lu.

To smooth out the otherwise sawtoothlike absolute abundances of odd and even atomic numbers (the Oddo-Harkins effect), the concentration of a REE in a rock is divided by the concentration of the same element in average chondritic meteorites (Table 2.7). This sample/chondrite ratio is then plotted on a logarithmic scale (Figure 2.23). **Chondrites** are used as the basis of comparison because they are thought to have accreted to form the inner planets in the solar system and thus have a chemical composition like that of the entire primitive Earth. If all REEs had the same partition coefficient in all minerals in a magma system, the chondrite-normalized pattern would be flat—a horizontal line. However, few magmatic rocks have such a pattern.

The sloping, arcuate, and even spiky patterns of rocks provide important information on the sources and processes in the origin of the magmas (Figure 2.23). For example, lunar basalt (Taylor, 1982) has a pronounced negative europium anomaly that provides an amazing insight into the early history of the Moon. It is believed that lunar basalt magmas were generated by partial melting from a Eu-depleted lunar mantle formed as a gravitative accumulation in the bottom of the primordial “magma ocean” in which crystallizing and floating plagioclase took up most of the compatible

Table 2.5 Partition Coefficients for Some Trace Elements

	U	Rb	K	Ba	Sr	Yb	Y	Nb	Eu	La	Ce	Zr	Ti	V	Cr	Ni
BASALT MAGMA																
Plagioclase	0.01	0.07	0.17	0.23	1.83	0.067	0.03	0.01	0.34	0.19	0.1	0.048	0.04			
Clinopyroxene	0.04	0.031	0.038	0.026	0.06	0.62	0.9	0.005	0.51	0.056	0.09	0.1	0.4	1.35	34	1.5-14
Orthopyroxene		0.022	0.014	0.013	0.04	0.34	0.18	0.15	0.05		0.02	0.18	0.1	0.6	10	5
Olivine	0.002	0.01	0.007	0.01	0.014	0.014	0.01	0.01	0.007	0.007	0.006	0.012	0.02	0.06	0.7	6-29
Magnetite						1.5	0.2	0.4	1.0	2.0	2.0	0.1	7.5	26	153	29
Garnet		0.042	0.015	0.023	0.012	11.5	9	0.02	0.49	0.01	0.03	0.65	0.3		2	
RHYOLITE MAGMA																
Plagioclase	0.093	0.041	0.1	0.31	4.4	0.09	0.1	0.06	2.1	0.38	0.27	0.1	0.05			
K-feldspar	0.02	0.5		4.3	3.76	0.0015			2.6	0.07	0.04	0.03				
Quartz	0.025	0.04	0.013	0.022		0.017			0.056	0.015	0.014		0.038			
Biotite	0.167	4.2		5.4	0.5	0.54			0.87	3.18	0.3				5.2	
Hornblende		0.014	0.08	0.044	0.022	8.38	6	4	5.14		1.5	4	7			
Zircon	340					527			16	17	17				190	
Apatite						24	40	0.1	30	14.5	35	0.1	0.1			
Allanite	15.5					31			111	2595	2279			15.5	380	
Titanite								6.3		4						

Data from Rollinson, 1993.

Table 2.6 Trace Element Characteristics Useful in Evaluating Petrogenesis of Rocks

ELEMENT	CHARACTERISTICS AND INTERPRETATIONS
Ni, Co, Cr	Typically highly compatible elements. High concentrations (e.g., Ni = 250–300 ppm, Cr = 500–600 ppm) of these elements indicate derivation of parental magmas from a peridotite mantle source. Declining concentrations of Ni and to a lesser extent Co in a rock series suggest olivine fractionation. Decrease in Cr suggests spinel or clinopyroxene fractionation.
PGE, Cu, Au, Ag	Strongly partitioned into immiscible sulfide melts. A series of mafic magmas that lack sulfides may show increases in these elements. In most other magma series, these are compatible elements that decline with increasing silica.
V, Ti	Typically compatible elements in ilmenite and titanomagnetite, although Ti can become enriched in some mafic magmas that lack these oxide minerals.
Nb	Incompatible element in most magmas. However, because it substitutes somewhat for Ti, residual titanates (such as rutile) may cause depletions of Nb in subduction-zone magma sources. Nb has a lower solubility in aqueous fluids than other equally incompatible elements.
Zr, Hf	Characteristically incompatible in mafic magmas and not readily substituting in mantle phases. In zircon-saturated (silicic) magmas both may behave as compatible elements.
P	Characteristically incompatible in mafic magmas but becomes a compatible element in intermediate and silicic magmas where apatite is a stable phase.
Ba	Substitutes for K in micas, K-feldspar, and to a lesser extent amphibole. A change from incompatible to compatible behavior in a magma series may indicate an increasing role for one of these phases.
Rb	Incompatible element in most magma, but it substitutes for K in micas and K-feldspar in silicic magmas, though not as strongly as Ba.
Sr, Eu	Substitute readily for Ca in plagioclase and K in K-feldspar. Declining Sr concentrations indicates feldspar removal from a series of related magmas. Sr is more incompatible under mantle conditions because of the absence of feldspar.
REEs	Generally, the <i>trivalent</i> rare earth elements are incompatible in basaltic magmas. Garnet more readily accommodates heavy REEs than light REEs and a steep REE pattern may indicate garnet remained in a mantle residue. Titanite prefers the middle REEs. Apatite, monazite, and allanite have very high partition coefficients for light REEs; consequently, light REEs are commonly compatible elements in rhyolitic magmas that have these minerals. Zircon and xenotime prefer heavy REEs but their abundance in natural magmas is rarely sufficient to make the heavy REEs behave as compatible elements.
Y	Generally behaves incompatibly, as do middle to heavy REEs. It has a high partition coefficient in garnet and to a lesser extent in amphibole. Its behavior is strongly affected by REE-rich accessory minerals such as apatite and especially xenotime.

Data from Green (1989).

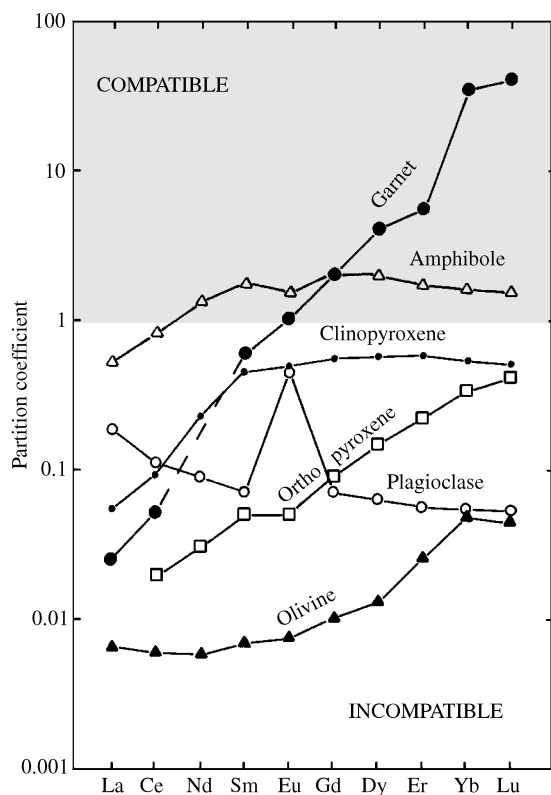
Eu; the plagioclase rock today forms the light-colored lunar highlands which contrast with the dark, basaltic mare lowlands. In contrast, the most widespread basalt on Earth, mid-ocean ridge tholeiitic basalt (MORB; Wilson, 1989), reflects extensive partial melting of mantle peridotite from which light REEs had been previously extracted. Yet another contrast is found in the negatively sloping pattern for **adakite** (Drummond and Defant, 1990), a type of dacite found in some subduction zones. Because its pattern is virtually a mirror image of the garnet coefficient pattern in Figure 2.22, petrologists believe that adakite magmas are generated by partial melting of the oceanic crust under high pressure where garnet is left behind after melting. Most of the incompatible light REE partition into the adakite partial melt and most of the compatible heavy REE stay behind in the garnet.

2.5.3 Other Normalized Trace Element Diagrams

The utility of the normalized REE diagram led to the development of similar **normalized trace element diagrams** that involve a wider variety of generally incompatible trace elements. One common approach is to normalize the trace element abundances in a rock sample with respect to **primitive mantle** concentrations (Table 2.7). These are average chondritic meteorite val-

ues but multiplied by a factor of 2.9. Adjustments must be made in K, Rb, and P because the two alkalis are volatile and may not have chondritic abundances in the Earth. Phosphorus may have been extracted from the mantle during formation of the core of the Earth. Other normalizations are with respect to chondrite or mid-ocean ridge basalts. In a primitive-mantle-normalized diagram (see Figure 13.2) a smooth, positively sloping pattern is obtained for mantle-derived mid-ocean ridge basalts (MORB). Generally, elements with the lowest partition coefficients are listed on the left and increasingly more compatible elements are found toward the right. However, it must be remembered that the partition coefficient for a particular element is not the same in every magma. A wide variety of similar diagrams have been used in the literature, so it is wise to pay careful attention to the exact scheme of normalization used for any trace element diagram.

Detailed discussion of the meaning of these trace element patterns is deferred to Chapters 11–13. Here, it is important to realize that there are significant differences between the trace element patterns of magmatic rocks—even in just one rock type, such as basalt—found in different tectonic settings and belonging to different petroctonic associations. Thus, mid-ocean ridge basalts are markedly impoverished in the most in-



2.22 Partition coefficients for REEs between minerals and basaltic melt. Garnet and plagioclase are the principal aluminous phases in basaltic magmas, but the former is stable at pressures above which plagioclase is stable. Note the striking contrast in their pattern of coefficients. Amphibole is another aluminous phase stable in hydrous systems. (Redrawn from Rollinson, 1993.)

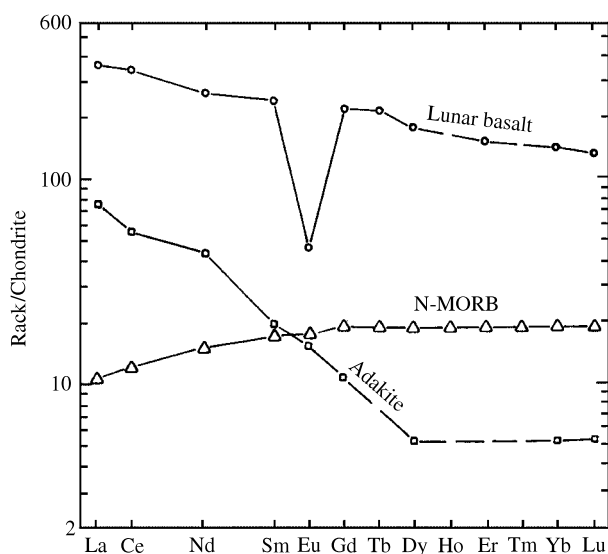
compatible elements, including Ba, Rb, and Th; otherwise their trace element pattern is quite smooth and nearly flat. MORB magmas are believed to be generated by extensive partial melting of mantle peridotite, but this would not create a depletion in the less compatible elements on the left. And neither would any crystallization effects. It is, therefore, believed that their mantle source must have experienced a previous partial melting event, or events, that preferentially extracted the most incompatible elements. This positively sloping pattern characterizes magmas derived from a **depleted source**—a magma-generating region that is depleted in the most incompatible elements. The depleted nature of the worldwide normal (N-MORB) source was one of the first fruits of studies of trace elements in rocks.

Calc-alkaline basalt magmas erupted in island arcs have dramatically different trace element patterns (see Figure 11.19). These basalts are **enriched** in the most incompatible elements, especially Ba, Rb, and K, but are strongly depleted in elements with high field strengths—Nb and Ta—relative to adjacent elements on the diagram. These depletions yield a spiked, irreg-

Table 2.7 Element Concentration (ppm) in Chondrite, Primitive Mantle, and Normal Mid-Ocean Ridge Basalt (N-MORB)

	CHONDRITE	PRIMITIVE MANTLE	N-MORB
Rb	2.32	0.635	0.56
Ba	2.41	6.989	6.3
Th	0.029	0.085	0.12
U	0.008	0.021	0.047
Nb	0.246	0.713	2.33
Ta	0.014	0.041	0.132
K	545	250	600
La	0.237	0.687	10.5
Ce	0.612	1.775	12.2
Sr	7.26	21.1	90
P	1220	95	510
Nd	0.467	1.354	15.6
Sm	0.153	0.444	17.2
Zr	3.87	11.2	74
Hf	0.1066	0.309	2.05
Eu	0.058	0.168	17.6
Ti	445	1300	7600
Gd	0.2055	0.596	17.9
Tb	0.0374	0.108	17.9
Dy	0.254	0.737	17.9
Y	1.57	4.55	28
Ho	0.0566	0.164	17.8
Er	0.1655	0.48	17.9
Tm	0.0255	0.074	17.9
Yb	0.17	0.493	17.9
Lu	0.0254	0.074	17.9

Data from Sun and McDonough (1989).



2.23 Very different **chondrite-normalized REE patterns** in three rocks. Compare patterns of partition coefficients in Figure 2.22, especially the mirror image of lunar basalt and plagioclase and of adakite and garnet.

ular pattern that, nonetheless, has an overall negative slope. This pattern is believed to reflect magma generation involving hydrous fluids in the mantle source overlying the downgoing lithospheric slab; the negative anomaly in Nb and Ta reflects a lower solubility of these elements in the migrating fluids.

✱2.6 ISOTOPES

Isotopes of an element are atoms whose nuclei contain the same number of protons but a different number of neutrons. Different isotopes are denoted with their atomic weights (protons + neutrons) as a superscript. Thus, all hydrogen atoms contain one proton in their nucleus and one electron that determines its chemical behavior. However, there are three H isotopes: hydrogen (^1H), deuterium (^2H), and tritium (^3H), which have zero, one, and two neutrons, respectively.

Isotopes are introduced in beginning geology courses because of their importance in determinations of the absolute age of rocks and minerals. In addition, like trace elements, isotopes serve as useful petrogenetic indicators of

1. processes of magma generation and evolution
2. T of crystallization
3. thermal history
4. other geologic processes, such as advective migration of aqueous fluids around hot magmatic intrusions

Investigations of trace elements and isotopes often go hand in hand because many of the petrologically important isotopes, except O and H, are of trace elements, namely, Rb, Sr, Pb, U, Th, Sm, and Nd. Geochemical investigations of trace elements and isotopes in magmas derived more or less directly from the mantle have provided significant constraints on the nature of this remote region of the interior of the Earth—once the exclusive and sole domain of geophysicists.

The isotopic proportions of elements in geologic materials are complex functions of their history and depend on whether the isotopes are unstable (radioactive) or stable and whether the isotopic system has remained closed.

2.6.1 Stable Isotopes

Stable isotopes do not decay. The stable isotope ratios of a particular element can only change by various physical and chemical **isotopic fractionation** phenomena in which one isotope is preferentially incorporated into one phase over another coexisting phase. For example, isotopes of ^{18}O are heavier than ^{16}O , and consequently molecules of H_2^{18}O are heavier than H_2^{16}O molecules. Because the vapor pressure, or escaping tendency, of a vibrating molecule is inversely proportional to its mass, evaporation of seawater enriches the overlying atmospheric vapor in the lighter molecules that contain ^{16}O

and ^1H isotopes, compared to the liquid seawater. Meteoric (rain) water derived from this vapor is also enriched in the lighter molecules and isotopes. Isotopic fractionation can occur between the isotopes of any element, but is greater for lighter elements, where there are larger relative differences in the masses of two isotopes. Hence, the mass difference between ^1H and ^2H is 100% and fractionation is considerable. Smaller fractionation occurs for heavier ^{16}O and ^{18}O , where the difference in mass is only about 12 percent. Isotopes of still heavier elements have even smaller relative mass differences; isotopic fractionation is too small to be detected for elements heavier than about Ca.

As a consequence of fractionation processes, stable isotopes can be used to trace the materials and processes involved in the evolution of many petrologic systems and the T at which they form. Because natural waters contain H, O, C, and S, the isotopes of these elements furnish valuable information regarding fluid-rock interactions in geologic systems. The importance of O exceeds that of the other isotopes because of its abundance in all kinds of rocks as well as natural fluids; it is the only stable isotope considered further here. See Faure (1986) for discussion of other stable isotopic systems.

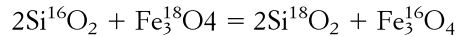
Oxygen Isotopes. Stable isotope fractionation occurs among the three isotopes of oxygen, ^{16}O , ^{17}O , and ^{18}O , whose *average* percentages in natural materials are 99.76%, 0.04%, and 0.20%, respectively; these proportions yield the atomic weight given in periodic tables of the elements. Geochemists define the isotope fractionation factor, $\alpha_{A-B} = R_A/R_B$ where $R_A = ^{18}\text{O}/^{16}\text{O}$ in phase A and $R_B = ^{18}\text{O}/^{16}\text{O}$ in phase B. Because these factors vary only in the thousandths place (generally between 1.000 and 1.004), stable isotope compositions are cited in the delta (δ) notation, wherein the isotope ratio *in a particular phase* is expressed as a fractional deviation from a standard of accepted composition

$$2.3 \quad \delta^{18}\text{O}\text{‰} = \left[\frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}} \right] \times 1000$$

Thus, the measured $\delta^{18}\text{O}$ value is expressed in parts per thousand, or per mil ‰. The standard used for comparison is usually Vienna Standard Mean Ocean Water (VSMOW), which has a composition similar to that of average ocean water. Positive $\delta^{18}\text{O}$ values are enriched in the heavy ^{18}O isotope, negative in light ^{16}O .

Fractionation of stable isotopes can occur during crystallization of minerals from liquids for much the same reason it does during evaporation. In crystals containing small light ions, such as Si^{4+} , the higher vibrational component of the internal energy can be reduced by bonding with heavier isotopes. Thus, in a rock in which the two phases quartz and magnetite

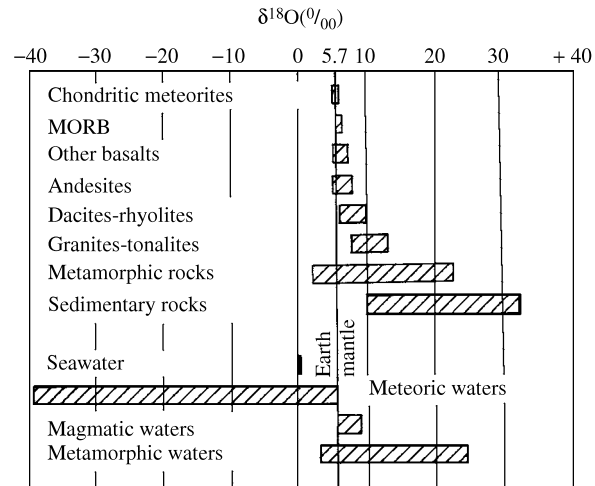
crystallized together under equilibrium conditions, the quartz will be more enriched in ^{18}O and the magnetite in ^{16}O . Fractionation is T -dependent but rather insensitive to P . A pair of minerals formed in nature at equilibrium can thus be used as a **geothermometer**. The basis for the O-isotope geothermometer is the T -dependent **isotope exchange reaction** between two minerals, such as quartz and magnetite



Exchange reactions of this sort commonly occur in the presence of some kind of liquid in which the isotopes can move about freely. Oxygen isotope ratios between many mineral pairs, including quartz-magnetite, plagioclase-magnetite, plagioclase-pyroxene, quartz-plagioclase, and quartz-muscovite have been measured experimentally over a wide range of temperatures. Consequently, the T at which coexisting minerals crystallized can be deduced from their isotopic ratios. Underlying assumptions in this geothermometer are that the coexisting minerals reached isotopic equilibrium with one another at some T and with the liquid agent, such as a melt or metamorphic aqueous fluid, and that the isotopic compositions of the minerals have not changed since equilibration. However, the second assumption is commonly not valid because many geologic systems are open to migrating fluids that perturb the isotopic ratios. In slowly cooled plutonic rocks, some reequilibration of isotopes may occur, leading to T estimates lower than those of initial crystallization. Moreover, some minerals reequilibrate more readily than others. For example, quartz is relatively resistant to isotopic reequilibration compared to biotite or magnetite.

Separation of crystals from coexisting melt in crystallizing magmas (fractional crystallization) results in only minor isotopic fractionation of most stable isotope ratios, oxygen included. In order of their tendency to concentrate ^{18}O from the melt, quartz is highest, then alkali feldspar, plagioclase, muscovite, pyroxene, hornblende, olivine, biotite, and ilmenite; magnetite is the lowest. Extensive separation of minerals from a mafic magma may yield a change of only 1 per mil or so in the residual melt. The same magnitude of changes is possible as a result of varying degrees of partial melting of source rocks.

It is therefore not surprising that the oxygen isotope ratio, $\delta^{18}\text{O}$, of most magmatic rocks has a limited range of only about +5‰ to +13‰ (Figure 2.24). Mantle peridotite and mantle-derived mafic magmas are about +6‰. In contrast, sedimentary rocks are much higher, shales +15 to +20‰ and carbonate rocks to as high as +33‰. These high ratios result from two factors: Fractionation factors for clay minerals and calcite in equilibrium with water are large and



2.24 Oxygen isotope composition of rocks and natural waters. (Redrawn from Rollinson, 1993, and Taylor and Sheppard, 1986.)

these minerals form in sedimentary environments at low temperatures where isotope fractionation is a maximum. It appears that the mantle is the source of most magmas but that some of the more silicic magmas having higher $\delta^{18}\text{O}$ values were contaminated by sedimentary rock.

Isotopic exchange reactions between magmatic rocks and hot aqueous fluids (hydrothermal solutions) advecting through them result in lowering of $\delta^{18}\text{O}$ values. Meteoric water (+6 to -40‰) advecting around shallow cooling magmatic intrusions (Figure 1.2; see also Figure 4.12) substantially lowers the $\delta^{18}\text{O}$ of the altered rock (Figure 4.14). Maps of $\delta^{18}\text{O}$ values can reveal fluid pathways.

2.6.2 Radiogenic Isotopes

Unstable, or radioactive, isotopes decay by nuclear processes into daughter **radiogenic isotopes**, which may be of the same or commonly of a different element as the parent. For example, radioactive ^{238}U decays into ^{206}Pb at a rate such that one-half of the parent ^{238}U is transformed into the daughter ^{206}Pb in about 4.5 Gy. This and other radioactive isotopic systems provide information on the absolute age of a mineral from that time the parent was initially lodged in it. (An absolute **age** measured backward from the present is expressed in **anna**; in International System [SI] units, 10^6 years = **Ma** [mega anna] and 10^9 years = **Ga** [giga anna]. An interval of time, such as the half-life just cited, is denoted in elapsed years, 4.5×10^9 y or 4.5 Gy.) As time passes the ratio of radioactive parent and daughter isotopes changes.

Because of their potentially different chemical behavior and mobility, parent and daughter isotopes might be susceptible to differential separation in an open isotopic system. For example, the decay of

radioactive ^{40}K in biotite crystals yields daughter ^{40}Ar , an inert, noble gas. Heating the biotite to modest temperatures ($>300^\circ\text{C}$) can promote the release, by diffusion, of the unbonded Ar from the crystal on geologic time scales. Comparisons of different minerals and isotopic systems having different **closure temperatures** provide insights into the thermal history of rocks (see, for example, Cliff, 1985).

Radioactive isotopes and their daughters behave differently as do other trace elements in geologic systems, making them valuable petrogenetic tracers. The most important difference lies in their contrasting compatibility in mantle-basaltic systems; thus, in the following, the degree of compatibility *increases to the right* and individual parent-daughter isotopic pairs are listed on the same line:

Rb >	Sr	
Th >	Pb	
U >	Pb >	
		Nd > Sm
		Hf > Lu

Hence, because Rb is the most incompatible, it is strongly concentrated in partial melts of the mantle that rise and solidify as crustal rock. In contrast, Sr, Sm, and Lu are least concentrated in the crust relative to the Rb-depleted mantle. Nd and Sm isotopes, on the other hand, are hardly fractionated from one another during partial melting and crystallization because of their very similar ionic radii. However, both are quite immobile and Nd-Sm systems, therefore, remain closed in many geologic environments where hydrothermal solutions and melting cause opening of the Rb-Sr system, mobilizing Rb but not Sr. The Th-Pb and U-Pb isotope systems are complex and the three elements have differing mobilities in addition to contrasting compatibilities; they are not discussed further in this textbook.

Rubidium-Strontium Systematics. Rubidium occurs in nature as the isotopes ^{85}Rb and ^{87}Rb ; the latter is radioactive and decays by beta emission to ^{87}Sr with a half-life of 48.8 Gy. The present relative abundance of these isotopes—72.17% ^{86}Rb and 27.83% ^{87}Rb —is the same in all rocks and minerals, regardless of age. Apparently, these heavy isotopes were thoroughly mixed in the primeval Earth and have not experienced fractionation since then regardless of the geologic processes that have acted upon them.

The same ionic charge of Rb^+ and K^+ and similar ionic radii (1.61 Å and 1.51 Å, respectively, based on eightfold coordination, Figure 2.20) means that Rb readily substitutes for K in micas and K-feldspar. Rocks and minerals that have high concentrations of K also tend to have relatively high Rb, although the K/Rb ra-

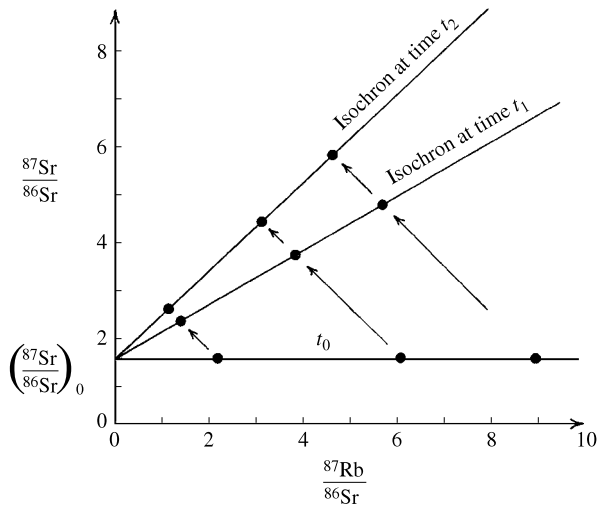
tio is not uniform in all materials, ranging over more than four orders of magnitude. The crystal chemical characteristics of Sr are a little more complicated than those of Rb, but essentially follow Ca, because of identical ionic charge and similar ionic radii (Sr^{2+} 1.26 Å; Ca^{2+} 1.12 Å). Consequently, Sr is relatively concentrated in calcic minerals such as plagioclase, apatite, and calcite; however, Ca^{2+} sites in calcic pyroxenes are too small for the slightly larger Sr^{2+} ions.

Strontium has four stable isotopes, ^{88}Sr , ^{87}Sr , ^{86}Sr , and ^{84}Sr , whose relative abundance is 82.5%, 7.0%, 9.9%, and 0.6%, respectively. But because ^{87}Sr is a decay product of ^{87}Rb , its exact abundance in a rock or mineral depends not only upon the amount of ^{87}Sr present when the material formed, but also upon the concentration of Rb and the age. Materials rich in Rb, such as micas and alkali feldspars, will obviously contain considerable ^{87}Sr , especially if they are old. As isotopic *ratios* are more accurately measured by mass spectrometers than the absolute amount of a single isotope, the abundance of ^{87}Sr is conventionally expressed as the ratio $^{87}\text{Sr}/^{86}\text{Sr}$. The number of atoms of ^{86}Sr in a mineral is constant, because it is a stable isotope not formed as a decay product of any other naturally occurring radioactive isotope. The relationships among the present day measurable $^{87}\text{Sr}/^{86}\text{Sr}$ ratio; the initial ratio ($^{87}\text{Sr}/^{86}\text{Sr}$)₀ when the rock or mineral formed at time zero; its present day, measurable $^{87}\text{Rb}/^{86}\text{Sr}$ ratio; the age in t years since the formation of the rock or mineral at time zero; and the decay constant λ ($= 1.42 \times 10^{-11} \text{ y}^{-1}$) for ^{87}Rb , is expressed by the equation

$$2.4 \quad ^{87}\text{Sr}/^{86}\text{Sr} = (^{87}\text{Sr}/^{86}\text{Sr})_0 + (^{87}\text{Rb}/^{86}\text{Sr})(e^{\lambda t} - 1)$$

This is a linear equation of the form $y = b + mx$, where $b = (^{87}\text{Sr}/^{86}\text{Sr})_0$ and $m = (e^{\lambda t} - 1)$. A plot (Figure 2.25) of $x = ^{87}\text{Rb}/^{86}\text{Sr}$ and $y = ^{87}\text{Sr}/^{86}\text{Sr}$ measured on separated minerals from one igneous rock, or on a group of genetically related whole rocks from a single igneous or metamorphic body that has behaved as a closed system since $t = 0$, yields a straight line called an **isochron**. The intercept (b) of the isochron on the y axis is the initial ratio ($^{87}\text{Sr}/^{86}\text{Sr}$)₀. From the slope of the line $m = (e^{\lambda t} - 1)$, the age of the rock from the time of crystallization can be calculated. Because of the long half-life of ^{87}Rb , the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured on a mass spectrometer for samples only a few million years old is essentially the same as the initial ratio.

The initial ratio ($^{87}\text{Sr}/^{86}\text{Sr}$)₀ is an especially valuable petrogenetic tracer because it is a record of the Rb/Sr ratio of the magma source. Magmas derived by partial melting of source rocks with high Rb/Sr ratios, or contaminated by such material, such as old continental crust, inherit this geochemical property in a high initial ratio. Sources in the peridotitic mantle, where Rb/Sr ratios are very low, yield magmas with low initial ratios.



2.25 Schematic Rb-Sr **isochron** diagram for cogenetic rocks or minerals decaying through time. Three samples of rocks or minerals (solid circles) having identical initial $(^{87}\text{Sr}/^{86}\text{Sr})_0$ ratios crystallized at the same time, t_0 , from cogenetic rocks or magma, after which the isotopic system remained closed. The initial $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of the three samples differed because of different Rb/Sr ratios; muscovite, for example, would have a greater ratio than plagioclase. Subsequent to time t_0 , individual rocks or minerals track along straight lines having a slope of -1 due to decay of ^{87}Rb to ^{87}Sr . At any one time, such as t_1 , and so on, points representing the analyzed samples define a straight line isochron whose positive slope is dictated by the age of the system since crystallization occurred to close it.

Although discussions in later chapters will explore specific implications of Rb-Sr isotopic compositions to magma genesis, it is pertinent here to present generalized models of Sr-isotope evolution in the Earth. In a simple model that assumes an initial meteoritic composition and no fractionation of Rb and Sr during the entire history of the Earth, all rocks would have the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratio today after its 4.5-Gy history. This uniformity in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is decidedly incorrect. Instead, a single-stage model can be assumed (Figure 2.26a) in which a partial melting event occurred in the mantle at, say, 1.5 Ga that generated magma of greater Rb/Sr ratio than the mantle source because of the differing incompatibility of these two elements. Solidification of this magma created crust whose $^{87}\text{Sr}/^{86}\text{Sr}$ ratio evolved at a greater rate along a steeper path because of the higher Rb/Sr ratio than in mantle peridotite. However, this single-stage model is still not valid because crustal rocks have a *range* of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, to as high as about 0.74, and mantle rocks and magmas derived from them have ratios of about 0.702–0.711. A multistage model must, therefore, apply in which Rb-enriched magmas have been repeatedly extracted from the mantle throughout Earth history (Figure 2.26b). The granitic continental crust has been derived, probably indirectly, from the mantle over most of the history

of the Earth; older crustal segments now have the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Samarium-Neodymium Systematics. There are many isotopes of these two light REEs, but the one of most relevance to geochronology and petrology is ^{147}Sm , which decays by alpha emission to ^{143}Nd with a half-life of 106 Gy. The abundance of the radiogenic daughter product is referred to by a ratio with the stable ^{144}Nd isotope, that is, $^{143}\text{Nd}/^{144}\text{Nd}$. The Sm-Nd isotopic system is similar to the Rb-Sr system just described and is handled in much the same manner. However, one important difference between the two isotopic systems is the much greater half-life for ^{147}Sm decay, which limits the usefulness in dating to rocks more than 1 Ga or so in age.

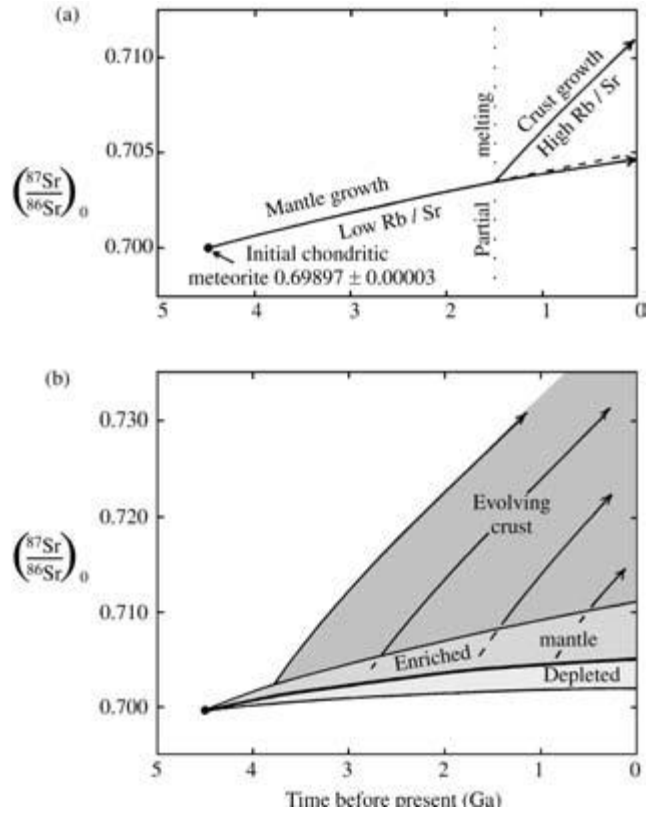
The initial ratio $(^{143}\text{Nd}/^{144}\text{Nd})_0$ serves as a valuable petrogenetic tracer. Rocks with high Sm/Nd ratios (i.e., light REE-depleted) develop higher isotope ratios with the passage of time, whereas rocks with low Sm/Nd ratios (light REE-enriched) develop lower isotope ratios (Figure 2.27). This behavior means that enriched sources like the continental crust have *lower* $(^{143}\text{Nd}/^{144}\text{Nd})_0$ but *higher* $(^{87}\text{Sr}/^{86}\text{Sr})_0$. Another important contrast with Sr isotopes is the very small difference in the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (0.510 to 0.514, or $<1\%$), which stems from the small variations in Sm/Nd ratios of 0.1 to 2.0 in rocks, in contrast to Rb/Sr ratios, which vary from 0.005 to over 100. The small differences in Sm and Nd are related to their similar crystal chemical behavior. Because of this similarity, there are no reservoirs on Earth especially rich in Sm or Nd like the Sr-rich oceanic waters that produce Sr-rich marine carbonates and the Rb-rich continental crust.

Sm-Nd isotopes offer significant advantages over other systems such as Rb-Sr and U-Pb because Sm and Nd occur in major minerals such as pyroxenes and plagioclase and are not easily mobilized. Comparison of Nd and Sr isotopic ratios can constrain models of magmatic evolution, for example, mantle partial melting and crustal contamination, to a better degree than use of Sr isotopes alone.

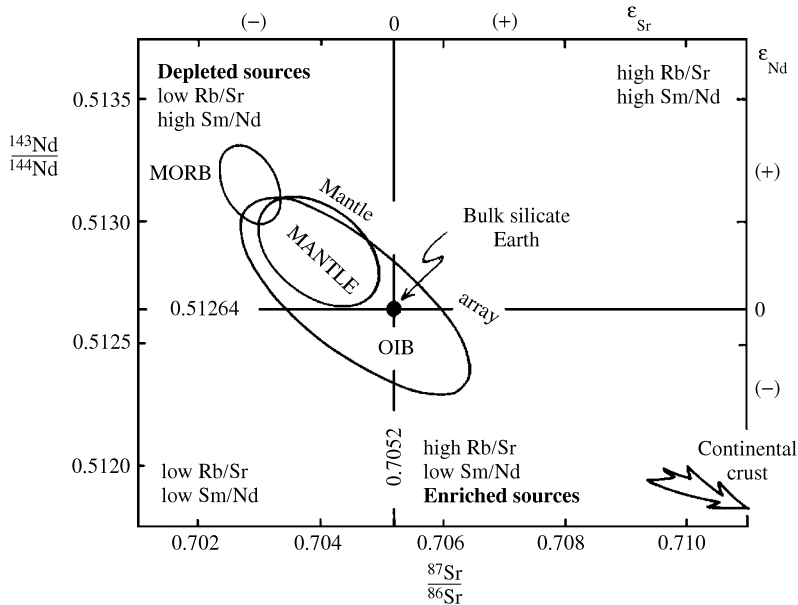
As a final note regarding Sr and Nd isotopic ratios, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in the remainder of this textbook will always refer to the *initial* ratio.

2.6.3 Cosmogenic Isotopes: Beryllium

Cosmogenic isotopes are produced when high-energy cosmic rays interact with nuclei of atoms in the atmosphere or on the surface of the Earth to produce new isotopes. Many of these cosmogenic isotopes are unstable and decay to other isotopes, including ^{14}C —which is the basis of a dating method for material less than about 40,000 years old. Isotopes of H (tritium), Al, Cl, and Be are also formed; only the latter is discussed here.



2.26 Schematic strontium isotope evolution diagrams for the Earth. Filled circle represents an assumed parental chondritic meteorite whose initial $(^{87}\text{Sr}/^{86}\text{Sr})_0$ ratio at 4.5 Ga, when the Earth accreted from primordial material, was 0.69897 ± 0.00003 . Note that growth lines are slightly curved because the amount of ^{87}Rb decaying to ^{87}Sr decreases through time. (a) Single-stage model with hypothetical partial melting event at 1.5 Ga. Thereafter, mantle growth is at a slightly lower rate because of extracted Rb from a depleted mantle. (b) Multistage model in which the mantle has been partially melted many times throughout its history to create a growing, evolving crust. Metasomatic processes create an incompatible-element-enriched mantle (Section 11.2.2); other parts of mantle are relatively depleted through partial melting processes.



2.27 Sr and Nd isotope ratio correlations. All terrestrial rocks are derived from a **primordial bulk silicate Earth**. The mantle array is defined by relatively depleted, mantle-derived, mid-ocean ridge basalt (MORB) and more enriched ocean island basalt (OIB), as well as fragments (xenoliths) of the suboceanic mantle (labeled MANTLE) brought up in erupted OIBs. Continental rocks plot well off the diagram to the lower right. The ϵ_{Sr} and ϵ_{Nd} notation refers to the difference between the measured $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in rock samples and the reference bulk Earth ratio (for further details see Rollinson, 1993). (Redrawn from Rollinson, 1993.)

Of the three isotopes of beryllium, only ^9B is stable, whereas ^7Be and ^{10}Be are radioactive isotopes constantly produced as cosmic rays fragment stable isotopes of oxygen and nitrogen in the atmosphere. ^7Be decays to stable ^7Li with a half-life of only 53 days. The more geologically useful ^{10}Be transforms by beta decay to stable ^{10}B with a half-life of 1.5 million years. After production, the cosmogenic Be isotopes are rapidly removed from the atmosphere by precipitation of rain and snow. Because Be is relatively insoluble in water, it is then absorbed or otherwise incorporated into organic and inorganic sediment particles that settle to the bottom of the oceans. As the oceanic crust is subducted and partially melted, the ^{10}Be isotopes are partitioned into ascending and erupting magmas, providing unequivocal evidence that oceanic sediment supplied at least some of the mass of subduction zone magma. Moreover, if detected, ^{10}Be isotopes provide insights into the time involved in subduction, magma generation, and ascent. If no sediment were subducted, no ^{10}Be would be found in any associated volcanic rocks, but, in fact, several investigators have found traces of ^{10}Be in rocks erupted above subduction zones. Of course, the absence of ^{10}Be does not prove that sediment was not involved because ^{10}Be has a very short half-life.

SUMMARY

Magmatic rocks have a broad continuous spectrum of chemical, mineralogical, and modal compositions that are produced by a virtually infinite variety of conditions in the magma source and subsequent evolutionary processes. Variation diagrams facilitate presentation of compositional data so that meaningful differences or similarities and evolutionary patterns can be discerned.

Rock classifications attempt to systematize these compositional continua, as well as recognizing a wide range of fabrics and field relations, in order to understand better the origin of rocks. One rock can be given several labels depending on the intent of the applied scheme of classification.

Magmatic rocks are subdivided on the basis of field relations into plutonic and volcanic, whose fabric is chiefly phaneritic, on the one hand, and aphanitic, glassy, or volcanoclastic, on the other. Mineralogical mnemonics are used to convey modal attributes. Specific rock-type names in plutonic/phaneritic rocks are based on the modal proportion of alkali feldspar, plagioclase, quartz, and feldspathoids for felsic rocks and the proportion of plagioclase, clinopyroxene, orthopyroxene, and olivine for mafic and ultramafic rocks. Other major rock-forming minerals nonessential to

their classification include amphibole, biotite, and Fe-Ti oxides. Rock-type names for volcanoclastic rocks depend on clast size. Names for volcanic/aphanitic (glassy) rock-types depend mostly on the relative amounts of $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ and SiO_2 .

The CIPW normative composition of magmatic rocks, together with actual mineral constituents, facilitates their classification according to degrees of silica and alumina saturation. Other coherent comagmatic kindreds and trends that can be discerned on variation diagrams include the alkaline rock suite, whose member rock types are enriched in alkalis relative to silica, and the subalkaline suite. This widespread suite of rocks, in which alkali concentrations are modest so that rocks are usually silica saturated to oversaturated, is further subdivided into the tholeiitic subsuite showing relative Fe enrichment and the calc-alkaline subsuite in which evolved rocks are less Fe-enriched and more felsic. Still other comagmatic kinships can be discerned with respect to variations in SiO_2 and K_2O . A particular rock type such as basalt can occur in different rock suites and can be found in different global tectonic settings. However, specific rock suites tend to be associated with specific tectonic settings, forming petrotectonic associations. Thus, tholeiitic basalt makes up most of the oceanic crust produced at spreading ridges; tholeiitic basalt and tholeiitic andesite (and locally dacite) compose island arcs at convergent ocean-ocean plate junctures; calc-alkaline basalt, andesite, dacite, and rhyolite (and their phaneritic equivalents) constitute medium- to high-K magmatic rocks at continental margin subduction zones; and midplate oceanic islands are of tholeiitic and alkaline basaltic rocks. Highly alkaline rocks occur in relatively stable continental cratons and in continental rifts where basalt and rhyolite also form a bimodal association.

Contrasting sources, global tectonic settings, and evolutionary processes affecting magmas are recorded in trace element and isotopic-tracers in rocks. In contrast to major elements, whose distribution between crystals and melt in a magma is controlled by phase equilibria, trace elements have more widely ranging concentrations, which reflect partitioning according to compatibility constraints between different major and accessory minerals and coexisting silicate melt. Trace element partitioning patterns can indicate specific minerals with which partial melts equilibrated at their source and which minerals might have been subsequently fractionated from the magma. Radiogenic isotope ratios can be used to establish the chronology of magmatic processes and place constraints on magma sources and interactions between a magma and its surroundings. The stable isotopes of oxygen serve as petrogenetic tracers as well as geothermometers of mineral growth.

CRITICAL THINKING QUESTIONS

- 2.1 What are the hindrances, rationale, and justification for classification of magmatic rocks? Is classification just meaningless busywork?
- 2.2 Briefly indicate the basis for each of the several classifications of magmatic rocks described in this chapter.
- 2.3 Contrast rock types with rock suites.
- 2.4 What are three fabric heteromorphs of granite?
- 2.5 From Figures 2.8 and 2.12, describe systematic variations in mode and silica among granite, granodiorite, and diorite. From Table 2.2, describe and explain systematic changes in major oxides.
- 2.6 Explain in detail how it is possible for a quartz-normative basalt to contain no real quartz in its mode, only plagioclase, pyroxene, olivine, and Fe-Ti oxides. A nepheline normative basalt of the same mode containing no actual nepheline. What is the role of pyroxene?
- 2.7 Discuss silica saturation in a simple model magma consisting of O, Si, Al, and K, which can potentially crystallize quartz, K-feldspar, leucite (KAlSi_2O_6), and kalsilite (KAlSiO_4). Create a diagram for this hypothetical system like Figure 2.14.
- 2.8 Discuss differences in the major and trace element compositions of basalt and relate these differences to global tectonic setting.
- 2.9 What is the relation between crustal thickness and K_2O at a given SiO_2 content for magmatic rocks in subduction zones?
- 2.10 What are the bases for distinguishing between compatible and incompatible trace elements? Give examples of each in rhyolitic and in basaltic magmas.
- 2.11 What are the rationale and the goal of investigations of trace elements in magmatic rocks? Of isotopes?

- 2.12 What factors control variations in the ratios of stable isotopes? Radiogenic isotopes?
- 2.13 Contrast the behavior and implications of Sm-Nd and Rb-Sr isotope systems.

PROBLEMS

- 2.1 Classify the garnet and spinel peridotites from Table 11.1 using Figure 2.10b.
- 2.2 Plot average granite and granodiorite in Table 2.2 in an enlarged photocopy of Figure 2.8 using the amounts of normative Q , Or , and Ab in lieu of modal Q , A , and P .
- 2.3 Calculate the normative composition of a magmatic biotite and hornblende from Appendix A. Classify these minerals, *as if they were rocks*, as to degree of silica saturation. Discuss how crystallization of these minerals in magmas controls the availability of silica for potential crystallization of quartz.
- 2.4 From problem 2.3 classify the selected biotite and amphibole as to degree of alumina saturation.
- 2.5 Calculate the normative compositions of the pantellerite in Table 13.10, the phlogopite-rich leucite lamproite in Table 13.11, and the shoshonite in Table 13.6. Classify these rocks in the total alkali-silica diagram (Figure 2.12). Discuss whether these rocks belong to the alkaline rock suite.
- 2.6 Calculate the bulk partition coefficients for Ni and for Rb in the garnet peridotite in Table 11.1 using partition coefficients in Table 2.5.
- 2.7 Construct a chondrite-normalized diagram for the spinel peridotite in Table 11.1. Describe this diagram. What rock in Figure 2.23 does the pattern of the spinel peridotite most closely resemble?