

# Chemical Petrology I: Major and Minor Elements

## Questions to be Considered in this Chapter:

1. How do we analyze rocks to determine their chemical composition?
2. How are rock analyses reported, and what do they tell us about the composition of igneous rocks?
3. How can we use the compositions of rocks and of groups of associated rocks to investigate the processes involved in their genesis?
4. How can we display the compositions of many associated rocks so that we can investigate trends in the data?
5. What quantitative methods are used to model observed compositional trends?
6. How can we use chemical criteria to characterize or classify igneous rocks and entire sequences of igneous rocks that appear to be related in the field?

**G**eology borrows heavily from other disciplines, applying the principles and techniques of physicists, chemists, and materials scientists, among others, to geological problems. Petrologists borrow most heavily from the field of chemistry, where the application of **geochemistry** to petrologic problems has proved so fruitful that modern petrology simply cannot be accomplished properly without it. In this chapter, I shall lay part of the groundwork for an understanding of the principles of chemistry that we apply to igneous and metamorphic rocks. This chapter begins with the chemical applications that address elements usually present in concentrations greater than 0.1 weight % (wt. %) in igneous rocks. The material in this chapter is critical to our ability to interpret and understand the processes of magma generation and evolution in the various igneous–tectonic settings. At times you may want to refer to the periodic table.

For convenience in what follows, elements are considered to be either major, minor, or trace elements, based on their concentration in rocks. Limits on the groups are arbitrary, but the following is a guide to the common behavior:

**Major elements** >1.0 wt. % (expressed as an oxide)

Typical examples: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MgO, CaO, Na<sub>2</sub>O, and K<sub>2</sub>O

**Minor elements** 0.1 to 1.0 wt. % (expressed as an oxide)

Typical examples: TiO<sub>2</sub>, MnO, P<sub>2</sub>O<sub>5</sub>, and perhaps the volatiles H<sub>2</sub>O and CO<sub>2</sub>

**Trace elements** <0.1 wt. % (usually expressed as an element)

**Major elements**, because they are present in high concentrations, control to a large extent the mineralogy and crystallization–melting behavior in igneous systems. They also control such properties as viscosity, density, diffusivity, etc. of magmas and rocks. **Minor elements** typically substitute for a major element in a mineral. (Mn, for example, substitutes for Fe or Mg in most mafic minerals.) If they reach a sufficient concentration, however, minor elements may form a separate mineral phase, present in minor amounts (called an **accessory mineral**). For example, if sufficient Zr is present, it causes the mineral zircon to form, sufficient P will generate apatite, and Ti may form titanite, rutile, or a Fe-Ti oxide, such as ilmenite. **Trace elements** are too dilute to form a separate phase, so they act strictly as substitutes for major or minor elements. Although major elements, minor elements, and trace elements are classified in accordance with the guidelines above, most petrologists consider TiO<sub>2</sub>, MnO, P<sub>2</sub>O<sub>5</sub>, and H<sub>2</sub>O minor elements, even in uncommon instances when they are present in concentrations greater than 1.0 wt. %. Likewise, K<sub>2</sub>O, which may be present in concentrations below 0.1 wt. % in some mafic rocks, is more abundant in most rocks and is thus considered a major element by many investigators, regardless of concentration.

As a result of the different roles played by major and trace elements, each provides distinct insights into various igneous processes. Major elements may be used to classify igneous rocks and study the chemical control on the physical properties of crystal–melt systems. They are also used to study the chemical evolution of melts (and minerals) during the crystallization or melting process. The concentration and distribution of trace elements may also be used to study the evolution of magmas. They have proved to be particularly effective as tracers that help to constrain magma sources or to discriminate between some magmatic processes.

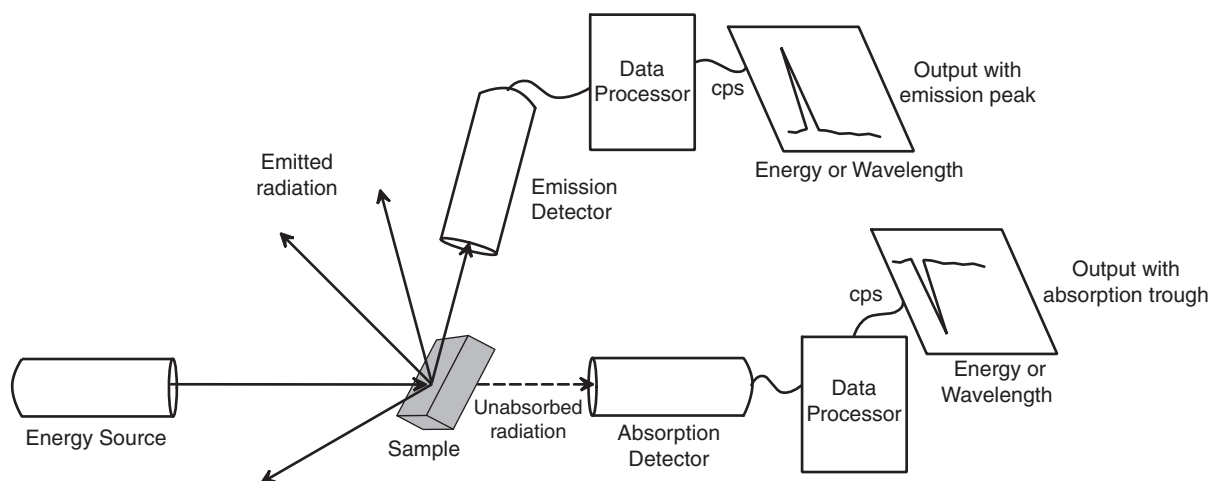
## 1 ANALYTICAL METHODS

Chemical techniques were first applied to rocks in 16th-century Europe in order to understand and exploit ore veins. It was only in the 18th and 19th centuries, however, that the majority of the elements were recognized and organized on the basis of similar properties (giving rise to the periodic table of the elements in 1869). The techniques for the accurate chemical analysis of rocks, minerals, volcanic gases, and aqueous solutions were developed in the past 150 years. The only available method prior to the 1920s and 1930s was classical volumetric and gravimetric analysis (commonly called **wet chemical analysis**). Preparation of liquids and gases for wet chemical analysis was relatively easy compared to that for rocks and minerals, which had to be dissolved in strong acids and diluted before the resulting liquid could be analyzed. Mineral analyses were particularly formidable because a reasonable quantity of the pure mineral (free of inclusions and other mineral fragments) had to be physically separated before the mineral could be dissolved and analyzed accurately. Wet chemical analyses involved analysis by the tedious and time-consuming processes of

titrating, or adding certain chemicals that would combine with a particular ion in solution to form an insoluble precipitate. The concentration of the ion in question could then be calculated either from the accurately determined volume titrated or the weight of the precipitate. When this was done for each of the principal elements in the sample, the analysis was complete. A single analysis could require over a day, and years of experience were needed to master the techniques to produce high-quality results. Needless to say, chemical analyses of rocks and minerals were not common when these techniques were the only ones available. Even then, analysis could be performed only for major and minor elements.

As technology advanced, wet chemical analysis was gradually augmented by, and eventually replaced by, **instrumental** techniques of analysis. Techniques useful to the analysis of rocks and minerals are based on the ability of atoms to either emit or absorb radiation with frequencies characteristic of the element responsible. Because these techniques involve emission or absorption of some particular portion of the electromagnetic spectrum, they are called **spectroscopic** techniques. They permit much more rapid analysis of geological materials, and they can determine the concentrations of various trace elements as well. Figure 1 illustrates, in a simplistic fashion, the general principles of emission and absorption upon which these instruments are based. All of them require an energy source that bombards the sample to be analyzed (also called the “unknown”) with energy and a detector capable of distinguishing the energy of the emitted or transmitted photons and determining the intensity of the radiation corresponding to a particular energy. The detector output provides a signal that is a measure of the emitted or absorbed radiation from the sample.

**Emission** requires that atoms in the sample being analyzed be “excited,” or raised to an unstable state by the absorption of some form of energy. The excited state usually involves the transfer of an electron from a lower energy orbital about the nucleus to one of higher energy. The excited atom then returns spontaneously to the unexcited (“ground”) state. Because energy must be conserved, the return is accompanied by emission of a photon of light, the energy (or wavelength) of which is related directly to the energy of the electron transfer (the difference between the energy levels of the two orbitals). Because the energy of electron orbitals are quantized, the radiated energy is characteristic of the element. Not every atom in the sample will continuously emit characteristic photons, but the number of photons with a particular energy emitted in a given period of time is proportional to the number of atoms of that element present in the sample (i.e., the concentration of the element). The raw data, then, are the rate of emission from the sample (usually in “counts per second,” [cps]) at a particular frequency or energy. Equating cps to concentration requires comparison of the emission rate of the “unknown” (sample) to the emission rate of a set of “standards” of known concentration. These standards may be natural samples of known composition (previously analyzed using wet chemical techniques) or



**FIGURE 1** Diagram illustrating the geometry of typical spectroscopic instruments. “Data processor” represents possible electronic signal amplifiers, filters, and data analysis electronics. Output is illustrated as a plot of intensity (typically in counts/second [cps]) of the emitted or unabsorbed or absorbed radiation ( $y$ -axis) versus energy, frequency, or wavelength ( $x$ -axis).

prepared by dissolving and diluting pure analytical reagents to specific concentrations.

The simplest (and therefore the first) instrument for spectral detection and analysis was the **optical spectrometer**. It uses a simple prism or a diffraction grating to disperse the visible-light spectrum emitted by an excited substance and photographic film to record the light of a given color (frequency). The intensity of the spot or line of a particular color on the developed film is proportional to the concentration of a certain element. Later, electronic detectors with photomultipliers were developed to determine the intensity more accurately and quantitatively and to permit detection of radiation emitted beyond the visible portion of the spectrum. One could excite a sample in the optical spectrometer by using intense heat or simply point the detector at a self-excited source, such as the sun and stars.

**Absorption** techniques work in a fashion similar to emission but determine the amount of energy *absorbed* by a sample. The energy is absorbed by atoms in the sample in order to reach an excited state (generally associated with an electron jump between orbitals), so that a particular element may absorb energy at characteristic frequencies as well (equal to the energy difference between the ground and excited states). In absorption instruments, electromagnetic radiation (usually light) is passed through a sample into a detector that measures the final intensity (Figure 1). The extent of absorption is compared to standards in order to compute the concentration of an element (or compound) in an unknown. Of course, the light source has to be of variable frequency in order to provide the energy that correlates with the electron shifts for a variety of elements.

A number of instrumental techniques, both emission and absorption, have been developed over the years, some of which are more suitable than others for certain elements, concentrations, and materials. The first fully instrumental techniques to be developed were flame photometry, emission spectroscopy, and colorimetry, none of which is used much today. These deal with the ultraviolet–visible–near-infrared portions of the spectrum. They can also be applied to elements

in far lower concentrations than can be analyzed by using wet chemical analysis. The **flame photometer** involves the aspiration of a solution into a flame (the energy source). The flame can provide only enough energy to excite the outer (valence) electrons of easily ionized elements, primarily the alkali metals. For example, the yellow-colored light observed when you strike a match is the 589 nm emission of sodium in the match head when excited by the heat of the flame. The photometer is capable of dispersing the emitted spectrum, focusing on the (sodium) emission line, and quantifying the emission. **Emission spectrometry** is similar to flame photometry, but the energy is supplied by a graphite electrode. The bright-white light emitted by the emission spectrometer testifies to a far more energetic source that can excite a much greater number of elements than can flame photometry. **Colorimetry** is based on the absorption of visible light associated with the color imparted to an aqueous solution by the addition of a chemical that forms a colored complex with the element to be analyzed.

Later, **atomic absorption (AA)** and **x-ray fluorescence (XRF)** spectroscopy were developed. In AA spectroscopy, a solution is aspirated into a flame or a graphite furnace, and a beam of light (of a predetermined wavelength) is also passed through the flame or furnace. The absorption (the reduction in intensity of the resultant light) is measured and compared to the reduction in standards. XRF irradiates a *solid* sample with x-rays that are sufficiently energetic to excite electron transitions in the *inner* electron shells (not just among the valence electrons) for a variety of elements in a sample. The ensuing return to the ground state results in emission of **fluorescent x-rays**, characteristic spectra in the higher-energy x-ray range. The emitted x-ray spectrum can no longer be dispersed by a prism or a light diffraction grating to isolate a particular frequency but requires an oriented crystal lattice to diffract it (in accordance with Bragg’s law). Once the spectrum is dispersed, an x-ray detector can be tuned to a particular frequency (based on the angle with reference to the diffracting crystal) and measure

the rate of emission corresponding to the energy of a particular element. Modern XRF units have sample chambers that hold many samples and are automated to evaluate a number of elements on each sample in a short period of time. The process is controlled by a computer that also performs data reduction and computes the concentrations. AA and XRF are reasonably accurate and precise and can reliably detect many elements in concentrations down to a few parts per million (see below). The lowest concentration that can be accurately determined for a given element by a particular technique is called the **detection limit**.

In the 1970s the **inductively coupled plasma (ICP)** technique became widely available. To use it, samples are dissolved and then mixed with argon gas as they are aspirated into a tiny radio frequency generator, where a plasma (similar to the gas in a fluorescent light tube) is created. This is a particularly effective means of exciting atoms. The emission line relating to each element is isolated by a diffraction grating and detected by a series of photomultipliers, each on a separate channel tuned for a specific element. All channels are simultaneously counted and fed to an on-board computer, where the data are reduced and the concentration of each element is calculated. A good modern ICP can produce a chemical analysis of more than 60 elements in a matter of minutes (once the sample has been prepared).

In addition to these spectroscopic methods that rely upon *electron* interactions, there are methods that rely upon *nuclear* interactions. Excited or unstable particle configurations within the nucleus of an atom may release either a photon or a particle when they *decay*, or revert to the ground state. We commonly refer to these releases as “radioactivity.” We can detect and measure the natural radioactivity of rocks and minerals by using a Geiger or scintillation counter. Of course this works only for isotopes of elements that are naturally unstable and emit radioactivity as they decay. Nuclear techniques have the advantage of determining the concentration of *isotopes* and not just elements. In a technique called **instrumental neutron activation analysis (INAA)**, the nuclei of a number of otherwise stable nuclides are excited by bombarding samples with an intense neutron flux in a nuclear reactor. The sample that is removed is “hot” in the radioactive sense, and the particles emitted as the atoms within it return to stable configurations can be analyzed spectroscopically in a fashion similar to XRF. This method is very accurate, with low detection limits for many elements.

In **mass spectrometry**, a sample is heated and ionized, and the ions are introduced into an evacuated chamber with a strong magnetic field. The stream of charged ions follows a curved path in the magnetic field. Due to their greater momentum, heavier ions follow a path with a larger radius of curvature. Ions of each mass are counted as they pass through slits in a charged detector. This instrument is not like the others in that it does not rely on emission or absorption, but it physically dissociates the sample and physically counts the particles of a particular mass. This is an expensive method, but it is the only reliable way to determine isotopic ratios for petrology and geochronology.

For petrology, most of the methods mentioned thus far require that a representative quantity of the sample be crushed and dissolved or fused. Of course a sample must be fresh and unaltered (unless you plan to study the alteration). Grain size and sample heterogeneity affects the sampling and preparation procedure. For very coarse-grained rocks, such as pegmatites, several kilograms may be required, and a sample splitter, a device that produces an unbiased portion, may have to be used. The result is an analysis of the complete rock (a **whole-rock analysis**).

As mentioned above, *mineral* analyses were far more difficult because they required separation of clean monomineralic samples. The advent of the **electron microprobe (EMP)** has changed this; the EMP provides an efficient, accurate, and rapid method of mineral analysis. With this instrument, a polished thin section of the sample is bombarded with a beam of electrons only  $\sim 2 \mu\text{m}$  in diameter. The electrons excite the atoms in a tiny spot on the sample (perhaps  $10 \mu\text{m}$  in diameter), which emit fluorescent x-rays, much as with XRF. In both XRF and EMP, the x-rays can be dispersed either on the basis of wavelength, using oriented crystals and Bragg’s law (**wavelength dispersive spectrometers [WDS]**), or on the basis of energy, using silicon semiconductor wafers (**energy dispersive spectrometers [EDS]**). WDS has better resolution of the elements but requires a separate crystal and detector channel for each element to be analyzed. Most WDS “probes” have four or more channels, each of which, after finishing the counting for one element, are re-tuned by computer to another wavelength and begin collecting again for a different element. After two to four such passes per channel, the excited sample spot has been analyzed for the 8 to 14 principal elements found in most minerals. EDS systems are less accurate than WDS systems, but they are compact and require only one small detector port. An EDS system can be mounted on a scanning electron microscope (SEM), and it adds to existing imaging devices the ability to do chemical analyses. The main advantage of EMP is that it can provide very rapid and reasonably accurate mineral analyses. Further, we can use it to analyze a traverse across a mineral, from core to rim, and determine the nature of any chemical zoning, if present. With advanced computer-driven electron beams, it is possible to create element distribution “maps” that portray the relative concentration of various elements of interest in a small area of the thin section (two color maps for a garnet are shown on the back cover of this text). The EMP has the further advantage that it is nondestructive, in that the thin section is undamaged (other than a few  $<20 \mu\text{m}$  pits if the electron beam intensity is high). The drawbacks are that it is not appropriate for whole-rock analysis, and the detection limits are high enough that it is not good for many trace elements.

A variation on the EMP idea is the **ion microprobe (IMP)**. This device bombards a sample surface with a stream of oxygen ions, literally blasting a crater and ionizing the target area. The ions are released into a mass spectrometer and analyzed by mass. This produces both an elemental analysis and an isotopic analysis. Ion probes are very expensive, and there are only a handful of them in operation, mainly in large government-supported laboratories.

Today, whole-rock analysis is done quickly and routinely, usually using a combination of XRF and ICP techniques. Some elements are more reliably analyzed by XRF and others by ICP. AA and colorimetry are also used in some laboratories. For a list of elements and the appropriate technique(s) for each, see Rollinson (1993). Mineral analyses are done on the EMP, and isotopic analysis requires a mass spectrometer. Oxidation states cannot be determined by using spectroscopic techniques, so  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , when desired, must still be determined by titration.

## 2 ANALYTICAL RESULTS

Raw data from instrumental techniques are in counts per second of an emitted spectral line (or the decrease in emission associated with absorption), and there is always some statistical variation in the output. Any two consecutive counting intervals produce slightly different total counts, both for the sample and the standards. When combined with electronic fluctuations in the instruments, a certain level of statistical uncertainty is invariably associated with the determined concentration for each element. Because the elements are analyzed separately, the resulting analysis would not be expected to total exactly 100.000%. In addition, not all elements are routinely determined. For example, electron microprobes require that the samples be coated with an electrically conductive material (typically carbon) to disperse the electron buildup resulting from the beam, so it is not possible to analyze for carbon (unless another coating is used). Also, the windows on the detectors, required to maintain a vacuum in them, absorb the weak x-rays produced by light elements (usually below atomic number 9), so these elements are not determinable using XRF or the microprobe. The concentration of oxygen is not determined directly either because it has an atomic number of 8, and it is present in the atmosphere and in the water in which samples are dissolved for AA and ICP. Rather, oxygen is calculated on a charge-balance basis and added to the analysis in the proportion required to balance the cations. If an analysis is less than 100%, it may be because of analytical uncertainty, unanalyzed constituents, or both.

Even though *elemental* concentrations are determined using instrumental techniques, the major and minor elements for silicate rocks and minerals are routinely reported as *wt. % oxides* (grams of the oxide per 100 g of the sample). This practice is a holdover from the days of wet chemical analysis, when the precipitates were typically oxides and were weighed to determine the concentration. Certainly, most cations in our oxygen-rich atmosphere are bonded to oxygen, and this is also true for cations in silicate minerals, so reporting the analyses as oxides makes a certain degree of sense. Oxides were so commonly addressed that most common ones have specific names ( $\text{SiO}_2$  = "silica,"  $\text{Al}_2\text{O}_3$  = "alumina,"  $\text{MgO}$  = "magnesia,"  $\text{CaO}$  = "lime,"  $\text{Na}_2\text{O}$  = "soda,"  $\text{K}_2\text{O}$  = "potash,"  $\text{P}_2\text{O}_5$  = "phosphate;" oxides of iron and manganese have no names . . . unless you consider "rust"). Our interest in rock and mineral compositions, however, is focused on the flow, exchange, and distribution of atoms (or ions), and these atomic (or molecular) proportions may be obscured by atomic

mass differences when reported in wt. %. The first step in most chemical calculations is thus to convert wt. % to atomic proportion. Some works report analyses or chemical ratios in molecular proportions directly, and care must be taken to notice the difference. Trace element concentrations are typically reported in *parts per million (ppm)* of the *element*, not the oxide. This is still on a weight basis, so ppm equals grams of the element per million grams of sample. A convenient conversion to remember is *1 wt. % is equivalent to 10,000 ppm*.

The first numeric column of Table 1 represents a typical analysis taken directly from the literature, in this case of a basalt. The major and minor element *oxides* are usually combined and listed in order of decreasing valence. Error estimates are seldom reported, but most analyses are good to three significant figures, with an error in the range of 1 to 5 relative percent. **Relative percent** means the percentage relative to the total *reported for that element*. For example, a relative error of 3% in the value for MgO in Table 1 equals 3% of 6.44, or 0.19 **absolute percent**. Thus the analysis might be expressed as  $\text{MgO} = 6.44 \pm 0.19$  wt. %. Many authors simply report analyses to two decimal places, so the values for silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and lime ( $\text{CaO}$ ) are given to four significant figures, which is more precise than can be justified by analytical uncertainty.

$\text{H}_2\text{O}$  is the most common volatile constituent in most rocks and minerals and may be expressed as  $\text{H}_2\text{O}^+$  and  $\text{H}_2\text{O}^-$ .  $\text{H}_2\text{O}^+$  represents **structural water**, present as  $\text{OH}^-$  bonded in

**TABLE 1** Chemical Analysis of a Basalt (Mid-Atlantic Ridge)

Oxide	Wt. %	Mol Wt.	Atom Prop.	Atom %
$\text{SiO}_2$	49.2	60.09	0.82	17.21
$\text{TiO}_2$	2.03	79.88	0.03	0.53
$\text{Al}_2\text{O}_3$	16.1	101.96	0.32	6.64
$\text{Fe}_2\text{O}_3$	2.72	159.70	0.03	0.72
$\text{FeO}$	7.77	71.85	0.11	2.27
$\text{MnO}$	0.18	70.94	0.00	0.05
$\text{MgO}$	6.44	40.31	0.16	3.36
$\text{CaO}$	10.5	56.08	0.19	3.93
$\text{Na}_2\text{O}$	3.01	61.98	0.10	2.04
$\text{K}_2\text{O}$	0.14	94.20	0.00	0.06
$\text{P}_2\text{O}_5$	0.23	141.94	0.00	0.07
$\text{H}_2\text{O}^+$	0.70	18.02	0.08	1.63
$\text{H}_2\text{O}^-$	0.95	18.02	0.11	2.22
(O)			2.82	59.27
Total	99.92		4.76	100.00
	<b>ppm</b>			<b>ppm</b>
Ba	5	137.33	0.04	0.8
Co	32	58.93	0.54	11.4
Cr	220	52	4.23	88.9
Ni	87	58.7	1.48	31.1
Pb	1.29	207.2	0.01	0.1
Rb	1.14	85.47	0.01	0.3
Sr	190	87.62	2.17	45.6
Th	0.15	232.04	0.00	0.0
U	0.16	238.03	0.00	0.0
V	280	50.94	5.5	115.5
Zr	160	91.22	1.75	36.9

Data from Carmichael et al. (1974), p. 376, col. 1.

hydrous minerals such as amphiboles and micas.  $\text{H}_2\text{O}^-$  is adsorbed, or trapped along mineral grain boundaries. Both are too light to be detected by spectrographic means.  $\text{H}_2\text{O}^-$  can be driven off by heating the powdered sample to about  $100^\circ\text{C}$  and determined by the weight loss accompanying this process. **Loss on ignition (LOI)** is the weight loss that occurs when the powdered sample is heated to about  $800^\circ\text{C}$ , at which point all of the remaining volatiles, including structural volatiles ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , etc.), are released. If LOI is determined without first weighing the post- $100^\circ\text{C}$  sample, LOI will include  $\text{H}_2\text{O}^-$  as well as the bonded volatile elements. Therefore, heating is usually done in two steps.

The total of 99.92 in Table 1 suggests that the analysis is good. If all major and minor elements are determined, an analysis is generally considered to be acceptable if the total falls between 99.8 and 100.2%. A total of 100.00%, on the other hand, does not mean that an analysis is error free but that the statistical errors for each element happened to offset in such a way as to coincidentally produce this total. On the other hand, a total of 94% may not be significantly in error, either, if a major constituent is not analyzed. For example, because  $\text{CO}_2$  is rarely analyzed in rocks or minerals, a good analysis for a limestone may total only 56% (the wt. % of CaO in  $\text{CaCO}_3$ ). Because microprobed amphiboles are hydrous, they commonly have totals near 98%, and micas may not have totals much higher than 96%.

Trace elements, when determined, are listed (typically in ppm) after the major/minor elements. Even when considered cumulatively, they are unlikely to compose a significant proportion of the sample, so they are generally not included in the total. It would be very time-consuming and expensive to determine *all* of the trace elements present in a rock or mineral, so one must choose the ones to be analyzed based on the purpose for which the analysis is intended. Trace elements are determined only when necessary, and many published whole-rock analyses do not include them. ICP and XRF analyses have become common, and the number of analyses that include trace elements is increasing because it requires little extra time to produce them. Isotopic analysis is still slow and expensive, so it is done only for specific applications. Because the electron microprobe does not analyze sparse trace elements or isotopes, the number of mineral analyses that include either is miniscule.

I have added the remaining two numeric columns in Table 1 to illustrate the conversion from wt. % oxides to atomic % Column 3 contains the molecular weights of the oxides (or elements for the trace elements). You can determine these by adding the atomic weights in the periodic table on the inside front cover. Column 4, atomic proportions, is calculated by dividing column 2 by column 3 (weight to moles) and multiplying each by the number of cations in the oxide formula. For Si, this number is  $49.2/60.09$ , for Al it is  $2(16.09/101.96)$ , etc. Oxygen is totaled in a similar fashion for each oxide (2 for each Si atom +  $3/2$  for each Al, etc.). These atom proportions are then added for the major and minor elements only (assuming that the trace elements have a negligible effect). Each value in column 5 is the value in column 4 divided by the sum of column 4 multiplied by 100, which converts the atom proportions

to atomic %. Converting to a molecular basis but retaining the expression as mol % oxides is easier. We need only divide each wt. % by the molecular weight and then normalize each to 100.

### 3 MAJOR AND MINOR ELEMENTS IN THE CRUST

Based on compilations of published rock analyses and estimates of the relative proportions of the rocks represented, a number of investigators have attempted to produce a representative analysis of the continental crust. Table 2 is one such example (for major elements only). Column 2 is an average of the estimates (expressed as oxides) from Poldervaart (1955) and Ronov and Yaroshevsky (1976). I calculated the approximate atomic % from these values in the manner discussed above. Note that these eight elements constitute nearly 99% of the total crust, so it should not be surprising to find that these elements are the major elements of most rocks and minerals that we shall encounter. Certainly, O and Si dominate, as reflected in the high percentage of silicate minerals in the crust. When expressed as oxides, seven major oxides would be expected to compose most crustal materials (column 2 in Table 2).

Table 3 shows some examples of the major and minor element compositions of some common igneous rocks, ranging from ultramafic to granitic and alkalic. These examples are taken from a study by LeMaitre (1976b), in which he determined average compositions based on more than 26,000 published analyses. Note that the seven major element oxides in Table 2 make up essentially all of the rocks listed. If the peridotite is representative of the mantle, these oxides are the dominant mantle constituents as well.  $\text{TiO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{MnO}$ , and  $\text{P}_2\text{O}_5$  are the other oxides typically present in minor concentrations, and they compose the minor elements of most igneous rocks.  $\text{Cr}_2\text{O}_3$  may be a minor element in ultramafics, but it is typically a trace element in most rocks. Fe is the only major or minor element that occurs widely in two different valence states. The ratio of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  increases with the **oxygen fugacity** in the rock or melt at equilibrium. Because  $\text{Fe}^{3+}$  is concentrated in Fe-Ti oxides, rocks with relatively high oxygen fugacities have less Fe available for silicates, which will reduce the mafic silicate content of a rock. When the titration required to determine oxidation state has been performed, Fe is reported as  $\text{Fe}_2\text{O}_3$

**TABLE 2** Estimated Relative Abundances of the Major Elements in the Continental Crust

Element	Wt. % Oxide	Atomic %
O		60.8
Si	59.3	21.2
Al	15.3	6.4
Fe	7.5	2.2
Ca	6.9	2.6
Mg	4.5	2.4
Na	2.8	1.9
K	2.2	1.0
Total	98.5	98.5

After Poldervaart (1955) and Ronov and Yaroshevsky (1976).

**TABLE 3** Chemical Analyses of Some Representative Igneous Rocks

Oxide	Peridotite	Basalt	Andesite	Rhyolite	Phonolite
SiO <sub>2</sub>	44.8	49.2	57.9	72.8	56.2
TiO <sub>2</sub>	0.19	1.84	0.87	0.28	0.62
Al <sub>2</sub> O <sub>3</sub>	4.16	15.7	17.0	13.3	19.0
Fe <sub>2</sub> O <sub>3</sub>	1.36	3.79	3.27	1.48	2.79
FeO	6.85	7.13	4.04	1.11	2.03
MnO	0.11	0.20	0.14	0.06	0.17
MgO	39.2	6.73	3.33	0.39	1.07
CaO	2.42	9.47	6.79	1.14	2.72
Na <sub>2</sub> O	0.22	2.91	3.48	3.55	7.79
K <sub>2</sub> O	0.05	1.10	1.62	4.30	5.24
H <sub>2</sub> O <sup>+</sup>	0.0	0.95	0.83	1.10	1.57
Total	99.36	99.02	99.27	99.51	99.20

Peridotite: average for Lizard (Green, 1964); other averages from LeMaitre (1976a).

(Fe<sup>3+</sup>, or *ferric*, iron) and FeO (Fe<sup>2+</sup>, or *ferrous*, iron). When it hasn't, most authors calculate all Fe as FeO\* (or FeO<sub>T</sub>: the asterisk and T subscript indicate that all Fe has been converted mathematically to FeO). Fe<sub>2</sub>O<sub>3</sub>\* may also be used; it means that all Fe is converted and reported as ferric. If we want to compare the Fe content of analyses using different conventions, Fe<sub>2</sub>O<sub>3</sub> can be converted to FeO by multiplying by 0.899. FeO can be converted to Fe<sub>2</sub>O<sub>3</sub> by multiplying by 1.1113. For example, we can convert Fe<sub>2</sub>O<sub>3</sub> to FeO for the peridotite in Table 3, and add it to the remaining FeO:

$$\text{FeO}^* = \text{FeO} + 0.8998 \cdot \text{Fe}_2\text{O}_3 = 6.85 + 0.8998 \cdot 1.36 = 8.07$$

Heating to determine LOI oxidizes some of the Fe, so Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios should either be determined before LOI, or Fe should be reported as total Fe.

Note in Table 3 that MgO and FeO\* decrease as silica and alkalis increase, going from a peridotite to a rhyolite. This is a common mafic-to-silicic trend in igneous rocks. Of course, this variation is reflected in rock mineralogy as well. The more silicic rocks generally contain more alkali feldspars plus quartz and fewer mafic minerals. The relationship between the composition of a rock and the compositions of its constituent minerals should be obvious: If we were to analyze all of the minerals that are in a particular rock, we could calculate the composition of the rock by combining the mineral analyses, factored for their percentage in the rock. Of course, it is much easier (and more accurate) to simply obtain a whole-rock analysis.

For volcanics, which may have a considerable glassy or amorphous component, a chemical analysis may be required if we are to discern the rock type. Many of the volcanics used for data in the averages presented in Table 3 were not entirely crystalline. Most of the rhyolites were either tuffs or glassy rocks, with very few minerals. They can best be identified as rhyolites based on their chemical com-

position. For example, if you take the silica content of the rhyolite in Table 3 (72.82%) and total alkalis (Na<sub>2</sub>O + K<sub>2</sub>O = 7.85%), and plot these values on a chemical classification of volcanics, they plot in the rhyolite field.

The chemical composition of rocks also permits the comparison of igneous rocks with their altered and metamorphosed equivalents. Although the mineral composition may vary with changes in pressure and temperature, the bulk rock chemical composition should remain largely unaltered (at least with respect to some critical, or immobile, elements). This may allow us to identify the original igneous precursor to a number of metamorphic rocks and perhaps correlate modern and ancient igneous provinces. In many cases, we may also be able to document the chemical changes that accompany alteration and metamorphic processes.

#### 4 NORMATIVE MINERALS

Because many volcanic rocks are too fine grained for us to recognize their mineral constituents, even microscopically, and may have a significant glassy component, a method exists to calculate an idealized mineralogy for such rocks so they can be compared with coarse-grained rocks. The mineralogy of coarse-grained rocks may also vary with pressure and temperature, making direct comparison difficult. The **norm** is an attempt to reconcile these differences to a consistent and limited set of minerals that reflect compositional variables only, facilitating the direct comparison of a broad spectrum of rocks. Norms can also be used to calculate an approximate mineralogy from published whole-rock analyses when the mineralogy is not reported. Because the norm is calculated on an anhydrous basis, it can be used to compare the mineralogy of rocks with different H<sub>2</sub>O contents. Because they reflect the chemical composition of a rock, norms have also been used in a number of classification schemes.

The norm was first developed by C. W. Cross, J. P. Idings, L. V. Pirsson, and H. S. Washington (Cross et al., 1902) at the beginning of the 20th century, as part of an elaborate igneous rock classification scheme. Their norm is called the **CIPW norm**, from the first letters of their last names. Although the norm-based classification scheme never met with popular approval, the norm itself lives on. They based their normative minerals on the typical minerals that might be expected to crystallize from an anhydrous melt at low pressure. Since that time, a number of variations and alternative norms have been proposed, some for special circumstances (such as high pressure). The original CIPW norm is still the one in standard use in the United States.

The *norm* is not to be confused with the *mode*. The **mode** is the actual mineral composition of a rock, based on the observed volume %. The norm is the idealized mineralogy calculated from the chemical composition of a rock. Because the chemical composition is reported in wt. % of the oxides, the CIPW norm is expressed in wt. % of the normative minerals. The mode and the norm may differ for a number of reasons, but the volume versus weight proportion is a consistent difference that distorts the relationship between a mode and a norm. The norm exaggerates the denser minerals compared to the mode. We could convert from wt. % to volume % by using mineral densities, but this is seldom done. An alternative norm, the **cation norm** or **Barth-Niggli norm**, expresses the normative minerals on an atomic basis. This superior method is popular in Europe.

The CIPW norm is calculated by following a rigidly prescribed set of rules that allocates the various oxides to a set of end-member and solid-solution minerals. To accomplish this, it combines the thrilling processes of mineral stoichiometry and business accounting. Such a rigid formal methodology is an ideal application for a computer program, and a number of norm programs are available. Oxygen fugacity and the oxidation state of Fe are generally not known, and estimates must usually be supplied for reasonable normative mafic mineral contents. Irvine and Baragar (1971) discussed a method to estimate the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio for a norm. Once computerized, the conversion between CIPW and cation norms should be an easy process, as is the conversion to approximate volume % (if mineral densities are available) for comparison to modes.

The norm simplifies and organizes the chemical composition of a rock in a way that emphasizes certain subtle chemical characteristics, particularly (but not limited to) **silica saturation**. A “silica-oversaturated” rock is one that contains quartz (or another silica polymorph) in the mode as a stable phase. “Silica-undersaturated” rocks contain a mineral that is incompatible with quartz, such as olivine or a feldspathoid. A rock that is just silica saturated may contain a trace of quartz but no undersaturated phase. If you look at the analyses in Table 3, which are silica saturated? Certainly, the degree of silica saturation must be correlated with the silica content in the analysis, but there is no simple silica concentration that will determine this. Whether quartz (or a polymorph) forms depends upon the silica content *but also*

*on what other elements are competing for silica to form a variety of silicate minerals.* For example, a rock with 100% silica will be pure quartz. If we then add 20% MgO, this combines with the silica to form enstatite. We could then determine whether free quartz would remain by calculating how much silica, if any, is present after a molecule of  $\text{SiO}_2$  was apportioned to each molecule of MgO to create  $\text{MgSiO}_3$ . If rocks contained only MgO and  $\text{SiO}_2$ , then there would be a critical silica concentration that we could relate to silica saturation: Any rock with over 60 wt. % silica (the fraction of silica in enstatite) has excess  $\text{SiO}_2$ , and would thus have quartz in it. But if we add  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ , they also combine with silica to form albite. Each atom of Na consumes three atoms of Si (and one of Al) to create albite ( $\text{NaAlSi}_3\text{O}_8$ ). Now the relation between silica concentration and saturation gets complicated and depends on the Si:Mg:Na:Al ratios. During the norm calculation, silica is sequentially apportioned to the various silicate minerals in a fashion similar to that just discussed for enstatite. The last mineral to be determined is quartz, which represents any excess silica left after the other oxides have had  $\text{SiO}_2$  allocated to them. Thus a norm can be used for a variety of rock compositions to estimate silica saturation. If quartz appears in the norm, the rock is considered oversaturated. Other normative minerals can be used to indicate silica undersaturation, high alkalinity, excess alumina content, etc. Many other aspects of rock chemical composition can be indicated by the various normative minerals.

The norm is held in varying levels of esteem by petrologists. Some value it highly and use it both to compare and classify igneous rocks. Others think it is outdated and adds little to the discussion of chemical characteristics that is not already apparent in a chemical analysis. Whether or not we like the norm, its common use in the literature requires that we be familiar with it. You will also see that it has some uses in this chapter. All of us “old timers” have calculated norms by hand, and many of us also require our students to do so. Whether this is because of the “you can’t understand it well until you do it” philosophy or “misery loves company” is difficult to tell. You can calculate a norm from an analysis such as those in Table 3 by following the procedure in Appendix B. By doing so, you can become familiar with the process and thereby get a better understanding of how to interpret the results. Problem 3 of this chapter is an alternative way to understand how the norm works without having to perform any arduous calculations.

## 5 VARIATION DIAGRAMS

Suppose you are engaged in a research project mapping and evaluating a sequence of volcanic rocks in a volcanic terrane, consisting of several small vents, cones, and small flows. You suspect the rocks to be genetically related to some local volcanic process or event of limited duration. You carefully map individual flows and collect a **suite** of rocks (a collection that is either genetically related or representative of an area) with



samples from each flow and cone layer. Now that it is possible to generate chemical (or mineralogical, geophysical, structural, etc.) data rather rapidly, and in quantity, it is possible to become swamped by your own data. Let's say you analyze all of your rocks and end up with more than 100 analyzed samples. Using a table of chemical analyses for a suite of rocks, similar to Table 3, is an excellent way to organize the data, but it is often difficult to see important trends, particularly if you have many analyses. When data for a series of cogenetic volcanic or plutonic rocks are analyzed, they usually show significant chemical variation. It thus becomes critically important to be able to display the data in a fashion that allows you to recognize trends in the variation so that you can describe and interpret them. There is no single best way to display data, and indeed it is something of an art. The objective is to find the parameters that show systematic variation so that you can investigate the underlying causes. Diagrams that do this are called **variation diagrams**.

There are three common formats for variation diagrams of chemical data in petrology. In the first, the **bivariate (Cartesian, or x-y) plot**, two parameters are plotted, one vertically (called the ordinate, or y-axis) and one horizontally (called the abscissa, or the x-axis). In the second, the **triangular diagram**, we can represent three parameters, one at each corner, but they can show only *relative* proportions, not absolute quantities, because the three parameters must be normalized so that they sum to 100% in order to plot as a unique point. The third common type of diagram is the *normalized multi-element diagram*.

Any correlations or trends in bivariate or triangular diagrams show up in the pattern of plotted points (if we choose the parameters wisely). More dimensions can be represented by contouring (as was done for temperature in the three-component phase diagrams), or projecting, but the diagrams can quickly become so complex that the benefits gained by adding meaningful data are quickly overcome by the loss in simplicity and the ability to visualize the correlations.

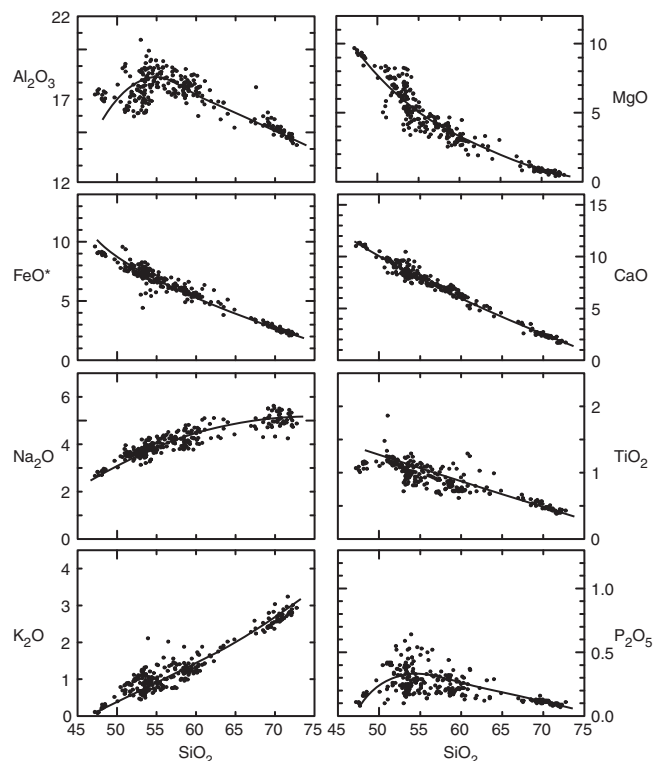
Additional chemical data can also be represented by combining chemical constituents that behave in a similar fashion (such as FeO + MgO + MnO as a single component). Of course, a compromise is involved when we do this as well. We can get some additional data, but we lose the ability to focus on effects attributable to individual constituents. There is no unique way to display data, and researchers are continually inventing creative ways to do it. Computers are useful in this process, allowing us to rapidly select and display data in a variety of formats, searching for correlations or patterns. Variation diagrams not only help us to recognize trends in geochemical data, but they can also help us to interpret recognized trends and evaluate the process or processes responsible.

## 5.1 Bivariate Plots

Any chemical constituents, such as major elements, trace elements, or even combinations of elements and element ratios, can be compared on bivariate diagrams. Perhaps the first such

diagram applied to petrologic chemical data was the **Harker diagram**, first used by Iddings (1892b) on a molecular basis but named after British petrologist Alfred Harker, who used weight percents and advocated their broad usage (Harker, 1900). This simple x-y diagram, which plots wt. % silica as the abscissa against the other major oxides, is still one of the most common variation diagrams in use today. Figure 2 is an example of a Harker diagram for the volcanic rocks of Crater Lake/Mt. Mazama. The first things that one notices in Figure 2 are that the rocks from Crater Lake span a significant compositional range (from basalts to rhyolites) and that there is a smooth trend in the variation of each of the major oxides. It would certainly require considerable study of a table of analytical results before one could recognize these trends. The diagram makes this obvious. Of course, there is some scatter, a combination of analytical error and the type of variation generally found in nature. Rarely in geology do data fall exactly on a nice line or curve. Nonetheless, the trends in Figure 2 are remarkably clear. Curves have been drawn for the trends of each oxide as a best fit to the data.

The smooth trends strongly suggest that the lavas at Crater Lake are genetically related in some fashion and that some process is at work, perhaps in a shallow magma chamber, that causes the continuous variation. **Primary magmas** are those derived directly by partial melting of some source, and they have no characteristics that reflect the effects of subsequent differentiation. Unless specified otherwise, the source is presumed to be the mantle. Magmas that have experienced some form of chemical differentiation along the trends in Figure 2 are referred to as **evolved magmas** or



**FIGURE 2** Harker variation diagram for 310 analyzed volcanic rocks from Crater Lake (Mt. Mazama), Oregon Cascades. Data compiled by Rick Conrey (personal communication).

**derivative magmas.** Magmas that are not very evolved are called **primitive**. The **parental magma** corresponds to the most primitive rock found in an area and, thus, the magma from which we suppose the others are derived.

Harker (1909) proposed that  $\text{SiO}_2$  increased steadily with magmatic evolution, and he thus used it as the abscissa to indicate the extent of evolution. The magma with the lowest silica content in Figure 2 is thus accepted as the *parental* magma. It may be impossible, however, to demonstrate conclusively that it is a true *primary* magma because it may also have evolved during ascent.

Although we cannot directly observe the dynamics of a magma chamber, we can gain considerable insight into the processes by studying the chemical characteristics of the various products of natural igneous systems, such as at Crater Lake or the Tuolumne Intrusive Series. One test is to determine whether the chemical and/or mineralogical trends are consistent with some process, such as crystal settling, mixing of two magmas, assimilation of the wall rock, etc.

Consider the manner in which a liquid varies in composition as minerals form during cooling of some simple experimental systems. If the crystals are removed from the melt, the process is called **fractional crystallization** (or **crystal fractionation**), and the composition of the remaining liquid system follows the **liquid line of descent**, usually along cotectic curves toward the eutectic minimum-temperature liquid composition. For most of the 20th century, in large part because of the great influence of N. L. Bowen, petrologists considered fractional crystallization to be the predominant method by which magmas **differentiate**, or change composition, in nature. If such a process were applicable to the rocks at Crater Lake, we could imagine a magma chamber at some depth beneath the area, in which early-forming minerals were separating from the magma (perhaps by sinking), and the evolving liquid escaped periodically to the surface, forming the cones, flows, and pyroclastics in the area.

Let's assume for a moment that fractional crystallization is responsible for the trends shown in Figure 2. Can we relate the observed trends to a reasonable sequence of extracted minerals? The decrease in  $\text{MgO}$ ,  $\text{FeO}^*$ , and  $\text{CaO}$  as  $\text{SiO}_2$  increases is consistent with the removal of early-forming minerals from the cooling liquid.  $\text{MgO}$  and  $\text{FeO}^*$  are incorporated into the typically early-forming olivine or pyroxene.  $\text{CaO}$  may have been removed by either a calcic plagioclase, a clinopyroxene, or both.

The apparent increase in  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  are artifacts of the necessity that the analyses must all total 100%. As the other elements are removed, any elements that are not incorporated into a crystallizing phase are **conserved**, or concentrated in the later liquids. These elements do not necessarily increase in any absolute sense; they just compose a greater proportion of the remaining liquid. For example, imagine that you have a bag containing an equal number of red and green candies. If you prefer the red ones, and you eat 10 of them for every 1 green candy you eat, the ratio of green to red candies remaining in the bag increases with time.

Without adding any more candy, you may have increased the *proportion* of green ones from 50 to 95%. On a *percentage* basis, it would appear that the green candies have increased, whereas they have actually *decreased* on an *absolute* basis (because you ate 1 for every 10 red ones). The fact that analyses must total 100%, and the effect this has on apparent trends in variation diagrams, is referred to as the **closure problem**, and it has been discussed in detail by Chayes (1964). The increasing  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  trends in Figure 2 suggest that the albite component in any plagioclase that may have formed and settled was low and that potassium feldspar either did not form or was very minor. Although the closure problem tells us that alkalis and other components that increase with progressive magmatic evolution need not be added to increase in percentage, this does not preclude their being added by assimilation or mixing processes either.

The  $\text{Al}_2\text{O}_3$  curve shows an interesting trend. First it increases, and then it decreases. Because  $\text{CaO}$  decreases continuously, we can reconcile these trends by speculating that clinopyroxene was removed early on, removing  $\text{Ca}$ , but not  $\text{Al}$ , and plagioclase began to crystallize later, removing both  $\text{Ca}$  and  $\text{Al}$ .

Many geologists believe that Harker diagrams amply demonstrate the crystal fractionation process. When we make analyses of igneous processes based on variation diagrams, however, we should be careful to distinguish *observations* from *interpretations*. Only then can we be clear on what is interpretive, and perhaps then we can explore the assumptions upon which the interpretations are based. The interpretation that relates the trends to a crystal fractionation process assumes that these analyses represent *consanguineous* lavas (i.e., lavas with a common ancestor) erupted from a magma chamber beneath the volcano at various stages of progressive evolution. This assumption is supported, but not proved, by the close spatial and temporal association of the rocks. Our interpretation further assumes that the silica content is related to the evolutionary process in such a way that the wt. %  $\text{SiO}_2$  increases as the magma evolves and that crystal fractionation is the sole process involved. By recognizing these assumptions, we can return to the chemical data, or even the petrography, or the field, and evaluate them in light of our assumptions and interpretations.

For example, if a crystal fractionation process is indeed responsible for the trends, care should be taken if porphyritic or coarse-grained rocks are included because these rocks may still include minerals that should have been removed by fractionation. In the case of porphyritic rocks, they may include some early-forming minerals and not others, if, perhaps, mineral density controlled the phenocryst separation (sinking) process. Some porphyritic rocks may actually have *accumulated* phenocrysts as they settled from higher levels or floated. Such rocks would plot off the true liquid line of descent, and the fit on a Harker diagram might improve if these rocks were excluded.

Phenocrysts of the minerals that are inferred to be fractionating should either be found in some of the lavas or be

shown by experiments to be stable phases in the magmatic systems in question. The trends in variation diagrams should also be consistent with experimental cotectic liquid lines of descent. Further, the more evolved rocks should be younger than the less evolved ones. Likewise, the trends should be amenable to *quantitative* simulation based on extraction of specific proportions of minerals that are naturally, experimentally, or theoretically compatible with the types of magmas present, as we shall discuss shortly. Can this be substantiated in the field? If not, how must the model be amended?.

In many systems, including layered mafic intrusions (where we can document the fractionation process) and several volcanic series, the silica content does not increase during most of the differentiation process. In such cases, a different index should be used, one that is more sensitive to the particular process at hand. Table 4 lists several chemical parameters that have been applied by various investigators as measures of progressive differentiation for some igneous province. Most of the indices are based on major elements, but a number of trace elements are also not incorporated into early crystallizing phases and thus concentrate in late melts. The high precision of modern analytical techniques has led several investigators to prefer some of these trace elements, such as Zr, Th, or Ce, as differentiation indices.

Any of the indices in Table 4 can be used as the abscissa in a bivariate diagram if the objective is to document magmatic evolution in an igneous series. Because different systems evolve in different ways, we might not expect a single parameter, such as wt. % SiO<sub>2</sub>, to work equally well in them all. Some may work better than others throughout a particular area, or some may be more sensitive at a particular stage of evolution. For example, the indices based on Mg/Fe ratios are most effective in the early evolution of mafic systems (where SiO<sub>2</sub> varies little), whereas the more alkaline parameters generally work best in the late stages of igneous evolution.

**TABLE 4** Some Indices of Differentiation Proposed in the Literature

Name	Formula
Felsic Index	$100 \frac{(\text{Na}_2\text{O} + \text{K}_2\text{O})}{(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})}$
Larson Index	$\frac{1}{3} \text{SiO}_2 + \text{K}_2\text{O} - (\text{FeO} + \text{CaO} + \text{MgO})$
Nockolds Index	$\frac{1}{3} \text{Si} + \text{K} - (\text{Mg} + \text{Ca})$
Mafic Index (MI)	$\frac{(\text{Fe}_2\text{O}_3 + \text{FeO})}{(\text{Fe}_2\text{O}_3 + \text{FeO} + \text{MgO})}$
MgO	Wt. % MgO
M (or Mg#, Mg', Mg*)	$100 \frac{\text{Mg}}{(\text{Mg} + \text{Fe}^{2+})}$ (can be fraction or %)
Solidification Index	$100 \frac{\text{MgO}}{(\text{MgO} + \text{Fe}_2\text{O}_3 + \text{FeO} + \text{Na}_2\text{O} + \text{K}_2\text{O})}$
% Normative Plag.	Normative <i>pl</i>
Differentiation Index	Normative $q + or + ab + ne + ks + lc$
Normative Felsic Index	Normative $100 \frac{(ab + or)}{(ab + or + an)}$
Conserved Trace Element	Zr, Th, Ce

Variation diagrams are extremely useful, both descriptively and as a basis for interpretation, but they should be used as the *first step* toward rigorous interpretation. Crystal fractionation is not the only method by which magmas differentiate. The wealth of recent geochemical data, in fact, suggests that fractional crystallization may not be the principal process responsible for subduction-related magma evolution, such as at Crater Lake. Conrey (unpub. manuscript), in a review of extensive chemical data, concluded that, although fractional crystallization may be important at the primitive end of the spectrum, mixing of mafic magma (mantle melts) and silicic magma (crustal melts) is the dominant process in the evolution of subduction-related magma series.

In addition, the differentiation process may not be restricted to a single shallow magma chamber, which is merely the last place of residence of a rising magma. New influx of mafic parental magma from a deep source may alter, or even reverse, some of the trends. Assessing the various processes that may be responsible for the evolutionary trends apparent in a particular igneous province is an important and difficult job, and the chemical trends are the principal method by which we attempt to distinguish and document them. *Variation diagrams work best when they are carefully designed to test a specific hypothesis.* Because several processes may be contributing to the evolution of a magmatic series, several types of variation diagrams may be employed to analyze the same data.

Careful observations of variation diagrams can provide further benefits as we focus on details in the data. For example, the peaked Al<sub>2</sub>O<sub>3</sub> curve in Figure 2 may simply be a result of the mathematical fit of the curve to data that are widely scattered at the low-silica end. We may want to analyze more rocks with low silica and carefully observe the Al-bearing minerals to provide some better constraint on the curve.

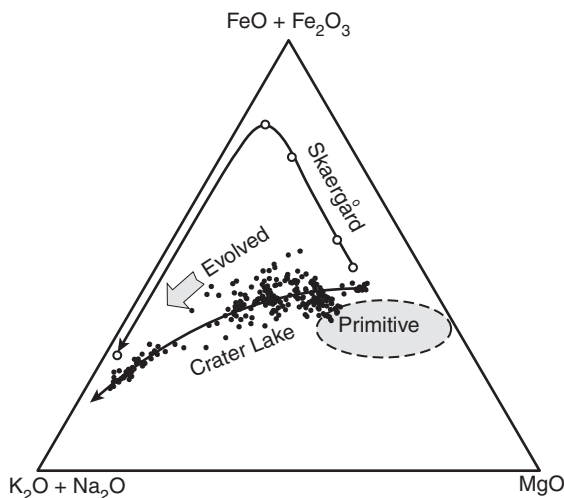
The gap between 62 and 66% SiO<sub>2</sub> is also provocative. Is this simply an accident of sampling, or is it real? If the latter, why? Was there simply a quiescent period during this stage of magmatic evolution, resulting in no eruption of lavas, or is there some developmental or mineralogical reason why no representative rocks exist from this interval? Based on more than 350 analyses from Crater Lake, Bacon and Druitt (1988) found a similar gap in whole-rock analyses but noticed that the *glass* compositions fill this gap and display a more continuous spectrum. Thus the whole-rock gap may be a discontinuity in *crystal* content (the mafics are richer in crystals than the felsics), which, Bacon and Druitt (1988) proposed, reflects a recharge period in the magma chamber, during which eruptions were rare. On the other hand, volcanics with SiO<sub>2</sub> contents between 48 and 58 wt. % are less common than basalts (<48%) and trachytes-rhyolites (>58%) in many subduction-related volcanic areas, not just Crater Lake. This compositional gap in volcanic series is commonly called the **Daly gap** (after Reginald Daly). The gap may be more apparent than real, reflecting the dynamics of fractional crystallization and the phases involved.

The abrupt appearance on an oxide mineral, for example, may cause the liquid line of descent to cross the Daly gap in terms of  $\text{SiO}_2$  content, with only a minor amount of fractionation. When a fractionation index other than  $\text{SiO}_2$  is used, the gap is usually lessened. If magma mixing is responsible for the trends in the more evolved end of the spectrum of subduction-related magma series, the Daly gap may easily be explained by the simple notion that magmas closer to the two mixed end-members are likely to be more common than intermediate mixtures.

In order to have interpretive significance, variation diagrams are best restricted to a single igneous locality or a somewhat broader set of igneous centers that are still apparently related to the same process. The term **petrogenetic province** (or petrographic province) is commonly used to refer to a geographic region in which the igneous rocks are related in space and time and are presumed to have a common genesis. The scope of this term is purposefully left rather vague: a single volcano is generally considered to be a bit restrictive, but the term can range from a specific phenomenon such as Crater Lake to the High Cascade volcanic arc or the Oregon High Lava Plateau, to the Jurassic volcanic arc of the western United States.

## 5.2 Triangular Plots: The AFM Diagram

The most common triangular variation diagram used by igneous petrologists is the AFM diagram (Figure 3), in which A (alkalis:  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ), F ( $\text{FeO} + \text{Fe}_2\text{O}_3$ ), and M ( $\text{MgO}$ ) plot as the corners of the triangle. The AFM diagram used by igneous petrologists should not be confused with the different AFM diagram used by metamorphic petrologists. Igneous AFM diagrams are generally cast on a wt. % basis, but they can also be created on a cation basis. Note that the AFM diagram actually accounts for *four* cation elements and that the relative proportions of Na and K are obscured due to the conviction (or hope) that the total alkali content is more informative than either one separately. Figure 3 includes data for both Crater Lake and the



**FIGURE 3** AFM diagram for Crater Lake volcanics (data from Figure 2) and the Skaergård intrusion, eastern Greenland.

Skaergård mafic intrusion of East Greenland. Here also, trends are noticeable, and the Crater Lake and Skaergård trends are clearly distinguished. Remember from the phase diagram of the olivine system that, for most mafic minerals,  $\text{Mg}/\text{Fe}$  is higher in the solid phase than the coexisting melt. Removal of the solid by fractional crystallization thus depletes  $\text{MgO}$  preferentially from the melt and enriches it in  $\text{FeO}$ , a trend evident in the Skaergård data. Alkalis are typically enriched in evolved liquids and enter into solid phases only during the late stages of crystallization. We can thus recognize the evolution curves on the AFM diagram. The parental magmas, if present, are closer to the  $\text{MgO}$  corner, and the most evolved ones are closer to the alkali corner. Note that, although the Skaergård trend shows a pronounced  $\text{Fe}$  enrichment in the early stages of magmatic evolution, the Crater Lake trend does not.

## 6 USING VARIATION DIAGRAMS TO MODEL MAGMATIC EVOLUTION

So far, our interpretation of variation diagrams has been inferential and qualitative. We have sought minerals capable of extracting certain components that could produce the increases or decreases in the evolutionary trends on variation diagrams. A more satisfactory evaluation would be to quantify the evolutionary process and test the proposed minerals to see if they can really produce the observed patterns. Two methods are commonly employed to assess the effects of mineral fractionation, using variation diagrams for magmatic suites. One, called Pearce element ratios, uses the slopes of variation trends based on fractionating mineral stoichiometry. The other is far more rigorous and varied in approach: direct mass-balance modeling that can be done graphically or by computer. This latter approach goes far beyond simply using variation diagrams, and sophisticated models have been developed.

### 6.1 Pearce Element Ratios (PERs)

Pearce (1968) proposed a method for using chemical data to indicate phases extracted from evolving liquids. This method is entirely empirical and uses element *ratios* to test hypotheses of mineral fractionation in a set of cogenetic analyses. The technique involves plotting on bivariate diagrams the ratios of certain elements, designed to test for the fractional crystallization of a particular mineral or minerals. The denominator of the ratio is always the same for both axes and is usually a single element (but may be more) and *not* contained in the fractionating minerals, but conserved in the remaining melt. This minimizes the closure problem discussed above. The numerators are linear combinations of elements that reflect the stoichiometry of the proposed fractionating mineral or minerals.

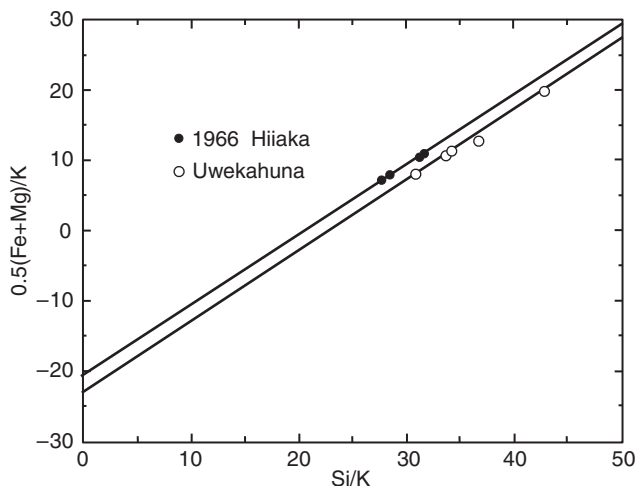
Because most minerals have a fairly simple stoichiometry, separation of a specific mineral will remove certain elements from the remaining melt in the proportion in which they are contained in that mineral, thereby leaving an imprint of that stoichiometry on the chemical variation in

the series of remaining melts that eventually comprise the suite of rocks. Trends on a properly devised PER diagram have slopes that give an immediate and quantitative indication of the mineral(s) that may have fractionated and thereby controlled the chemical variations in the set.

For example, olivine,  $(\text{Fe}, \text{Mg})_2\text{SiO}_4$ , contains  $(\text{Fe} + \text{Mg})/\text{Si}$  in the atomic ratio 2/1, so olivine fractionation removes  $(\text{Fe} + \text{Mg})/\text{Si}$  from the remaining melts in that proportion, defining a trend with a slope of +2 on a plot of  $(\text{Fe} + \text{Mg})/\text{K}$  as the ordinate versus  $\text{Si}/\text{K}$  as the abscissa (on an atomic basis) of the derivative liquids. Either elements or oxides can be used in PER diagrams, as long as molecular proportions are used and not weight percents. Figure 4 is a plot of  $0.5(\text{Fe} + \text{Mg})/\text{K}$  versus  $\text{Si}/\text{K}$  for two sets of Hawaiian basaltic magmas. Because the mafic component is halved in Figure 4, a slope of 1.0, not 2.0, would be in accordance with olivine fractionation. Note that the two sets have distinct original  $(\text{Fe} + \text{Mg})/\text{Si}$  ratios, so they plot as two separate lines, but each fits well to a slope of 1.0, supporting the notion of olivine fractionation within each set.

Like any variation diagram, PERs do not *prove* that a particular mineral is fractionating, or even that fractional crystallization is at work. They merely indicate whether the chemical composition of a suite of lavas is consistent with such a process. PERs are strictly empirical and may be better at excluding mineral extracts than at proving them. When the pattern of points does *not* conform to the slope one would expect from the fractionation of a particular mineral, it provides compelling negative evidence that the magmatic suite is *not* the result of fractionation of that mineral. If the data plot on the predicted trend, then the data are compatible with hypothesis of fractionation of the mineral, but, again, do not prove it.

As a more complex example of the application of PERs, we turn to another set of Hawaiian basalts erupted from Kilauea from 1967 to 1968 (Nicholls, 1990). In this set, Ti, K, and P appear to be conserved, such that  $\text{Ti}/\text{K}$  and



**FIGURE 4** Pearce element ratio (PER) diagram of  $0.5(\text{Fe} + \text{Mg})/\text{K}$  versus  $\text{Si}/\text{K}$  for two Hawaiian picritic magma suites. From Nicholls and Russell (1990).

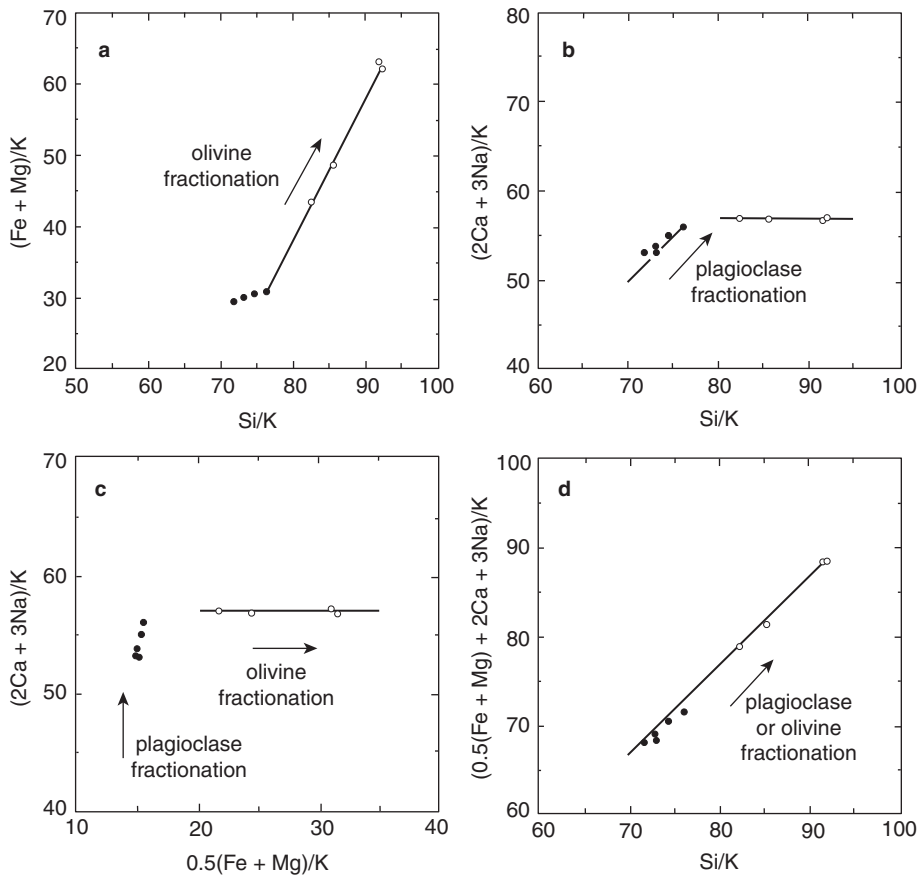
$\text{P}/\text{K}$  remain essentially constant for the set of analyses. This suggests that the set of rocks is genetically related because they have these consistent ratios. Figure 5 is a set of 4 PER diagrams for the Kilauean volcanic rocks. Figure 5a is a plot similar to Figure 4 (except that the mafics are not halved). A slope of 2 is thus compatible with olivine fractionation. Indeed, the picrites (light circles) fall on such a line, but the basalts appear to fall on a line with a shallower slope. This suggests that another mineral is fractionating in the basalts, either along with or instead of olivine.

Figure 5b is a PER diagram designed to test for the fractionation of plagioclase. In anorthite, the ratio of Ca to Si is 1:2. In albite the ratio of Na to Si is 1:3. If we plotted  $\text{Ca}/\text{K}$  versus  $\text{Si}/\text{K}$ , a slope of 0.5 would be compatible with anorthite fractionation. By plotting  $2\text{Ca}/\text{K}$  versus  $\text{Si}/\text{K}$ , a slope of 1 would then be compatible. Because the plagioclase composition also varies as fractionation proceeds, so would the  $\text{Ca}/\text{Si}$  ratio of the plagioclase, the linearity in a  $2\text{Ca}/\text{K}$  versus  $\text{Si}/\text{K}$  diagram would be lost, and a curve would result. If we plot  $3\text{Na}/\text{K}$  versus  $\text{Si}/\text{K}$ , a slope of 1 would also result if albite were fractionating. So if we now plot  $(2\text{Ca} + 3\text{Na})/\text{K}$  versus  $\text{Si}/\text{K}$ , a slope of 1 would result if *any* plagioclase composition between pure anorthite and pure albite were to be fractionating. This has been done in Figure 5b. The dashed line with a slope of 1 closely fits the basalt data, meaning that they are compatible with plagioclase fractionation. The data actually show a slightly shallower slope than the line, suggesting that some other phase is also fractionating. The picrites have a slope of zero, suggesting no plagioclase fractionation in them.

Figure 5c combines Figures 5a and 5b. A vertical line is compatible with plagioclase-only fractionation (no change in Fe or Mg), and a horizontal line is compatible with mafic-only fractionation (no change in Ca or Na). The non-vertical slope of the basalts suggests that a *mafic* phase is fractionating with plagioclase in the basalts because Fe and Mg are affected. Figure 5d is a more comprehensive plot. This repeats the Ca-Na process described above for a variable plagioclase stoichiometry but includes the  $(\text{Fe} + \text{Mg})/\text{Si}$  stoichiometry of olivine to create a combined parameter  $(0.5(\text{Fe} + \text{Mg}) + 2\text{Ca} + 3\text{Na})/\text{K}$  that should vary in a 1:1 ratio with  $\text{Si}/\text{K}$  if any combination of anorthite, albite, and olivine is removed. Figure 5d is compatible with such a process for both the basalt and picrite data. This suggests that olivine fractionates with the plagioclase in the basalts because pyroxene would remove  $0.5(\text{Fe} + \text{Mg})$  versus Si in a 2:1 ratio rather than a 1:1 ratio.

PERs, and the resulting diagrams, can be used to critically evaluate the minerals that might be fractionating to relate a set of cogenetic lavas. The ratios that can be plotted are limited only by the stoichiometry of the minerals and the ingenuity of the investigator. The reader should be aware, however, that any technique involving ratio correlation can be misleading. As pointed out by Chayes (1971), Butler (1982, 1986), and Rollinson (1993), even when a set of variables shows no correlation, *ratios* of those variables with components in common tend to be correlated, sometimes even highly correlated. In other words, because the denominators are the same in both the ordinate and abscissa of PER diagrams, they may indicate a correlation where none really





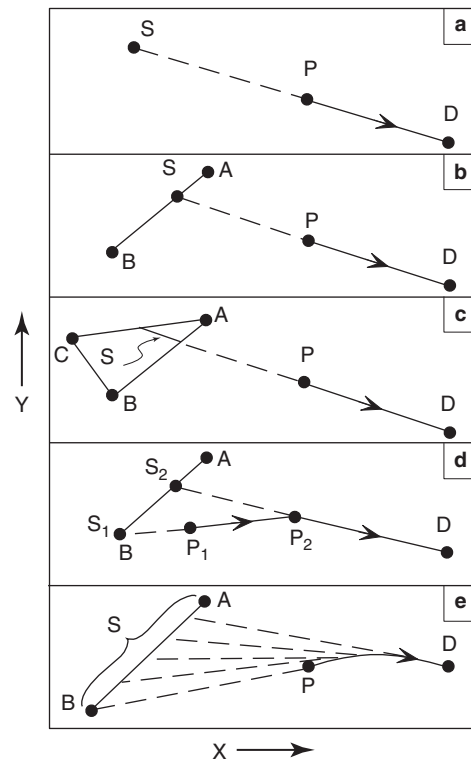
**FIGURE 5** PER diagrams for basalts (dark circles) and picrites (light circles) erupted from Kilauea, Hawaii, between November 1967 and August 1968. After Nicholls (1990).

exists. The PER approach is a good way to test hypotheses and can serve to eliminate a bad hypothesis, but it can only support, not *prove*, a good one. When scattered data on Harker-type diagrams suddenly become linear on PER diagrams, one should not jump to the conclusion that this correlation necessarily demonstrates that a particular mineral is fractionating. Rather, it should be treated as a suggestion, to be evaluated using other textural and chemical criteria.

### 6.2 Graphical and Mathematical Models of Magmatic Evolution

If some process of magmatic evolution is responsible for the trends on variation diagrams, we should be able to quantitatively model the process by subtracting some components to cause the resulting melt to follow the given path. Variation diagrams, particularly bivariate diagrams, provide an excellent basis for these models. In this section, I shall present the methodology, with emphasis on the graphical analysis of crystal fractionation.

The basic method by which a particular model of magma evolution, such as fractional crystallization, is tested is an extension of the simple lever principle to determine the relative proportions of coexisting phases in experimental phase diagrams. The principles involved are illustrated in Figure 6, which shows five different plots on a Harker-type variation diagram, using the hypothetical components X and Y (as either weight or mol %). In all of the diagrams, P represents the parental



**FIGURE 6** Stacked variation diagrams of hypothetical components X and Y (either wt. % or mol %). P = parent, D = daughter, S = solid extract, A, B, C = possible extracted solid phases. For explanation, see text. From Ragland (1989). Reprinted by permission of Oxford University Press.

sample, and  $D$  is the derived one.  $S$  represents the solid bulk composition removed from the parent to produce the derived liquid (the “bulk mineral extract”).  $A$ ,  $B$ , and  $C$  represent the composition of individual minerals that may be in the extract.

In Figure 6a only a single mineral ( $S$ ) forms and is removed from the parent magma ( $P$ ). The composition of the melt, upon loss of  $S$ , must move *directly* away from  $S$ , so that  $S$ - $P$ - $D$  must define a straight line. A derived melt of composition  $D$  can be formed when sufficient  $S$  has been extracted from  $P$ . The  $D/S$  ratio is readily calculated by using the lever principle:

$$\frac{D}{S} = \frac{\overline{SP}}{\overline{PD}} \quad (1)$$

where  $\overline{SP}$  is the length of the line  $S$ - $P$ , etc. Likewise, the percentage of  $D$  and  $S$  are derived by:

$$\%D = 100\overline{SP}/\overline{SD} \quad (2)$$

and:

$$\%S = \overline{PD}/\overline{SD} = 100 - \%D$$

The line  $S$ - $P$ - $D$  is commonly called the **control line** for mineral  $S$  fractionation.

In Figure 6b, *two* minerals ( $A$  and  $B$ ) are removed from  $P$  to create  $D$ . The bulk mineral extract,  $S$ , must fall somewhere on the line connecting the two minerals that compose it.  $S$  can be determined by extrapolating the line  $D$ - $P$  back to where it crosses the line  $A$ - $B$ . We can determine the  $S/D$  ratio by using Equations (1) and (2). We can also determine the  $A/B$  ratio in  $S$  by using:

$$\frac{A}{B} = \frac{\overline{BS}}{\overline{AS}} \quad (3)$$

An equation similar to Equation (2) can be used to recast the ratios as percentages. Note that Equations (1) and (3) (or their % counterparts) can be used in conjunction to determine the relative amounts of all three phases,  $D$ ,  $A$ , and  $B$ .

In Figure 6c, three minerals ( $A$ ,  $B$ , and  $C$ ) are extracted. The bulk mineral extract,  $S$ , in this case cannot be uniquely determined because the extrapolation of the line  $D$ - $P$  intersects the triangle  $ABC$  in a *line* (the solid line in Figure 6c).  $S$  must lie on this line, but we cannot know where because any point on the line could, when extracted, produce  $D$  from  $P$ . As a result, we cannot determine the  $A$ : $B$ : $C$  ratios, nor the  $S/D$  ratio, without some further information.

Figure 6d represents a **sequence** of two minerals being extracted from  $P$ . This is analogous to a binary eutectic-type situation. First, bulk mineral extract  $S_1$  (mineral  $B$ ) crystallizes and is removed, driving the parental melt from point  $P_1$  directly away from  $B$  toward  $P_2$ . At  $P_2$ , mineral  $A$  joins  $B$  in such a way that the  $A/B$  ratio in the extract equals  $S_2$ . Now the melt at that time ( $P_2$ ) moves directly away from  $S_2$ , toward the final derived melt  $D$ . The resulting liquid line

of descent on the variation diagram shows a definite kink at  $P_2$  and is not a straight line, as in the previous cases that involve only a single bulk mineral extract. At any point along either path, the relative proportions of the coexisting phases can be determined by using Equations (1) to (3).

Figure 6e illustrates the effect of extracting a solid solution, or two minerals in which the ratio varies continuously (as would occur with a curved cotectic). In this case, the bulk mineral extract moves along the line from  $B$  toward  $A$ . As it does so, the melt composition must move directly away from a shifting bulk extract point, resulting in a curved liquid line of descent, similar to those for  $Al_2O_3$ ,  $MgO$ , and  $Na_2O$  in Figure 2.

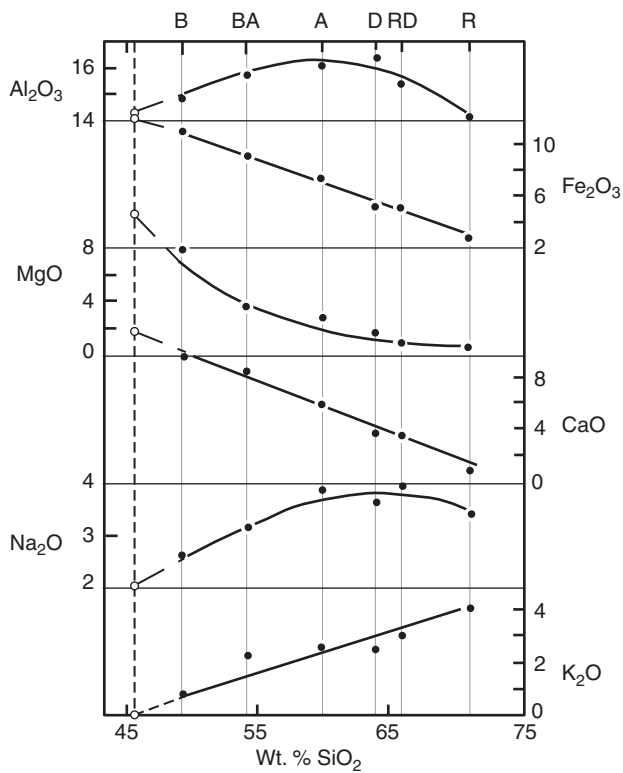
This simple graphical example is the basis for more rigorous numeric solutions. Complex combinations of mineral sequences and solid solutions can be specifically modeled mathematically using the computer, by extending this treatment. We can analyze the simple processes in Figure 6 graphically or mathematically. If the number of phases gets beyond three, the mathematical method is far superior.

The technique described can be used equally well to model **crystal accumulation**. In this case,  $D$  in Figure 6 would be the initial parent magma, and  $P$  would be the accumulative rock that formed by the addition of cumulate crystals  $S = A, B$ , etc. The only way to tell the difference between fractional crystallization and crystal accumulation would be based on textures. **Fractional melting** could be modeled with  $P$  as the parent,  $D$  the extracted melt, and  $S, A, B$ , etc. the solid assemblage left behind. Assimilation of wall rocks and magma mixing can also be modeled, or any combination of processes. Sophisticated computer models have been developed to quantitatively model observed trends in terms of single or combined processes.

As an example of the graphical treatment of fractional crystallization, I offer one developed by Ragland (1989), which, along with Cox et al. (1979), should be consulted for further amplification of the methods. The example begins with a suite of cogenetic rocks, ranging from a basalt to a rhyolite, from a typical subduction-related volcano. The analyses (selected from samples with <5% phenocrysts) are given in Table 5. These data are then plotted on a set of Harker diagrams in Figure 7. Smooth curves are fitted to the trends for each oxide. Note that three curves are linear, three are curved, and two show a maximum. We can now proceed to analyze these rocks based on the following three assumptions:

1. The rocks in Figure 7 are related to each other by a process of crystal fractionation.
2. The trends in Figure 7 represent liquid lines of descent.
3. The basalt is the parental magma from which the others are derived.

There are two methods to evaluate the hypothesis that fractional crystallization is responsible for the trends in Figure 7. Both involve stepwise analysis from each rock type to the next, more evolved one. This avoids the complexities involved with curved liquid descent lines and continuously shifting extract compositions required to produce them. Rather, they are



**FIGURE 7** Stacked Harker diagrams for the calc-alkaline volcanic series of Table 5 (dark circles). From Ragland (1989). Reprinted by permission of Oxford University Press.

treated as a series of straight-line segments connecting each analysis. We shall do this only for the basalt (*B* in Table 5 and Figure 7) to basaltic andesite (*BA*) increment, which should suffice for the purpose of illustration.

The first method is the most general. It assumes that the point representing *B* (the parent) must lie on a straight line between *BA* (the derived melt) and *S* (the bulk mineral extract), as was demonstrated in Figure 6. If we want to find *S*, then, it must lie on the low-SiO<sub>2</sub> extrapolation of the line drawn from *BA* through *B*. Of all the analyses in Figure 7, three have positive correlations with SiO<sub>2</sub> in the *B-BA* range: Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O. If we extrapolate lines from

**TABLE 5** Chemical Analyses (wt. %) of a Hypothetical Set of Related Calc-Alkaline Volcanics

Oxide	B	BA	A	D	RD	R
SiO <sub>2</sub>	50.2	54.3	60.1	64.9	66.2	71.5
TiO <sub>2</sub>	1.1	0.8	0.7	0.6	0.5	0.3
Al <sub>2</sub> O <sub>3</sub>	14.9	15.7	16.1	16.4	15.3	14.1
Fe <sub>2</sub> O <sub>3</sub> *	10.4	9.2	6.9	5.1	5.1	2.8
MgO	7.4	3.7	2.8	1.7	0.9	0.5
CaO	10.0	8.2	5.9	3.6	3.5	1.1
Na <sub>2</sub> O	2.6	3.2	3.8	3.6	3.9	3.4
K <sub>2</sub> O	1.0	2.1	2.5	2.5	3.1	4.1
LOI	1.9	2.0	1.8	1.6	1.2	1.4
Total	99.5	99.2	100.6	100.0	99.7	99.2

B = basalt, BA = basaltic andesite, A = andesite, D = dacite, RD = rhyo-dacite, R = rhyolite. Data from Ragland (1989).

*BA* back through *B* to more primitive compositions, all three will eventually extend to zero. K<sub>2</sub>O proves to be the limiting value in this example because the *BA-B* line extrapolates to zero potassium in Figure 7 first, at 46.5% SiO<sub>2</sub> (dashed line), the highest silica value of the three. At lower silica values, the concentration of K<sub>2</sub>O in the extract would be negative, which is clearly impossible for any analysis. If we next assume that there was no potassium in the bulk mineral extract (a reasonable assumption for a basalt), this indicates that 46.5% is the silica concentration for our extract. Using a vertical line on Figure 7 at 46.5% SiO<sub>2</sub>, we can graphically determine the concentrations of the other oxides in the bulk mineral extract by the intersection of their variation curves with this line (unfilled circles in Figure 7).

A more accurate approach to this method is a mathematical one using Table 5 and the linear equation applied to chemical variables *X* and *Y* and rocks 0, 1, and 2:

$$(X_2 - X_1)/(Y_2 - Y_1) = (X_1 - X_0)/(Y_1 - Y_0) \quad (4)$$

If we perform the calculation for 1 = *B*, 2 = *BA*, and 0 = bulk mineral extract (in which the wt. % K<sub>2</sub>O = 0) and substitute SiO<sub>2</sub> for *X* and K<sub>2</sub>O for *Y*, we can calculate X<sub>0</sub>, the value of SiO<sub>2</sub> when K<sub>2</sub>O = Y<sub>0</sub> = 0. From Table 5 we get:

$$(54.3 - 50.2)/(2.1 - 1.0) = (50.2 - X_0)/(1.0 - 0)$$

for which X<sub>0</sub> = 46.5 wt. % SiO<sub>2</sub>.

If we take this value for X<sub>0</sub>, we can use Equation (4) to get any other oxide as Y<sub>0</sub>. For example, MgO:

$$(54.3 - 50.2)/(3.7 - 7.4) = (50.2 - 46.5)/(7.4 - Y_0)$$

for which Y<sub>0</sub> = 10.8% MgO.

Using either the graphical or mathematical approach for all major oxides, we get the chemical composition for a bulk mineral extract reported in Table 6. Note that all oxides are positive, except for K<sub>2</sub>O = 0, as was our aim. At this point, a norm calculation comes in handy (columns 3 and 4 of Table 6), so we can express the chemical composition as an approximate mineralogy. (We may prefer another norm scheme, such as a high-pressure norm, if we suspect a deep fractionation

**TABLE 6** Bulk Mineral Extract Required for the Evolution from *B* to *BA* in Table 5

Oxide	Wt. %	Cation Norm	
SiO <sub>2</sub>	46.5	<i>ab</i>	18.3
TiO <sub>2</sub>	1.4	<i>an</i>	30.1
Al <sub>2</sub> O <sub>3</sub>	14.2	<i>di</i>	23.2
Fe <sub>2</sub> O <sub>3</sub> *	11.5	<i>hy</i>	4.7
MgO	10.8	<i>ol</i>	19.3
CaO	11.6	<i>mt</i>	1.7
Na <sub>2</sub> O	2.1	<i>il</i>	2.7
K <sub>2</sub> O	0.0		
Total	98.1		100

Data from Ragland (1989).

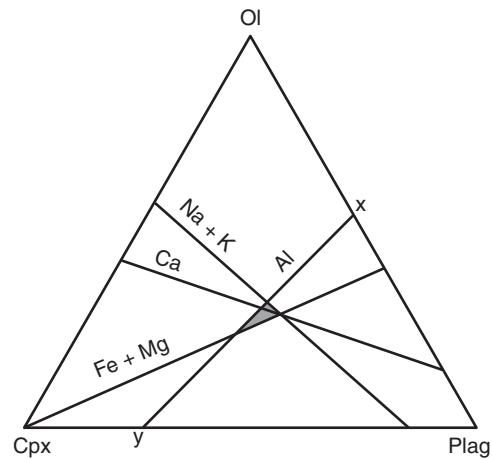


process.) Note that olivine, diopside, and plagioclase dominate the bulk mineral extract, which is reasonable for a basalt phenocryst assemblage. Because the norm is a cation norm, the composition of the plagioclase =  $100 \text{ an}/(\text{an} + \text{ab}) = \text{An}_{62}$ , perhaps a bit low for a basalt (for which plagioclase is usually in the  $\text{An}_{70}$  to  $\text{An}_{85}$  range), but it's close. The  $h_y$  component may not require orthopyroxene but may be included as a component in the clinopyroxene (especially if it's a pigeonite).

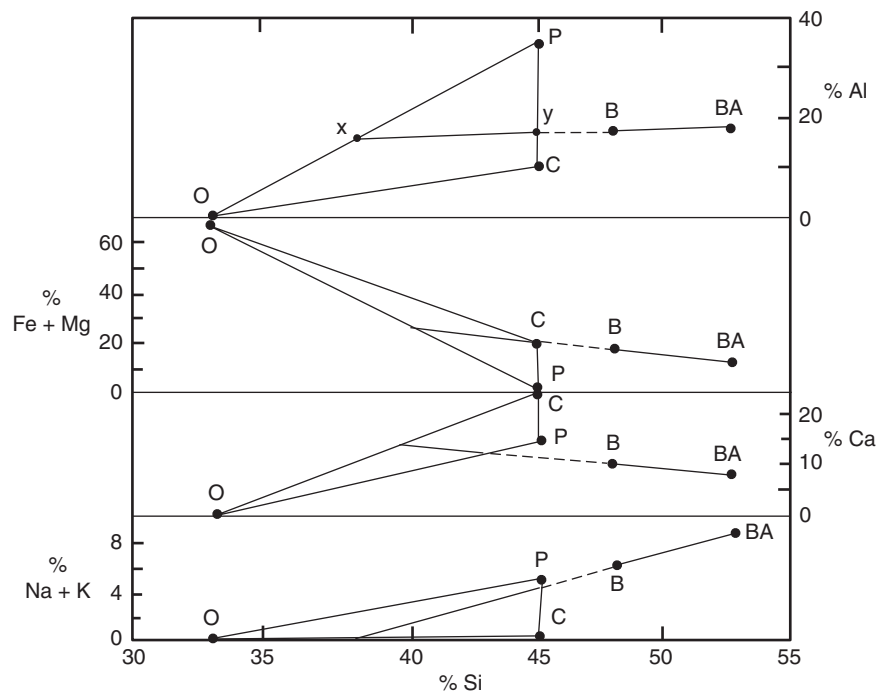
A more precise method can be used if there is a phenocryst assemblage associated with the basalt. If the compositions of the phenocrysts have been analyzed using a microprobe, they can be plotted on the same variation diagram as  $B$  and  $BA$  and used to solve the liquid line of descent, either graphically (as in Figure 6) or mathematically. As stated previously, the trends in Figure 7 are considered reliable examples of the evolved liquids only if the rocks contain few phenocrysts. Thus only samples with <5% phenocrysts were used. However, these phenocrysts can now be useful. Let's say we have phenocrysts of olivine, augite, and plagioclase in the basalt  $B$ , and we have only a few augite and plagioclase phenocrysts in the basaltic andesite  $BA$ . Figure 8 is a variation diagram created by Ragland for this example. In it,  $B$  and  $BA$  are plotted, along with the three phenocryst compositions. For variety, the compositions have been recast as molecular %, but this is not necessary. Using wt. % oxides would work equally well. Ragland combined Fe + Mg to minimize errors associated with Fe oxidation state. K + Na were also combined because they are both susceptible to subsolidus alteration, and combining them may serve to minimize these effects. It is possible to do this only when both elements behave in a similar fashion. In this case, both Na and K increase. If we were to model the  $RD$  to  $R$  path, instead of  $B$  to  $BA$ , Na would decrease, and K would increase (Figure 7), and combining them should then be avoided.

If you compare Figures 6c and 8, you will see the similarities. Figure 8 produces four triangles (for Al, Fe +

Mg, Na + K, and Ca), with four lines on which possible values for  $S$ , the bulk mineral extract, may lie. Because the triangles are different sizes and shapes, they cannot be directly compared. If the four triangles are converted to equilateral triangles of the same size, however, they can be superimposed. The four solid extract lines can be added to the equilateral composite (Figure 9) by noting the relative intercepts of each line on the two sides of the triangle that it pierces in Figure 8. For example, in the  $\text{Al}_2\text{O}_3$  section of Figure 8, the ratios of the line lengths  $\overline{Py}/\overline{PC}$  and  $\overline{Px}/\overline{PO}$  define the line  $x$ - $y$  in any shape of triangle  $POC$ . Ideally, when added to the triangle, the four lines intersect at a point equal to  $S$ , the bulk extract. If they don't intersect at a point, the area bounded by the intersecting lines defines the zone containing  $S$ , which should be relatively small (shaded in Figure 9). The ratios of olivine,



**FIGURE 9** Equilateral triangle showing the solution to the bulk mineral extract (shaded area) best fitting the criteria for the variation diagrams in Figure 8. From Ragland (1989). Reprinted by permission of Oxford University Press.



**FIGURE 8** Variation diagram on a cation basis for the fractional crystallization of olivine, augite, and plagioclase to form  $BA$  from  $B$  (Table 6). From Ragland (1989). Reprinted by permission of Oxford University Press.

plagioclase, and augite can then be determined from S.

This graphic example illustrates the process by which fractionation processes can be modeled. The graphic method is more instructive, but the mathematical process is more efficient, for it can be extended to several components and phases, and it can address combinations of processes, such as fractional crystallization and magma mixing, or wall-rock assimilation (Bryan et al., 1969; Wright and Doherty, 1970; DePaolo, 1981c; Nielsen, 1990). The methods involve the best least-squares fit of analyzed minerals to a regression line of successive analyzed lavas. Care must be taken when several simultaneous processes are considered, for more than one unique solution may be possible. Like PERs, the graphic and numeric models provide a test for a hypothesis, eliminating some hypotheses effectively, but they cannot prove that a particular process was operating. Later quantitative approaches have attempted to model mineral–melt equilibria based on thermodynamic data extracted from experimental melting data (see Ghiorso, 1985; Nielsen, 1990; Ghiorso and Sack, 1995). A “forward” approach may be employed, using a model to predict a liquid line of descent, which is then compared to a natural suite.

## 7 MAGMA SERIES

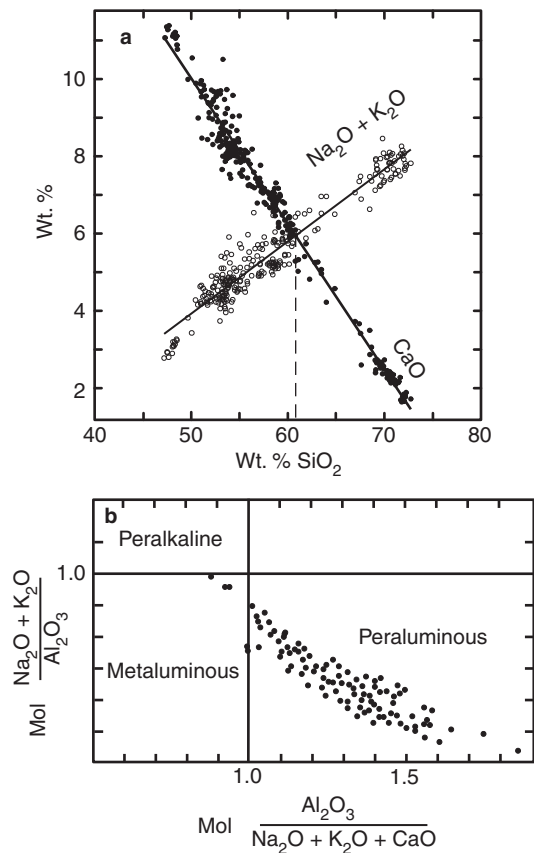
You should already know how chemical composition can be used to classify and name individual igneous rocks, a method that is particularly useful for volcanic rocks that may have few identifiable minerals. The different trends in Figure 3 for two sets of samples, Crater Lake and Skaergård, each show a fairly continuous, yet distinct, chemical variation that strongly implies a genetic relationship or an evolutionary process. This is an invitation to attempt a different type of chemical classification, one that distinguishes whole *families* of magmas (and the resulting rocks). A group of rocks that share some chemical (and perhaps mineralogical) characteristics and shows a consistent pattern on a variation diagram, suggesting a genetic relationship, can be referred to as a **magma series**. Synonymous terms include *association*, *lineage*, *magma type*, and *clan*. The American Commission on Stratigraphic Nomenclature (1961) preferred the term *group* to *series*, but this usage is no longer common.

The concept that many igneous rocks fall into distinct kindred series and that each series follows some characteristic evolutionary path from a unique type of parent magma through a series of more evolved silicic derivative types was first proposed by Iddings (1892a). He recognized the chemical nature of this distinction and proposed that all igneous rocks fell into either an **alkaline series** or a **subalkaline series**. The initial distinction of most series was made in the field on the basis of mode of occurrence and mineralogical characteristics. Harker (1909), intrigued by large-scale patterns, divided the Cenozoic volcanics bordering the oceans into “Atlantic” (alkaline) and “Pacific” (subalkaline) “branches.” The seminal 1924 memoir on the Scottish Isle of Mull (Bailey et al., 1924) recognized that the various Eocene intrusions and lavas of the Inner Hebrides fell into two groups, the “Plateau Magma Series”

(alkaline) and the “Main Magma Series” (subalkaline). Kennedy (1933) considered these two types to be worldwide in scope and proposed the “tholeiitic” (Plateau, or subalkaline) and “olivine-basalt” (Main, or alkaline) “magma types.” Basalts, with their high liquidus temperatures, are considered to be the parental magmas from which the more evolved types within a series are derived. Bowen (1928) provided sound experimental support for this concept, and, under his great influence, the process of crystal fractionation was accepted as the dominant process by which the various series evolved. As mentioned above, there is reason to doubt that fractional crystallization is the sole process of magmatic evolution, and it may not even be the dominant one in many provinces, giving way to magma mixing or assimilation in some types of magmatism.

Although many series were distinguished on field and mineralogical characteristics, the chemical characteristics and influence were equally obvious, particularly the alkalinity and silica content, because these features were distinctive throughout a series. The influence of silica and alkali content are reflected in the names of the two original major series. Subsequent work has only reinforced the early series concept, but we now consider the large-scale groupings of Harker and Kennedy as overly simplified (i.e., that subalkaline rocks occur in the Atlantic, and alkaline rocks in the Pacific). Alkaline rocks are richer in alkalis and are commonly silica undersaturated, whereas subalkaline rocks are silica saturated to oversaturated. If the series are indeed unique, they should be distinguished by their evolutionary patterns on variation diagrams, which might also permit further analysis of the evolutionary processes.

Peacock (1931) used a plot of CaO and  $(\text{Na}_2\text{O} + \text{K}_2\text{O})$  versus  $\text{SiO}_2$  (Figure 10a) to somewhat arbitrarily distinguish four chemical classes, based on a single parameter, the “alkali–lime index” (the wt. %  $\text{SiO}_2$  at which the increasing alkali curve met the decreasing CaO curve on a Harker diagram). He called the classes **alkalic** (alkali–lime index <51), **alkali-calcic** (51 to 56), **calc-alkalic** (56 to 61), and **calcic** (>61). Note that the Crater Lake data in Figure 10a yield an alkali–lime index of ~60.7, indicating that the series is just to the calc-alkalic side of the boundary between Peacock’s calcic and calc-alkalic classes. Shand (1927) grouped igneous rocks based on the total *molar* alkali versus alumina content as either **peralkaline** [ $\text{Al}_2\text{O}_3 < (\text{Na}_2\text{O} + \text{K}_2\text{O})$ ], **per-aluminous** [ $\text{Al}_2\text{O}_3 > (\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ ], or **metaluminous** [ $\text{Al}_2\text{O}_3 < (\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$  but  $\text{Al}_2\text{O}_3 > (\text{Na}_2\text{O} + \text{K}_2\text{O})$ ], a classification that is useful mostly for very felsic rocks (Figure 10b). The molar alkali–alumina ratio,  $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3$ , is called the **peralkalinity index**. The term **agpaitic** has been used as a synonym for peralkaline (and the agpaitic index, or coefficient, as initially proposed, indicated the same thing as the peralkalinity index). More recently, however, the agpaitic character of alkaline rocks considers mineralogical and other chemical parameters, such as Ca, Ba, Sr, Rb, and Cs, which may substitute for Na and K in several alkaline silicate minerals, and the IUGS now recommends that agpaitic rocks be restricted to a specific class of peralkaline nepheline syenites characterized by complex Zr and Ti minerals (see Sørensen, 1974, 1997).



**FIGURE 10** (a) Plot of CaO (solid circles) and (Na<sub>2</sub>O + K<sub>2</sub>O) (open circles) versus SiO<sub>2</sub> for the Crater Lake data used in Figures 2 and 3. Peacock (1931) used the value of SiO<sub>2</sub> at which the two curves crossed as his "alkali-lime index" (dashed line). (b) Alumina saturation indices (Shand, 1927), with analyses of the peraluminous granitic rocks from the Achala Batholith, Argentina (Lira and Kirschbaum, 1990).

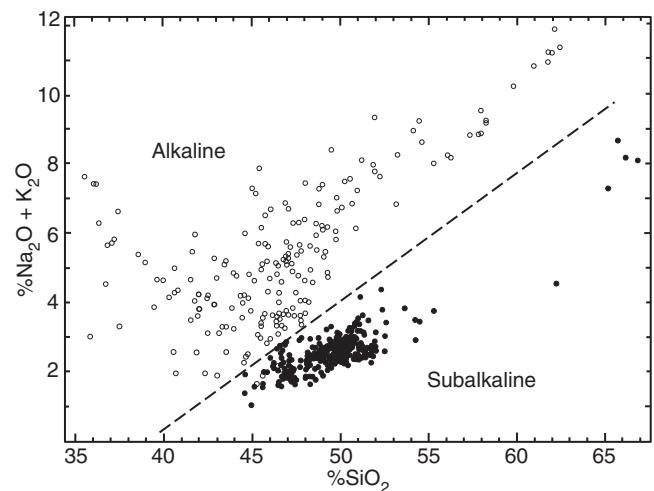
Since these pioneering works, a number of investigators have attempted to identify and classify magma series based on chemical characteristics. Other series have been proposed, based, among other things, upon the dominant type of alkali. Some of the terms were considered to be true magma series, whereas others served more to describe the chemical characteristics of an igneous rock or province. Such different applications of the same terms led to obvious confusion. Most investigators continue to recognize Iddings's (1892a) original two series, alkaline and subalkaline, and accept that the subalkaline can be further divided into the tholeiitic series and calc-alkaline series. Beyond that, there is less agreement as to what constitutes a series and how series are distinguished.

In 1971, Irvine and Baragar attempted to systematize the growing diversity of nomenclature of magmatic rocks and series, and they recommended a classification to the National Resource Council of Canada. Using major element composition and Barth-Niggli (cation) norms, they attempted to provide a reasonable classification of magma series and methods by which they could be distinguished. They accepted the original alkaline and subalkaline series and the subdivision of the subalkaline series into the tholeiitic and calc-alkaline series. They also recognized a **peralkaline series**, based on the

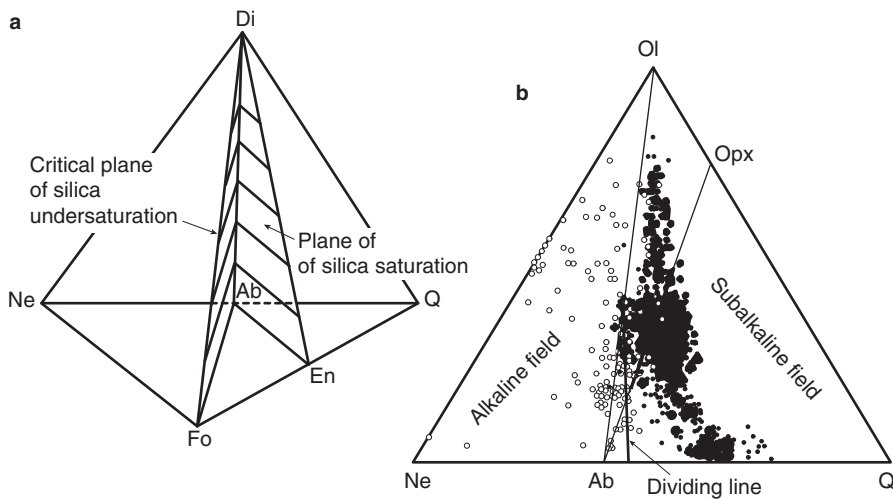
alumina content, as defined above, though it is less common. They also provided a chemical definition for conventional rock names (as parts of the series), but, because it overlaps with the chemical classification by the IUGS, we shall disregard that aspect of the work.

The alkaline and subalkaline series are distinguished in a total alkali versus silica diagram in Figure 11. In this diagram, the alkaline rocks plot distinctly above and the subalkaline rocks below the dividing lines chosen by MacDonald (1968) and Irvine and Baragar (1971).

Figure 12a is the Ne-Di-Fo-Qtz tetrahedron, called the **basalt tetrahedron** because it is so useful in characterizing basalts. The Di-Ab-En plane is called the **plane of silica saturation** because to the right of it, a silica polymorph is stable (indicating SiO<sub>2</sub> oversaturation), whereas to the left, the silica-undersaturated phase olivine is stable without a silica polymorph. The Di-Ab-Fo plane is called the **critical plane of silica undersaturation**, and to the left of this plane, the alkaline and silica-undersaturated feldspathoid mineral nepheline is stable. Figure 12b is the Ne-Fo-Qtz base of the tetrahedron. The alkaline and subalkaline rocks, when plotted on this diagram using the (cation) normative minerals *ne*, *ol*, and *q*, are distinguished by the dividing line shown (proposed by Irvine and Baragar, 1971). This line is close to the critical plane of silica undersaturation. Alkaline rocks plot to the left of this plane and are thus silica undersaturated. These two series should be distinct, at least at low pressures, because of the **thermal divide** along the line Ab-Ol (see Figure 13) that prevents liquids from crossing it as they cool. Rather, liquids on the flanks of this divide descend away from it as they cool, evolving toward either the silica-saturated or the alkaline and silica-undersaturated eutectic. Subalkaline rocks can be olivine bearing or quartz bearing, depending upon which side of the plane of silica saturation they occupy. The common evolutionary sequence in the alkaline series begins with an alkali olivine basalt and proceeds through trachybasalts and trachyandesites, to trachytes or



**FIGURE 11** Total alkalis versus silica diagram for the alkaline (open circles) and subalkaline rocks of Hawaii. After MacDonald (1968). Copyright © The Geological Society of America, Inc.



**FIGURE 12** (a) The basalt tetrahedron (after Yoder and Tilley, 1962). (b) The base of the basalt tetrahedron on which are projected from Cpx the compositions of (cation) normative minerals, determined from whole-rock analyses of subalkaline rocks (black) and alkaline rocks (gray) from Figure 11. After Irvine and Baragar (1971).

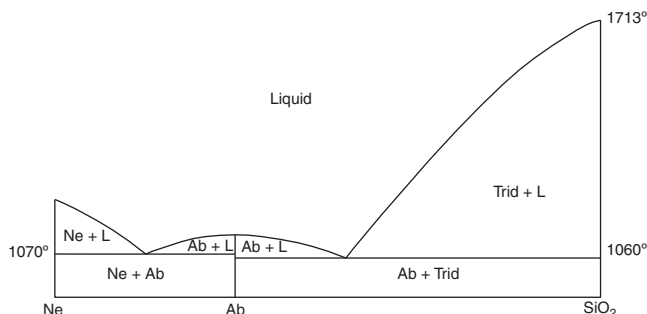
phonolites. The common sequence for the subalkaline series is the more familiar basalt → andesite → dacite → rhyolite family.

The subalkaline series was further subdivided into a **tholeiitic** and a **calc-alkaline series** by Tilley (1950). Although these two subdivisions cannot be distinguished in either the alkali-silica or the *ne-ol-q* diagrams (despite Peacock's 1931 attempt), they do plot as distinct fields in the AFM diagram (Figure 14) and on a plot of  $\text{Al}_2\text{O}_3$  versus the composition of the (cation) normative plagioclase (Figure 15).

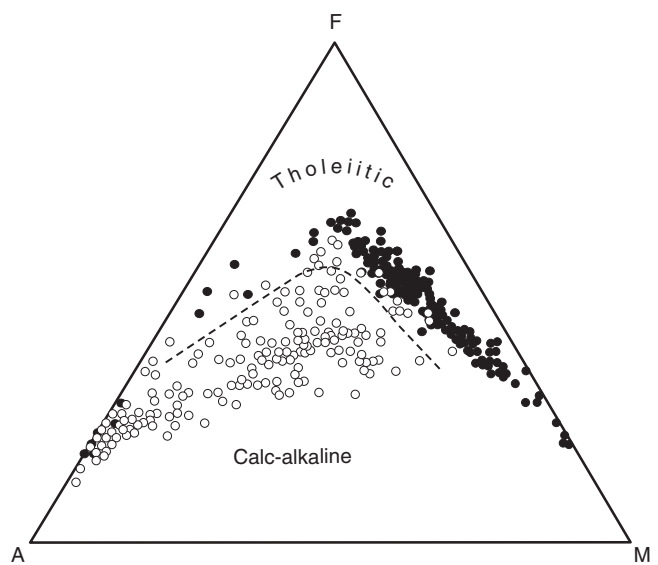
If we compare on AFM diagrams in Figures 3 and 14, we see that the Skaergård trend is clearly tholeiitic, and the Crater Lake trend is calc-alkaline. Both series progress along the basalt–andesite–dacite–rhyolite trend, but there are distinctive mineralogical and chemical differences between the two series that are most evident for intermediate compositions. The parental end-members converge toward the M corner, making distinction among them on an AFM diagram problematic. Likewise, Irvine and Baragar (1971) found it impossible to consistently distinguish the more siliceous members of the two series because they converge after the different iron enrichment paths that characterize the intermediate stages (Figure 14). As pointed out by Sheth et al. (2002), Figures 14 and 15

distinguish tholeiitic from calc-alkaline series on the basis of criteria other than CaO versus alkalis. Although they may effectively do so, and those distinctions may lead us toward understanding the responsible processes, neither should really be used to *define* a rock series as calc-alkaline without addressing both CaO and alkalis (as the original Peacock criteria do).

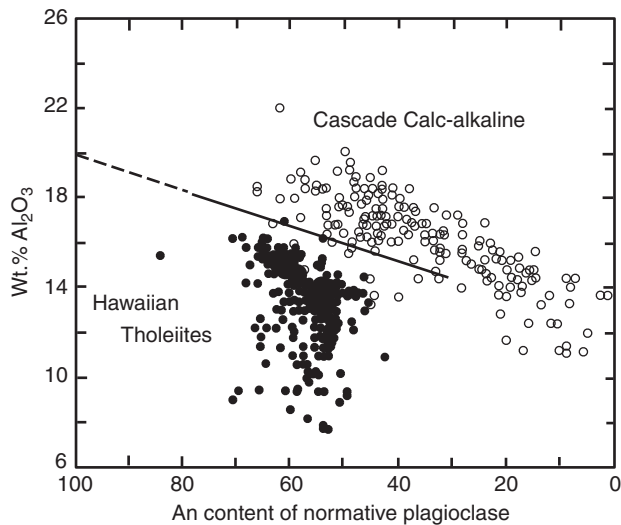
Irvine and Baragar (1971) further divided the alkali series into a **sodic series** and **potassic series**, and Middlemost (1975) recommended adding a **high-K series** as well (Figure 16). The remaining terms, such as *peraluminous*, *metaluminous*, etc., although they may yet be shown to characterize some distinctive magma series, are more useful as descriptive terms when some chemical characteristic is emphasized for a particular igneous rock or province.



**FIGURE 13** The thermal divide at the albite composition on the Ne-Q system.



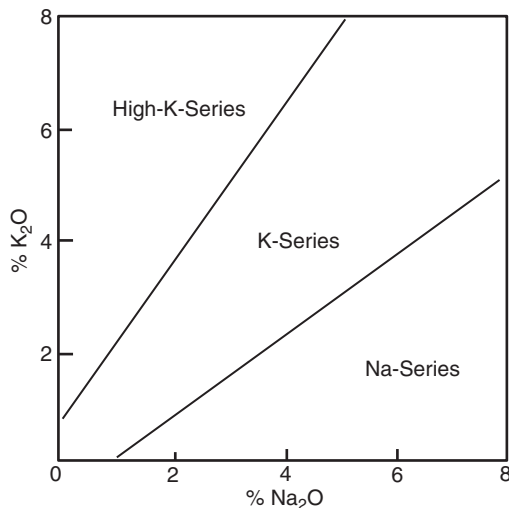
**FIGURE 14** AFM diagram showing the distinction between selected tholeiitic rocks from Iceland, the Mid-Atlantic Ridge, the Columbia River Basalts, and Hawaii (solid circles) plus the calc-alkaline rocks of the Cascade volcanics (open circles). From Irving and Baragar (1971).



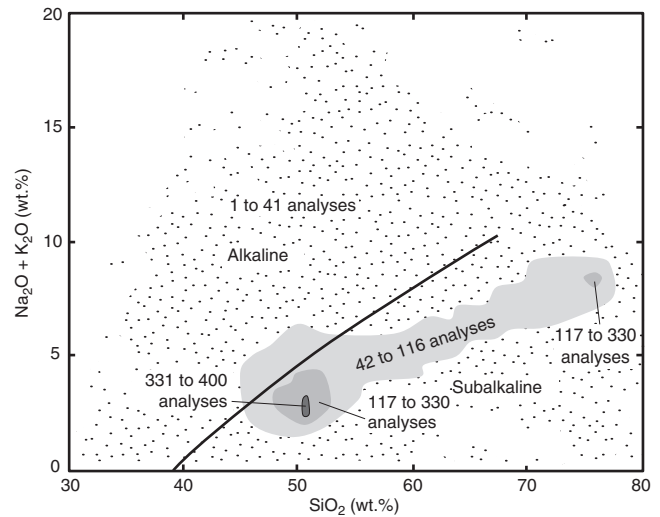
**FIGURE 15** Plot of wt. %  $\text{Al}_2\text{O}_3$  versus anorthite content of the normative plagioclase, showing the distinction between the tholeiitic and calc-alkaline series. From Irvine and Baragar (1971).

Although the alkaline, tholeiitic, and calc-alkaline magma series predominate the igneous history of the Earth, transitional types can be found. Diagrams such as Figures 11 to 16 suggest a clear separation of the series types, but when additional data are added, the distinction becomes less clear. Figure 17 is a plot of more than 41,000 analyses of igneous rocks compiled from the literature on an alkali versus silica diagram, such as that used in Figure 11 to distinguish the principal alkaline and subalkaline magma series. Besides noting that the subalkaline rocks are more common than the alkaline, we see that any supposed gap separating these two dominant series is missing. In fact, a modest concentration of analyses lie on a portion of the boundary line of Irvine and Baragar (1971).

In addition, the commonly accepted series are too narrowly defined to accommodate all magmas, or even all



**FIGURE 16** Wt. %  $\text{K}_2\text{O}$  versus  $\text{Na}_2\text{O}$  diagram subdividing the alkaline magma series into High-K-, K-, and Na-sub-series. After Middlemost (1975). Copyright © with permission from Elsevier Science.



**FIGURE 17** Plot of more than 41,000 igneous rock analyses on an alkali versus silica diagram. The alkaline–subalkaline dividing line of Irvine and Baragar is included. After LeMaitre (1976b). Copyright © with permission from Springer-Verlag.

magma series, particularly among the highly variable alkaline rocks of the continental interiors. Thus, although the classification into magma series may be useful, it is far from perfect. Classifications, with their convenient “pigeon-holes,” are commonly difficult to apply unambiguously to nature. Classifications also focus our attention on *similarities*, when individual *differences* may be equally important, if not more so. Although the basalts of Mauna Kea, the Columbia River Plateau, and the Mid-Atlantic Ridge are all tholeiitic, they do not have identical origins, chemistries, or evolutionary paths. However, it is still convenient to use the three main magma series (at least). Despite the somewhat gradational distinctions at times, a significant number of magmas fall into one of these series. Each series is characterized by a particular parent basalt and shows a sequence of derivative magmas that follow a liquid line of descent from the parent. This leads us to the conclusion that there must be some important physical and chemical controls on the development of a number of primary and derivative magmas. The search for patterns and correlations, however general, is a fundamental scientific approach, and the patterns represented by magma series are real, even if they are not universal. These patterns must reflect some basic Earth processes that we cannot afford to overlook. If we look at the tectonic setting of the various series in Table 7, we find some other correlations.

First, calc-alkaline magmas are essentially restricted to subduction-related plate tectonic processes. This must carry some genetic significance and will certainly be a factor in any model for subduction zone magma genesis. Recognition of calc-alkaline characteristics in the composition of ancient volcanic rocks may help determine their tectonic framework and aid the historic interpretation of an area. Second, tholeiitic magmas are practically the exclusive magma type associated with divergent boundaries. Although some alkaline rocks are found, they play a

**TABLE 7** Magma Series in Specific Plate Tectonic Settings

Characteristic Series	Plate Margin		Within Plate	
	Convergent	Divergent	Oceanic	Continental
Alkaline	yes	no	yes	yes
Tholeiitic	yes	yes	yes	yes
Calc-alkaline	yes	no	no	no

After Wilson (1989), p. 11.

subordinate role, usually in the initial stages of continental rifting. This too, must provide some useful clues to the genesis of magmas at mid-ocean ridges.

Magma series are important to our understanding of igneous petrogenesis. Earlier, as we first regarded the spectrum of igneous rocks that occur on Earth, I asked a basic

question: Does the observed diversity derive from a single primitive parent by a variety of diversification methods, or are there several parents, each with its own lineage of diversification products? It would appear that the latter is the case and that there are at least three principal magma series, and perhaps several other minor ones.

## Summary

Petrologists use the chemical composition of rocks and minerals to characterize and categorize individual types, to identify series of related rocks, and to model processes that relate the rocks in a consanguineous series. Analyses were initially performed by using tedious gravimetric methods but are now quickly and routinely accomplished by using instrumental spectroscopic techniques based on emission or absorption of energy when directed at prepared samples. Analyses are typically reported in wt. % oxide for the major elements (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MgO, FeO, CaO, Na<sub>2</sub>O, and K<sub>2</sub>O) and minor elements (TiO<sub>2</sub>, MnO, P<sub>2</sub>O<sub>5</sub>, H<sub>2</sub>O, and CO<sub>2</sub>), and they are reported as parts per million (ppm) of the element for trace elements. A norm is a method of recasting a chemical analysis into a set of hypothetical minerals. Norms are useful in categorizing volcanic/glassy rocks that have not fully crystallized, and they also have other uses in igneous rock classification and modeling.

Graphical display of accumulated chemical data in suitable variation diagrams may prove helpful in discerning trends that may discriminate between possible evolution mechanisms relating members of a suite of rock samples collected in an area. Bivariate (*x-y*) diagrams are commonly

used, particularly ones in which various components are plotted versus some chemical parameter that is considered a measure of chemical fractionation (e.g., SiO<sub>2</sub>, Zr, Mg#). Ternary diagrams, such as the AFM diagram, are also common. By using bivariate diagrams, such as Harker or Pearce element ratio diagrams, we can evaluate specific differentiation mechanisms (e.g., fractional crystallization of certain minerals) deemed responsible for the chemical evolution within a suite of supposedly consanguineous rocks. Quantitative graphical and computational methods extend the power of this approach and can determine such things as the exact amounts of minerals of specific compositions that could, if fractionated, relate the rocks within an evolving suite.

Petrologists use the term *petrogenetic province* to refer to a geographic region in which igneous rocks are apparently related. They apply the term *series* to a broader category of characteristic evolutionary path from a type of parent magma through a sequence of more evolved derivative types. The most popularly recognized series are alkaline and subalkaline series, and the subalkaline type may be subdivided further into tholeiitic and calc-alkaline series.

## Key Terms

Major, minor, and trace elements	Primary magma	Pearce element ratio (PER)
Spectroscopic analysis	Derivative magma	Magma series
Detection limit	Primitive	Alkaline series
Loss on ignition (LOI)	Parental	Subalkaline series
Norm (CIPW)	Conserved elements	Tholeiitic series
Mode	Closure problem	Calc-alkaline series
Silica saturation	Consanguineous	Thermal divide
Suite	Daly gap	Peralkaline/agpaitic
Variation diagram	Petrogenetic province	Peraluminous



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## Review Questions and Problems

Review Questions and Problems are located on the author's web page at the following address: <http://www.prenhall.com/winter>

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## Important "First Principle" Concepts

- Major element behavior is different from that of trace elements. Because of their high concentrations, major elements (and, to a lesser extent, minor elements) determine the physical properties of magmas and the minerals that crystallize from them. Differentiation processes resulting in the evolution of magmas within a petrogenetic province are largely controlled by major element concentrations and may be detected by noting variations in major elements across a suite of cogenetic igneous rocks.
  - We can qualitatively and quantitatively model fractionation processes to evaluate the potential of specific processes to produce the compositional evolutionary trends observed in such an igneous suite.
  - Trends revealed in variation diagrams are best used to critically evaluate a specific hypothesis. They may provide grounds to reject or support the hypothesis, but cannot prove that it has occurred.
  - A rock containing sufficient  $\text{SiO}_2$  to combine with the other elements to create silicates (such as feldspars and pyroxene) and yet have excess  $\text{SiO}_2$  left over will manifest that excess as quartz (either in the mode or norm). Such a rock is considered *silica oversaturated*. Rocks with insufficient  $\text{SiO}_2$  will develop minerals unstable with quartz, such as olivine or a feldspathoid. Just-saturated rocks will develop feldspars and mafics such as pyroxene but neither quartz nor olivine/feldspathoid.
  - *Primary* magmas are magmas derived directly from a source (typically the mantle) without evolving after separation from that source. Most suites of cogenetic (consanguineous) rocks display a range of compositions from *primitive* to *evolved* (or *derivative*) compositions. *Parental* magmas are the most primitive ones found in an area and are considered the local type from which the others evolved.
  - Three common magma series are popularly recognized: alkaline, calc-alkaline, and tholeiitic. Numerous other series have been proposed by investigators desiring more detail.
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## Suggested Further Readings

### Analytical Methods and Major Element Analysis

- Cox, K. G., J. D. Bell, and R. J. Pankhurst. (1979). *The Interpretation of the Igneous Rocks*. Allen & Unwin. London.
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### Variation Diagrams, Magma Series, and Classification

- Carmichael, I. S. E., F. J. Turner, and J. Verhoogen. (1974). *Igneous Petrology*. McGraw-Hill. New York. pp. 32–50.
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- Wilcox, R. E. (1974). The liquid line of descent and variation diagrams. In: *The Evolution of the Igneous Rocks. Fiftieth Anniversary Perspectives* (ed. H. S. Yoder). Princeton University Press. Princeton, NJ.
- Young, D. A. (2003). *Mind over Magma. The Story of Igneous Petrology*. Princeton University Press. Princeton, NJ. (Several chapters cover the historical development of many concepts and methodologies.)
- See also Ragland (1989) and Cox et al. (1979), above.