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Paul A. Schroeder
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1 What Are Clays and What Is the Critical Zone?

1.1 Introduction

1.1.1 What Is a Mineral?

To most people, the term “mineral” is something that is added to their breakfast cereal to fortify their diet. To a mineralogist 50 years ago, the term specified a naturally occurring inorganic solid material with a generally fixed chemical composition and internal crystalline order. To a mineralogist today, the term now includes the subtleties of human influence on natural mineral formations, which might range from pure synthesis in a lab to an outdoor occurrence, such as those formed in an acid mine drainage site. A mineralogist today also recognizes that biological processes are responsible for the formation of many minerals, either as controlled processes (e.g., the formation of animal teeth, bones, or shells) or induced processes (e.g., the formation of opal-A in a hot spring or pyrite in a salt marsh from microbial activities). Materials once thought to lack an internal crystal structure are now revealing order at the nanoscale with the aid of new technologies (Heaney, 2015). This book is about clays in the Critical Zone (CZ). We begin by discussing the definitions of “clay,” “clay mineral,” and “Critical Zone.” As for many other words and expressions, there are differing definitions for these terms, depending on perspective and context. Clay science is the study of clays and clay minerals, so let‘s start with asking about these terms and their definitions by those who study clays in the Critical Zone.

1.1.2 What Is Clay?

Clay scientists operationally define the term “clay” as a fine-grained material having the physical property of being generally plastic when wet, hardened when dried or fired, and composed of particles (mostly minerals) that are commonly micron-scale or less in size. Speaking of size, let’s first discuss the size of the things we will look at. Gauging size is not always intuitive for many people, particularly when the unaided human eye can’t see an object because it’s too small or too large. The smallest thing humans can see with the naked eye is a grain of sand whose individual particles range from a lower limit of 63 microns (μm) to an upper limit of 2 millimeters in size. A micron is one-millionth of a meter (10^{-6} m), which is about the average size of one prokaryotic cell (i.e., a single-celled bacteria and archaea), or one-hundredth the diameter of an average single human hair. In comparison, the upper limit for clay-sized particles is generally accepted to be less than 2 μm.

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Micron-length scales also define the size range of infrared radiation energy wavelengths within the electromagnetic spectrum (EM). We will see that interactions between EM energy and matter are scale-dependent; those interactions are how we learn much about things we can't see, like clay minerals.

Exponents, logarithms, and natural logs can be wonderful and useful tools in the study of clays, particularly when faced with huge ranges of scale in length, time, or mass. Exponential forms can describe natural growth and decay processes, such as radioactivity, as well as the accumulation or breakdown of pollutants in a soil profile. Most people know exponents in the context of the accumulation of interest in their savings account (i.e., it takes money to make money) or perhaps by the familiar interest cost added to unpaid credit card bills. If you have not had a chance to practice the basics of log scales, then see the supplemental document clay.uga.edu/CCZ/logs.pdf for a short tutorial, with the cautionary note that this information is not a substitute for solid courses in applied mathematics.

Figure 1.1 is a compilation of "the size of things" about which a scientist might have interest. Spatial scales (as well as mass and temporal scales) are so vast in nature that measurements are often presented in log dimensions, such as the length scale in Figure 1.1 ($\log_{10}$ meters). It is important to study the illustration and return to it often. Why? Although the particle size of clay is often defined as < 2 μm, this certainly does not mean that particles larger than clay are outside the interest or realm of clay science and the Critical Zone. Also, it is important to note the response of matter to the absorption of electromagnetic (EM) radiation, which is included in Figure 1.1. Grasping the size of something (e.g., the nanometer-scale distance between atoms in a clay mineral or the meter-scale thicknesses of clay seams buried at kilometer-scale depths) and the wavelength of the energy interacting with that material (e.g., EM or seismic waves) provides the first step toward developing an understanding of physical theories and is the basis for most analytical techniques.

1.1.3 The Size of Things

The upper limit of clay particle sizes is reported at different values in various disciplines. Guggenheim and Martin (1995) discuss the definitions of clay (also referred to as the fine fraction) and clay minerals. They note that a sedimentologist may choose < 4 μm for the upper limit of clay-sized particles, while colloid chemists may use < 1 μm. The International Organization for Standardization (ISO) uses < 2 μm as the upper cutoff for the fine fraction.

Particles are three-dimensional. So, what is really meant by the expressions "< 2 μm," "fine fraction," and "clay fraction"? The caveat to understanding these terms is that they are operationally defined as particles with equivalent spherical diameters (ESD), assuming Stokes' law (Equation 1.1). In this case, we assume that a < 2 μm spherical particle is settling in a Newtonian fluid (e.g., nonturbulent water) where stresses, arising from flow at every point, are linearly proportional to the local strain rate. In other words, the particle flow is laminar (i.e., not turbulent) and the viscosity (i.e., resistance to fluid deformation) does not change with the rate of flow. Stokes' law is an accurate model to account for viscosity

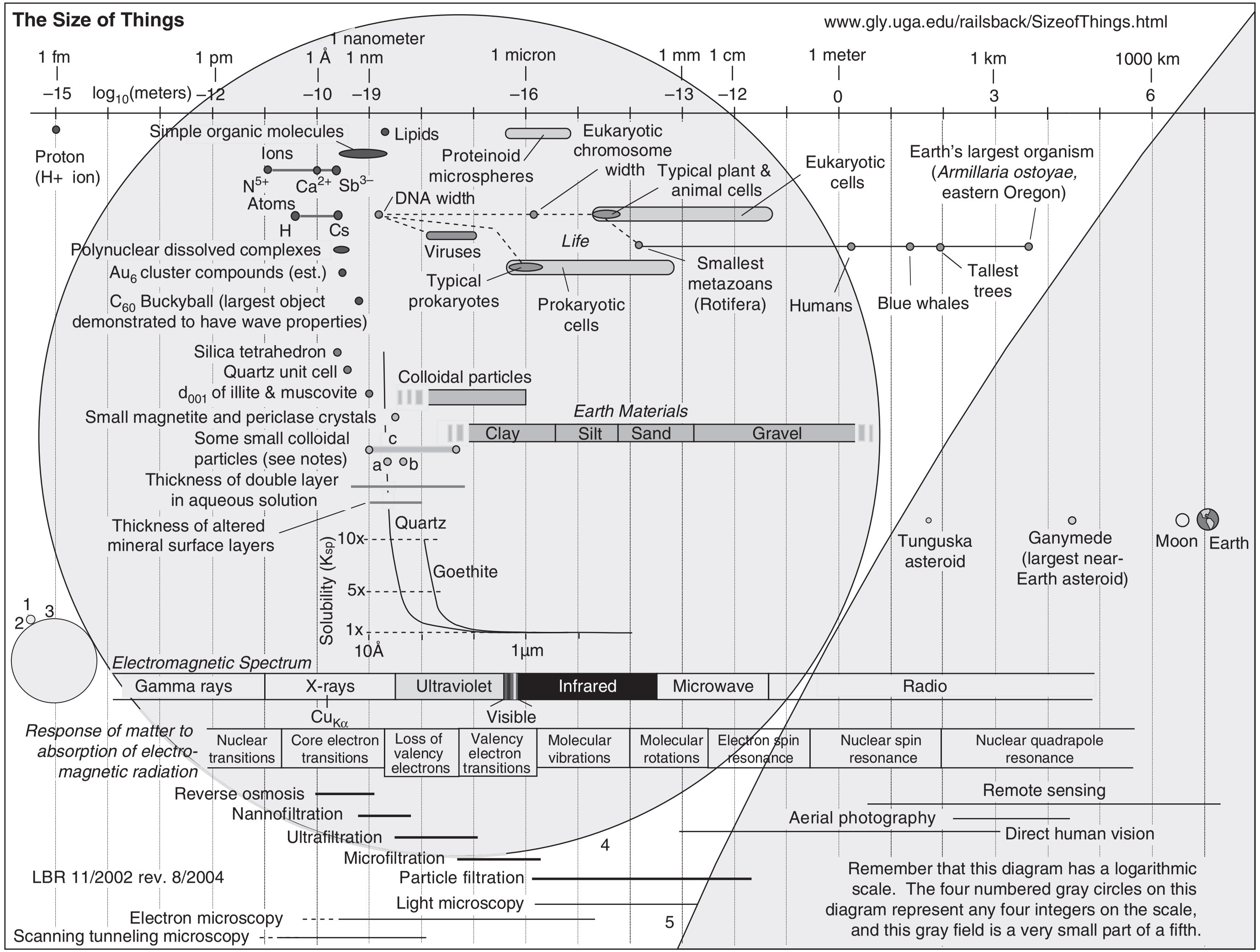

Figure 1.1 The size of things. The diagram shows the size of objects from protons to the Earth. Noted observations include the size of biological entities, the size of particles, and the range of molecular entities. The lower part of the diagram includes the electromagnetic spectrum, which gives insight into how we observe materials. For example, the absorption of infrared radiation provides details about the molecular coordination of elements in clay minerals and their surrounding electronic environment. Reproduced from Railsback, www.clay.uga.edu/CCZ/.

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effects such that in the presence of a gravitational field (or a force field created by centrifugation), the terminal velocity of a particle can be determined by its diameter and density. Stokes' law is given as

$$V = \frac{g(\rho_r - \rho_w)d^2}{18P} \tag{1.1}$$

where V = terminal velocity (cm s^{-1}), g = gravitational field (cm s^{-2}), ρ_r = particle density (g cm^{-3}), ρ_w = water density (g cm^{-3}), d = spherical particle diameter (cm), and P = fluid viscosity (poise, recalling 1 *poise* = g s^{-1} cm^{-1}).

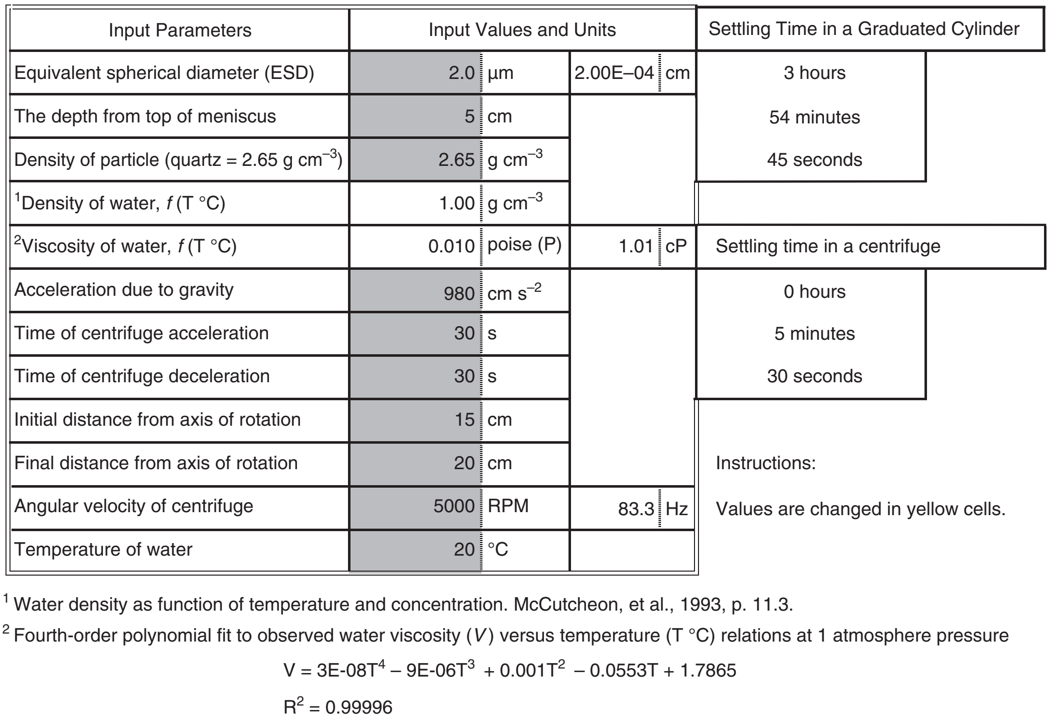
The most important factors determining settling rates are the density and size of the particles and the water viscosity. Water viscosity is very dependent upon temperature (T). Fortunately, there are well-known equations to predict the viscosity and density of water with changing temperatures. Particle densities and the shapes of natural material are generally unknown ahead of time. Therefore, by general agreement, we assume that all the particles are perfectly spherical and have the same density as quartz (2.65 g/cm^3). Clearly this is not the case, but the goal is to have a particle-size separation protocol that is the same for everyone. This is an important point, because if we all agree to the same set of assumptions, then reproducibility can be achieved among labs. To report that the clay fraction was separated to < 2 μm using Stokes' law, be sure to report it as < 2 μm ESD. The readers of your report will understand your underlying assumptions. This operational definition applies to other clay subfractions that may be reported (e.g., < 0.5 μm ESD or < 0.1 μm ESD).

Let's put Stokes' law into practice solving the settling time of an ideal 2 μm ESD particle at a room temperature of 20 °C. In this case, we need to pick a settling distance from the top surface of a homogeneously dispersed suspension of sample and water (i.e., a slurry). Remember that the fluid must be Newtonian, so a slurry that is too thick or has too many coarse particles might violate this assumption. On the other hand, a slurry that is too thin may not produce adequate sample mass to study. As a rule, if your sample is clay-rich, a ratio of ~20 to 50 g solid mass per liter of water is a good starting point to prevent the slurry from being too thick. If your sample is sand-rich, then first sieving ~50 to 100 g per liter of water to remove the > 63 μm fraction helps prevent turbulence in the water otherwise caused by the large fast-settling particles. Other considerations for achieving a well-dispersed suspension may arise in cases in which you do not have ample mass. How to overcome some of these challenges is discussed further in Chapter 3. The point here is that for everyone to agree to an operational definition of "clay fraction" (i.e., the < 2 μm ESD fraction), we can't disregard our assumptions. A properly dispersed suspension is paramount for using Stokes' law.

Rearranging the Stokes' law equation for time (t, seconds) and distance from the top surface of a settling slurry (l, cm) gives the following equation:

$$t = \frac{18Pl}{g(\rho_r - \rho_w)} \tag{1.2}$$

This equation can readily be entered into a spreadsheet like the one illustrated in Figure 1.2. The calculation of settling times for clay-sized particles at room temperature in a graduated cylinder reveals long settling times that are on the order of hours to days. To speed things up, we resort to a centrifuge to increase the forces involved. Stokes' formula can be rearranged



Input Parameters	Input Values and Units			
Equivalent spherical diameter (ESD)	2.0	µm	2.00E–04	cm
The depth from top of meniscus	5	cm		
Density of particle (quartz = 2.65 g cm^{-3})	2.65	g cm^{-3}		
[1]Density of water, *f* (T °C)	1.00	g cm^{-3}		
[2]Viscosity of water, *f* (T °C)	0.010	poise (P)	1.01	cP
Acceleration due to gravity	980	cm s^{-2}		
Time of centrifuge acceleration	30	s		
Time of centrifuge deceleration	30	s		
Initial distance from axis of rotation	15	cm		
Final distance from axis of rotation	20	cm		
Angular velocity of centrifuge	5000	RPM	83.3	Hz
Temperature of water	20	°C		

Settling Time in a Graduated Cylinder
3 hours
54 minutes
45 seconds

Settling time in a centrifuge
0 hours
5 minutes
30 seconds

Instructions:

Values are changed in yellow cells.

[1] Water density as function of temperature and concentration. McCutcheon, et al., 1993, p. 11.3.

[2] Fourth-order polynomial fit to observed water viscosity (*V*) versus temperature (T °C) relations at 1 atmosphere pressure

$$V = 3E\text{-}08T^4 - 9E\text{-}06T^3 + 0.001T^2 - 0.0553T + 1.7865$$

$$R^2 = 0.99996$$

Figure 1.2 A spreadsheet using Stokes' law allows for the calculation of time for an operationally defined ESD particle, assuming a given temperature and settling distance in water. The example here shows a settling time of almost four hours for 2 μm ESD particles at a depth of 5 cm in a graduated cylinder. The terminal velocity of very fine clay particles settling in room-temperature water can be extremely slow. For example, a 0.2 μm ESD particle takes almost 15 days in a graduated cylinder. Using a centrifuge can reduce the settling time. With initial and final rotor dimensions of 15 and 20 cm, respectively, and spinning at 5000 RPM, about five minutes is required to settle 2 μm ESD particles. Stokes' law is nonlinear, so take the time to download the spreadsheet used here at www.clay.uga.edu/CCZ/stokes.xls. Parameterize the values for your lab and experiment by changing variables of particle size, temperature, depths, and rotor speeds to gain a sense of how Stokes' law works. The equation for viscosity does not describe the property exactly and is valid only in near-room-temperature ranges (Korson et al., 1969).

into an equation to calculate settling time. Given t_a = the time of centrifuge acceleration (s), t_d = time of centrifuge deceleration (s), η = viscosity of water (poise), R_1 = initial distance of particle from axis of rotation (cm), R_2 = initial distance of particle from axis of rotation (cm), r = radius of particle (cm), and N = angular velocity (revolutions per minute, RPM). The relationship was presented by Hathaway (1955) and is found as

$$t = \frac{\eta \log\left(\frac{R_2}{R_1}\right)}{3.81 r^2 N^2 (\rho_r - \rho_w)} + \frac{2(t_a + t_d)}{3} \tag{1.3}$$

This relationship can be coded into the same spreadsheet used to calculate settling times falling due to gravity (see Figure 1.2). Settling times are highly dependent upon water viscosity (i.e., temperature). To settle extremely fine particles (e.g., < 0.1 µm) you will need very high rotor speeds and long spin times, which creates heat in the centrifuge. A refrigerated centrifuge and well-balanced opposing-spin sample masses are a must. Your sample slurries, for example, might weigh 50 grams. They must be paired oppositely and weighed exactly the same to ± 0.1 g or less, depending upon the rotor speed. Be prepared for some high-price sticker shock, as these centrifuges are relatively expensive and require periodic maintenance. Although beyond the scope of this book, the Sharples centrifuge is a very high-RPM machine designed for large volumes of fluid slurries and the separation of nanoparticles in oils, food products, and fluids (as in the medical virus and blood recovery industries). Obtaining large masses of very fine particles is a difficult task in clay science. Approaches to this challenge are addressed later in this book.

1.1.4 Colloids and Nanoparticles

Colloids and nanoparticles occur when a material's particles become so small that they can be considered molecular aggregates. Colloids are operationally defined as fine material that stays in suspension with its surrounding medium (solid, liquid, or gas). As you will learn is the case of water solutions in the Critical Zone, the properties of a suspension are dependent upon the concentrations and types of dissolved ions in the solution. The surface charges of the particles play an important role. Since the mid-1990s, the terms "nanoparticle" and "nanocrystals" have come into popular use. Nanocrystals denote materials that have a crystalline order in the nanometer particle-size range (10^{-9} m). These materials are commonly detected by methods such as electron optics and are now routinely recognized with the advent of second-generation electron microscopes and synchrotrons.

Many advances in science (hence civilization as we know it) have come about by improving our ability to spatially resolve our environment. A good example is the scientific advancement made in the sixteenth century that accompanied the invention of telescopes and optical microscopes. As our ability to image and describe the order, disorder, and composition of materials across different scales improves, then so does our understanding of material. We are just starting to understand the nature of the nanoscale and the concept of nano-ordering. In other words, clay structures that we once perceived to be disordered or amorphous using a low-resolution scale of observation may be nanocrystalline when studied at higher resolution. A good example is found in the comparison of scattering X-rays versus scattering electrons. This will be discussed further in Chapter 3, but at this point suffice it to say that a material may be amorphous in structure when examined by scattered X-rays but crystalline when examined by scattered electrons. The next step in resolution is seeing order in the world on the picoscale.

1.1.5 Clay Rheology

Clay-sized particles can be comprised of numerous natural materials, so there is a second aspect to the answer to the question "What is clay?" that involves physical properties. Clay

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is operationally defined by rheology (i.e., the study of stress-deformation relationships). With appropriate water content, clays will plastically deform and harden when dried or fired. There is nothing inherent about the composition of clay; however, clay is often made up of clay minerals and may also include organic matter and other particles that do not impart plasticity. Rheometry is the quantitative measurement of flow and deformation of matter; hence it is used to study clays. Wet clays behave as non-Newtonian fluids. There are numerous instruments designed to measure their flow and deformation, which is the challenge of rheologists, who attempt to examine states of matter. These rheological states can range from the temperature of liquid helium to that of molten glass, in a space as small as a living cell or as large as that of concrete mixes. The Atterberg limits test is a common physical procedure designed to quantify the liquid, plastic, solid, and shrink behavior of clay-rich materials such as soils. Figure 1.3 provides a good overview of how particle composition, particle size, and the surrounding environment affect rheological properties. The plasticity of clay is a fundamental property that is defined as that which allows a material to be repeatedly deformed without rupture when acted upon by a force sufficient to cause deformation and to retain its shape after the force has been removed. Clay scientists refer to “fat” clays that are highly plastic (e.g., ball clays) and “lean” clays that are much less plastic (e.g., kaolins). Andrade et al. (2011) provide an excellent review of clay plasticity and note its importance to engineering and science. Choices of measurement methods for evaluating clays vary; therefore, application (i.e., the simulation of conditions or deformation) and cost criteria must be considered when investigating clay rheology.

1.1.6 Clay Minerals

The term “clay mineral” is most commonly used to denote a family of hydrous aluminosilicates (more specifically hydrous phyllosilicates) and minerals that impart the rheological criterion of plasticity when wet and hard or when dried or fired. Most clay minerals are found in nature with particle sizes in the < 4 μm range. However, there are clay minerals consisting of crystals larger than clay size. Clay minerals are chemically and structurally similar to the true micas and brittle micas, which are hydrous phyllosilicates. We can learn much about clay minerals from the macroscopic study of chlorites and common true micas, like muscovite, phlogopite, and biotite.

There are many other materials of geological and biological importance in the Critical Zone that are clay sized but that are not “clay minerals” by the definition given earlier. These other clay-sized minerals and materials include other silicates such as quartz, feldspars, and zeolites. Also of interest are nonsilicates – such as hydrous sulfates, hydroxides, carbonates, oxyhydroxides, hydrous oxides, amorphous compounds, and organic minerals – and biological entities like biochar, prokaryotes, and viruses. Another material is biochar, an earth-surface, clay-sized material produced by natural and anthropogenic pyrolysis (burning) of biomass that is found in many environments on our planet’s surface. Because all of these materials are often intimately associated with clay minerals, they are included in the domain of clay mineralogy and the study of clays in the Critical Zone.

Why are clay minerals clay sized? To answer this question, it is necessary to understand the concepts of surface free energy (discussed in further detail later in this book). The short

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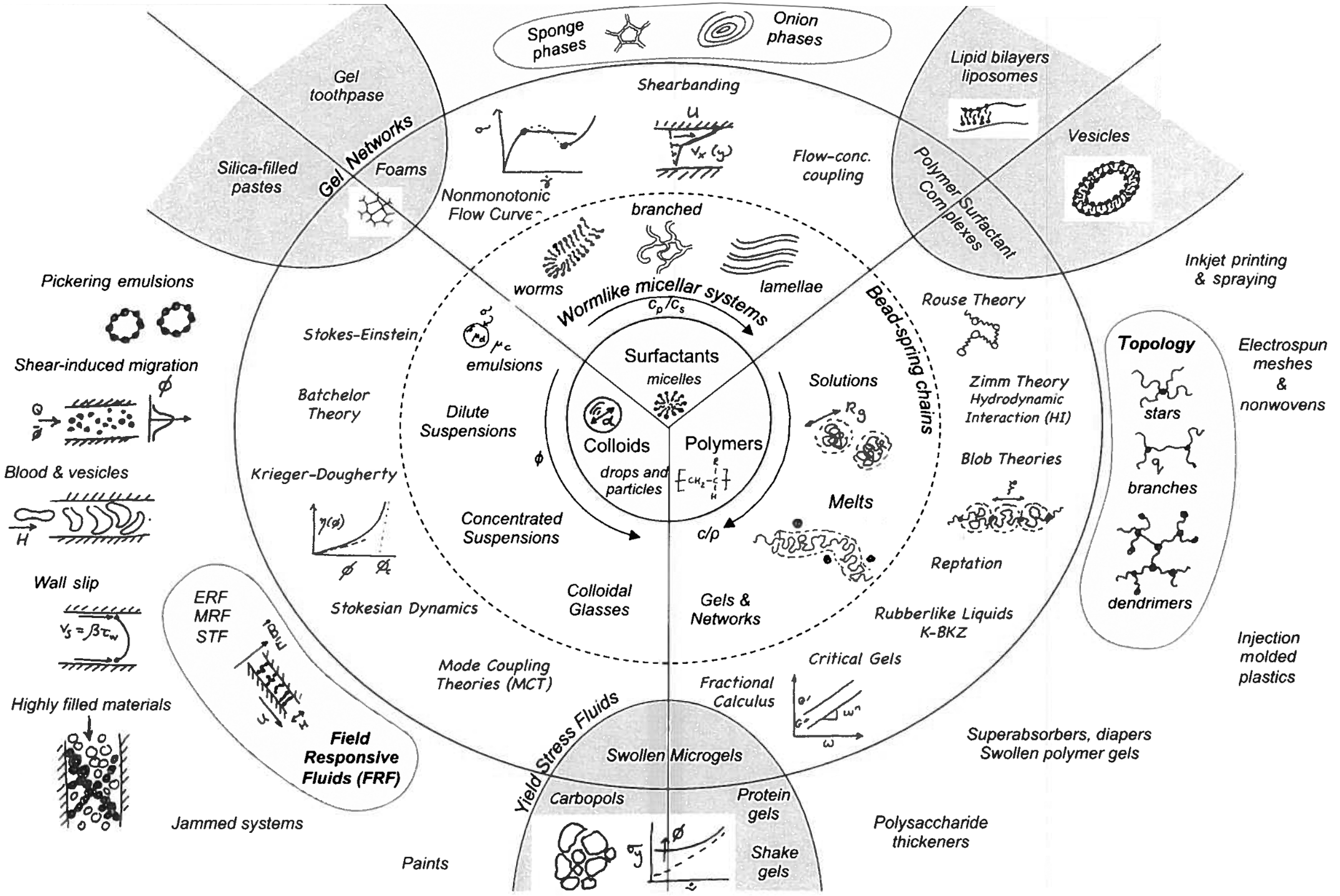

Figure 1.3 Gareth McKinley's "Hitchhiker's Guide to Complex Fluids." The center is subdivided into polymer-colloid-surfactant–scale entities (in the center of the diagram). In principle, clay minerals occur with similar dimensions and occupy the lower left portion of the diagram. Clays can interact with other materials to create gels, suspensions, emulsions, solutions, and micellar systems (the second sphere of the diagram). There are numerous theories that simulate rheological behaviors (the third sphere of the diagram), which have applied uses. The outermost sphere of the diagram depicts macroscale systems, each with application to materials that reside in the Critical Zone. These include man-made paints, pastes, pigments, absorbents, and gels as well as natural biological and mineral material (McKinley, 2015). For a traditional graphical representation of the classification of rheological properties, see Bilmes (1942).

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answer has to do with reactive surface areas of minerals and where steps form on the crystal surfaces. The planar surfaces of clay minerals (comprised of geochemically stable aluminum- and silicon-rich sheets) have a less reactive area (fewer steps) than their edges, so their total relative surface area prone to dissolution is small. Equant-shaped minerals have more reactive surfaces (more steps) than planar minerals and are more likely to react, particularly as their particle sizes are small. In other words, the surface step to volume ratio makes equant shapes more vulnerable to dissolution than planar shapes as particle sizes become clay sized.

If you were to ask every clay scientist, “What is the definition of a clay and a clay mineral?” then you’d likely get a different answer from each person. The philosophy here is to be inclusive of all materials and strive to understand their fundamental chemical structure and the nature of their interfaces. A resource for navigating clay and clay mineral nomenclature is the Clay Minerals Society (CMS) Glossary for Clay Science Project. This resource is updated periodically (www.clays.org) to keep it up to date with terms and their meanings, which change with time. Just as the Critical Zone encompasses different environments, so does clay terminology. Legal and commercial professions have a need for accurate definitions, so terms that can’t be reconciled by nomenclature committees are not included in the CMS Glossary. International bodies such as the International Mineralogical Association (IMA), CMS, and Association Internationale pour l’Étude des Argiles (AIPEA) attempt to establish definitions. Also evolving at this time is the larger concept of a controlled vocabulary, through which knowledge is organized for use by information science (e.g., the System for Earth Science Registration, www.earthchem.org or www.geosamples.org). Regardless of the names, the better you understand minerals that are clay sized (which will be the subject of the discussions that follow), then the better you will understand their behavior in the environment.

1.1.7 Why Are Clay Minerals So Important?

If we look at the volume of the solid part of the Critical Zone, we can see that clay minerals constitute about 16 percent of its total. Figure 1.4 depicts an approximation of the relative abundance of rock types on the Earth’ s surface. A 20 km thickness of the Earth’s crust is considered the “surface” because it is the region from which we extract natural resources and dump our waste (i.e., most of the mass in the Critical Zone). If 20 percent of the upper 20 km crust on the Earth is igneous and metamorphic rock, then that leaves 80 percent of all upper crust as sedimentary rock. If half of these sedimentary rocks are sandstone and limestone, then that leaves 40 percent of all upper rocks as shale. If nearly two thirds of shale is composed of framework silicates – including quartz, feldspars, oxides, and other silicates – then that leaves the remaining as clay minerals. Therefore, 16 percent of all surface rocks are comprised of clay minerals. When we consider that clay minerals are also abundant in soils and hydrothermal alteration zones associated with igneous and metamorphic rocks, then the percentage of clay is greater. This analysis admittedly ignores organics and water, but the point is that clay minerals are clearly a major component of the Earth’s surface. If clay minerals’ particle surface area is considered, given their small size, their relative surface area abundance is even greater.

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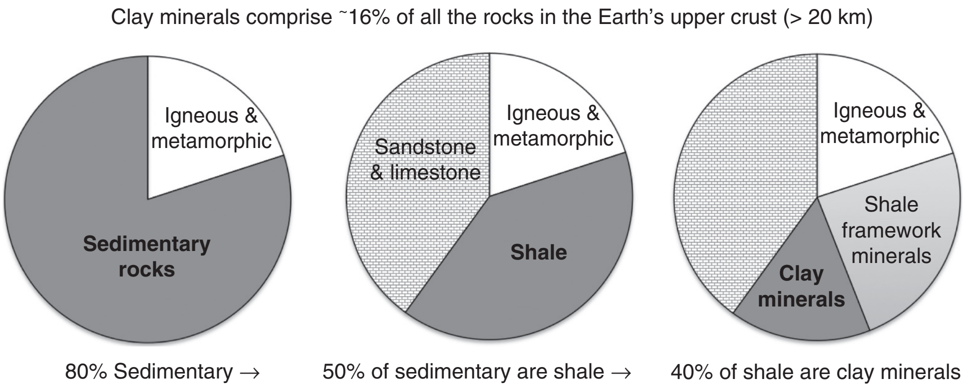

Figure 1.4 Approximate amounts of rocks in the Earth's crust. Values derived from Garrels and Mackenzie (1971), pp. 1–397.

1.1.8 Who Studies Clays?

The field of clay science is truly multidisciplinary (Figure 1.5). You are equally likely to encounter a geologist, civil engineer, soil scientist, chemist, agronomist, pharmacologist, biochemist, microbiologist, food scientist, astrobiologist, or material scientist at a clay science meeting. Such a meeting would have students and international participants from all around the world. Attendees would also be likely to come from a variety of professions, including those in industry, government, and academia. Industry scientists remind us that, at the end of the day, society needs clay products and that clay science and economics are not disconnected. Government scientists interface with the political and regulatory aspects of clay products and clays in our environment, and also reach out to the public concerning clay science's role in policy making. Academic scientists pursue basic research and train clay scientists for future generations. End-members of this ternary group rarely exist. Combining professions with the different fields of clay science should be appealing to anyone with a desire to advance Critical Zone science.

As a supplemental activity, a ternary diagram is provided in Figure 1.6 as a short exercise to perform either by yourself or with a group of clay scientists (students, teachers, or professionals). The intent is to remind us why we study clays and to keep in mind the reality of what drives people to pursue clay science. Perhaps Moore and Reynolds (1997) captured it well by saying, "[S]cience is a human activity, strongly influenced by culture. There are significant amounts of ambition, greed, luck, envy . . . underlying the work that gets done and is called science." Adding to this notion is the fact that dedication, excitement, and a steady work ethic are important traits needed to advance all sciences, including clay science.