Water, Air, and Geochemical Cycles



Elizabeth Kay Berner and Robert A. Berner

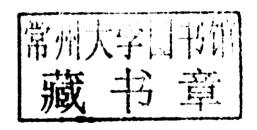
Second Edition

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To Abby, Katie, Sarah, Zach, Marshall, Charlotte, and Audrey

Preface to the Second Edition

During the past three decades, there has been a veritable explosion of books on environmental problems. However, this book is different in that it approaches the environment almost entirely in terms of global geochemical cycles both as they occur naturally and as they are affected by human activities. Here we emphasize such important problems as global warming, acid rain, rock weathering, erosion, eutrophication of both lakes and estuaries, and ocean acidification.

This book is intended for those who have a fundamental understanding of elementary chemistry, but it requires no other background in science, whether it be in biology, geology, meteorology, oceanography, hydrology, soil science, or environmental science. Our approach is multidisciplinary and covers all of these fields, but we do it from an elementary standpoint. Mathematical complexity is held to an absolute minimum, with the only requirement being some previous training in chemistry at the college freshman, or even the advanced high school, level. The book is appropriate as a primary or secondary text in junior- or senior-level undergraduate courses, or beginning graduate courses, in environmental geochemistry, environmental geology, global change, biogeochemistry, water pollution, geochemical cycles, chemical oceanography, and geohydrology. Because we provide extensive data on natural fluxes of chemicals, the book is also of reference value to researchers on global geochemical and environmental problems.

Much of this book is devoted to the natural behavior of the Earth's surface. We attempt to quantify the rates by which the major constituents of rocks, water, air, and life are transferred from one reservoir to another and to track down the sources of each constituent. We feel that a knowledge of geochemical cycles in the prehuman state is necessary before one can discuss how humans have perturbed these cycles.

The present book is a second edition of our 1996 book by the same title. Here we have put in extra effort to update the increasing amount of information being published on important global environmental problems. This includes,

among other things, an exhaustive study of changing climate and atmospheric chemistry by the Intergovernmental Panel on Climate Change (ICPP) in 2001 and 2007; new findings on how the problem of acid rain is being ameliorated somewhat; further information on the euthrophication of lakes, rivers, and estuaries; major advances in the study of chemical weathering; and the new global environmental problem of ocean acidification.

The material in this book has been used in courses over the past three decades by E. K. Berner at Wesleyan University and the University of Connecticut and by R. A. Berner at Yale University. We are grateful for the various suggestions made to us by both students and teaching assistants during the preparation of this book and its predecessor. Special thanks are due to Danny Rye for help in photograph preparation.

Elizabeth Kay Berner Robert A. Berner North Haven, Connecticut April 12, 2011

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Introduction to the Global Environment: The Water and Energy Cycles and Atmospheric and Oceanic Circulation

Introduction

In this book we shall be concerned with the principal constituents of rocks, water, and life as they circulate through the land, the sea, and the air. In other words, our concern will be with the geochemistry of the Earth's surface and how it operates naturally and how it has been perturbed by human activities. The approach is global in scope, and because of their special importance in Earth surface geochemical cycles, water and air will receive major attention. Water moves from the atmosphere to the land surface as rain containing pollutants added to the air by humans. Humans also add other gases and solids to the atmosphere that result in changes in atmospheric composition and climate. The air flows from one place to another, distributing pollutants over wide areas. Water once on the ground reacts with minerals contained in rocks, via a process known as chemical weathering, with a change in chemical composition of the water and with soil formation. Plants circulate elements between the atmosphere and soils. Water eventually makes its way into rivers, which obtain dissolved pollutants as well as suspended material derived from humanaccelerated erosion. The rivers then deliver their load to the oceans, where a variety of chemical and biological processes occur. Overall, it is these fluxes of water and air that ultimately act to maintain the overall chemical and physical conditions at the Earth's surface.

Throughout most of this book we will concentrate on the principal constituents transported by water and air. These are sodium, potassium, calcium, magnesium, silicon, carbon, nitrogen, sulfur, phosphorus, chlorine, and, of course,

hydrogen and oxygen. We shall point out how the global cycles of some of these elements have been perturbed by humans, resulting in such things as greenhouse gases, acid rain, eutrophic lakes, and oceanic acidification. Although they are of geochemical and environmental interest, we shall not be concerned with minor and trace elements (e.g., lead and mercury) or exotic synthetic chemicals (e.g., pesticides), since our goal is not all-inclusive environmental coverage. (The interested reader is referred to books such as those by Laws 2000 and Mackenzie 2011 for detailed discussion of environmental problems.) Rather, the approach is that of geochemists trying to understand how global chemical cycles operate and how they affect the major constituents of rocks, water, air, and life.

Because of their importance to climate and chemical changes in the global environment, emphasis in this chapter will be placed on the atmosphere and the oceans, and how their circulation operates; a discussion of the water and energy cycles of the Earth and their role in meteorology and oceanography will be included. The chapter, then, helps to set the stage for discussions of such subjects as the atmospheric greenhouse effect (chapter 2), acid rain (chapter 3), and chemistry of the oceans (chapter 8).

The Global Water Cycle

Major Water Masses

Earth is the only planet in the solar system having an abundance of liquid water on its surface; about 70% of the Earth is covered by liquid water. Because of the particular combinations of temperature and pressure on the planet's surface, water can exist here in three states: as liquid water, as ice, and as water vapor. This is in sharp contrast to the surface of the planet Mars, for example, which is so cold and dry that water can exist there only as ice or as water vapor.

Water is by far the most abundant substance at the Earth's surface. There are $1444 \times 10^6 \text{ km}^3$ of it in its three phases: liquid water, ice, and water vapor. As shown in table 1.1, most of the Earth's water (97%) is stored as seawater in the oceans. The remaining 3% is either on the continents or in the atmosphere. The amount of water in the atmosphere, in the form of water vapor, is very small in comparison with the other reservoirs, only around 0.001% of the total. However, it plays a very important role in the water cycle, as we shall see.

Of the fresh water stored on the continents, around two-thirds is in the form of ice in ice sheets, polar ice caps, and glaciers. Most of the rest of the continental water is present either as subsurface groundwater or in lakes and rivers. It is this small part of the Earth's total water (1%) that humans draw on for their water supplies. Here we shall focus on water near the Earth's surface and how it moves within and between the various reservoirs.

Fluxes between Reservoirs

Water does not remain in any one reservoir but is continually moving from one place to another in the hydrologic cycle. This is illustrated in figure 1.1. (For a more detailed discussion, see chapter 5 for runoff; also Penman 1970,

Table 1.1 Inventory of Water at the Earth's Surface

Reservoir	Volume 10 ⁶ km ³ (10 ¹⁸ kg)	Percent of Total
Oceans	1400	96.95
Mixed layer	50	
Thermocline	460	
Abyssal	890	
lce shelves (floating) ^a	0.7	0.048
Ice caps and glaciers ^b	0.09	0.006
Ice sheets ^a	27.6	1.9
Greenland	2.9	
Antarctica	24.7	
Groundwater	15.3	1.06
Lakes	0.125	0.009
Rivers	0.0017	0.0001
Soil moisture	0.065	0.0045
Atmosphere total ^b	0.0155	0.001
Terrestrial	0.0045	
Oceanic	0.0110	
Biosphere	0.002	0.0001
Approximate Total	1444	

Source: NRC 1986; Berner and Berner 1987; Lemke et al. 2007.

Baumgartner and Reichel 1975, NRC 1986, and Chahine 1992). Water is evaporated from the oceans and the land into the atmosphere, where it remains for only a short time, on the average about eleven days, before failing back to the surface as snow or rain. Part of the water falling onto the continents runs off in rivers and, in some places, accumulates temporarily in lakes. Some also passes underground only to emerge later in rivers, lakes, and the ocean. The remaining portion of the precipitation on the continents is returned directly to the atmosphere via evaporation. Over the oceans, evaporation exceeds precipitation, with the difference being made up by input via runoff from the continents. An idea of the sizes of these various fluxes of water (mass transported per unit time) is shown in figure 1.1.

In order to conserve total water, evaporation must balance precipitation for the Earth as a whole, since the total mass of water at the Earth's surface is believed to be constant over time. The average global precipitation rate, which is equal to the evaporation rate, is 0.506×10^6 km³/yr. For any one portion of the Earth, by contrast, evaporation and precipitation generally do not balance. On the land, or continental part of the Earth, the precipitation rate $(0.108 \times 10^6 \text{ km}^3/\text{yr})$ exceeds the evaporation rate $(0.071 \times 10^6 \text{ km}^3/\text{yr})$, whereas over the oceans evaporation $(0.435 \times 10^6 \text{ km}^3/\text{yr})$ dominates over precipitation $(0.398 \times 10^6 \text{ km}^3/\text{yr})$. The difference in each case $(0.037 \times 10^6 \text{ km}^3/\text{yr})$ comprises water transported from the oceans to the continents as atmospheric water vapor, or that returned to the oceans as river runoff (see fig. 1.1). Although inaccurately

a Lemke et al. 2007.

b As liquid volume equivalent of water vapor.