

---

Bruce Velde · Alain Meunier

## The Origin of Clay Minerals in Soils and Weathered Rocks



---

Bruce Velde · Alain Meunier

# The Origin of Clay Minerals in Soils and Weathered Rocks

With 195 Figures and 23 Tables



Springer

---

## Authors

### Bruce Velde

Ecole Normale Supérieure (ENS)  
Département Terre-Atmosphère-Océan  
Laboratoire de Géologie  
24, rue Lhomond  
75231 Paris Cedex 05, France  
E-Mail: [velde@geologie.ens.fr](mailto:velde@geologie.ens.fr)

### Alain Meunier

Université de Poitiers  
UMR 6532 HydrASA – Bâtiment Géologie  
40, Avenue du Recteur Pineau  
86022 Poitiers Cedex, France  
E-Mail: [alain.meunier@univ-poitiers.fr](mailto:alain.meunier@univ-poitiers.fr)

ISBN: 978-3-540-75633-0

e-ISBN: 978-3-540-75634-7

Library of Congress Control Number: 2008928139

© 2008 Springer-Verlag Berlin Heidelberg

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitations, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer. Violations are liable to prosecution under the German Copyright Law.

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Cover picture: © marilyn barbone – Fotolia.com

Cover design: deblik, Berlin

Typesetting: Uwe Imbrock, Stasch · Verlagsservice, Bayreuth ([stasch@stasch.com](mailto:stasch@stasch.com))

Production: Agata Oelschläger

Printed on acid-free paper 30/2132/AO – 5 4 3 2 1 0

[springer.com](http://springer.com)

---

## Preface

Of course such a book as we propose here is not the product of just two people working together, although the experience has been a great pleasure for us. We would like to thank our many collaborators and students who have encouraged our effort by their, often, sharp criticism. We hope that we have used their comments to good effect. Especially we would like to thank Pierre Barré for his help, enthusiasm and consent for the use of much of his thesis material in formulating the last chapter of the book. Dominique Righi was instrumental in giving us ideas, useful comments and vigorous debate for a great number of our ideas and during the periods of formulation of our conclusions. Our approach is from mineral chemistry and hence has greatly benefited from discussions with people who know soils and plants. The project of this book was realized and encouraged with the help of Wolfgang Engel who, unfortunately is not with us to see its finalization. We greatly regret his passing.

This book is not in the general pattern of accepted knowledge and analysis of the phenomena which affect the occurrence of clays in the surface environment. We stress the role of plants at the bio-interface and the importance of microsystems at the water/rock interface. We believe that the literature at our and anyone's disposal shows that the system of clay formation and reaction is highly dynamic, especially at the surface. Clay alteration profiles are slow to form, thousands to hundreds of thousands of years, but they react quickly at the surface to chemical change, essentially engendered by plants. This is the message. Clays can react in short periods, years to tens of years, and hence should be considered as part of the active surface environment. Land use can be impacted by management for periods as short as those of elected officials in governments. Thus soil scientists and ecologists can forcefully argue for better management on a year to year basis and the results can be shown within the period of an appointed official's term. Therefore a clear understanding of plant and soil interactions and the fundamental alteration processes is vital to stewardship of one of the most precious parts of nature, the soil zone.

We hope that this book and some of the ideas presented will inspire young people to look more closely at the surface environment in a quest for a more rational and viable use of soils. Surface clay minerals appear to react very rapidly to changes in environments, specifically changes in plant regime in soils. The high reactivity of this kind makes clay minerals potential indicators of changes in the Earth's surface paleo-conditions and those engendered by the action of agricultural man.



---

# Contents

<b>Introduction .....</b>	<b>1</b>
<b>1 Fundamentals of Clay Mineral Crystal Structure and Physicochemical Properties .....</b>	<b>3</b>
Introduction .....	3
1.1 The Common Structure of Phyllosilicates .....	3
1.1.1 From Atomic Sheets to Layers .....	4
1.1.2 Negatively Charged Layers .....	8
1.1.3 The Different Layer-to-Layer Chemical Bonds .....	10
1.2 Polytypes and Mixed Layer Minerals .....	11
1.2.1 Layers of Identical Composition: Polytypes .....	11
1.2.2 Layers of Different Composition: Mixed Layer Minerals .....	13
1.3 Crystallites – Particles – Aggregates .....	15
1.3.1 Crystallites: The Limit of the Mineralogical Definition .....	15
1.3.2 Particles and Aggregates .....	16
1.4 The Principal Clay Mineral Species .....	17
1.4.1 The Cation Substitutions .....	17
1.4.2 The Principal Mineral Species of the 1:1 Phyllosilicate Group .....	19
1.4.3 Principal Mineral Species of the 2:1 Phyllosilicates Group without Interlayer Sheet .....	20
1.4.4 The 2:1 Phyllosilicates with an Interlayer Ion Sheet (Micas) .....	21
1.4.5 Phyllosilicates with a Brucite-type Interlayer Sheet (2:1:1) .....	23
1.4.6 The Fibrous Clay Minerals: Sepiolite and Palygorskite .....	25
1.5 Typical Properties of Intermediate Charge Clay Minerals .....	26
1.5.1 Hydration and Swelling .....	26
1.5.2 The Crystallite Outer Surfaces .....	28
1.5.3 The Ion Exchange Capacity .....	30
1.6 Particularities of Clay Minerals: Size and Continuity .....	34
1.6.1 Clay Minerals are always Small .....	34
1.6.2 The Reduced Number of Layers in the Stacks	
Typical of Clay Minerals .....	37
1.6.3 From Order-Disorder to Crystal Defects .....	38
1.6.4 Composition Heterogeneity at the Scale of a Single Layer .....	41
1.7 How Do Clay Minerals Grow? .....	46
1.7.1 Phyllosilicate Growth Principles .....	46

1.7.2	Speculative Interpretation of Growth Processes – Crystal Morphology Relations .....	50
1.7.3	Nucleation Processes in Clay-Bearing Rocks .....	53
1.8	Summary: Clay Minerals in Soils and Weathered Rocks .....	56
1.8.1	The 2:1 Clay Structure and Its Importance in Soils .....	56
1.8.2	The Illitic Minerals in Soils and Weathered Rocks .....	57
1.8.3	Expandable Minerals (Smectites – Vermiculites) .....	61
1.8.4	Hydroxy Interlayered Minerals .....	62
1.8.5	Mixed Layer Minerals in Soils .....	67
1.8.6	Kaolinite and Kaolinite/Smectite Mixed Layer Minerals (K/S) .....	68
1.8.7	Allophane and Imogolite .....	69
1.8.8	The Non-Phyllosilicate Minerals in Soils and Weathered Rocks .....	71
1.8.9	Stability of Clay Minerals Formed under Weathering Conditions .....	73
	Suggested Reading .....	73
<b>2</b>	<b>Basics for the Study of Soil and Weathered Rock</b>	
	<b>Geochemical Systems</b> .....	75
	Introduction .....	75
2.1	Definition of the Systems .....	76
2.1.1	The Size of the Systems under Consideration .....	76
2.1.2	The Solutions in Systems of Different Size .....	87
2.2	The Physicochemical Forces Acting in the Systems .....	91
2.2.1	Basic Definitions .....	91
2.2.2	The Chemical Potential .....	94
2.2.3	A Particular Chemical Potential: The pH .....	99
2.2.4	The Oxidation-Reduction Potential (Redox) .....	105
2.3	Mineral Reactions in Alteration Systems .....	108
2.3.1	Conditions at Equilibrium .....	108
2.3.2	Kinetics of Alteration Reactions .....	110
	Suggested Reading .....	111
<b>3</b>	<b>The Development of Soils and Weathering Profile</b> .....	113
	Introduction .....	113
3.1	Physical Description of Soils and Weathering Profiles .....	114
3.1.1	The Development of Weathering Profiles .....	114
3.1.2	The Development of Soils .....	118
3.1.3	Conclusion in a YES or NO Question Series .....	122
3.2	Dynamics of the Alteration Process under Temperate Conditions: An Investigation Comparing Soil and Rock Alteration in Profiles .....	123
3.2.1	Alteration in Temperate Climates .....	123
3.2.2	Kinetics of Alteration Processes .....	125
3.2.3	Kinetics of Soil Formation .....	127
3.3	The Inter-Relation of the Dynamics of the Alteration-Soil Profile Sequence .....	132
3.3.1	Overview of Soil and Weathering Mineralogy .....	132
3.3.2	The Mineralogy of Soil Horizons .....	134

3.3.3	Mineralogical and Chemical Differences between Alteration and Soil Zones .....	135
3.4	What Are the Clay Mineral Assemblages? .....	137
3.4.1	Formation of Different Clay Mineral Phases in A Horizon .....	137
3.4.2	General Schema of Alteration Zone and Soil Relations .....	140
3.4.3	Overview of Alteration in the Soil Zone in Temperate Climates .....	142
	Suggested Reading .....	142
<b>4</b>	<b>Clay Mineral Formation in Weathered Rocks:</b>	
	<b>Water–Rock Interaction</b> .....	143
	Introduction .....	143
4.1	Weathered Rock Profiles in Temperate Climates .....	144
4.1.1	Weathering at the Landscape Scale .....	144
4.1.2	The Parent Rock Control on Weathering Profiles .....	147
4.1.3	The Climate Control on Weathering Profiles .....	152
4.1.4	From Macro- to Microscopic Scale .....	155
4.2	The Internal Destabilization of Primary Minerals (Primary Plasmic Microsystems) .....	156
4.2.1	Porosity-Permeability and Microsystems in Crystalline Rocks .....	156
4.2.2	Petrography of Contact Microsystems .....	163
4.2.3	Petrography of the Primary Plasmic Microsystems .....	167
4.3	Mineral Reactions in the Secondary Plasmic Microsystems .....	193
4.3.1	Petrography of the Secondary Plasmic Microsystems .....	194
4.3.2	Clays Forming in Secondary Plasmic Microsystems .....	196
4.4	The Ultimate Weathering Stages .....	203
4.4.1	The Fissural Microsystems: Cutans .....	203
4.4.2	Accumulations (Absolute and Residual) .....	207
4.5	The Weathering of Porous Sedimentary Rocks .....	214
4.5.1	Gluconitic Sandstones .....	214
4.5.2	Weathering of Marls .....	217
4.6	Possible Models for Weathering Processes .....	219
4.6.1	From Heterogeneity to Homogeneity .....	219
4.6.2	Mass Balance and Weathering Rates .....	222
4.6.3	From Qualitative to Quantitative Models .....	225
4.7	Summary of the Water/Rock Interaction Clay-Forming Processes .....	237
	Suggested Reading .....	239
<b>5</b>	<b>Plants and Soil Clay Minerals</b> .....	241
	Introduction .....	241
5.1	Dynamics of Clay Reactions in the Soil (Plant/Clay Interaction) Zone of the A Horizon .....	241
5.1.1	Disequilibrium in Plant–Soil Zone Clays .....	241
5.1.2	Dynamics of Clay Reactions in the Soils .....	242
5.2	Clay Mineral Types in the Plant–Soil Interaction Zone .....	247
5.2.1	Illite .....	247
5.2.2	Kaolinite .....	248

5.2.3	Oxides and Oxyhydroxides .....	249
5.2.4	Mixed Layer Minerals .....	249
5.3	Soil Clay Mineral Assemblages by Ecological Type .....	255
5.3.1	Prairie Soils .....	256
5.3.2	Forest Soils .....	261
5.4	Chemical Control in Soil Horizon by Plant Action .....	265
5.4.1	Silica .....	266
5.4.2	Potassium .....	267
5.4.3	Element Loss and Element Gain .....	270
5.5	Agricultural Influences .....	272
5.5.1	Prairie Soil Clay Mineralogy in Agriculture .....	272
5.5.2	Effect of Fertilizer on Clay Minerals .....	278
5.5.3	Plants and Soil Clay Minerals: Some Thoughts for Further Consideration .....	281
	Suggested Reading .....	281
6	<b>Clays and Climate – Clay Assemblages Formed under Extreme Humidity Conditions</b> .....	283
	Introduction .....	283
6.1	Impact of High Rainfall on Clay Mineralogy .....	283
6.1.1	Soil Development as a Function of Rainfall .....	283
6.1.2	Very High Rainfall .....	285
6.2	Rainfall and Vitreous Rocks (Andosols) .....	288
6.2.1	Andosol Characteristics .....	288
6.2.2	Weathering Processes Affecting Vitreous Rocks under Constantly Humid Conditions .....	290
6.2.3	Mineralogy and Hydration State of Andosols .....	293
6.3	Weathering Trends as a Function of Time .....	294
6.3.1	Weathering Trends as a Function of Time under Tropical Conditions .....	294
6.3.2	Weathering Trends in Semi-Arid and Arid Climates .....	295
6.3.3	Summary .....	298
	Suggested Reading .....	299
7	<b>Physical Disequilibrium and Transportation of Soil Material</b> .....	301
	Introduction .....	301
7.1	Slope Effects and Physical Disequilibrium .....	301
7.1.1	High Slopes in Mountains .....	301
7.1.2	Moderate Slopes .....	302
7.1.3	Wind and Water .....	303
7.1.4	Movement of Coarse Grained Material .....	306
7.2	Fine Grained Material .....	306
7.2.1	Wind Transport and Loess .....	307
7.2.2	Reaction Rates due to Plant/Loess Interaction .....	308
7.2.3	River Transport and Salt Marsh Sediments .....	312
7.3	Catena Movement of Fine Grained Material on Slopes .....	314

7.3.1	Topographically Controlled Soil Sequences .....	314
7.3.2	Slope and Smectite Genesis (Catenas) .....	314
7.4	Summary .....	318
	Suggested Reading .....	319
<b>8</b>	<b>The Place of Clay Mineral Species in Soils and Alterites .....</b>	<b>321</b>
	Introduction .....	321
8.1	Where Clay Mineral Types Occur in Alterites and Soils .....	321
8.1.1	The 2:1 Minerals .....	322
8.1.2	Kaolinite and Kaolinite/Smectite Mixed Layer Minerals .....	325
8.1.3	Gibbsite .....	325
8.1.4	Iron Oxyhydroxides .....	326
8.1.5	Imogolite and Allophane .....	326
8.1.6	Chlorites .....	327
8.1.7	Palygorskite, Sepiolite .....	327
8.2	Clay Minerals Present in Soils as a Response to Climate .....	328
8.2.1	Physical Factors and Their Effect on Alteration and Soil Clay Mineral Facies .....	328
8.2.2	Weathering Trend (Water – Silicate Chemical Trends) .....	330
8.3	The Impact of Plant Regime on Clay Minerals in Soils .....	334
8.3.1	Reactivity of Clay Minerals in Ecosystems .....	334
8.3.2	Convergence of Soil Clay Mineralogies .....	337
8.3.3	Effect of Chemical Translocation by Plants on Clay Mineral Stabilities .....	338
8.3.4	Equilibrium and Disequilibrium of Soil Clays .....	343
8.4	The Structure of Alteration and Clay Formation .....	344
8.4.1	Water/Rock Interaction .....	344
8.4.2	Source Rock and Clays .....	345
8.4.3	Plant/Soil Interaction .....	345
8.4.4	Clay Transport .....	346
8.4.5	Kinetics of Clay Change in the Soil Zone .....	347
8.4.6	Minerals Present and Their Change in the Soil/Plant Interaction Zone .....	347
8.4.7	Conclusions .....	349
8.5	Perspectives for Clay Mineral Science in Surface Environments: Challenges for the Future .....	349
8.5.1	Soils and Crops .....	349
8.5.2	Soils as a Natural Safety Net for Modern Society .....	351
	Suggested Reading .....	351
<b>Annexes</b> .....	<b>353</b>	
<b>Annex 1 – Polytypes</b> .....	<b>353</b>	
Definition .....	353	
An Example: The Mica or Illite Polytypes .....	353	
References .....	355	

<b>Annex 2 – Mixed Layer Minerals .....</b>	357
Conditions of Interstratification .....	357
Random Stacking Sequence (Ro) .....	357
Ordered Stacking Sequences (R <sub>1</sub> ) .....	357
References .....	360
<b>Annex 3 – Cation Exchange Capacity .....</b>	361
The Chemical Reaction of Cation Exchange .....	361
Deviation from Ideality .....	362
The Variable Charges .....	363
References .....	364
<b>Annex 4 – Hydroxy-Interlayered Minerals (HIMs) .....</b>	365
The XRD Properties of Hydroxy-Interlayered Minerals .....	365
The Incorporation of Al Ions in the Interlayer Region of HIMs .....	365
The Crystallochemical Composition of HIMs .....	371
The Mixed Layer Model .....	372
Conclusion .....	373
References .....	373
<b>Annex 5 – Phase Diagrams Applied to Clay Mineral Assemblages .....</b>	375
Fundamentals .....	375
Clay Minerals: The Stable Phases at Surface of the Earth .....	377
References .....	378
<b>Annex 6 – Kinetics .....</b>	381
Fundamentals .....	381
The Fick's Laws .....	382
Suggested Reading .....	384
<b>References .....</b>	385
<b>Subject Index .....</b>	403

---

## Introduction

As outlined in Chap. 1, clays are historically considered to be formed of  $<2\text{ }\mu\text{m}$  particles. The use of the optical microscope for petrographic observations at the end of the 19th century defined the limit of a recognizable crystal and mineral. Crystals whose size was lower than the resolution of the optical microscope,  $2\text{ }\mu\text{m}$ , were unidentifiable and called clays. Because of this size-dependent definition, clays include different mineral species: silicates, oxides, carbonates. The largest part of the material of our investigation is called a phyllosilicate, i.e. silicate material which has a sheet like aspect, thinner than long and large. However such materials which are found in the small grain size fraction, though most often of small size, can at times reach several tens of micrometers in diameter. The same types of mineral can be found as high-temperature phyllosilicate equivalents, minerals such as micas and chlorites which can be found in centimetric sizes. Thus size is not a definite description of the silicate minerals found and formed at the Earth's surface. In a very general manner, one can say that phyllosilicates of high temperature origin, greater than  $40\text{ }^{\circ}\text{C}$ , are of diagenetic or metamorphic origin and are not stable under surface conditions. They tend to interact chemically at conditions where atmospheric water is present. It remains for us to show the differences between clay minerals whose origin is at the Earth's surface and those formed under other conditions. The first identification of a surface clay mineral is that it has a small grain size, generally  $<2\text{ }\mu\text{m}$ .

Even if the reasons for small crystal size which are constantly observed are not fully understood at present, it is certainly the major characteristic of surface clay minerals. Because small size induces very great crystal surfaces, most of the remarkable chemical and physical properties of clay minerals are related to surface interactions. This was discovered very early during the first ages of human technical development: the plasticity of water-clay mixtures which was exploited during the Neolithic period for the production of pottery. Soils, and consequently clay minerals, are the support of the most fundamental activities of mankind: agriculture, ceramics and housing. Even today about 40% of the Earth's inhabitants live in dwellings composed in part by earth, i.e. clay assemblages with other materials. Therefore, the question of the origin of clay minerals is as important as that of the origin of humanity. Clay minerals are hydrated silicates. They contain hydrogen assigned to OH groups which contribute to the electronic stability of the framework of the crystal lattice (Grim 1953). However, they often contain molecular water associated with cations located between the basic structural layers of the minerals. It is clear that hydrogen and hence water is essential for clay mineral formation. Generally speaking, clay minerals form from aqueous solutions interacting with other, pre-existing, silicate species by dissolution-recrystalliza-

tion processes. Thus, the origin of clay minerals is related to water-rock interactions. In order to understand the mechanisms of fluid-rock interactions it is important to determine the driving force of these reactions typical of Earth surface conditions. Particularly, the role of chemical potential gradients must be considered in order to determine the stability domains of each species of clay mineral. One should keep in mind that clay minerals are first of all minerals, that is to say solids, able to react to changes in the conditions of their environment. Such changes are classically described in burial diagenesis where surface alteration clays are progressively transformed into illitic ones under increasing burial conditions, i.e. changes in temperature.

The most important geological occurrence where clay minerals are formed is that of rock weathering and soil formation. However, one must not forget that clay minerals are formed under the influence of hydrothermal action, i.e. the interaction of water and rock at conditions below the Earth's surface. Here one major clay resource is that of kaolinite, a mineral which has been used in many different industrial applications. Further, one finds significant alteration (weathering) of ocean bottom basalts creating proto-clay minerals which act as a sink for potassium in ocean water transfer, leaving sodium as the major alkali present in the greatest surface zone of the Earth. Diagenetic alteration of volcanic ash forms a near mono-mineralic material called bentonite (smectite) which has received recent attention in use for waste repositories for radio-active materials. Thus, atmospheric interaction with rocks is not the only source of clay minerals. However, the most likely interaction that humans are likely to have with clays is with those formed under conditions near those of the human environment, alteration of rocks to form soils.

We would like to attempt an explanation of the interactions of silicate and water at the surface of the Earth in systems generally described as weathering. This is the site of surface clay mineral formation. Water is the major motor of reaction, allowing and engendering chemical change. The minerals formed are stable at low temperatures, probably below 40–80 °C compared to those present in diagenetic series. However, the rapid change of mineralogy, on a geological scale at least, indicates subtle changes in the mineral structure as determined by X-ray diffraction, the major identification tool for clay minerals. Such change is the result of different chemical equilibria. Our objective is to clarify the factors which engender the change and persistence of surface clay minerals. In order to do this it is useful to understand the specificity of clay mineral structures and chemistry. The second step is to determine the chemical variables found under surface conditions which can produce and act upon surface clay minerals once formed. If one understands the origin of surface clays, and their stabilities, it will be possible to use them to better advantage in the coming era of environmental awareness.