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# **Structural and Determinative Mineralogy with Emphasis on Layer Silicates**

*A thesis submitted for the degree of Doctor of Science at the University of Adelaide*

Richard Anthony Eggleton

September 1998

**This thesis is dedicated to Glen, Rachel and Cate, for their support, love, and understanding, and to the inspirational Sturges W. Bailey.**

This thesis contains no material that has been accepted for the award of any other degree or diploma in any university or other tertiary institution, and to the best of my knowledge and belief, contains no material previously published or written by another person except where due reference has been made in the text.

I give consent to this copy of the thesis, when deposited in the University Library, being available for loan and photocopying.

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- 1 Eggleton R. A. (1968) Phase Determination for Pseudo-symmetric Centrosymmetric Crystals. *Acta Crystallographica* **A25**, 543-547.
- 2 Eggleton, R. A. (1972) The crystal structure of stilpnomelane: Part II. The full cell. *Mineralogical Magazine* **38**, 693-711.
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- 4 Guggenheim, S., Bailey, S. W., Eggleton, R. A., and Wilkes, P. (1982) Structural aspects of greenalite and related minerals: *Canadian Mineralogist* **20**, 1-18.
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- 8 Guggenheim, S. and Eggleton, R. A. (1986) Structural modulations in iron-rich and magnesium-rich minnesotaite: *Canadian Mineralogist* **24**, 479-497.
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- 25 Eggleton, R. A. and Boland, J. N. (1982) The weathering of enstatite to talc through a series of transitional phases. *Clays and Clay Minerals* **28**, 173-178.
- 26 Eggleton, R. A. and Keller, J. (1982) The palagonitization of limburgite glass, a TEM study. *N. Jb. Min. Monatshefte* **H7**, 321-336.
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- 35 Robertson, I.D.M. and Eggleton, R. A. (1991) Weathering of granitic muscovite to kaolinite and halloysite and of plagioclase-derived kaolinite to halloysite. *Clays and Clay Minerals* **39**, 113-126.

## Abstract

Research into the structure and formation of fine-grained layer silicates has revealed chemical and stereochemical features that determine their behaviour in natural systems. Particularly in low-grade metamorphic environments, where Fe and Mn are divalent, layer silicates having these cations in their octahedral sheets form complex structures. Investigations by X-ray diffraction and electron microscopy have discovered the structures of seven modulated layer silicates. Because of dimensional misfit between a larger octahedral sheet and a smaller tetrahedral sheet, modulations develop in the tetrahedral sheet, their spacing determined by the extent of misfit. Stresses placed on the interatomic bonding as a result of this generally lead to minute crystals being formed, and in some minerals the crystalline order is very short-range (greenalite, caryopilite) and in others a non-crystalline curved morphology results (serpentine, halloysite, hisingerite).

During rock weathering, fine-grained layer silicates crystallise by processes that are directly related to the structure of their parent silicate. TOT silicates (pyroxenes, amphiboles, micas) transform topotactically to layer silicates and iron oxyhydroxides. Precipitated species may adopt an epitaxial relation to the altering mineral. Alteration products of close-packed structures (e.g. olivine) and those with octahedral chains or sheets (e.g. kyanite) also form in epitaxial relationships to the parent. Framework silicates (feldspars, cordierite, zeolites) alter by a dissolution-precipitation process involving an amorphous intermediary. Classification of silicates into these groups shows their weathering behaviour and chemistry more clearly than by reference to the commonly used silica polyhedral classification.

A succession of minerals is developed during the weathering of the silicates, each having fine grain-size and large specific surface area. Weathering reaction rates will depend on the rate of the slowest step in this succession. Hosts for a variety of trace elements are created in these transient species, and recognising their presence gives the potential to better understand element migration and retention in the regolith.

## Introduction

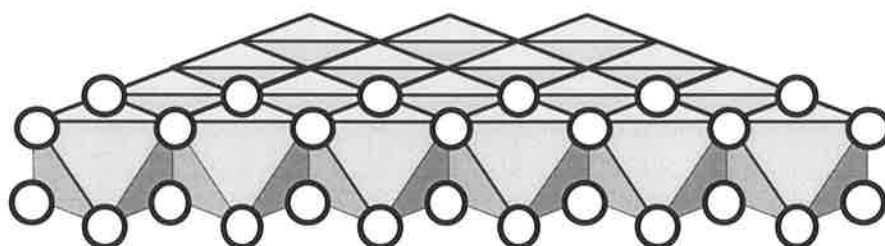
This thesis presents a body of research into the nature and origins of minerals of a group variously known as layer silicates, sheet silicates, or phyllosilicates. The papers which reported the research are in three groups. In Group 1 are papers on the subgroup of the layer silicates which are known as the *modulated layer silicates*, a term introduced by Guggenheim and Eggleton (1986, paper 8, Table 2). The balance of authorship for all submitted papers is indicated in the Tables of papers. Group 2 comprises papers largely on the nature of fine-grained layer silicates - the *clay silicates*. The research for this group of papers has benefited from collaboration with other scientists, and from higher degree student research under my supervision. Group 3 is papers on the weathering of rocks and minerals, and on the formation of clay minerals. The research streams of the three Groups were prosecuted contemporaneously, and the knowledge and insights from each informed the other. Central to all has been the use of the techniques of X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM).

The thesis is arranged in five chapters, each devoted to particular aspects of the research. Chapter one deals with the techniques which have been fundamental to the research: XRD and HRTEM. Chapter 2 considers the modulated layer silicates, emphasising the relationships between these minerals and other silicates that have emerged through the research. Chapter 3 addresses the advances in the understanding of clay silicates, and Chapter 4 is on the alteration of other silicates and the consequent formation of layer silicates. The three facets of the research are drawn together in Chapter 5, with a discussion of some of the implications of the work.

### LAYER SILICATES

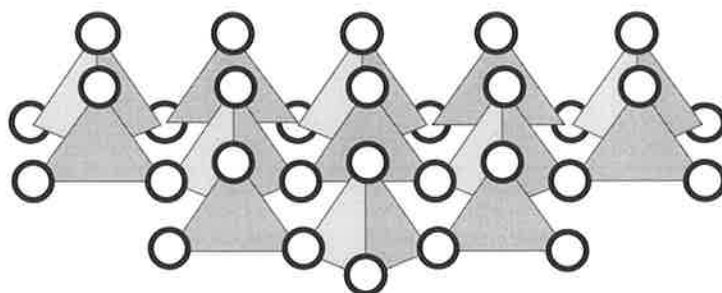
The basic crystal structure of the layer silicates was elucidated in the 1930s (Pauling, 1930), and it is now recognised that this mineral group, which includes most of the clay silicates, have closely related structures. All have two structural units; an octahedral sheet and a tetrahedral sheet.





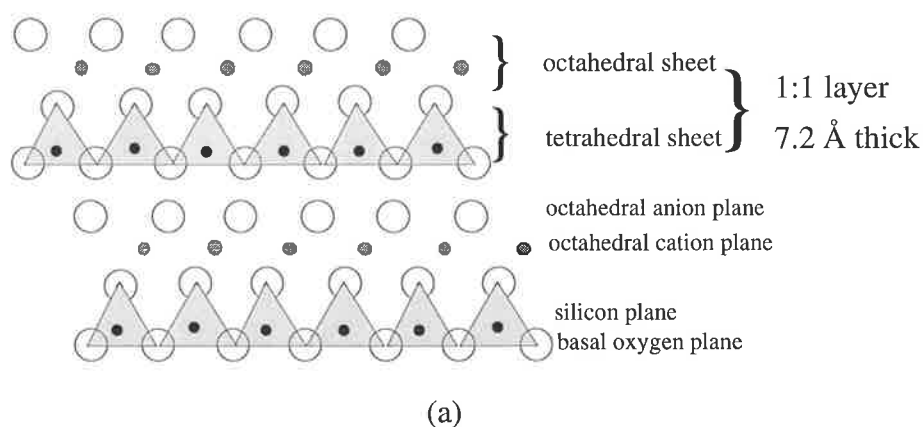
**Figure 1** Octahedral sheet of a layer silicate

The octahedral sheet (Fig 1) comprises a plane of cations in octahedral coordination with planes of anions on either side, and the tetrahedral sheet (Fig 2) similarly has two anion planes, but with the cations between in 4-fold or tetrahedral coordination.



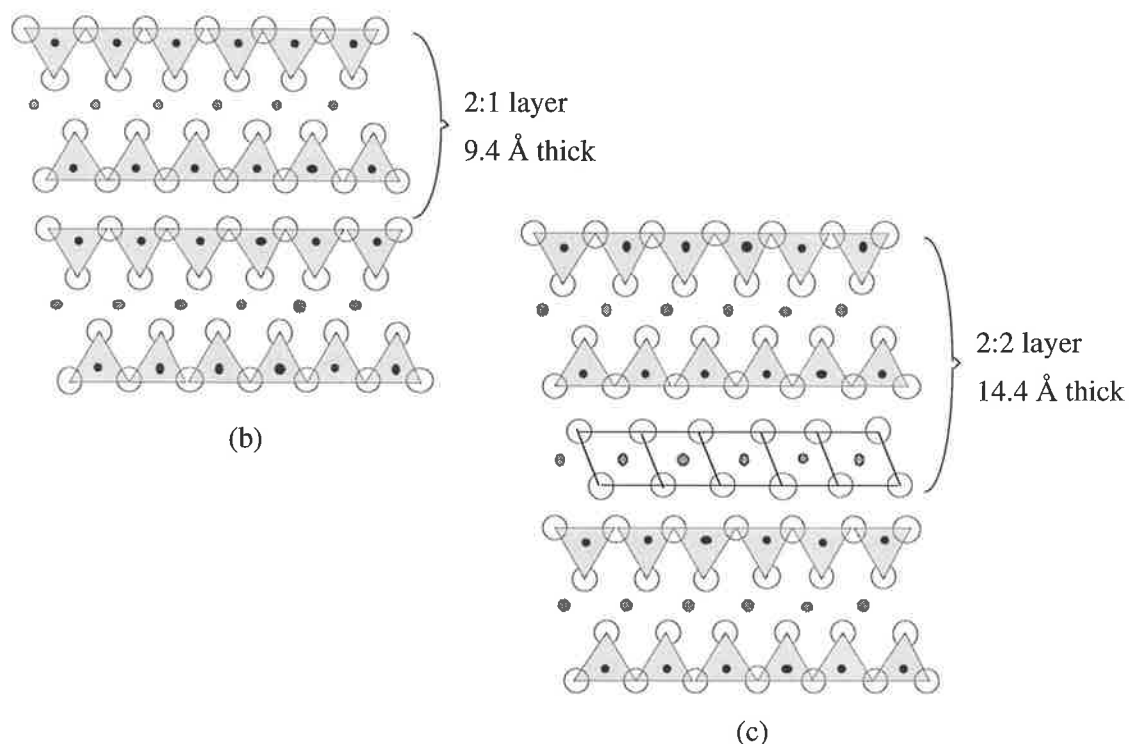
**Figure 2** Tetrahedral sheet of a layer silicate

The two sheets combine to form layers in which one plane of oxygens in the octahedral sheet is also a plane of oxygens in the tetrahedral sheet (Fig 3).



**Figure 3** Structure of layer silicates.

(a) kaolinite, a 1:1 dioctahedral layer silicate;



**Figure 3 (cont)** Structure of layer silicates.

(b) talc, a 2:1 trioctahedral layer silicate;

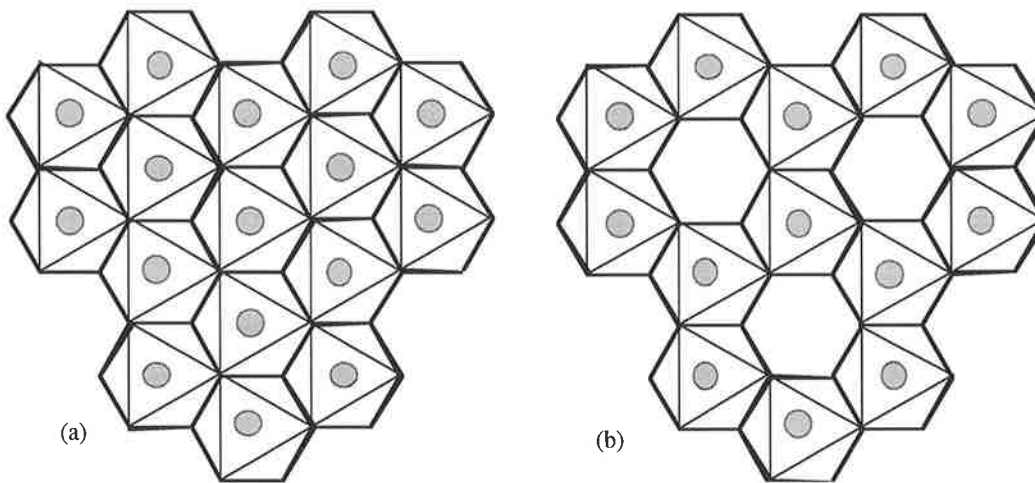
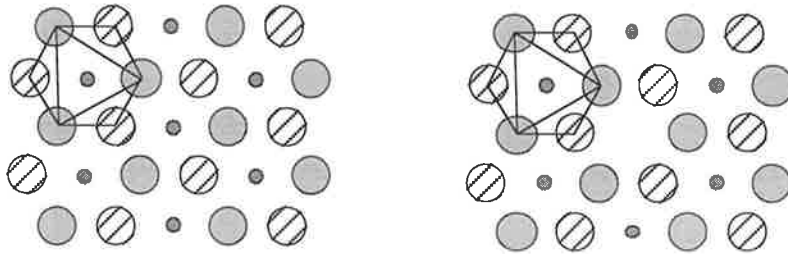
(c) chlorite, a 2:2 layer silicate.

A terminology for describing layer silicates has arisen from the work of the AIPEA Nomenclature Committee (Bailey, 1980). All components of the structure are planar (Fig 3):

- atoms are referred to as lying in *planes*
- two planes of anions with a plane of cations coordinated between them to form linked polyhedra are referred to as *sheets*
- sheets linked by common anion planes are referred to as *layers*.

The normal layer silicates (as contrasted with the modulated layer silicates) are classified on two criteria. The first identifies the occupancy of the octahedral sheet. An isolated octahedral sheet, such as in the mineral brucite ( $\text{Mg}_3(\text{OH})_6$ ), has trigonal symmetry, and a unit cell containing three  $\text{Mg}_3(\text{OH})_6$  octahedra. By contrast, the mineral gibbsite ( $\text{Al}_2(\text{OH})_6$ ), while also having trigonal symmetry and three octahedra in its unit cell, has one octahedron vacant.

Octahedral sheets having all three octahedra occupied are called *trioctahedral*, those with only two occupied are *dioctahedral*. (Fig 4)



**Figure 4** (a) trioctahedral sheet. (b) dioctahedral sheet.

The second classification criteria refers to the sequence of octahedral sheets and their flanking sheets of [SiAl] tetrahedra.

Known configurations for octahedral and tetrahedral sheet sequences are only three (Fig 3):

- one octahedral sheet with one flanking tetrahedral sheet (1:1 layer silicates);
- one octahedral sheet with two flanking tetrahedral sheets (2:1 layer silicates); and,
- 2:1 layers with octahedral sheets between (2:2 layer silicates).

Variations available to each layer type are:

- the nature of the octahedral cation, dominantly Al or Fe<sup>3+</sup> in dioctahedral sheets, and Mg or Fe<sup>2+</sup> in trioctahedral sheets. Mn<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>3+</sup>, Cr<sup>3+</sup>, Ti<sup>4+</sup> are common minor components in the octahedral sheet; and,
- substitution in the tetrahedral site of Si by Al, leading to a positive charge deficiency compensated by either a large low-charged cation between 2:1 layers (micas), or by positive charge generated in the octahedral sheets of 2:2 layer silicates by a R<sup>2+</sup> ↔ R<sup>3+</sup> substitution (chlorite).

## Chapter 1

### Techniques

Almost all the research presented here has required study of minerals with a particle size below the resolution of an optical microscope. That is, with the exception of the study of the crystal structures of stilpnomelane and ganophyllite, none of the material has been of sufficiently large crystal size to allow examination by the standard methods of single-crystal X-ray diffraction analysis, or indeed of such size as to allow the physical separation of the target mineral from its associates. X-ray powder diffraction has been an invaluable tool in the work, and for the most part this technique has been applied in conventional ways. A major consequence of small particle diffraction is the broadening of the diffraction maxima, with resultant changes in peak position and intensity. Essential to the understanding of such patterns is the Fourier Transform concept of diffraction (e.g. Lipson and Taylor, 1958), an approach first applied to modulated layer silicates in research on stilpnomelane (2), with the theory expounded in paper 1. This appears to have been the first report of an experiment using laser light to illuminate a structure model and so produce an optical diffraction pattern which could be compared to an observed XRD pattern. At a time when computation was unable to manage large crystal structures in a reasonable time, this was a pioneering technique, also applied to the determination of the structures of greenalite (4) and minnesotaite (8). With the advent of higher-speed computation, the diffraction patterns for the modulated structures of bementite (9) and parsettensite (10) were computed using normal Bragg diffraction theory. For greenalite-caryopilite (13), this theory was extended to perform calculations for one entire crystal of limited dimension (~10,000 atoms), reproducing by computation the electron diffraction results obtained for individual 15 nm diameter particles. This is an original approach to structure modelling.

The one-dimensional full XRD profile calculations for nontronite (14) showed that both crystal structure and particle size can be accessed by careful experimentation and comparison with theory. Similar calculations for kaolinite (18) allowed an estimate of particle size distribution for a kaolinite clay aggregate. As with the work on greenalite (4, 13) these studies are unique in comparing the calculated diffraction pattern from a complete aggregate of N atoms with the observed pattern. The normal approach is to calculate the Bragg intensity and position for an ideal crystal, then broaden this peak by a particle size formula. The nontronite work (14) was also the first to recognise that the act of preparing a clay

sample for diffraction could introduce inter-particle diffraction, and foreshadowed the "fundamental particle" concept (Nadeau et al, 1984).

Transmission electron microscopy (TEM) is also a long-standing technique in the study of fine-grained minerals. Prior to the work reported here, all TEM work on clays had made use of dispersed particles, examining them by diffraction and imaging before and after shadowing, or by microtoming. Dispersed platy clay minerals can only be prepared as aggregates normal to their XY plane, and the technique prevents any viewing of relationships between grains. Microtoming has the twin disadvantages of providing a relatively thick sample, and of introducing the likelihood of sample damage by shearing.

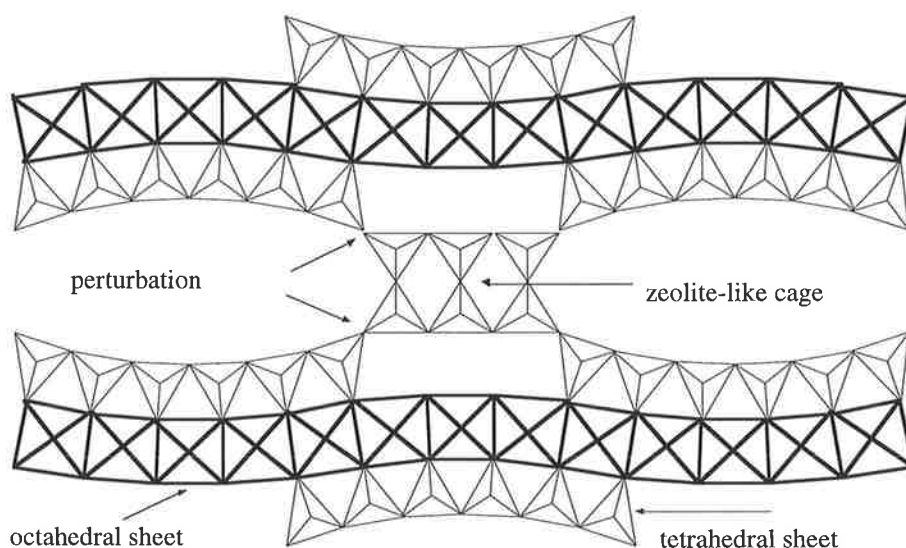
The method of ion-beam thinning can be used for mineral materials (see for example Buseck et al, 1988); it avoids the disadvantages of both dispersion and microtoming, and most of the work of this thesis has made use of ion-thinned materials. The application of this technique to clays and weathered rocks was the first to be reported (22 et seq.), and allowed major advances in understanding the processes of mineral alteration because spatial relationships were preserved at the nanometre scale. The technique has also been of immense value to studies of modulated layer silicates, by providing extensive thin (10 nm) areas of sample suitable for high resolution imaging (4, 8, 10).

## Chapter 2

### Modulated layer silicates

#### INTRODUCTION

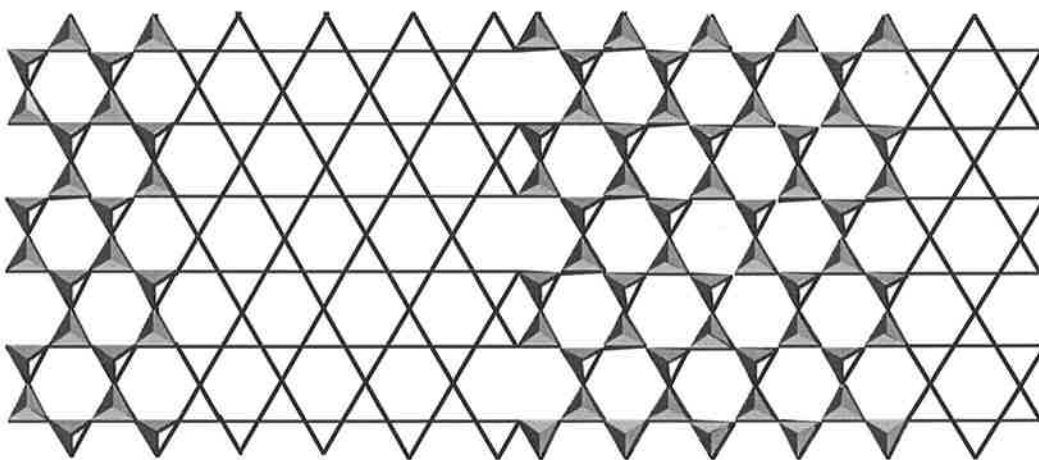
A modulated layer silicate is one in which a periodic perturbation occurs in the structure (4, 12). Such a perturbation always occurs in the tetrahedral sheet, and is a response to dimensional misfit between tetrahedral and octahedral sheets. A smaller tetrahedral sheet forces the larger octahedral sheet to dish or curve to retain registry between the two, but after several tetrahedra, the distortion becomes too great for the tetrahedral sheet to maintain its connections and the tetrahedra invert (Fig 5).



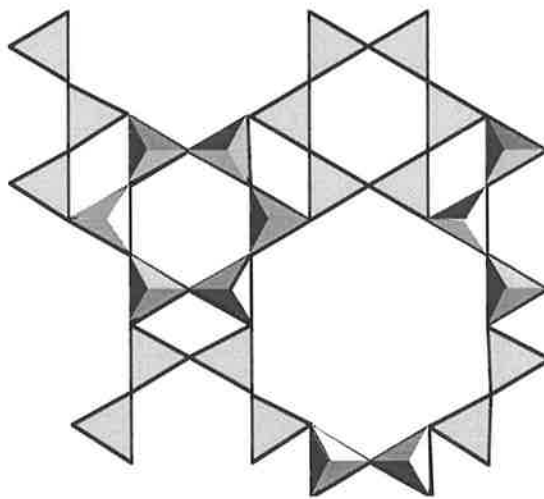
**Figure 5** Modulated structure in which 6 tetrahedra coordinate to one side of an octahedral sheet before inversion of the tetrahedra at the perturbation. Inverted tetrahedra link to produce a zeolite-like cage. The tetrahedral sheet has more tetrahedra per unit length than does the octahedral sheet, in this case 9 tetrahedra span 8 octahedra.

The first modulated structure to be determined was that of antigorite (Zussman, 1954; Kunze, 1956), a mineral in which uninterrupted octahedral sheets are linked by tetrahedral sheets in the form of narrow strips (of the order of nine tetrahedra wide) pointing in opposite directions, linked laterally into a sheet. Pyrosmalite and zussmanite were the second and third minerals to have been described with a periodic perturbation of the tetrahedral sheet

(Takeuchi, 1969; Lopes-Veira and Zussman, 1969). In contrast to antigorite, in both these minerals only a single group of six adjacent tetrahedra coordinate to one octahedral sheet before a perturbation occurs to reverse the orientation of the tetrahedra. Almost all other research on modulated layer silicates is that by Eggleton and Guggenheim collated in this thesis. The work up to 1988 is summarised in publication 12.



(a)



(b)

**Figure 6** Tetrahedral sheet arrangements in (a) antigorite, and (b) pyrosmalite.

It is a characteristic of modulated layer silicates that their crystals are imperfect. Most form in low-grade metamorphic rocks and reach crystal sizes smaller than a micrometer. Those that grow to millimetre size (stilpnomelane, pyrosmalite, ganophyllite and bannisterite) generally



have stacking faults that render their diffraction patterns diffuse. For example, the stilpnomelane crystal used for the broad-scale structure interpretation of the mineral (not included in this thesis) was the only one of some 420 crystals examined to have sufficiently regular stacking to allow the research to proceed. These imperfections prevent the use of single-crystal XRD analysis, and require electron diffraction and imaging to establish structural detail. A result of this is that none of the structures established in the papers that comprise this thesis can be said to have been unequivocally proven in the way that most crystal structures have been. Models have been erected that conform to the stoichiometry, electron diffraction and X-ray diffraction data, and which match the electron structure images. The models also conform to expected topologies, and some (11) have been found to have consistent and reasonable bond-lengths using the method of distance least squares.

**Table 1** Papers on modulated layer silicates.

1 Eggleton R. A. (1968) Phase Determination for Pseudo-symmetric Centrosymmetric Crystals. <i>Acta Crystallographica</i> <b>A25</b> , 543-547.	<i>A new approach to phase determination, original, useful in particular instances. Used to solve the full crystal structures of stilpnomelane (5) and brazilianite .</i>
2 Eggleton, R. A. (1972) The crystal structure of stilpnomelane: Part II. The full cell. <i>Mineralogical Magazine</i> <b>38</b> , 693-711.	<i>This paper built on an earlier publication, and reported a new and unique silica sheet structure.</i>
3 Eggleton, R. A. and Chappell, B. W. (1978) The crystal structure of stilpnomelane: Part III: Chemistry and physical properties. <i>Mineralogical Magazine</i> <b>42</b> , 361-368.	<i>The third publication on stilpnomelane, this paper related crystallography and chemistry. Chappell's contribution was to provide the X-ray fluorescence analyses of the stilpnomelane mineral concentrates essential to the story. My contribution about 80%</i>
4 Guggenheim, S., Bailey, S. W., Eggleton, R. A., and Wilkes, P. (1982) Structural aspects of greenalite and related minerals: <i>Canadian Mineralogist</i> <b>20</b> , 1-18.	<i>My contribution was in the high resolution electron microscopy and in developing a structural model. The order of authors reflects the intellectual input; 20-25%</i>

<p>5 Eggleton, R. A. and Guggenheim, S. (1986) A re-examination of the structure of ganophyllite: <i>Mineralogical Magazine</i> <b>50</b>, 307-315.</p>	<p><i>In this and the following papers with Guggenheim, the intellectual content is difficult to divide, and 50-50 is close enough. We choose senior author on fairly irrational grounds. In this case I was first because I insisted that Kato's earlier structural model couldn't be right and so initiated the work.</i></p>
<p>6 Guggenheim, S. and Eggleton, R. A. (1987) Modulated 2:1 layer silicates: Review, systematics, and predictions. <i>American Mineralogist</i> <b>72</b>, 724-738.</p>	<p><i>Another 50-50 joint publication with Guggenheim.</i></p>
<p>7 Guggenheim, S. and Eggleton, R. A. (1986) Cation exchange in ganophyllite: <i>Mineralogical Magazine</i> <b>50</b>, 517-520.</p>	<p><i>Guggenheim suggested we try ion-exchange during a sabbatical year in my laboratory. We interpreted and wrote this short paper together.</i></p>
<p>8 Guggenheim, S. and Eggleton, R. A. (1986) Structural modulations in iron-rich and magnesium-rich minnesotaite: <i>Canadian Mineralogist</i> <b>24</b>, 479-497.</p>	<p><i>This was Guggenheim's project, brought on sabbatical. We worked closely and equally together.</i></p>
<p>9 Heinrich, A., Eggleton, R. A., and Guggenheim, S. (1994) Structure and polytypism in bementite; a modulated layer silicate. <i>American Mineralogist</i> <b>79</b>, 91-106.</p>	<p><i>Heinrich worked on this project as a Post-doctoral study, basing it on the structure I had deduced from TEM results. 40%</i></p>
<p>10 Eggleton, R. A. and Guggenheim, S. (1994) The use of electron optical methods to determine the crystal structure of a modulated phyllosilicate: parsettensite <i>American Mineralogist</i> <b>79</b>, 426-437.</p>	<p><i>Sub-equal collaboration 60%</i></p>

<p>11 Guggenheim S. and Eggleton, R. A. (1994) A comparison of the structures and geometric stabilities of stilpnomelane and parsettensite: A distance least-squares (DLS) study. <i>American Mineralogist</i> <b>79</b>, 438-442.</p>	<p><i>Sub-equal collaboration 40%</i></p>
<p>12 Eggleton, R. A. and Guggenheim, S. (1988) Crystal Chemistry, classification and identification of modulated layer silicates. in <i>S.W.Bailey,(ed.) Hydrous Phyllosilicates exclusive of micas. Reviews in Mineralogy</i> <b>19</b>, 675-725, Min. Soc. America.</p>	<p><i>As with the earlier papers with Guggenheim, this was a roughly equal collaboration.</i></p>
<p>13 Guggenheim, S. and Eggleton R.A. (1998) The crystal structures of greenalite and caryopilite: A system of regularly interstratified crystalline and semi-amorphous sheets <i>Canadian Mineralogist</i> <b>36</b>, 163-179.</p>	<p><i>Guggenheim and I worked closely together on this project while he was on sabbatical in my laboratory. I continued the work after Guggenheim returned, developing the software and modelling the structure. 60%</i></p>

## 2.1 STILPNOMELANE - PAPERS 2, 3, 11.

The structure of the tetrahedral sheet described in paper 2, and its implication for the chemical stability of stilpnomelane (3), introduced several new concepts to silicate mineralogy:

- the combination of a large tetrahedral "island" linked by 5-, 6-, and 8-member tetrahedral rings;
- the organisation of the linking rings into cages, combining elements of zeolite and layer silicate structure;
- the evidence for step-wise oxidation of ferrous iron, as a consequence of differing environments for the octahedral cations; and,
- the ability for a layer silicate structure to accommodate either Fe<sup>2+</sup> or Fe<sup>3+</sup> in a trioctahedral sheet.

## 2.2 GREENALITE - PAPERS 4, 13

Unlike stilpnomelane, greenalite and caryopilite occur only as extremely fine-grained minerals, requiring transmission electron microscopy for their visualisation and understanding. Greenalite had, prior to this work, been regarded as the ferrous iron equivalent of kaolinite, and caryopilite as the Mn analogue. Bailey and Guggenheim (pers. com.) had deduced the fundamentals of the stacking of kaolin-like layers on the basis of poor single-crystal XRD photographs and XRD powder diffraction. They also recognised that the structure had modulation, and from the nature of the electron diffraction data, a lack of long-range order in the XY plane. Modelling of trial structures therefore included both a degree of randomness within the tetrahedral sheet, and disorder between 1:1 layers. The initial success of this approach reported in paper 4 was based on optical diffraction simulation of models built on the basis of chemistry and electron microscope images. In the second attack on these complex minerals, the results of our higher resolution electron microscopy compelled a modification of the earlier models, accounting better for lack of order in the XY-plane. The model testing for work reported in paper 13 was based on diffraction calculations for a complete crystal, as explained in chapter 2. Greenalite and caryopilite are the only layer silicates known to have disorder in both the stacking of the layers and within the plane of the layers.

## 2.3 GANOPHYLLITE - PAPERS 5, 7.

Kato (1980) published a description of the structure of the subcell of ganophyllite; one of the few modulated layer silicates to occur in well-crystallised form. Eggleton and Guggenheim (5) reassessed the structure in the light of its physical properties and stoichiometry, and by using Kato's single crystal data to form Patterson and Fourier syntheses. A new type of modulated structure was revealed, in which tetrahedral strips were linked laterally by 5-, 6-, and 7-member rings of silica tetrahedra. As in stilpnomelane, the linking rings cross-link to similar rings of the next tetrahedral sheet, introducing a zeolite-like cage containing K (or Na in the case of the iso-structural eggletonite).

## 2.4 MINNESOTAITE - PAPER 8.

Minnesotaite had been described by Gruner (1944) as the ferrous iron equivalent of talc. Most crystals of minnesotaite are extremely small, but Guggenheim and Bailey (1982) had obtained sufficient single crystal and powder XRD data to allow them to postulate a large

superlattice and to determine refined subcell parameters. Electron diffraction reported in paper 8 then provided the evidence to establish a smaller correct supercell, while high resolution images led to the correct structure. Unlike talc, which has the adjacent tetrahedral sheets of successive 2:1 layers weakly joined by residual bonds, minnesotaite has four tetrahedra wide 2:1 strips linked by single tetrahedra mid-way between them, another unique structure.

## 2.5 BEMENTITE- PAPER 9.

A structure for bementite was proposed in 1963 by Kato, and revised in 1980 by Kato and Takeuchi . Neither of these papers presented a crystal structure that was consistent with the observed parameters. Examination of electron diffraction data and structure images obtained by electron microscopy, as well as consideration of the mineral's cell dimensions and chemistry, led to a new model for the structure of the tetrahedral sheet (Eggleton and Guggenheim 1988) having linked 5-, 6-, and 7-member tetrahedral rings. The particular pattern of tetrahedral rings and inversions induces a  $24^\circ$  rotation between alternate octahedral sheets, a feature hitherto unknown in layer silicates. This model was further developed by Heinrich working with Eggleton in a study which explained both the tetrahedral-octahedral relationships, and the arrangement of stacking faults found in bementite.

## 2.6 PARSETTENSITE-PAPERS 10, 11.

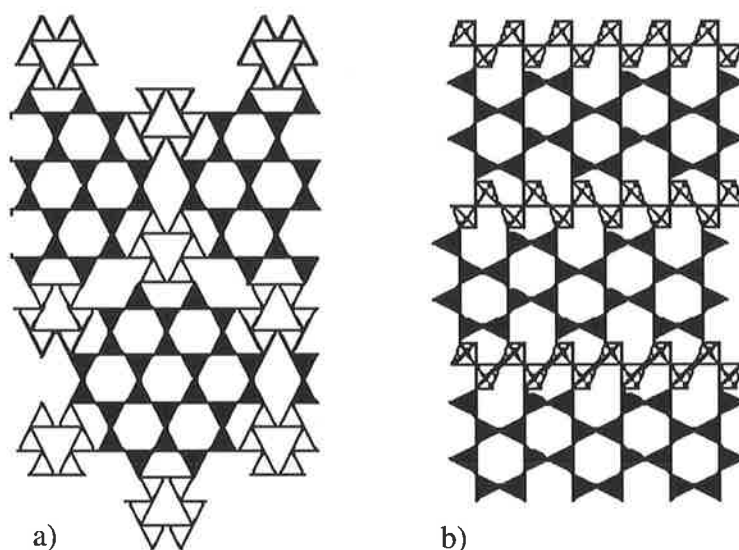
By chemistry and X-ray pattern, parsettensite resembles a manganese stilpnomelane. In paper 10, a model for the structure of this mineral was established, which explained its relation to stilpnomelane as well as detailing the differences. The approach to structure determination continued the pioneering aspects of the earlier papers on modulated layer silicates, using electron optics to deduce, test and establish the structure model. Because electron diffraction data are not such as to permit refinement of the model structures, paper 11 provided a further test of the parsettensite structure's internal consistency, as well as that of stilpnomelane, through the technique of distance least squares which allows a test of the topological arrangement through atom position adjustment to optimise interatomic distances.

## 2.7 REVIEWS - PAPERS 6, 12.

Paper 6 presents a synthesis of the factors influencing the structure of the tetrahedral sheets of the modulated layer silicates, as well as an initial classification scheme. Paper 12 extended

the classification to include both known and geometrically possible but unknown tetrahedral sheet structures. Modulated layer silicates can be divided into two groups:

- those having tetrahedral islands, made of silica tetrahedra linked into 6-rings. Islands may be one 6-ring wide (zussmanite, pyrosmalite), or larger (greenalite, stilpnomelane, parsettensite). Islands are linked to each other by inverted tetrahedra producing the modulations (Fig 7a);
- those having infinite (unmodulated) strips of tetrahedra linked laterally by inverted tetrahedra which introduce modulations (Fig 7b).



**Figure 7a** Modulated layer silicates

(a) linked islands (b) linked tetrahedral strips.

These review papers also show that modulations arise because of misfit between an FeMn-octahedral sheet and a largely Si-tetrahedral sheet. The greater the dimensional misfit, the smaller is the island or the narrower the strip width that can coordinate to the octahedra before linkage becomes impossible and the tetrahedra are required to invert (Fig 5).

## Chapter 3

### Clay silicates

#### INTRODUCTION

Clay is defined by sedimentologists as a particle size, generally  $2\mu\text{m}$ , but by mineralogists as a (mineral) material which becomes plastic when wet. These different definitions are generally consistent with each other; the clay silicates are layer silicates, have a particle size  $<2\mu\text{m}$  in diameter, and most exhibit plasticity. Such clays are commonly poly-mineralic. The papers grouped in this chapter describe clay silicates which are essentially monomineralic, and in most the thrust of the research was to understand both the atomic structure and the layer stacking arrangements, using normal X-ray structure analysis for the former aspect and Fourier transform analysis for the latter.

**Table 2** Publications on clay silicates.

14 Eggleton, R. A. and Bailey, S. W. (1967) Structural aspects of dioctahedral chlorite. <i>American Mineralogist</i> <b>52</b> , 673-689.	<i>Equal input from both authors; experimental data and concepts from Bailey, mathematical processing and interpretation by Eggleton.</i>
15 Eggleton R. A. (1977) Nontronite: Chemistry and X-ray diffraction. <i>Clay Minerals</i> <b>12</b> , 181-194.	<i>This paper, as well as adding extra evidence for the accepted structure of nontronite, drew attention to the effects of superimposed clay tactoids on an X-ray diffraction pattern.</i>
16 Eggleton, R. A., Pennington, J. H., Freeman, R. S., and Threadgold, I. M. (1983) Structural aspects of the hisingerite-neotocite series. <i>Clay Minerals</i> <b>18</b> , 21-31.	<i>The intellectual content of this paper was mine; Pennington and Freeman, Technical Officers, provided X-ray diffraction and fluorescence analysis results, Threadgold (University of Sydney) provided 2 samples and a density measurement. 80%</i>

<p>17 Eggleton, R. A. (1987) Noncrystalline Fe-Si-Al oxyhydroxides: <i>Clays and Clay Minerals</i> <b>35</b>, 29-32.</p>	<p><i>This paper introduced a new interpretation of several amorphous silicates related to or precursors of the clay layer silicates.</i></p>
<p>18 Ren, S. K., Eggleton, R. A., and Walshe, J. L. (1988) The formation of hydrothermal cookeite in the breccia pipes of the Ardlethan Tin Field, New South Wales, Australia. <i>Canadian Mineralogist</i> <b>26</b>, 407-412.</p>	<p><i>Ren, a Ph.D. student supervised by Walshe, found and analysed the cookeite, I contributed the mineralogical characterisation, about 60% of the work.</i></p>
<p>19 Walker, P. H., Taylor, G., and Eggleton, R. A. (1989) Properties and origin of a very fine-grained kaolinitic deposit: <i>Sedimentology</i> <b>36</b>, 889-906.</p>	<p><i>The author sequence is significant here, I contributed about 25% in describing the crystallographic properties of the kaolinite.</i></p>
<p>20 Eggleton, R. A. and Ashley, P. M. (1989) Norrishite: a new Mn-mica, <math>K(Mn^{3+}_2Li)Si_4O_{12}</math>, from the Hoskins mine, New south Wales, Australia. <i>American Mineralogist</i> <b>74</b>, 1360-1367.</p>	<p><i>Ashley initiated this work by recognising the new mica. I described it, contributing 80% of the work.</i></p>
<p>21 Eggleton, R.A. and Tilley, D.B. (1998) Hisingerite: ferric kaolin mineral with curved morphology. <i>Clays and Clay Minerals</i>. <b>46</b>, 400.</p>	<p><i>This study of type hisingerite was largely done by me, with Tilley contributing some of the electron microscope images . 80%</i></p>

### 3.1 DIOCTAHEDRAL CHLORITE - PAPER 14

This was a study in which powder XRD of both random and oriented material was used. The application of a continuous Fourier Transform for the calculation of broad diffraction maxima allowed an interpretation of the layer stacking sequence in interstratified chlorite-montmorillonite, while the analysis of the chlorite component structure was achieved by applying normal structure analysis theory to powder data.



### 3.2 NONTRONITE - PAPER 15

Clay minerals are typically prepared for X-ray diffraction analysis by deposition on a flat substrate from a water suspension. There has been considerable discussion about the extent to which the layer stacking of material presented to X-rays after such treatment resembles the organisation of the natural sample. As well as providing high quality chemical data, this research gave support for one of the then current alternate models for the structure of nontronite. It also showed, through an analysis of inter-particle diffraction effects, that the material as deposited on the substrate was dominated by 6-layer packets which diffracted as a unit.

### 3.3 POORLY DIFFRACTING MINERALS - PAPERS 16, 17, 21

X-ray diffraction signals only become sufficiently intense for detection if the individual diffracting units repeat for an appreciable distance. For layer silicates, diameters of 0.1  $\mu\text{m}$  and thicknesses of at least 4 or 5 repeating layers satisfies this criterion. Some minerals, having layer silicate chemistry and properties yield no, or very weak, XRD signals, and these papers addressed several such materials. A common feature found in these studies of poorly diffracting clay minerals was that they showed a spherical structure under TEM. Linear repetition of unit cells does not occur in spherical configurations, thus the poor diffraction result was explained by the fabric of the material. Though most of the materials studied in this group of three papers had not been previously described, hisingerite had been first reported in 1807. For the past two centuries its character had remained enigmatic because of its apparent amorphous nature. In paper 21, the structure of hisingerite was shown to be similar to that of spherical halloysite, thus adding a new member to the dioctahedral clay minerals (Table 3).

**Table 3** dioctahedral clay minerals

	Al	Fe <sup>3+</sup>
1:1 Platy	<b>kaolinite</b>	not known
1:1 Spherical	<b>halloysite</b>	<b>hisingerite</b>
2:1	<b>montmorillonite</b>	<b>nontronite</b>

### 3.4 CLAY CHARACTERISATIONS - PAPERS 18, 19

These two papers provided crystallographic information about unusual clay mineral occurrences, adding to the general understanding of the species concerned. Paper 18 became the starting point for later research into the ultra-structure of kaolinite and the reasons for its high exchange capacity in certain deposits. That research was prosecuted by a PhD student.

### 3.5 NORRISHITE - PAPER 20

This work described the properties of a significant end-member mica ( $\text{K}(\text{Mn}^{3+}_2\text{Li})\text{Si}_4\text{O}_{12}$ ), being trioctahedral yet having two trivalent cations in the octahedral sheet and having neither (OH) nor F in the 12 anion sites. This unusual mica provides further evidence for the crystal chemical behaviour of manganese in layer silicates. Knowledge of the structural behaviour of  $\text{Mn}^{2+}$  won in studies of manganiferous modulated layer silicates was important in understanding the environment of formation of this layer silicate. The methods used were standard.

## Chapter 4

### Mineral weathering

#### INTRODUCTION

Studies of the weathering of rocks and minerals have occupied earth scientists for almost 200 years. Perhaps one of the earliest was Buchanan (1807) who observed the red weathering masses of Indian rocks and called them laterite. In this century, soil scientists have been prime movers in developing an understanding of the chemistry of weathering and in the relative solubility of the primary rock minerals (for example Jenny, 1941). By the 1970s, using optical microscopy, X-ray diffraction, and transmission electron microscopy of particles, mineralogists had found the composition and identity of weathering products, as well as gaining some knowledge of the chemical reactions of weathering. What was lacking was any knowledge of the atomic mechanisms involved in mineral weathering. While it was recognised that some minerals, for example quartz, weathered by congruent dissolution, others, for example feldspar, weathered incongruently to clay minerals with release of silica. The clays, in turn, weathered to gibbsite ( $\text{Al}(\text{OH})_3$ ) with further silica release.

It was common to see the equation for feldspar weathering written as:



a true enough statement of starting materials and end products, but not a reaction that took into account natural system behaviour.

The research that forms the subject of this chapter was conceived as an entirely new direction in weathering research, taking advantage of recent developments in electron microscope technology, in the theory of the interaction of electrons with matter, and in preparing refractory materials for electron microscope examination. The program's aim was to understand the process of silicate weathering at as detailed a level as possible, down to the atomic scale.

**Table 4** Publications on weathering

<p>22 Eggleton R. A. (1975) Nontronite Topotaxial after Hedenbergite. <i>American Mineralogist</i> <b>60</b>, 1063-1068.</p>	<p><i>This was the first of a series of publications using transmission electron microscopy, aimed at establishing pathways of formation of clay minerals from primary precursors. No work of this nature existed before, although the general relationships between parent and offspring had been drawn by earlier workers from</i></p>
<p>23 Eggleton R. A. (1979) The ordering path for igneous K-feldspar megacrysts. <i>American Mineralogist</i> <b>64</b>, 906-911.</p>	<p><i>This paper grew from initial studies of feldspars intended as the basis for the work published at 15. The results developed a new direction, followed up in 16.</i></p>
<p>24 Eggleton, R. A. and Buseck, P. R. (1980) High resolution electron microscopy of feldspar weathering. <i>Clays and Clay Minerals</i> <b>30</b>, 11-20.</p>	<p><i>For this work, Buseck provided laboratory facilities and costs, and discussed the results. This initial work into feldspar weathering was the basis for later publications by students. Later selected as a benchmark paper. My contribution 95%.</i></p>
<p>25 Eggleton, R. A. and Boland, J. N. (1982) The weathering of enstatite to talc through a series of transitional phases. <i>Clays and Clay Minerals</i> <b>28</b>, 173-178.</p>	<p><i>This was one of the earliest publications demonstrating the evolution of biopyriboles by hydration. Boland contributed some electron microscopy, diffraction and discussion, but project initiation, the bulk of the microscopy and of the interpretation was mine, 70%.</i></p>
<p>26 Eggleton, R. A. and Keller, J. (1982) The palagonitization of limburgite glass, a TEM study. <i>N. Jb. Min. Monatshefte</i> <b>H7</b>, 321-336.</p>	<p><i>This study arose from a visit to Dr Keller's laboratory. He provided the samples and the geological setting, I examined the materials and interpreted the process of palagonitization. 90%.</i></p>

<p>27 Eggleton, R. A. and Smith, K. L. (1983) Silicate alteration mechanisms: <i>Sciences Geologique, Mem. 71</i>, Strasbourg, 45-54.</p>	<p><i>This was a summary paper of my understanding at that time of the processes leading to clay mineral formation. Smith, a Post-Doctoral Fellow in my lab, had provided data for two of the examples. 80%.</i></p>
<p>28 Eggleton, R. A. (1984) The formation of iddingsite rims on olivine: a TEM study: <i>Clays and Clay Minerals 32</i> 1-11.</p>	<p><i>In this paper the exact nature of the petrographic term iddingsite was displayed, and the process by which olivine weathered to smectite clay and goethite elucidated. This is a pivotal paper for the understanding of the weathering of ferromagnesian minerals to clay minerals.</i></p>
<p>29 Eggleton, R. A. and Banfield, J.F. (1985) The alteration of igneous biotite to chlorite. <i>American Mineralogist 70</i>, 902-910.</p>	<p><i>Banfield was then an Honours student, and did the preliminary work for this paper as a training exercise. I extended the project after she left, ultimately contributing about 75% of the work</i></p>
<p>30 Eggleton, R. A. (1985) The relation between crystal structure and silicate weathering rates: In Colman and Dethier, (eds) <i>Rates of Chemical Weathering in Rocks and Minerals</i>. 21-40. Academic press.</p>	<p><i>A summary of one aspect of my work on mineral weathering and clay formation to that date.</i></p>
<p>31 Eggleton, R. A., Varkevisser, D., and Foudoulis, C. (1987) The weathering of basalt: changes in bulk chemistry and mineralogy. <i>Clays and Clay Minerals 35</i>, 161-169.</p>	<p><i>This and paper 32 stemmed from my ARC grant into the processes of basalt weathering. Varkevisser was a Research Assistant who prepared thin sections and provided electron microprobe data, Foudoulis, Technical Officer, ran X-ray diffraction analyses. 80%</i></p>

<p>32 Smith, K.L., Milnes, A. R. and Eggleton, R.A. (1987) Weathering of basalt: Formation of iddingsite. <i>Clays and Clay Minerals</i> 35, 418-428.</p>	<p><i>This publication built on the work of 24 and 30, and was largely Smith's work. I guided the research and re-wrote the manuscript. 30%</i></p>
<p>33 Banfield J. F. and Eggleton, R. A. (1988) Transmission electron microscope study of biotite weathering. <i>Clays and Clay Minerals</i> 36, 47-60.</p>	<p><i>This was part of Banfield's Master's Thesis work. Largely her work under my guidance.</i></p>
<p>34 Banfield J. F. and Eggleton, R. A. (1990) Analytical transmission electron microscope studies of plagioclase, muscovite and K-feldspar weathering. <i>Clays and Clay Minerals</i> 38, 77-89.</p>	<p><i>A second paper from Banfield's Master's thesis, again with input from me in TEM interpretation and process. 25%</i></p>
<p>35 Robertson, I.D.M. and Eggleton, R. A. (1991) Weathering of granitic muscovite to kaolinite and halloysite and of plagioclase-derived kaolinite to halloysite. <i>Clays and Clay Minerals</i> 39, 113-126.</p>	<p><i>Robertson was a PDF in my lab, working on this as part of an ARC grant. He did the microscopy and we interpreted the results together. He wrote the paper. My contribution 35%</i></p>

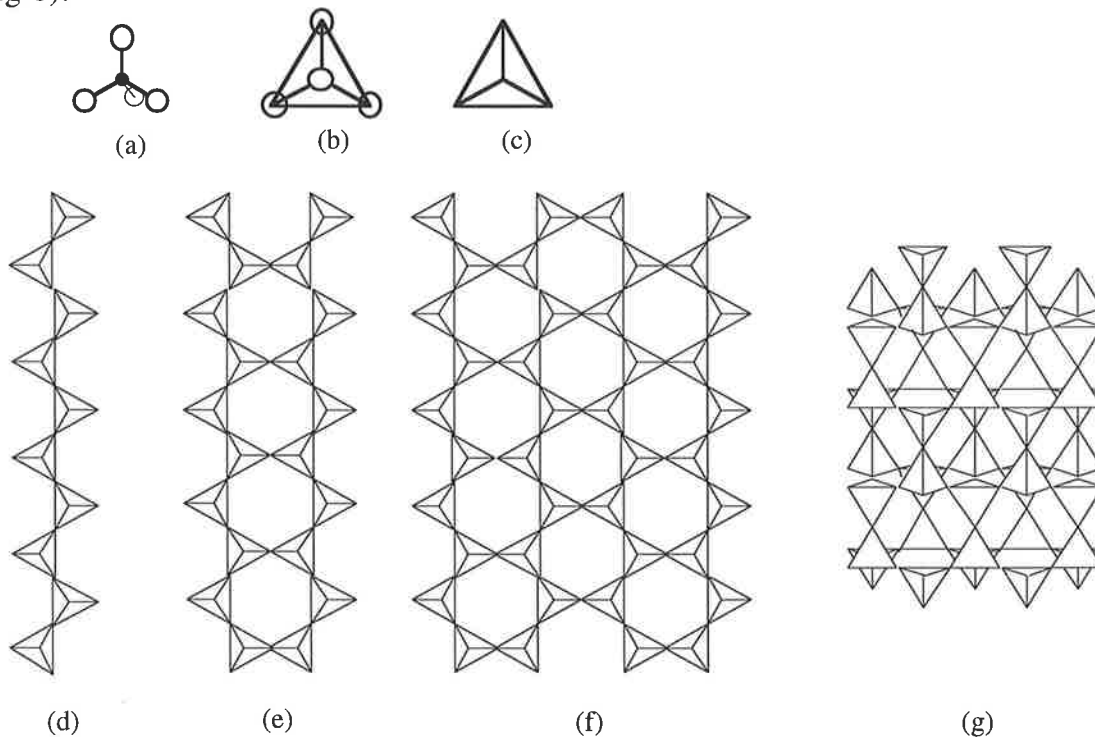
#### CLASSIFICATION OF THE SILICATES

In order to summarise the essential outcomes of this research, it is first useful to re-examine the classification of the silicate minerals.

Scientists erect classification schemes primarily to help in understanding the articles being classified. Early classifications of minerals were based on the morphology of their crystals, then as knowledge of chemistry grew, classification became based on their chemical composition, and this classification is still in wide-spread usage. Chemical classification is useful because it separates minerals into groups which have somewhat common modes of origin (e.g.. halides are mostly evaporites, many sulfides are localised together), and into groups which have similar reactions to weathering (halides mostly dissolve, sulfides oxidise).

The advent of X-ray diffraction and crystal structure analysis allowed a new classification based on the crystal structures of the minerals. This proved particularly useful for understanding the silicates, for it showed clear distinction between chemically similar minerals (such as amphiboles and pyroxenes) and gave a crystal chemical basis for the evolution of the mafic silicates during progressive crystallisation of igneous rocks.

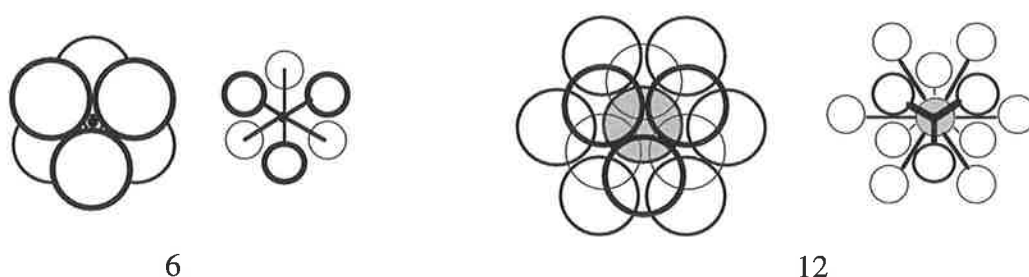
The structural classification of the silicates is based on the degree of polymerisation of silica tetrahedra, and is essential for understanding physical properties and atomic bonding (Fig 8).



**Figure 8** Classification of silicates according to tetrahedral polymerisation.

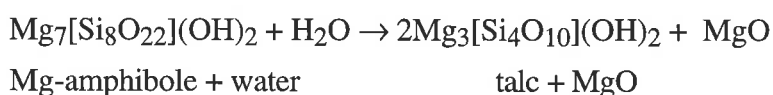
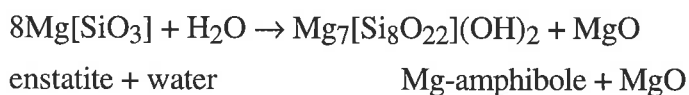
- (a) Silica tetrahedron viewed as four oxygens coordinated to a central silicon.
- (b) Tetrahedron viewed as a coordination tetrahedron with the oxygens at the apices.
- (c) Silica tetrahedron simplified.
- (d) single chain polymer.
- (e) double chain.
- (f) tetrahedral sheet.
- (g) tetrahedral framework.

Because the silica tetrahedra are unvarying in composition except for Al $\leftrightarrow$ Si substitution, most of the chemical variation in silicate minerals is ignored in the tetrahedral classification. Broadly speaking the remaining elements occur in either octahedral coordination to the anions, or in rather open cavities, with coordination to the anions ranging from 8 to 12. The smaller cations (Mg and the transition metals) are mostly found in octahedral coordination, the alkalis and alkaline earths in the larger cavities (Fig 9).



**Figure 9** 6-fold (octahedral ) and 12-fold coordinated sites in silicates.

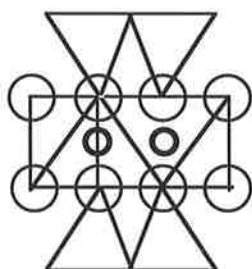
The tetrahedral polymerisation classification of silicates is useful because it is based on that part of the structure which undergoes the least variation within each group, and distinguishes the major structural and chemical variation between groups: the polymerisation of silica tetrahedra, and the ratio of silicon to oxygen. But when it comes to their behaviour during weathering, the silicate linkage classification obscures both similarities between minerals in different silicate groups, and differences between minerals in the same group. For example, the magnesium-pyroxene enstatite (single-chain silicate, MgSiO<sub>3</sub>) can weather to Mg-amphibole (double chain), which in turn weathers to talc (layer silicate). The classical description of these changes is to emphasise the Si:O increase from 1:3 to 4:11 to 2:5, and the progressive polymerisation of the tetrahedra. But in emphasising change, similarities are concealed and the actual process masked. The reaction expressed more completely is:



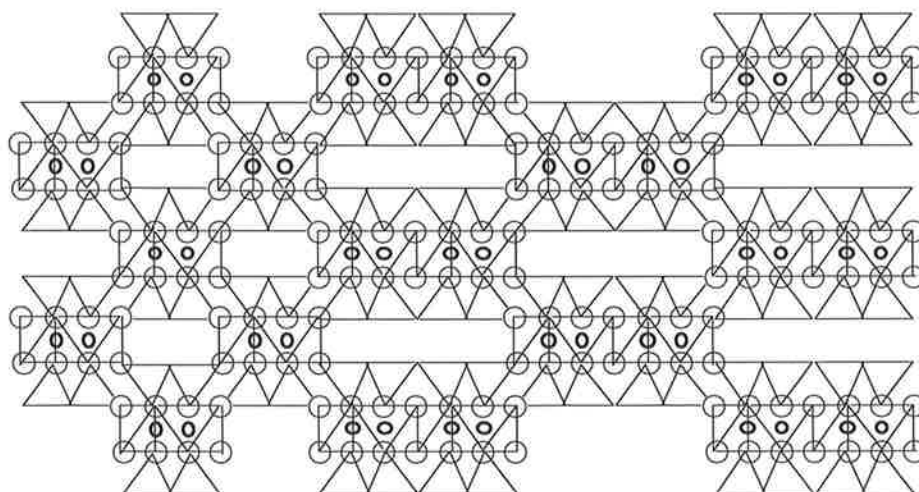


Here there is no addition of silica, nor a change in silica to anion ratio. The chemical exchange is only two hydrogens for one magnesium at each step, the Si:(O,OH) ratio is constant at 1:3.

In an extension of the concept of polyhedral polymerisation for silicate classification, Eggleton (1975- paper 20), Veblen and Burnham (1978), and Thompson (1978), developed the recognition that for pyroxenes, amphiboles and biotite, the major structural unit was not simply the linked tetrahedra, but the linked triplet of a metal octahedron flanked by two silica tetrahedra. This triplet has become known as the TOT, and the three silicate groups are sometimes collectively referred to as the biopyriboles (Fig 10). When viewed along the axis of the linked TOT sequences, considerable similarity is evident in the structures of pyroxenes, amphiboles and layer silicates (Fig 11). It is clear from the diagrams that the three structures can join laterally without a structural discontinuity, and the truth of this is evident in high resolution electron micrographs of weathered pyroxenes and amphiboles (See for example 23).



**Figure 10** TOT unit of a silicate



**Figure 11** Pyroxene and amphibole linked as TOT units

The structural similarities among these minerals are reflected in their similar hydration reactions, a similarity that is less obvious when they are put in different mineral groups emphasising their different tetrahedral classification. Considering only the ideal Mg-varieties, at the early stages of weathering, enstatite alters first to Mg-amphibole, which in turn alters to talc. This is a progression from a single chain silicate [ $\text{SiO}_3$ ], to a double chain silicate [ $\text{Si}_4\text{O}_{11}$ ] and then to a layer silicate [ $\text{Si}_2\text{O}_5$ ], a description which highlights changes in the Si:O ratio and in the tetrahedral linkages. Viewed from a perspective of the TOT structure, the reaction is seen as one of rearrangement of parallel slabs of TOTs, with the progressive replacement by hydrogen of the Mg in the relatively open 8-coordinated site between the TOTs.

Many minerals have a structure based on closest packing of their anions; included in this group are the iron and aluminium oxyhydroxides and many silicates, for example olivine. In the early stages of weathering, alteration can proceed apparently without change in the oxygen packing arrangements (28, 32).

Zoltai and Stout (1984) pointed out that a number of silicates were more sensibly classified on the basis of their overall polyhedral linkages, rather than on their silica tetrahedral polymerisation. Thus they regard cordierite and beryl as a framework silicates, though they are traditionally regarded as cyclo-silicates, having 6-rings of silica tetrahedra. When the Al-tetrahedra in cordierite and the Be-tetrahedra in beryl are considered, the linkages are seen to be those of a framework. Metal - oxygen octahedra may join at corners or edges, but rarely at faces; tetrahedra join only at corners in the mineral silicates. Broadly speaking, following Zoltai and Stout, structures dominated by corner-shared polyhedra may be described as frameworks, whereas those having significant polyhedral edge-sharing may relate to close packing or to chain or sheet structures. Typical corner-shared polyhedral structures are those of the feldspars and garnet. Edge sharing of octahedra occurs in andalusite and sillimanite and these structures, like the pyroxenes, are characterised by octahedral chains. Olivine, topaz, and kyanite structures can be related to close-packing of the anions.

Where parent and offspring mineral have a common structural character, it may help in understanding the processes of weathering to emphasise these similarities, rather than the chemical differences between the minerals.

Primary	Regolith
	<u>TOT silicates</u>
pyroxene	vermiculite
amphibole	smectite
mica	illite
chlorite	
	<u>Close-packed minerals</u>
olivine	goethite
kyanite	hematite
spinel	gibbsite
topaz	boehmite
ilmenite	lepidocrocite
	maghemite
	diaspore
	<u>Octahedral edge-shared</u>
andalusite	kaolinite
sillimanite	halloysite
titanite	
	<u>Frameworks</u>
quartz	quartz
garnet	opal CT
feldspar	
zeolites	
beryl	
cordierite	

This mineral classification helps show the similarities in crystal structure inherited through a weathering reaction. For example, at first sight it may be surprising to find vermiculite, normally the weathering product of biotite, in the saprolite of an olivine-pyroxene-plagioclase ultramafic rock. The explanation lies in the relatively easy transition from pyroxene to vermiculite via rearrangement of TOT chains to sheets.

#### WEATHERING REACTIONS

This research has enabled the division of mineral weathering mechanisms into two: those processes requiring dissolution and reconstruction, and those which proceed in the solid state by conversion from one structure to the next. Broadly, the framework silicates weather by the first mechanism, the TOT and close-packed silicates by the second. During the course of the research which comprises this section of the thesis, a sequence of weathering reactions has been discovered for many of the common rock-forming silicates. Some of the sequences listed below are in still unpublished graduate student studies under my supervision, and these are cited appropriately. Table 5 presents these sequences where they have been elucidated,

and for completeness includes rock-forming minerals for which no research has yet been undertaken. There are a few studies from other laboratories, and these are also cited. In the table, the symbol → means the transformation proceeds essentially in the solid state by diffusion and/or TOT displacement. The symbol ® means that complete destruction of the parent occurs as, or before, the offspring mineral forms.

**Table 5** Rock-forming mineral weathering transitions.

NESO SILICATES			
Olivine			
reductive	→	chlorite/vermiculite	unpublished
oxidative	→	smectite + goethite	28, 32
Sphene	®	anatase + smectite	Tilley and Eggleton, in prep.
Garnet	®		Velbel 1984
Sillimanite		no data	
Andalusite		no data	
Kyanite		no data	
Epidote		no data	
PYROXENES			
Enstatite	→	10-Å layer silicate	25
Hedenbergite	→	nontronite	22
Augite	→	pyriboles, smectite	Wang, 1988
AMPHIBOLES			
Tremolite-Actinolite		no data	
Hornblende	→	pyriboles, smectite	Wang, 1988
LAYER SILICATES			
Muscovite	→	kaolinite	34, 35
Biotite	→	vermiculite ?® goethite	33, Aspandiar 1992
Chlorite	→	vermiculite ?® goethite	Aspandiar 1992
Serpentine		no data	
Stilpnomelane	→	nontronite	22
FRAMEWORK SILICATES			
K-feldspar	®	amorphous ® smectite	33, Wang, 1988
Plagioclase	®	amorphous ® smectite	27, 33, Wang, 1988
Cordierite	®	halloysite	18, 27
Nepheline	®	halloysite	Wang, 1988
Zeolites		no data	

## Chapter 5

### Implications

#### INTRODUCTION

The three research thrusts discussed in this work are obviously linked by being studies of layer silicates, and by the techniques used in those studies. They are also linked through the insights they give into the behaviour of very fine-grained layer silicates. The structure, composition, morphology and adsorption properties of regolith minerals have great influence on the processes that occur in this most important blanket of weathered rock. This chapter addresses some of these issues.

#### PARTICLE SIZE AND MORPHOLOGY

The growth and development of layer silicates has been shown in these collated papers to depend very heavily on the lateral dimensions of the component sheets. In essence, where the sheets find a mechanism that enables a perfect match between the apical oxygens of the tetrahedral sheet and the anions of the octahedral sheet, crystals grow flat and large. Where the process of fitting introduces strain, crystals are small, and are curved, or have arcuate segments.

The bulk of the common layer silicates grow as millimetric crystals, minerals such as the 2:1 micas and 2:2 chlorite. All have aluminium substituting for silicon in their tetrahedral sheet, which allows expansion of the sheet to fit the dimensions of the larger MgFe octahedral sheet. In-plane rotation of the tetrahedra then allows the tetrahedral sheet to adjust precisely to the dimensions of the octahedral sheet, be it large, as in biotite, or small as in muscovite (6, 12). These structures remain flat because not only do their sheets fit, but the octahedral sheet is sandwiched between two tetrahedral sheets, preventing curling. Similarly the modulated layer silicates stilpnomelane, ganophyllite and bannisterite, have flexible tetrahedral sheets permitting precise registry with their large octahedra, and these minerals also form crystals of moderate size. Nonetheless, within these structures, the strain of fitting Si-tetrahedra to FeMn octahedra is evident in the arching of the octahedral sheet, the avoidance of "sandwiching", and the prevalence of layer disorder. Though these minerals have tetrahedral sheets on either side of the octahedral sheet, most octahedra only have a tetrahedron on one side, the other side faces the interlayer region. Here the tetrahedra have

inverted because of the strain that would result from having tetrahedra on both sides. (See Fig 5, in which only one out of every four octahedra has tetrahedra on both sides )

Chrysotile and halloysite are 1:1 layer silicates in which the accommodation between tetrahedral and octahedral sheet is effected by curling the layers into rolls. Distortion of the tetrahedral sheet allows it to extend (in chrysotile) or contract (in halloysite) in one of its planar directions so that registry between the sheets is achieved along the axis of the tubular crystal, but the resulting contraction or expansion in the other dimension introduces strain causing curling.

The fine-grained modulated layer silicates (greenalite, caryopilite, bementite, parsettensite, minnesotaite) all show the characteristic property of "one-sided" octahedral sheets (described above for stilpnomelane, ganophyllite and bannisterite). That is, only very limited regions of the octahedral sheet actually have tetrahedra linked on both sides. This allows a segment of the octahedral sheet and its adjacent tetrahedra to curve or dish sufficiently for the smaller tetrahedral sheet to coordinate. The relative size of the two sheets dictates the extent of the region of accommodation (12). An apparent consequence of the strains developed in such structures is that crystals reach only very small dimensions, mostly sub-micron.

The extreme consequence of misfit is the formation of spherically aggregated layer silicates, as occurs in spherical halloysite (32), hisingerite (16, 21), allophane (Wada, 1977), and some poorly characterised pre-cursor clays (17). The detailed character of spherical halloysite is unknown, but it appears probable that the bonding effects of interlayer water, coupled with impurity atoms in the octahedral sheet such as iron, prevent the lateral accommodation of the tetrahedral sheet found in tubular halloysite.

Hisingerite has so far only been found in the form of complete or part concentric spheres. This highly unusual structure, reminiscent of some buckminsterfullerenes, results from the misfit between a larger ferric-iron octahedral sheet and a pure silicon tetrahedral sheet. A similar phenomenon is seen in the devitrification of volcanic glass, where spherical structures evolve into balls of nontronite (26). Examination of even more poorly crystalline aluminium and ferric silicates shows incipient organisation into spherical structures (17), suggesting that at the early stages of growth, the lowest energy form for layer silicates is that of a sphere.

The study of solid state reactions between minerals takes as its starting point the assumption that the reactants are crystalline. That is, they are composed of regularly repeating structural units, extending for many unit cells in three dimensions. Most of the minerals of this thesis differ from this model; some only in having layer disorder, some in having disorder in two directions, and others in being spherical, a configuration that is not crystalline in the accepted sense, but which is still a regular, presumably stable, arrangement. Reaction rates depend on the slowest step in the reaction. Most crystal growth is rate limited by the supply of nutrients to the growing crystal, but this thesis has shown that some regolith layer silicates evolve through a morphological sequence, passing through a spherical state before becoming crystalline in the normally accepted meaning of the word. The rate of the first stage of organisation, from gel to spherical structure, would appear to be diffusion limited, rather than nutrient limited. The reaction from spherical to flat, where it occurs, may depend on the introduction of a threshold activation energy, such as is needed for the transition from orthoclase feldspar to microcline (23).

#### IMPLICATIONS FOR THERMODYNAMICS

Most of the minerals that are the subject of this thesis have never had thermodynamic properties measured for them, although several are the theoretical end members of important mineral series. Minnesotaite, long regarded as the ferrous iron analogue of talc, and greenalite, the ferrous analogue of serpentine, have been shown to have entirely different structures and significantly different compositions and cell volumes from those assumed previously. Thermodynamicists, lacking observational data, have provided calculated constants based on these assumed (wrong) parameters assuming the same structure as an Al or Mg equivalent (e.g. Nriagu, 1975; Helgeson et al, 1978). Similarly, hisingerite, chemically the ferric analogue of kaolinite, has such a radically different structural form that its thermodynamic properties must differ markedly from a presumed platy ferric analogue of kaolin. Predictions about stability fields for these minerals, or reactions between them and other minerals, awaits the development of thermodynamic parameters that take the real structures and compositions into account.

## IMPLICATIONS FOR ENVIRONMENTAL SCIENCE

In this context, 'environmental science' is taken to include all aspects of the behaviour of chemicals in solution in the regolith. Solution chemistry impacts on agriculture, mineral exploration, pollution control, and soil amelioration. Ions and organic molecules in the regolith may remain in solution, in which case they may interact with everything they bathe, or they may be sequestered by regolith minerals or biota. Retention of trace elements in minerals depends on the available mineral species (Table 6), and much of the research of this thesis has discovered hitherto unknown pathways and products of mineral weathering which yield intermediate phases, often metastable, all of extremely small particle size. Such intermediates, such as hisingerite formed during the weathering of many Fe-bearing minerals, are, or may be, highly adsorbing of cations, and can provide a temporary residence from which it may be difficult to displace the ion. But once the host mineral has itself broken down due to further weathering, the temporary resident is free to leave. Pathways of this kind, although barely investigated, may prove critical in understanding the availability of regolith chemicals.

**Table 6** Distribution of some elements according to their regolith mineral hosts.

	In major mineral as		In minor mineral as	
	major element	trace element	major element	trace element
Li			lithiophorite	
B	borax			
C	calcite, dolomite			
F	lost			
Na	lost			
Mg	smectite, palygorskite, dolomite			
Al	kaolin, smectite, illite, halloysite, gibbsite, amorphous		alunite	
Si	all silicates			
P			apatite, monazite, crandallite group	
S	gypsum		alunite, jarosite	
Cl	halite			
K	illite, jarosite		alunite	
Ca	calcite, gypsum			
Sc		Fe oxides	?anatase	



Table 6 (cont.)

In major mineral as			In minor mineral as	
	major element	trace element	major element	trace element
Ti			anatase, ilmenite, rutile	
V		smectite	carnotite, montroseite	Mn oxides
Cr		smectite	chromite	Mn oxides
Mn	pyrolusite, birnessite			
Fe	goethite, hematite, ferrihydrite			
Co				Mn oxides
Ni		smectite, Fe oxides	pimelite, garnierite	Mn oxides
Cu		smectite, Fe oxides	malachite, azurite	Mn oxides
Zn		smectite, Fe oxides	smithsonite	Mn oxides
Ga		with Al		
Ge		with Si		
As		Fe oxides	various arsenates	
Se		Fe oxides		
Sr				Mn oxides
Y			phosphates	Mn oxides
Zr			zircon, baddeleyite	
Mo		Fe oxides		Mn oxides
Ag				Mn oxides
Sn			cassiterite	
Sb				Mn oxides
Ba			barite, gorceixite	Mn oxides
REE			rhabdophane, florencite, gorceixite, lanthanite	Mn oxides
Au			gold	
Pb			cerussite, anglesite, phosphates, arsenates	Mn oxides
Th			thorite?	
U			carnotite, phosphates	zircon

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