

XRD AND ELECTRON-MICROSCOPY INVESTIGATIONS OF LAYER SILICATES

PREFACE

In 1997, the 11th International Clay Conference was held in Canada for the first time. The Mineralogical Association of Canada acted as one of the official “sponsors” of this major meeting. In that context, my colleague Hoyatollah Vali and I volunteered to organize a one-day special session of the power of a combined XRD - TEM approach in the study of layer silicates. Contributors were also asked to provide a summary of their presentation for the Conference Proceedings volume. I sensed that some speakers would be frustrated if they were limited to an extended abstract of their contribution. For example, how could they hope to present SEM, TEM and XRD documentation needed to make their point with the space limitations imposed on them?

Thus there emerged in my mind the concept of a thematic issue of *The Canadian Mineralogist*, which you now have before you. In consultation with guest Associate Editor H. Vali, I decided to translate the idea of “sponsorship” of a major conference into something tangible. Furthermore, I decided to extend an invitation to other possible contributors who, for one reason or another, were unable to attend the Ottawa meeting.

One plenary conference at the 11th International Clay Conference focused on the concept of fundamental particles. The development and merits of the concept were presented by its originator, Dr. Paul Nadeau. However, in the opinion of some attendees, there was insufficient discussion of this theme in Ottawa. Our issue thus starts off with a thought-provoking essay by Dr. Donald R. Peacor on the merits of the concept of fundamental particles, and in particular on the implications of TEM data accumulated since the concept was first described in print fifteen years ago. There are still many lingering questions concerning the meaning and implications of “fundamental particles”. It was my wish to use this open forum for a healthy discussion of some divergences of opinion concerning this important concept. Dr. Peacor’s discussion is followed by a reply by Dr. Nadeau, and another by Drs. F. Nieto and J. Cuadros.

The rest of the issue contains articles that address the theme “XRD and Electron-Microscopy Investigations of Layer Silicates”. Some of these articles focus on the complicated issues raised in the discussion and replies about fundamental particles. Just what is interstratified illite-smectite? Just what is measured by X-ray diffraction and transmission electron microscopy once the sample preparation for those techniques is done? Also included are papers on chlorite, lizardite, antigorite, and kaolinite. The last paper focusses on a geographically relevant issue, the mineralogy and consequent geotechnical behavior of Champlain clay-bearing clastic sediments of Pleistocene age, subject to major landslides in the St. Lawrence Lowlands of easternmost Ontario and Quebec.

I take this opportunity to thank the authors for their cooperation and willingness to contribute to this thematic issue and to *The Canadian Mineralogist*. I acknowledge the help of Hoyatollah Vali, and of the many referees who volunteered their time and effort to provide authors with suggestions on how best to increase the impact of their contributions, and thus, ultimately, to

make this a better thematic issue.

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IMPLICATIONS OF TEM DATA FOR THE CONCEPT OF FUNDAMENTAL PARTICLES

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ABSTRACT

There are two critical aspects of the concept of fundamental particles (fp): (1) in the original “working test” proposed, “separates” should demonstrate a single-crystal $hk0$ pattern in TEM (*i.e.*, coherent interlayers), and (2) if “separation” of particles occurs, it should occur only along smectite-like interfaces, which are incoherent. Unfortunately, “separates” are, with rare exceptions, referred to as fp without any test, whereas data imply that some separates of smectite-rich clays (especially) give $hk0$ SAED patterns reflecting a polycrystalline (turbostratically stacked) array. More importantly, coherency across even smectite interlayers is commonly demonstrated in original rocks by: (1) TEM lattice-fringe images with “cross-fringes”, (2) euhedral crystals of I/S, smectite, and illite, and (3) ubiquitous SAED patterns with discrete, but non-periodic hkl reflections. Layer sequences of S, I/S, and I have both incoherent and coherent interfaces, the proportion of the former decreasing with increasing grade; *i.e.*, they are neither entirely translationally periodic nor turbostratically stacked. During separation, cleavage may occur along coherent interfaces in smectite (likely) as well as illite, so that even where the working test for fp is valid, such crystallites may be only portions of more extended coherent sequences as they occurred in original rocks. The term fp should therefore be used only where appropriate tests have been carried out. Even in those rare cases, such confirmation implies only a minimum measure of thicknesses (in separates) of coherent sequences in equivalent original rocks. Because separation affects the thickness of crystallites, layer sequences and coherency, separates reconstituted for XRD analysis may be inappropriate measures of relations in original rocks, and therefore may lead to erroneous conclusions regarding genetic (crystal growth) relations. Before such features in separates are used in any predictive fashion, it is therefore essential to determine the ways in which layer relations in original rocks are modified by disarticulation and subsequent reconstitution for powder XRD analysis. Only where tests confirm consistency with the original definition of fp, and where the relation of such units has been verified as directly reflecting units in original rocks as originally implied, should the term “fundamental particle” be used. These criteria have only rarely been met. The term “separate” confers, on the other hand, an unbiased, unadorned and accurate description of the state of samples prepared for XRD analysis. It should be used in most cases, at least until additional tests of sufficient numbers and kinds of samples have been obtained that confirm the occurrence of fp.

Keywords: fundamental particles, coherent interlayers, smectite, illite/smectite, illite.

FUNDAMENTAL PARTICLES AND THE ADVANCEMENT OF GEOSCIENCE:
RESPONSE TO "IMPLICATIONS OF TEM DATA FOR THE CONCEPT OF
FUNDAMENTAL PARTICLES"

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ABSTRACT

A scientific response to suggested modifications of the fundamental particles theory for clay minerals, and limitations regarding its usage in the literature, demonstrates that such modifications may be unnecessary, and potentially harmful to communication of research results. The value of this mineralogical model, as well as its physical description of complex clay mineral properties in diagenetic and other environments, would be compromised or unduly restricted by adopting the suggested criteria for its usage. In the absence of a demonstrably superior and confirmed alternative model, it is recommended that fundamental particle hypotheses have priority within geoscience disciplines, as it provides a quantitative, verified, and independently validated basis from which to evaluate the nature, behavior, and origin of clay minerals in a variety of geological settings.

Keywords: fundamental particles, MacEwan crystallites, mixed layer clays, electron microscopy, X-ray diffraction, illite, smectite, diagenesis, nomenclature of clay minerals.

EVOLUTION, CURRENT SITUATION, AND GEOLOGICAL IMPLICATIONS OF THE “FUNDAMENTAL PARTICLE” CONCEPT

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ABSTRACT

The fundamental particle concept has evolved from its original formulation in order to take into account experimental evidence, in particular lattice-fringe images and the polar character of I/S. This process has brought the concept closer to the traditional mixed-layer view, the difference in interpretation lying only in the three-dimensional coherence across “fundamental particles”. Recent evidence suggests that there is coherence through smectite layers. We thus consider that the fundamental particle model does not contribute to an understanding of I/S genesis.

Keywords: fundamental particle, illite, mixed-layer, smectite.

A COHERENT TEM- AND XRD-DESCRIPTION OF MIXED-LAYER ILLITE/SMECTITE

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ABSTRACT

We present a model for the low-charge (smectite?) layers in mixed-layer illite/smectite based on an integration of observations from transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). This model is an attempt to account for the apparent discrepancies in the structural descriptions based solely on one technique or the other, in which the low-charge interlayers appear to be coherent interfaces by TEM but incoherent interfaces by XRD. In our model, the low-charge boundaries between adjacent 2:1 layers are semicoherent owing to rotational disorder (*i.e.*, they are turbostratically stacked), but the degree of rotational disorder is limited. Such a model is consistent with both TEM and XRD observations and with an intuitive model of the interlayer-site occupancy: if a low-charge interlayer must have approximately $\frac{1}{4}$ to $\frac{2}{3}$ of the total sites occupied to satisfy charge balance, then the rotational disorder must be less than $\sim 10\text{--}15^\circ$.

Keywords: illite, smectite, X-ray diffraction, transmission electron microscopy, mixed-layer I/S.

MODIFICATION OF ILLITE–MUSCOVITE CRYSTALLITE-SIZE DISTRIBUTIONS BY SAMPLE PREPARATION FOR POWDER XRD ANALYSIS

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ABSTRACT

Mean crystallite sizes of illite–muscovite have been obtained by direct measurements using TEM on ion-milled (original rock) samples and separates prepared for XRD analysis, and by XRD profile analysis of separates in a prograde sequence of metapelites from southern New Zealand. The mean crystallite sizes determined by the analyses of XRD peak profiles increase with metamorphic grade, consistent with the trend determined by TEM from ion-milled rock samples. However, the sizes obtained by TEM on the ion-milled rock samples are approximately two to four times larger than those by XRD profile analyses. This difference is greater in higher-grade than lower-grade samples. The mean size of crystallites measured using TEM on the separates that were used to obtain XRD profiles correspond well to those from XRD profile analyses. Further TEM and AFM observations of separates show that crystals have been broken across and cleaved along (001) planes. These relations indicate that the XRD data were obtained from samples that differ significantly from the original rock samples; the data indicate that sample preparation for XRD analysis significantly altered the original size-distributions. Crystallite-size distributions are poor approximations to lognormal in original rocks, but are modified to lognormal or nearly lognormal distributions in separates. Interpretation of growth conditions from size distributions of separates is therefore subject to error. Only size distributions of unseparated samples, or separates where the effects of the separation process are known, should be used as

indicators of growth conditions.

Keywords: illite–muscovite, crystallite size, size distribution, XRD analysis, TEM measurement, diagenesis, low-grade metamorphism, anchizone, epizone, New Zealand.

CRYSTALLITE THICKNESS AND DEFECT DENSITY OF PHYLLOSILICATES IN LOW-TEMPERATURE METAMORPHIC PELITES: A TEM AND XRD STUDY OF CLAY-MINERAL CRYSTALLINITY-INDEX STANDARDS

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ABSTRACT

The thickness distribution and defect density of illite crystallites (both illite–smectite and illite–muscovite phases) and chlorite are presented for a set of clay-mineral crystallinity-index standards, as determined by TEM and XRD methods for both the whole rock and disaggregated clay-sized fractions. The pelitic standards, selected from the Variscan rocks of southwestern England, display the full array of typical microstructural transformations that characterize the prograde transition from diagenesis (zeolite facies) to epizonal (greenschist facies), with increasing thickness of crystallites and decreasing concentration of lattice imperfections. Crystallite thickness, measured from TEM lattice-fringe images in the c^* direction of both illite and chlorite, commonly deviate from lognormal distributions, with positive skewness toward small sizes. These distributions are considered to reflect complex histories of nucleation and growth, as well as structural modifications due to rock strain. Crystal damage caused by rock disaggregation, in the form of splitting along crystallite boundaries and other planar defects, can be observed in all clay-sized separates. The degree of damage increases as a function of increasing size of crystals, and clearly enhances the differences in mean thickness of the crystallites between the whole rock and clay-sized fractions, particularly in anchizonal and epizonal slates. Although clay separates yield smaller mean thicknesses of crystallites and show thickness distributions with lower degrees of skewness and standard deviation than measured from matrix of the pelitic rocks, the aaa and bbb_2 shape parameters (the mean and variance of the natural logarithms of the sizes) for both grain-size fractions define a common crystal-growth path when plotted in $aaa - bbb_2$ space. This feature shows that ultrasonic disaggregation has not modified the shape of the thickness distributions in a way that has influenced the interpretation of the mechanisms of crystal growth and deformation. NEWMOD modeling of XRD profiles based on TEM constraints show a relatively good correspondence between the size of X-ray-scattering domains and crystallite thicknesses in most cases. XRD-determined area-weighted mean thicknesses of crystallites

calculated using an integral peak-width method yield sizes that correspond to those measured directly from TEM measurements. However, the refined Warren–Averbach method of MUDMASTER, adopted for the analysis of PVP-saturated clays, produced profiles that do not match well the TEM-determined distributions. Refinements to the method are required before accurate thickness-distributions can be extracted from the narrower XRD reflections of metamorphic phyllosilicates.

Keywords: phyllosilicates, clay minerals, crystallite thickness, defect density, transmission electron microscopy, X-ray diffraction, crystallinity-index standards, low-temperature metamorphism, pelites.

CHANGES IN LAYER ORGANIZATION OF SEPARATES OF Na- AND Ca-EXCHANGED SMECTITE DURING SOLVENT EXCHANGES FOR EMBEDMENT IN RESIN

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ABSTRACT

The embedding process designed for impregnation in resin of hydrated clays for TEM observation, comprises four steps of exchange by solvents and resin. Clay pastes of Na- and Ca-exchanged Wyoming smectite were prepared at low suction pressures (3.2 and 100 kPa, respectively), and their layer organization was examined at different steps of the embedding process. X-ray diffraction was used in order to follow the evolution of layer distances and particle orientation during solvent exchanges. At 3.2 kPa as well as at 100 kPa, the water-saturated clay exhibits interlayer distances of 1.9 nm. After methanol exchange, interlayer distances collapsed to 1.6–1.7 nm. With 1,2-epoxypropane and resin saturation, clays behave in a similar way as with methanol. Examination of layer-stacking coherency by measurement of peak widths indicates that the first exchange by methanol is the most critical step in the embedding process because it induces reduction of the layer distances and aggregation, especially in the case of dilute Na-exchanged clay. The final polymerization of resin introduces further slight changes in organization of the clay.

Keywords: smectite, organization, embedment, solvent, resin, X-ray diffraction.

SIGNIFICANCE OF *n*-ALKYLAMMONIUM EXCHANGE IN THE STUDY OF 2:1 CLAY MINERAL DIAGENESIS, MACKENZIE DELTA – BEAUFORT SEA REGION, ARCTIC CANADA

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ABSTRACT

We have undertaken an XRD and HRTEM study of 2:1 clay minerals from argillaceous rocks of the Reindeer D–27 well, Mackenzie Delta – Beaufort Sea (MDBS) region, Arctic Canada. Separates of the fine clay fraction (<0.05 μm) after treatment with *n*-alkylammonium cations consist of 2:1 clay mineral assemblages which span the major steps in the evolution of smectite to illite (S → I). Diffraction patterns of the <0.05 μm fractions treated with octylammonium ($n_c = 8$) and octadecylammonium ($n_c = 18$) cations from intermediate (2659.4 m) to maximum depths (3832.8 m) in well D–27 suggest the presence of R1 and R3 ordered illitic phases. Lattice-fringe images reveal the presence of multiple metastable phases of low- and high-charge expandable 2:1 clay minerals, a short-range rectorite-like R1 ordered phase, “*n*-alkylammonium illite” and illite in zones that overlap with burial depth. Expandable 2:1 clay minerals decrease in abundance with depth of burial and were not observed in samples at maximum depth. Illitic and micaceous phases of variable layer thickness and origin are present at all depths. A rectorite-like R1 ordered phase dominates at the intermediate stage in the evolution of S → I at a depth of 2659.4 m, and apparently coherent sequences (packets) of illite with three to seven layers (R3 ordered) dominate at the maximum depth of 3832.8 m. Packets of “*n*-alkylammonium illite” are only identified in lattice-fringe images of samples from maximum well-depth. The prograde evolution of metastable 2:1 clay minerals with depth, which constitutes the conversion of S to I in the MDBS region, corroborates previous postulates that the principal mechanism of reaction is dissolution–crystallization.

Keywords: *n*-alkylammonium-cation exchange, smectite, rectorite-like R1 ordered phase, “*n*-alkylammonium illite”, illite, HRTEM, XRD, Reindeer D–27 well, Mackenzie Delta – Beaufort Sea region, Arctic Canada.

K–Ar AGES OF UNTREATED AND *n*-ALKYLAMMONIUM-TREATED 2:1 CLAY MINERALS, MACKENZIE DELTA – BEAUFORT SEA REGION, ARCTIC CANADA

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ABSTRACT

K–Ar ages of untreated 2:1 clay minerals of the <0.05 mmmm size-fraction separated from argillaceous rocks of the Reindeer D–27 well, Mackenzie Delta – Beaufort Sea region, Arctic Canada, generally increase with increasing depth of burial, from 19 ± 3 at *ca.* 1935 m to 65 ± 1 Ma at *ca.* 3832 m. Although the ages are lower than the stratigraphic ages, XRD patterns and TEM images of the same material suggest that the K–Ar ages are mixed ages. These result from a mixture of detrital and diagenetic illite. The K–Ar ages of the 0.05–0.1 mmmm fraction generally decrease with increasing burial, but are older than the stratigraphic ages. K–Ar ages of the <0.05 and 0.05–0.1 mmmm size fractions after intercalating octadecylammonium cations ($n_c = 18$) also vary with burial depth. The ages of the 0.05–0.1 mmmm fraction decreased slightly from 120 ± 2 to 115 ± 3 Ma at shallow depth (*ca.* 1935 m), and decreased from 95 ± 2 to 55 ± 3 Ma at slightly greater depth (*ca.* 2065 m). A decrease in age may be due to the exchange of K and Ar by the intercalation of $n_c = 18$ cations into the interlayers of an illitic phase of detrital origin. At maximum depth (*ca.* 3832 m), the age of the 0.05–0.1 mmmm fraction increased slightly from 100 ± 2 to 106 ± 3 Ma after treatment with $n_c = 18$. The increase in K–Ar age with treatment is more evident in the <0.05 mmmm fraction, which increased from 19 ± 3 to 92 ± 4 Ma at *ca.* 1935 m

and from 65 ± 3 to 97 ± 3 Ma at *ca.* 3832 m. This suggests that exchange of interlayer K and radiogenic Ar by $n_C = 18$ has occurred in a “young” illitic phase of diagenetic origin. The change in age is less significant in the deeper sample because it is dominated by an authigenic illitic phase, and the removal of K and Ar by $n_C = 18$ is incomplete. The K–Ar dating of IS and illite from argillaceous rocks of a burial-diagenetic sequence after treatment with long-chain alkylammonium cations may help to better constrain the timing of post-depositional events in the diagenetic history. It is possible to distinguish between diagenetic and detrital illitic subpopulations in shales with small amounts of detrital illite, as well as constraining the age of the detrital illitic component.

Keywords: K–Ar dating, illite, “alkylammonium illite”, smectite, octadecylammonium cations, TEM, Pt–C replica, Reindeer D–27 well, Mackenzie Delta – Beaufort Sea region, Arctic Canada.

ABSTRACT

CHAMOSITE FROM OOLITIC IRONSTONES: THE NECESSITY OF A COMBINED XRD–EDX APPROACH

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ABSTRACT

Chemical compositions of fine flakes of chlorite within chamositic coated grains from ironstones in regressive and condensed Ordovician and Jurassic sequences in Poland, Germany, Czech Republic and India were established by energy-dispersion analysis (EDX). The chemical data are inaccurate, mainly owing to the presence of intergrowths with other mineral phases. Structural formulae of trioctahedral chlorites calculated from the EDX data show apparent vacancies in the octahedral site. A more accurate chemical composition was obtained using an X-ray-diffraction (XRD) method. Relationships between d_{001} and b and the chemical composition of trioctahedral chlorites enabled the determination of their structural formulae. A comparison of the experimental powder-diffraction patterns with calculated patterns allows the assignment of chlorites from Paśłek to subfamilies C and D, and of chlorites in samples from other localities, to subfamily D. A sample from Paśłek was identified as a mixture of two chlorite polytypes: $1A_C$ -I-ho (82%) and $1M_D$ -II-ho (8%) with quartz (10%). Both polytypes reveal homo-octahedral occupancy of cations, and differ slightly in their chemical composition, which is manifested in different values of d_{001} and b . The combination of XRD and EDX methods of determination of chemical composition of chamosite is superior to EDX analyses alone. From a simple measurement of d_{001} and b , one obtains five major chemical components: ^{IV}Al , ^{VI}Al , Mg and Fe^{2+} not contaminated by mineral intergrowths. The EDX approach in addition provides information on specific heavy elements.

Keywords: chlorite, chamosite, coated grains, crystal chemistry, energy-dispersion analysis, X-ray diffraction.

SURFACE MICROTOPOGRAPHY OF ILLITE CRYSTALS FROM DIFFERENT MODES OF OCCURRENCE

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ABSTRACT

By means of transmission electron microscopy (TEM) and the gold-decoration technique, the surface microtopography of illite crystals from various environments was investigated. On the crystal surfaces, gold decoration successfully revealed growth steps of ~1 nm in height. The illite samples investigated exclusively exhibit growth spirals of either polygonal or circular form, with varying separation of steps. The spiral morphological characteristics were critically analyzed in relation to their mode of occurrence. Crystals from massive metasomatic specimens (aggregation texture with very low porosity) are characterized by circular growth-spirals with a narrow separation of steps, whereas those from veins and druses (aggregation texture with high porosity) are characterized by polygonal growth-spirals with a wide separation of steps. Hexagonal and lath-shaped crystals were controlled by polygonal spiral-growth; on the other hand, irregular platy crystals are characterized by circular or malformed circular spiral-growth. The morphology of illite crystals seems to reflect the spiral-growth process under the various conditions.

Keywords: illite, microtopography, spiral growth, Au-decoration method, morphology, hydrothermal environment, metasomatism.

SYNTHESIS AND PROPERTIES OF REGULARLY INTERSTRATIFIED (R=2)
MARGARITE (0.67) – BEIDELLITE, A 34 Å PHASE

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ABSTRACT

A regularly interstratified (R=2) margarite(0.67)/beidellite was hydrothermally synthesized at 400–500°C under 1 kbar pressure. The starting material was a mixture of kaolinite, calcium oxide or calcium carbonate, and alumina gel. X-ray powder-diffraction data of a sample saturated with Mg showed that the spacings of basal reflections vary depending on sample preparation. The first-order reflection was observed at 34.6 Å under air-dry condition with 60% relative humidity, 29.1 Å after heating to 600°C, 36.4 and 37.0 Å after solvation with ethylene glycol and glycerol, respectively. The spacing of the 060 reflection was 1.478 Å, indicating its dioctahedral nature. Chemical data gave a structural formula of $\text{Mg}_{0.18}(\text{Ca}_{1.84}\text{Na}_{0.22}\text{K}_{0.12})(\text{Al}_{5.97}\text{Fe}^{3+}_{0.01}\text{Mg}_{0.03}\text{Ti}_{0.06})(\text{Si}_{7.35}\text{Al}_{4.65})\text{O}_{30}(\text{OH})_6$. A differential thermal analysis showed a few endothermic peaks below 200°C and in the range 500–650°C, and an exothermic peak at 1070°C. XRD and chemical data indicate that the sample is composed of margarite-like and beidellite-like layers in a proportion 0.67:0.33. Infrared absorption of the sample showed major bands at 670–700 cm⁻¹ and 900–930 cm⁻¹ regions, which are similar to the known values of margarite. These data suggest that the phase exhibits a large extent of substitution of Si by Al.

Keywords: regular interstratified phyllosilicate, R=2 margarite(0.67) – beidellite, synthesis, 34 Å phase.

CALCULATED H-ATOM POSITIONS IN MICAS AND CLAY MINERALS

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ABSTRACT

The Static Structure-Energy Minimization (SSEM) technique was used to calculate the H-atom positions in phlogopite, clinocllore, kaolinite, margarite, muscovite and dickite using four interaction terms: Coulombic interaction, repulsion, covalency and polarization. Interaction within the OH groups was calculated using a Morse potential. Two steps were taken to locate the H-atom position(s): (1) relaxing the H positions from those of the hydroxyl O-atoms with symmetry constraints, and (2) relaxing the H positions obtained in step (1) without symmetry constraints for the H atoms only. Phlogopite, clinocllore and kaolinite give results that agree well with the neutron-diffraction values. The split-site model of margarite was successfully reproduced. In muscovite, two H-atom positions are predicted, represented with a split H-atom model in space group $C2/c$. For dickite, six H-positions are predicted rather than the four that are observed by diffraction. This result helps explain the apparent disagreement between the diffraction experiment that located four unique H-atom positions, and the IR experiments that suggest six OH-stretching bands.

Keywords: Static Structure-Energy Minimization, H-atom positions, micas, clays, chlorite.

EFFECT OF TEMPERATURE ON THE STRUCTURES OF LIZARDITE-1*T* AND LIZARDITE-2*H*₁

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ABSTRACT

Lizardite-1*T* from Val Sissone, Italy, and lizardite-2*H*₁ from the Monte dei Tre Abati ophiolite complex, Colli, Italy, were studied by single-crystal X-ray-diffraction methods to 480° and 525°C, respectively. The 1*T* polytype refined to a residual value *R* of 0.050 (*wR* = 0.058) at 480°C in space group *P*31*m*, and the 2*H*₁ polytype refined to an *R* of 0.031 (*wR* = 0.035) at 525°C in space group *P*6₃*cm*. Mean thermal-expansion coefficients for the cell parameters are $a = b = 0.37 \times 10^{-5}/\text{deg}$, $c = 1.13 \times 10^{-5}/\text{deg}$ for 1*T*, and $a = b = 0.70 \times 10^{-5}/\text{deg}$, $c = 1.67 \times 10^{-5}/\text{deg}$ for 2*H*₁. For the 1*T* polytype, ditrigonal ring distortions (tetrahedral rotation angle, *aaa*) change from -1.5 to near 0° from 20 to 480°C, whereas the *aaa* value for the 2*H*₁ polytype decreases from 1.8 to 1.3° at near 300°C, and remains constant at 1.3° to 475°C. The O–O distances for O–H–O linkages across the interlayer increase linearly from 3.08(1) to 3.15(1) Å from 20 to 475°C for the 2*H*₁ polytype. In contrast, the 1*T* polytype shows near-constant values for similar O–O distances of 3.06(1) Å to 360°C. From 360 to 480°C, this distance increases at nearly the same rate as with the 2*H*₁ polytype, from 3.06 to 3.09(1) Å. On the basis of longer O–O distances, the 2*H*₁ polytype exhibits weaker hydrogen bond linkages across the interlayer at all temperatures than the 1*T* polytype. Thermal expansion is related to optimum hydrogen bonding (O–H–O linkages) across the interlayer, which is affected by both thermal effects (dynamic displacements) and structural constraints. Structural constraints are predominately controlled by tetrahedral rotation within the plane of the sheet and the consequent movement of basal atoms of oxygen, which results from an adjustment of the tetrahedral and octahedral sheets to different modes of thermal expansion. Thermal effects dominate over structural constraints for the 2*H*₁ polytype. In contrast, it is tentatively concluded that structural adjustments dominate to about 300°C in the 1*T* polytype, above which thermal effects dominate because the tetrahedral sheet is extended fully and interlayer bonding has weakened sufficiently.

Keywords: lizardite, serpentine, high-temperature, structure, polytypes, hydrogen bonding, X-ray diffraction.

TEM AND XRD STUDY OF ANTIGORITE SUPERSTRUCTURES

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ABSTRACT

Samples of antigorite exhibiting variety in superstructures, taken from low-grade to high-grade serpentinites from southwestern Japan, were studied by X-ray diffraction (XRD), selected-area electron diffraction (SAED), and high-resolution transmission electron microscopy (HRTEM). Indexed XRD patterns indicate an A cell parameter of the supercell in the range 35.4 – 53.6 Å, and the following dimensions of the subcell: $5.407 < a < 5.466$, $9.238 < b < 9.262$, $7.241 < c < 7.279$ Å, $91.07 < \beta < 91.65^\circ$. SAED patterns show a wider range of A parameters, from 28 to 61 Å ($5.0 < M < 11.4$, $M = A/a$). Antigorite with a 40.0 – 42.5 Å supercell ($M = 7.5$) is the common structure in southwestern Japan. A new method for supercell measurement by powder XRD is proposed. M values show a linear relation with the XRD-derived parameter, $M = 14.26 - 2.41 D$. A sample of antigorite with $A = 43$ Å ($M = 8$) belongs to space group Pm . Diffraction patterns (single-crystal XRD and SAED) and c -axis HRTEM images of antigorite having $M = (2n + 1)/2$ indicate that the true periodicity of the superstructure along the X direction is $2A$, corresponding to two waves, and the space lattice is C -centered.

Keywords: antigorite, XRD, SAED, HRTEM, supercell, superstructure, Japan.

EVIDENCE FOR ATOMIC-SCALE RESOLUTION IN ATOMIC-FORCE MICROSCOPY OF LAYER SILICATES

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ABSTRACT

We have recorded atomic force microscopy (AFM) images of the surfaces of kaolinite and lizardite. Typically, the AFM images of the rings of basal-O atoms of these structures have two-fold rotational symmetry, and there is an apparent difference in height between adjacent tetrahedra. These are anomalous features not found in the known structures, and comparison with calculated images of graphite suggest that both features are due to the interaction of a double-atom AFM tip with the atoms of the surface of the sample. However, in some cases we have recorded the first images of the O-atoms in the basal-O plane of sheet silicates at atomic-scale resolution. Currently, there are two views of such AFM images: (1) they show arrays of individual atoms; (2) they show arrays of averaged atom positions. There are two interpretations for the second view. The first relates to the use of two-dimensional fast-Fourier transforms (2DFFT) to enhance detail in the image, the argument being that the use of 2DFFT introduces spurious features *and* averages the atomic positions. The other interpretation is that the periodic repeat-units of the structure being scanned set up harmonic vibrations in the cantilever and produce an image of an average structure. We have recorded a *single* image that shows two *different* atomic repeat-units in different parts of the raw image. Enhancement using 2DFFT significantly increases the resolution of each part of the image but maintains the two discrete images of the different structural elements; it does not average the separate parts of the image. In another image, we have recorded atoms that are displaced from the expected atomic position, a feature that would not be recorded if averaging took place. We conclude that these images represents individual atoms on the surface.

Keywords: lizardite, kaolinite, atomic-force microscopy, atomic-scale resolution, two-dimensional fast-Fourier transforms.

GREISEN AND POST-GREISEN ALTERATION IN THE SÃO VICENTE DE PEREIRA KAOLINITE DEPOSIT, PORTUGAL

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ABSTRACT

The São Vicente de Pereira kaolinite deposit, located at the northwestern border of the Ossa Morena zone, in Portugal, is the site of important hydrothermal alteration, developed at the expense of migmatitic rocks and related to a system of Hercynian polyphase deformation and shear zones. Two stages of hydrothermal alteration are evident: 1) greisen-type alteration is represented by quartz + muscovite containing F and Cl, and by quartz + tourmaline; 2) post-greisen alteration and advanced argillic alteration led to the formation of well-ordered or poorly ordered kaolinite. The quartz + muscovite assemblage was investigated by XRD and electron-microprobe analyses. The mica shows intermediate characteristics between muscovite and lepidolite. It has a relatively low content of Si (3.10–3.20 *apfu*), a high proportion of ^{VI}Al, a very low Fe content, and an absence of Mg. Quartz–tourmaline-rich greisen occurs in veinlets that cross-cut migmatites showing advanced argillic alteration. Two generations of tourmaline having different morphologies and different Fe contents can be identified. Well-ordered kaolinite formed at the expense of muscovite exhibits a “booklet” morphology, as revealed by SEM and TEM observations. The hydration of well-ordered kaolinite led to halloysite-7Å. Results of oxygen and hydrogen isotopic analyses attest to the formation of kaolinite from metamorphic pore-fluid.

Keywords: greisen, post-greisen alteration, kaolinite, halloysite-7Å, X-ray diffraction, electron microprobe, electron microscopy, isotopic ratios, oxygen, hydrogen, deposit, Portugal.

MINERALOGY, GRAIN-SIZE DISTRIBUTION AND GEOTECHNICAL BEHAVIOR OF CHAMPLAIN CLAY CORE SAMPLES, QUEBEC

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ABSTRACT

Samples of Champlain Sea sediment from St-Barnabé, Quebec, near the Canadian Shield contact of the Champlain Sea basin, and from Henryville, Quebec, near the Appalachian Mountains contact, are dominated by the tectosilicates (47–82%). At Henryville, quartz and plagioclase are dominant, with lesser K-feldspar; among the phyllosilicates, the 4–0.5 mmm fraction contains, in decreasing order, chlorite, illite, and expandable clay, except in the near-surface weathered zone, where the expandable clay is in greatest quantity. In the <0.5 mmm fraction, expandable clay also dominates in the surface and basal zones of the sediment. At St-Barnabé, plagioclase is dominant, with lesser amounts of quartz and K-feldspar; the phyllosilicate component of the 4–0.5 mmm fraction is dominated by illite, with much lower proportions of chlorite and expandable clay at all depths, whereas in the <0.5 mmm fraction, the proportion of expandable clay increases relative to illite and chlorite, although it generally is not dominant. The sensitivity of the sediment decreases as the relative abundance of expandable clays increases. Oxide concentrations are low, on the order of 1% of the total sample; although relatively more abundant in the smaller size-fractions, the quantity increases at a lesser rate than the surface area. The relatively small amount of oxides present suggests that, at these levels, they probably affect soil behavior by a cementing action that is analogous to a “spot welding” process at interparticle contacts.

Keywords: Champlain Sea, Leda clay, mineralogy, geotechnical behavior, size fractionation, tectosilicates, expandable clays, oxide minerals, Quebec.