THE CHARGE OF COMPONENT LAYERS OF ILLITE-SMECTITE IN BENTONITES AND THE NATURE OF END-MEMBER ILLITE

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Abstract—The nature of component layers of mixed-layer illite-smectite and their possible evolution in the course of illitization have been debated since the 1960s. The present study is a new attempt to solve these problems, using samples collected from diverse geological formations around the world. Twenty three purified illite-smectites from bentonites and hydrothermal rocks, covering the complete range of expandability, were analyzed chemically, including NH_4^+ determination, and their structural formulae were calculated. The exchangeable cations (EXCH) were plotted *vs.* the fixed cations (FIX) yielding the following experimental regression:

$EXCH = -0.43 \times FIX + 0.41$ (R² = 0.98)

FIX and EXCH depend on the charge of the illite (Q_i) and smectite (Q_s) interlayers, and the fractions of these interlayers in the bulk clay leading to:

$\text{EXCH} = -Q_{\text{s}}/Q_{\text{i}} \times \text{FIX} + Q_{\text{s}}$

Analysis of these relations and independent measurements of the total specific surface area (TSSA) indicate that the layer charges of both types do not change in the course of illitization. The smectite layer charge is equal to 0.41 and the illite layer charge is equal to 0.95 per $O_{10}(OH)_2$. End-member illite has a well defined composition that is close to intermediate between muscovite and phengite, with fixed cations content greater than that specified in the AIPEA classification of layer silicates:

FIX_{0.95}(Si_{3.25}Al_{0.75})(Al_{1.81}Fe_{0.01}Mg_{0.19})O₁₀(OH)₂

The established relationship allows the calculation of the mean number (N) of 2:1 layers in all fundamental particles and also the fraction of smectitic layers (f_s) from FIX:

$$N = Q_i/(Q_i - FIX)$$
 $f_s = (Q_i - FIX)/Q_i$

N and f_s can be used to calculate TSSA, and all three parameters can also be calculated from cation exchange capacity and from X-ray diffraction peak positions, utilizing the regressions established here. **Key Words**—CEC, Charge Density, EGME, Illite, Illite-smectite, Layer Charge, NEWMOD, Smectite, Specific Surface Area, Surface Area, Water Sorption, XRD.

INTRODUCTION

Attempts to characterize the chemistry of the component layers of illite-smectite (I-S) began with that by Mehra and Jackson (1959), who concluded from K_2O and surface-area measurements of illites that all K_2O comes from the non-expandable (illitic) layers and all samples with <10 wt.% K_2O contain some expandable layers. Weaver (1965) made the first attempt to calculate the smectitic and illitic components from the overall structural formula of illite-smectite and the layer ratio evaluated by XRD. A smectitic layer charge (Q_s) of 0.46/ $O_{10}(OH)_2$ and an illitic layer charge (Q_i) of 0.84 were established, similar to the $Q_s = 0.36$ and $Q_i = 0.88$ established by Brown and Weir (1963) for rectorite.

The first systematic chemical study of a series of illite-smectites was published by Hower and Mowatt (1966), who plotted fixed cations (FIX = K+Na) vs. percent of smectite layers evaluated by XRD ($\%S_{XRD}$)

and obtained by linear extrapolation $Q_i = 0.75$. Those authors concluded that the illite end-member of the mixed-layer series was a mineral species distinct from true mica, and observed that cation exchange capacity (CEC) correlates well with S_{XRD} . Środoń *et al.* (1986) using a similar approach on a broader set of samples, covering the entire range of S_{XRD} , found that the FIX *vs.* S_{XRD} relationship is not linear but concave, and suggested that it was due to the presence of two types of illite layers with $Q_i = 0.55$ in random (R0) I-S and $Q_i =$ 1.00 in ordered (R >0) I-S.

Velde and Brusewitz (1986) concluded from chemical and XRD data that $Q_i = 0.7$ and that Q_s is stable during illitization, but varies from 0.3 to 0.7 between different sample sets. Meunier and Velde (1989) arrived at similar conclusions by chemiographic analysis: $Q_s =$ 0.33-0.66 and $Q_i = 0.87$. Different relationships were found for soil-derived I-S, using a non-linear optimization of chemical data (Laird *et al.*, 1991): $Q_s = 0.48$ and $Q_i = 0.47$.

Nadeau and Bain (1986) were the first to measure ammonium as a minor fixed cation in I-S and the first to observe that XRD appears to overestimate the proportion of illite layers, compared to direct TEM measurements of

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the thickness of fundamental particles. Their results suggested that Q_i and Q_s are similar and that they increase in the course of illitization from ~0.5 to ~0.9. Srodoń et al. (1992) also used transmission electron microscopy to calculate %S, but found that Q_i and Q_s are stable at 0.89 and 0.4, respectively. Identical values were obtained by Ylagan et al. (2000), who applied the same technique to a set of I-S samples from a hydrothermal alteration zone. Loucks (1991) suggested that the vacant illite interlayer sites ($Q_i < 1.00$) were occupied by hydronium and molecular water, or by molecular water only (Slonimskaya et al., 1978; Drits and McCarty, 2007). The most recent report of the AIPEA Nomenclature Committee dealing with clay nomenclature (Guggenheim et al., 2006) defined illite as 'interlayer-deficient mica' with a layer charge of 0.6-0.85.

Cetin and Huff (1995) used the alkylammonium technique to investigate the expandable layer charge during diagenesis and concluded that at ~10% S_{XRD} it changes from smectitic to vermiculitic. Sato *et al.* (1996) carried out a similar study using several tests (K-saturation, Greene-Kelly test, alkylammonium) and concluded that smectite becomes more beidellitic before the onset of illitization; its layer charge increases from 0.28 to 0.37, and this process continues during illitization. Meunier *et al.* (2000), analyzing a broad range of published data, came to the conclusion that in the course of diagenesis smectite layers first evolve into vermiculite layers and then undergo illitization.

Review of the literature suggests that the nature of the component layers of I-S is still ambiguous, along with their evolution during illitization. The results of another attempt to solve this puzzle are presented below, and built on the results of Środoń and McCarty (2008), who demonstrated how to use CEC and H₂O and EGME sorption for an accurate measurement of the layer charge and the total specific surface area (TSSA) of pure smectites. Combining this approach with a careful chemical analysis of a broad set of pure samples offers a new insight into the crystal chemistry and evolution of I-S. Most of the symbols used in this paper were defined in the appendix of the paper by Środoń and McCarty (2008).

MATERIALS AND METHODS

Twenty three samples or rocks containing I-S of different layer ratios, and possibly free of other mineral admixtures, were selected for this study. Most are bentonites of various ages and a few come from a hydrothermal clay deposit in Hungary. Two reference smectites (Wyoming and Cheto) were also studied. Table 1 lists the details and gives relevant references.

The rocks were crushed in a hand mortar and treated chemically to remove carbonates, organic matter, and Fe oxides (Jackson, 1975). After initial removal of the excess electrolyte by centrifugation, the $<0.2 \ \mu m$ frac-

tions were separated. A small portion was then coagulated with NaCl, while most of the clay suspension was converted into Ca form by four exchanges with 1 N CaCl₂. Both Na and Ca clays were purified by centrifugation followed by dialysis, monitored by a conductometer, and finally freeze dried. The purity of the clay fractions was checked by X-ray diffraction (XRD), using side-loaded, random preparations. The XRD identification of illite-smectite was performed using 4.5 cm long sedimented preparations (10 mg clay/cm²), under conditions of ethylene-glycol saturation and after dehydration by heating. The XRD patterns of the oriented Ca-saturated preparations were registered over a 2-50°2 θ CuK α range for 3 s/0.02°2 θ step on a Thermo X'tra diffractometer equipped with two Soller 1.3° slits, 0.9 mm divergent slit, 0.3 mm receiving slit, 1.05 mm divergent scatter slit, and 1 mm receiving scatter slit. The peak positions were found to be accurate within $\pm 0.02^{\circ}2\theta$, based on quartz impurities present in a few samples. The oriented slides of K-saturated samples spiked with silicon powder (NIST standard SRM 640c) were heated at 150°C and 250°C and immediately registered under N₂ atmosphere over a $2-52^{\circ}2\theta$ CuK α) range using 5 s/0.01°20 steps on a Thermo X'tra diffractometer equipped with two Soller 2° slits, 0.8 mm divergent slit, 0.2 mm receiving slit, 4 mm divergent scatter slit, and 0.5 mm receiving scatter slit.

The loss on ignition of Na and Ca samples (from the air-dry state to 1 h at 1100°C) and the %K₂O of the ignited Ca samples (Sherwood Model 420 flame photometer) were measured. The total specific surface area (TSSA) was measured by a technique combining the approach used by Tiller and Smith (1990, free surface EGME sorption) and Newman (1983, water sorption). Clay samples in Ca form were first equilibrated at 47% RH over a saturated solution of lithium nitrate. After overnight equilibration, all samples were weighed and placed in the desiccator again. Next, the weight of H₂O released during heating to 200°C followed by isothermal heating at 200°C for 0.5 h was established using a programmable thermobalance, and the hot sample was placed in the desiccator used for the EGME determination. After equilibrating all samples with EGME, the sample weights were measured again. Using this approach, sorption of both H₂O and EGME can be referred to the same weight of clay, obtained at 200°C, which is close to the absolutely dry weight, thus independent of changes in relative humidity (Srodoń and McCarty, 2008). Finally, the CEC was measured by the Co-hexamine technique of Orsini and Remy (1976) and Bardon et al. (1983) on the same sample split, and referred to the same weight at 200°C. The optimum Cohexamine solution concentration was estimated from the sorption data. Testing performed on separate sample splits proved that CEC measured on EGME samples is essentially the same as measured on the H₂O samples $(CEC_{EGME} = 0.998 \times CEC_{H_2O} + 2.15, R^2 = 0.998).$

Major element analysis was performed by inductively coupled plasma mass spectrometry (ICP-MS) on ignited Ca samples fused with a Li metaborate-tetraborate flux at Activation Laboratories, Canada. NIST 70a (K feldspar) and 76a (burnt refractory) standards were used to check the accuracy of these analyses.

The same laboratory measured the C, N, and S contents by LECO CNS-2000 from air-dry Na samples and the major element contents, including Co, by the Li metaborate-tetraborate fusion XRF technique on the samples after the Co-hexamine exchange and purification by dialysis.

Fourier-transform infrared (FTIR) spectroscopy of selected samples was conducted using the KBr pellet technique. The pellets (0.8 mg sample/300 mg potassium bromide) were prepared by dehydration of the clays (by heating for 24 h at 110°C) and of the KBr powder (by heating for 24 h at 550°C). The pellets were further dehydrated by storing at 195°C overnight. The spectra were recorded in a dry N₂ atmosphere using a Fourier Transform Infrared Spectrometer Bio Rad FTS 135. For each sample 32 scans were collected in the range $400-4000 \text{ cm}^{-1}$ at a resolution of 2 cm⁻¹.

RESULTS

Chemical analyses, independent checks for the presence of NH_{4}^{+} , and structural formulae

All of the original chemical analyses and the mineral impurities detected by XRD are listed in Table 1. The accuracy and precision of the ICP data were checked by triple analyses of two NIST standards. The analyses were found to be within 5 relative % of the certified values for all components >1%, except for K₂O, for which the error reached 9 relative %. Most errors were random; only Al₂O₃ and K₂O contents were found to be

systematically underestimated. Al_2O_3 data were then increased by 3 relative %, which is a correction factor based on the certified and the measured values for the two NIST standards. The K₂O data obtained by flame photometry were used, which for the two NIST standards fall within the certified values. The following correlation between the two K₂O data sets was established (both obtained for ignited samples):

$$%K_2O$$
 (FP) = 1.036 × $%K_2O$ (ICP) + 0.0893 R² = 0.996

The precision of the C, N, and S measurements was checked by double analyses of six samples and found to be within 0.03% absolute for C and 0.01% for N and S.

The C contents of all samples were found to be <0.2%. The N content of bituminous coals, which corresponds to the range of diagenesis studied, does not exceed 2% (Burchill and Welch, 1989). N can, therefore, be considered as representing inorganic ammonium fixed in illite and the %N in air-dry Nasamples can be recalculated to $%(NH_4)_2O$ in the ignited sample and added to the silicate major elements.

To validate these assumptions, two independent methods (FTIR and XRD) were used to check for the presence of NH_4^+ in the illite interlayer space. Six samples (with large and small N contents) were analyzed by FTIR and the spectra were consistent with the chemical data: the intensities of NH_4^+ bands at 1430, 3048, and 3307 cm⁻¹ are proportional to the %(NH₄)₂O established from chemical analysis (Figure 1).

For five heated, K-saturated samples (four NH_4^+ -rich and one NH_4^+ -poor), *d* spacing and peak-profile analyses were carried out on oriented XRD patterns, following the method proposed by Drits *et al.* (1997a, 2005). This method requires the slides to be heated at 150°C and warns against the use of temperatures which are too high (300°C). Because one sample (Małe Ciche) clearly did



Figure 1. FTIR spectra of dehydrated KBr discs of $<0.2 \ \mu m$ fractions, illustrating the complete range of detected substitution of NH⁴₄ (the bands at 1430, 3048, and 3307 cm⁻¹) for K⁺. The spectra are normalized to the OH-stretching band at 3630 cm⁻¹ after removing a flat background. The percentage of (NH₄)₂O from Table 1 is reported next to the sample names. A residual water band can be observed at 3450 cm⁻¹ and a kaolinite band (Silesia 25) at 3701 cm⁻¹.

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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	905 06 256 006 677 049 154 000 677 049 913 1020 046 023 013 954 1154 018 566 1210 2568 003 - 1497 005 153 010 156 011 650 013 050 157 1190 2568 003 - 1497 055 1154 018 601 050 053 053 915 1154 018 001 050 155 011 653 010 77, 1190 2568 003 - 1497 055 114 447 006 017 050 958 1437 006 051 100 164 397 006 2 , 0.1 1500 253 163 147 006 017 050 958 1437 008 051 100 164 397 006 2 , 0.1 1500 253 155 143 100 055 056 012 260 002 010 003 955 1557 005 001 0144 2011 1961 2568 003 - 1950 2555 155 153 349 011 533 044 005 015 005 038 1557 005 001 0144 2011 1951 2556 010 - 1500 2555 155 153 349 011 533 044 005 057 003 991 457 010 001 010 1144 2011 1951 3554 004 - 1510 2555 155 155 349 011 231 011 221 000 015 003 951 147 001 010 100 1124 1201 1951 953 004 109 7555 155 155 349 011 231 011 221 004 013 001 2012 005 013 991 457 011 08 001 011 144 2011 1951 953 003 01 493 7556 010 1951 1953 5554 003 001 252 9147 001 124 2011 1951 953 903 003 - 11930 2555 155 349 015 311 010 321 000 310 010 123 01 1231 001 1231 001 1231 001 1231 001 1231 001 124 1231 001 1251 1951 953 910 003 001 1244 1201 154 1950 155 114 1447 001 125 155 010 0102 101 124 1251 001 0101 124 1251 001 1251 1950 101 124 1251 124 1251 124 1251 001 0107 198 013 010 1259 204 1499 013 010 1259 204 1499 1469 013 010 1259 204 1499 1469 013 010 1259 204 1499 1469 013 010 1259 204 1499 1469 013 010 1259 204 1499 1469 013 010 1259 204 1499 1469 013 010 1259 204 1499 1469 144 144 144 144 144 144 144 144 144 14	0.1	32.68	0.97	1.52	0.02	8.65	0.06	0.26	0.015	0.062	0.03	99.01	11.42	0.11	0.03	<0.01	71.6	119.5	28.56	0.00	I	1.497
1137 088 230 004 861 004 034 0070 035 004 9313 1020 040 001 577 1190 256 0121 0256 003 003 931 1134 010 159 011 639 040 165 011 544 010 066 0177 0106 0177 0106 0177 0195 4 930 001 97, A, Q 1498 039 110 1134 147 005 052 040 013 040 165 011 544 0130 050 037 035 030 1448 011 066 0177 035 9301 1134 477 001 051 030 9301 1134 477 001 051 030 9301 1134 477 001 051 030 9301 1134 477 001 051 030 9301 1134 477 001 051 030 9301 1136 010 010 010 01106 1887 5564 005 A, Ch 1497 035 551 010 143 021 033 002 9301 1455 011 143 011 051 031 041 030 035 030 9301 1457 011 048 011 051 012 130 010 010 143 011 051 011 051 031 011 051 031 041 930 030 9301 1447 011 041 031 01106 1887 5564 005 A, Ch 1497 035 551 010 438 021 039 003 030 9301 1447 001 000 1151 0171 1951 931 011 231 011 231 010 233 033 9301 1447 001 000 010 1106 1887 5564 005 A, Ch 1497 035 551 173 030 010 4127 2313 012 251 010 013 012 038 119 016 011 1321 006 037 010 1104 1837 5564 013 A, Ch 1499 2356 217 233 010 012 231 010 013 012 039 931 1447 001 000 1154 1897 5567 003 030 014 011971 1951 930 03 03 01 1474 2350 039 03 01 1499 2358 2380 030 K 1490 2358 2380 235 011 493 011 231 000 035 010 9301 1447 001 031 011 237 2343 7778 035 Ch Q 1499 2358 235 011 249 003 030 0101 1147 2350 2380 2380 238 231 000 011 249 2358 2380 030 K 1490 2358 235 011 249 031 001 001 1147 2350 030 030 001 011 1472 2343 7778 030 Ch Q 1499 2358 235 011 240 03 230 030 030 0140 010 1574 2353 030 030 K 1490 2358 235 011 249 031 240 133 230 030 030 001 001 1273 2283 735 010 01 01 124 235 000 035 010 9301 1442 235 010 001 201 124 1497 235 000 035 010 935 010 935 010 930 01400 035 010 9301 1442 001 1373 2283 738 030 K 1490 2358 2358 235 030 030 031 01141 232 235 738 030 K 1490 2358 735 010 235 735 73 738 035 011 041 1498 7264 9314 740 011 141 1487 235 010 124 1498 235 238 238 030 145 Ch Q 1499 235 235 238 238 238 000 030 031 040 010 130 235 238 238 238 000 140 000 135 235 238 238 238 000 124 01 1490 235 235 238 238 238 000 124 01 1490 235 235 238 238 238 000 124 01 1498 236 235 238 238 238 000 124 01 1490 2	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		29.92	0.96	2.26	0.09	6.97	0.49	1.50	0.004	0.672	0.05	99.54	11.54	0.08	0.24	0.02	70.7	143.9	29.98	0.05	A, Q	1.500
303 093 596 004 828 004 839 004 003 005 9915 1113 019 004 400 677 109 034 003 100 197, 302 1438 0051 103 143 005 005 010 0158, 3970 006 2, Ch 1500 236 013 54 013 54 013 54 013 54 013 556 013 147 005 05 06 01110 104 1887 556 001 97, 302 1439 1439 1507 008 001 011 75 1823 556 005 76 0, Ch 1500 253 163 143 006 015 013 951 143 006 015 010 0110 104 1887 556 005 006 2, Ch 1497 255 155 101 143 17 005 05 010 101 153 13 011 21 000 001 003 003 951 1447 001 010 011 011 961 1887 556 005 76 01 1497 255 155 100 110 110 115 1823 556 001 1497 1952 600 1499 1499 255 1173 183 114 000 015 003 930 1447 001 100 010 011 1961 1887 556 001 1499 1499 255 1173 183 011 433 011 433 011 433 011 433 011 433 011 433 011 433 011 433 011 433 011 433 011 433 011 258 004 003 901 1071 1961 1961 1961 1961 1961 1961 1990 250 1199 308 009 428 000 013 001 1447 007 003 4001 1174 1835 540 005 005 01 1990 256 149 1499 256 240 349 011 278 003 4001 1174 1259 2041 1499 256 249 345 011 278 003 301 1971 1961 1961 1961 1961 1990 150 013 010 1971 1961 1991 1991 1991 1991 1991 1991	303 093 506 004 828 004 828 004 001 066 005 99.5 11.54 018 010 067 071 072 1190 29.40 003 - 1948 005 100 156.4 001 197. A Q 1498 005 110 159 011 657 013 010 015 05 005 010 1047 1952 46.0 1190 - 1500 025 1135 13 010 135 74 013 2.49 0006 0177 005 98.51 1456 011 018 001 1047 1952 46.0 05 001 7, 1973 056 0, Ch 1907 255 155 13 574 013 2.49 0006 0130 003 98.7 1458 010 106 1887 5564 005 A Ch 1907 255 155 145 011 513 011 513 017 261 0006 0150 003 98.7 1456 011 018 001 106 1887 5564 005 A Ch 1907 255 155 143 010 55 117 3 10 17 261 0006 0150 003 98.7 1456 011 018 001 1071 1961 987 5564 005 A Ch 1907 255 157 173 114 417 001 114 122 0106 0150 003 98.7 1456 011 018 001 1071 1961 987 5564 005 A Ch 1907 255 155 145 011 513 011 531 011 531 011 531 011 321 0019 004 013 004 907 1447 005 003 901 1477 2502 756 011 1961 1887 5564 005 Ch Q 1499 756 110 93 300 1124 1895 540 03 001 127 1498 005 001 1971 1961 987 903 001 1971 1961 993 000 005 001 1971 1961 993 000 001 1021 1427 2243 7778 005 Ch Q 1499 756 241 242 016 112 313 001 331 0014 003 003 001 401 1474 2300 756 701 Q 1499 725 333 012 257 010 101 123 1000 005 003 903 1011 145 930 703 701 901 127 243 7778 005 Ch Q 1499 725 233 312 368 011 127 247 310 004 005 003 903 1017 1498 007 003 4001 1971 252 300 756 71 Q 1499 725 235 312 300 120 001 127 256 79 715 003 001 - 1497 235 313 012 247 016 011 1373 252 258 920 000 001 - 1497 235 007 2401 1971 252 253 000 140 007 034 003 903 003 001 1001 175 2243 7778 005 Ch Q 1499 725 133 012 247 010 011 1574 253 007 2401 1971 252 253 000 140 007 034 001 1971 252 253 000 140 000 005 000 905 000 905 000 900 005 000 900 005 000 900 005 001 901 175 2243 7778 000 - 1497 2524 1497 254 149 149 149 149 149 149 149 147 123 000 100 101 175 252 757 7911 149 120 120 120 110 120 120 120 110 121 123 001 121 123 000 100 110 121 123 001 1001 1		31.78	0.88	2.30	0.04	8.61	0.04	0.24	0.007	0.050	0.04	99.13	10.20	0.04	0.02	<0.01	56.6	121.0	25.68	0.03	I	1.497
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	2000 110 129 011 639 0.04 662 013 147 0006 0177 005 905 1458 011 000 1684 702 1348 3051 001 Py $\Lambda_{1}Q$ 1498 250 149 350 004 652 013 147 0006 0177 005 905 1437 011 0141 7011 444 7011 447 006 010 0104 71 1952 4603 001 01 1141 2011 1417 001 - 1500 2558 158 013 574 013 574 013 200 0106 017 005 005 000 011 1141 2011 1447 001 - 1500 2558 158 013 901 101 431 011 018 1877 3564 001 - 1500 2558 158 34 011 433 011 321 0006 057 003 9931 4475 011 018 010 106 1175 1823 3564 003 $\Lambda_{1}C$ 1499 2558 165 240 011 231 010 201 258 010 901 1014 121 258 000 0501 000 058 003 991 4475 011 1071 1951 951 903 003 - 1500 2558 158 34 011 231 017 256 000 057 005 053 9931 4475 011 171 155 1823 3564 003 $\Lambda_{1}C$ 1499 2555 165 241 251 213 017 256 004 051 003 9931 4475 011 1259 2041 557 005 01 1249 1499 248 258 312 012 257 008 031 1004 0134 004 933 000 4011 141 127 2243 773 80 001 171 155 172 010 100 101 171 1258 003 001 171 125 2041 557 003 01 1499 1499 238 152 004 001 1071 1951 7232 258 258 220 035 001 172 235 335 011 126 044 331 0009 055 004 901 177 165 001 1973 2582 788 003 κ 1499 238 232 335 011 126 004 331 0009 056 004 930 10017 1498 003 004 011 171 275 250 035 001 1974 219 253 375 012 128 253 335 011 1278 000 055 004 931 0009 056 014 937 000 001 1973 2582 788 001 011 171 258 003 001 001 171 258 003 1001 171 258 003 001 001 171 258 003 001 001 171 258 003 001 001 171 258 003 001 001 171 258 258 227 253 783 001 000 058 001 990 1433 000 001 1973 2562 003 001 001 171 258 2528 780 003 001 001 171 258 2528 780 003 001 001 171 258 2528 780 003 001 001 171 258 2528 780 003 001 001 1149 252 2558 251 000 001 001 100 171 258 003 001 001 171 258 258 258 250 003 001 101 170 001 - 1498 258 258 251 000 008 003 001 001 171 258 258 258 250 003 001 001 171 258 258 258 250 003 001 001 1149 252 258 258 250 003 001 201 001 171 258 258 258 250 003 001 201 001 171 258 252 258 250 003 001 201 001 171 258 252 258 250 003 001 201 001 171 258 252 258 250 003 001 201 201 201 201 201 200 200 200 200		30.33	0.93	2.86	0.04	8.28	0.08	0.34	0.010	0.063	0.05	99.15	11.13	0.19	0.04	<0.01	67.7	119.0	29.40	0.03	I	1.498
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		30.90	1.10	1.59	0.11	6.93	0.40	1.46	0.011	0.601	0.08	98.51	11.54	0.18	0.19	0.74	70.2	134.8	30.51	0.01	Py, A, Q	1.498
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		26.20	1.40	3.60	0.04	6.62	0.13	1.47	0.006	0.177	0.05	99.05	14.68	0.11	0.06	0.05	100.0	168.4	39.70	0.06	Q, Ch	1.500
2305 140 356 0.13 5.74 0.13 2.49 0.006 0.233 0.02 98.03 15.07 0.05 0.06 0.01 1144 201.1 44.47 0.04 - 1.501 232 0.04 1.93 0.34 0.01 5.13 0.17 2.61 0.006 0.05 98.16 14.73 0.10 0.00 2117.5 18.23 5.56 0.04 K, Q 1.499 255 1.65 3.49 0.11 5.13 0.17 2.61 0.006 0.057 0.03 99.10 14.75 0.11 0.08 0.01 17.5 18.23 5.56 0.04 K, Q 1.499 255 1.65 3.49 0.11 5.13 0.17 2.61 0.006 0.057 0.03 99.01 14.75 0.03 0.01 17.1 196.1 5.039 0.03 - 1.500 255 1.65 3.49 0.11 5.13 0.11 2.21 0.04 0.051 0.03 99.01 14.77 0.04 1.699 0.05 - 0.1 1499 0.15 2.52 0.019 0.039 9.207 14.69 0.05 0.03 0.01 17.1 196.1 5.93 0.03 - 0.1 1499 2.56 2.41 2.42 0.16 3.13 0.11 3.21 0.004 0.051 0.03 9.207 14.47 0.07 0.03 0.01 14.27 2.43 77.78 0.05 - 1.499 2.245 2.36 3.16 0.12 3.13 0.013 0.019 0.06 9.35 15.12 0.04 0.03 0.01 14.27 2.243 77.78 0.05 7.4 1499 2.245 2.35 3.10 0.04 2.01 14.27 2.243 77.78 0.03 - 0.1 1497 2.25 2.33 0.13 2.67 0.03 2.01 14.27 2.243 77.78 0.03 - 1.499 2.245 2.35 3.11 0.044 0.03 8.85 13.2 0.04 0.01 126.7 2.243 77.78 0.03 - 0.1 1497 2.25 2.35 2.33 2.33 2.33 2.33 2.31 2.67 9.06 9.30 0.04 0.01 197.1 2.26 0.03 0.01 14.27 2.243 77.78 0.03 - 1.497 2.221 2.25 2.35 0.11 1.66 0.04 0.03 8.85 13.2 0.04 0.01 190.1 25 2.25 2.003 0.03 - 0.01 197.1 2.28 0.03 - 0.01 171.6 2.78 0.01 190.1 2 - 1.497 2.221 2.25 2.35 0.11 1.66 0.04 0.03 8.50 1.90 0.00 0.00 190.1 2 - 1.497 2.221 2.25 2.35 2.31 2.36 0.01 2.20 0.01 9.976 1.433 0.07 0.21 0.01 176 2.78 0.01 2.01 176 2.78 0.01 2.01 2 - 1.497 2.221 2.25 2.35 0.11 0.04 0.02 8.01 0.00 10.1 175 2.24 2.01 9.01 0.01 176 2.72 2.21 2.25 2.24 2.25 2.24 2.25 2.24 2.25 2.24 2.25 2.24 2.25 2.24 2.25 2.24 2.20 0.00 0.05 0.02 9.92 1.04 0.02 0.01 176 2.72 2.24 2.01 2.01 0.01 175 2.21 1.497 2.20 1.21 2.20 2.21 2.25 2.24 2.20 2.20 2.22 2.24 2.24 2.20 2.20	23.05 1.40 3.56 0.13 5.74 0.13 2.49 0.006 0.233 0.02 98.03 15.07 0.05 0.06 0.00 1144 201.1 44.47 0.04 - 1300 23.206 1.90 1.8 0.34 0.01 5.13 0.17 2.61 0.006 0.05 98.16 14.78 0.01 0.010 0.02 117.5 18.23 5.54.5 0.03 - 1500 25.23 1.53 0.03 - 1500 25.23 1.53 0.01 4.43 0.03 - 0.01 107.1 96.1 5.33 5.46 0.03 - 0.01 1.901 25.9 0.03 - 1.1300 25.23 1.53 0.01 4.23 0.03 0.04 2.8 0.04 0.05 0.03 9.92.0 14.47 0.05 0.03 9.001 107.1 96.1 5.32 5.54.5 0.03 0.03 - 1.1300 25.21 1.73 0.01 2.52 0.03 0.03 - 1.1300 25.21 1.73 0.01 2.52 0.03 0.03 0.03 9.92.0 14.47 0.05 0.03 9.001 125.9 2.041 5.57 0.05 0.03 - 1.1499 2.778 0.05 0.03 0.01 125.9 2.41 1.50 0.03 0.01 125.9 0.03 0.01 125.9 0.03 0.01 1427 2.43 7.78 0.05 0.03 0.01 1499 2.243 2.35 0.01 2.253 2.40 3.45 0.004 0.05 0.03 9.92.0 14.47 0.07 0.03 0.01 1427 2.243 7.78 0.05 0.03 0.01 1499 2.243 2.35 0.03 0.01 125.9 0.03 0.01 125.9 2.38 0.03 0.01 1427 2.43 7.78 0.05 0.03 0.01 2.249 2.35 0.01 2.259 2.358 0.01 127.1 2.26 0.03 0.01 9.976 1.499 2.244 2.30 2.35 0.01 2.267 0.03 2.00 9.956 0.04 9.976 0.01 2.01 125.9 2.268 2.201 0.01 - 1.1497 2.243 2.35 0.01 0.01 2.01 0.01 0.01 127.1 2.243 7.78 0.03 0.01 2.1497 2.243 2.35 0.01 0.01 7.01 17.1 2.25 0.03 0.01 9.976 0.01 9.976 0.01 9.976 0.01 9.976 0.01 197.1 2.253 2.34 0.00 0.03 0.01 9.976 0.01 175.9 2.257 9.973 0.01 - 1.1497 2.243 2.36 0.000 0.03 0.00 9.976 0.01 9.01 157.1 2.243 2.30 2.200 0.01 0.01 1.149 2.227 2.243 2.37 0.01 2.21 2.39 2.37 0.00 0.03 0.00 9.976 0.01 9.01 157.1 2.243 2.27 9.973 0.01 - 1.1497 2.243 2.31 0.31 0.31 0.30 0.00 0.00 0.01 0.01 157.1 2.243 2.27 9.973 0.01 - 1.1497 2.243 2.19 0.00 0.05 0.00 9.923 1.15.9 0.00 0.00 0.01 175.9 2.257 9.973 0.01 - 1.1497 2.243 2.11 0.00 0.00 1.140 0.01 175.9 2.257 9.923 0.01 - 1.1497 2.243 2.11 0.00 0.00 1.141 0.23 0.01 175.9 2.277 9.923 0.01 - 1.1497 2.243 2.11 0.00 0.00 1.141 0.23 0.01 157.9 2.244 0.00 0.00 0.01 0.1 1.149 2.241 2.31 0.00 0.01 0.1 1.149 2.31 0.00 0.02 0.00 1.1497 2.243 2.243 0.00 0.00 0.01 0.1 1.149 2.241 2.31 0.00 0.00 0.00 0.01 1.214 2.300 0.00 0.01 0.01 1.149 2.210 0.01 2.210		22.71	1.34	4.47	0.05	6.26	0.02	2.60	0.002	0.100	0.02	98.50	14.37	0.08	0.01	0.01	104.7	195.2	46.03	0.01	I	1.500
3206 190 1.8 045 4.14 0.38 141 0006 0616 005 98.72 14.56 0.11 018 001 1106 188.7 55.64 0.05 $\Lambda_{\rm C}$ Ch 1497 253 163 349 011 513 017 261 0006 0057 003 99.91 4.77 011 008 -0.01 1751 1823 55.00 045 $\Lambda_{\rm C}$ Ch 1499 262 11.7 305 011 513 011 513 011 51 011 253 003 003 01 127 1518 1825 54.02 005 -0.1148 1500 2553 165 349 011 513 011 513 011 511 008 -0.01 1751 1853 54.02 005 -0.1148 1500 2563 11.7 305 011 493 012 252 0019 0043 004 953 013 003 -0.01 127 143 253 1523 7582 003 -0.1148 1499 2568 251 172 210 016 015 313 006 311 0016 015 010 312 004 013 006 311 0016 013 003 -0.01 1477 243 778 005 -0.1149 249 248 236 110 1 228 003 301 01427 243 778 003 -0.1149 245 240 34 011 278 003 311 0004 0058 003 903 010 1427 243 778 003 -1.1498 245 240 34 011 278 006 311 0004 0058 003 903 010 1477 243 7582 003 K 1499 243 333 012 257 004 033 988 1819 006 003 -0.01 157 243 7582 003 K 1499 243 533 312 256 293 333 011 278 003 300 1004 0058 004 9976 1645 007 002 -0.01 1677 243 7582 003 001 -0.11497 2535 014 032 9883 134 010 200 005 014 001 157 2587 010 107 01 -1.1498 2214 235 013 011 278 003 300 1004 058 004 9976 1645 007 002 -0.01 1679 2568 9278 001 -1.1498 2214 236 011 043 003 342 0009 0055 004 9976 1645 007 002 -0.01 175 2587 000 003 -1.1498 2214 236 013 011 010 7 01 175 2587 010 01 -1.1498 2214 239 313 011 043 000 342 0009 0055 004 9976 1645 007 002 -0.01 1616 700 155 2588 010 001 -1.1498 2213 013 011 010 7 01 175 2787 10107 010 -1.1498 2214 239 313 011 043 000 342 0007 024 010 901 -0.01 1407 201 -1.1498 2213 013 011 021 000 124 002 903 010 -0.01 1001 -0.01 1408 168 014 003 003 000 0055 000 9953 004 -0.01 -0.01 1401 175 2787 10107 001 -1.1498 2214 239 035 010 000 120 000 120 010 100 175 9 2568 9278 000 -1.1498 2214 239 333 011 044 000 200 001 -0.01 1401 220 001 201 100 100 101 100 175 9 2568 9278 000 003 000 003 000 100 100 1195 2283 234 000 003 000 003 000 000 000 000 100 100	23.20 1.99 1.58 0.45 4.34 0.38 1.41 0.06 0.615 0.03 9.8.16 4.478 0.11 0.18 0.01 110.6 188.7 55.64 0.05 Λ Ch 1.997 25.8 1.68 2.59 0.11 5.13 0.17 2.61 0.006 0.057 0.03 9.91 4.477 0.10 0.01 107.1 196.1 55.93 0.03 - 1500 25.51 1.77 3.05 0.11 5.13 0.17 2.51 0.004 0.057 0.03 9.991 4.477 0.07 0.03 0.01 107.1 196.1 55.93 0.03 - 1500 25.51 1.77 3.05 0.11 3.13 0.17 2.51 0.004 0.051 0.03 9.991 4.479 0.07 0.03 0.01 112.5 18.27 3.55 0.04 Ch 1.997 25.5 1.19 0.05 2.51 1.77 3.05 0.11 2.31 0.015 2.52 0.019 0.051 0.03 9.920 4.447 0.07 0.03 0.01 14.27 2.43 77.78 0.05 Ch Q 1499 276 2.44 2.43 2.43 2.43 2.43 2.43 2.43 2.43		23.05	1.40	3.56	0.13	5.74	0.13	2.49	0.006	0.233	0.02	98.03	15.07	0.05	0.06	<0.01	114.4	201.1	44.47	0.04	I	1.501
28.58 168 2.50 0.10 4.83 0.21 0.93 0.004 0.105 0.03 99.16 14.78 0.10 0.00 11.75 182.3 53.65 0.04 K.Q 1499 255 1.65 3.49 0.11 5.11 961 30.39 0.01 201 154 1895 54.02 0.03 0.15 1008 0.05 0.01 1154 1895 54.00 0.03 0.11 299 3.08 0.09 4.28 0.06 255 0.04 0.05 10.01 10.01 0.01 1154 1895 54.00 0.03 0.11 249 20.25 0.01 1493 0.15 0.05 0.01 1154 1895 54.00 0.05 0.01 1499 256 1.498 256 1.498 256 1.199 3.08 0.01 2.313 0.01 3.21 0.015 0.192 0.03 9.920 14.47 0.07 0.03 $<0.01 1154$ 1895 54.00 0.05 0.03 0.11 493 0.15 0.192 0.06 9.33 115.1 0.004 0.051 0.03 0.01 1154 1895 54.0 0.05 0.03 0.1 1499 248 2.54 2.41 2.42 2.15 0.06 3.311 0.004 0.058 0.03 0.011 7 148 0.03 0.01 142.7 2243 77.78 0.05 Ch, Q 1499 248 2.54 2.40 2.41 2.72 0.01 3.12 0.004 0.058 0.03 0.011 7 148 0.03 0.01 147.2 254 0.03 K 1498 2.54 0.10 2.313 0.004 0.054 0.03 9.88 18.19 0.06 0.03 $<0.01 1474$ 2515 0.03 K 1498 2.54 0.10 2.57 0.01 9.97 0.01 2.91 2.57 0.01 1497 2.55 0.03 K 1498 2.54 0.10 2.217 2.25 3.35 0.11 0.64 0.03 3.00 0.05 0.01 9.01 7 148 2.56 0.03 0.01 150 2.528 3.51 0.12 2.57 0.01 2.14 2.57 0.01 2.148 2.55 0.03 0.01 2.149 2.53 0.11 0.64 0.03 0.04 0.07 0.02 0.01 0.00 10.601 1773 2.82 7 8.001 0.01 -0 1498 2.238 0.11 0.43 0.04 3.52 0.004 0.05 0.02 9.94 15.8 0.03 0.01 $<0.01 1716$ 2.787 0.01 2.917 0.01 -0 1498 2.217 2.55 0.03 0.01 2.01 17.6 2.587 0.01 2.01 17.6 2.587 0.01 -0.1 1498 2.217 2.55 0.03 0.01 2.01 2.217 2.55 0.50 0.01 2.01 17.6 2.587 0.01 2.01 17.6 2.587 0.01 0.01 17.6 2.587 0.01 -0.1 1498 2.219 0.01 -0.1 1498 2.219 0.00 0.05 0.01 2.001 2.01 2.01 17.6 2.587 0.01 2.01 2.01 17.6 2.587 0.01 2.01 2.01 17.6 2.587 0.01 2.01 2.01 2.01 2.01 2.01 2.01 2.01	28.58 168 2.50 0.10 4.83 0.21 0.93 0.004 0.105 0.03 98.16 4.78 0.10 0.10 0.02 1175 18.23 53.55 0.04 K.Q 1.909 25.251 15 3.91 0.11 431 0.12 251 0.005 0.051 0.03 90.01 154 189.5 54.02 0.03 9 1.509 0.25 251 1.99 3.08 0.09 4.28 0.06 6.051 0.03 90.01 154 189.5 54.02 0.05 9 1.498 255.01 1.99 3.06 0.01 121 3.1 0.11 2.21 0.06 0.351 0.03 9.01 1474 255.01 0.05 0.01 1474 255.0 0.03 7.4 1498 254.1 1498 0.03 0.01 1474 255.0 0.03 K 1.498 254.1 2.54 0.03 3.11 0.004 0.058 0.01 90.01 1474 255.0 0.03 K 1.498 254.1 2.57 0.03 K 1.498 257 0.03 7.4, 0 1.499 254.1 2.58 0.04 0.01 3.21 0.004 0.058 0.01 90.01 1474 255.0 0.03 K 1.498 257 0.03 7.4, 0 1.499 253 3.51 0.01 0.01 2.01 157 3.282 78.0 0.03 K 1.498 257 0.03 2.214 2.39 3.35 0.11 1.60 0.04 3.21 0.009 0.056 0.04 99.76 1.468 0.01 0.01 2.01 177 2543 75.0 0.03 1.491 1474 255.0 0.03 1.491 1474 255.0 0.03 0.01 4.00 1177 195.1 257 0.03 0.01 177 195.1 258 253 3.57 0.12 1.28 0.02 3.00 0.055 0.04 9.06 14.66 0.03 0.01 0.01 1674 251.9 29.73 0.01 -1 1497 255.1 2.243 3.57 0.12 1.28 0.02 3.00 0.055 0.04 9.976 14.56 0.07 0.02 4.01 1674 251.9 9.73 0.01 -1 1497 255.1 209 3.77 0.01 -1 1497 255.1 209 3.77 0.01 0.01 -1 1498 255.8 0.01 0.01 1.61 2.243 3.31 3.00 3.02 0.03 0.01 4.00 14.06 0.03 0.01 4.00 1674 261.9 9.73 0.01 -1 1497 255.1 299 3.77 0.01 0.01 -1 1497 255.1 299 3.77 0.01 0.01 2.14 3.14 123.12 0.02 -1 1497 256.1 299 3.73 0.13 0.01 0.00 3.8 0.00 0.05 0.02 9.04 4.01 0.01 1601 175 2.24 2.97 0.00 -1 1497 256.1 299 3.75 0.00 0.03 0.02 0.00 9.56 0.01 9.00 160.1 175 2.244 0.00 0.01 10.01 1.149 3.00 0.01 -1 1497 256.1 299 3.71 0.00 0.05 0.00 0.05 0.00 9.56 0.01 9.00 0.00 0.00 0.01 0.01 175 2.244 0.00 0.01 10.1 1144 123.12 0.02 -1 1498 10.00 0.01 10.01 1.149 3.01 0.00 1.140 0.00 0.01 1.1493 10.00 0.01 1.1493 10.00 0.00 1.1493 10.00 0.01 1.1493 10.00 0.01 1.1493 10.00 0.00 1.1493 10.00 0.00 1.1493 10.00 0.00 1.1493 10.00 0.00 0.00 0.00 1.1493 10.00 0.00 0.00 0.00 0.00 1.1493 10.00 0.00 0.00 0.00 0.00 0.00 0.00 1.1493 10.00 0.00 0.00 0.00 0.00 0.00 0.00 0.		32.06	1.90	1.58	0.45	4.34	0.38	1.41	0.006	0.616	0.05	98.72	14.56	0.11	0.18	0.01	110.6	188.7	55.64	0.05	A, Ch	1.497
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	2555 165 349 011 513 017 261 0.006 0.057 0.03 99.91 14.75 0.11 0.08 $< 0.01 10.71$ 196.1 50.39 0.03 $- 11500$ 26.21 17.8 0.05 0.15 0.19 0.04 0.05 0.04 90.07 14.69 0.05 $< 0.01 15.9 - 1150$ 26.1 0.01 15.1 196.1 50.39 0.03 $- 11499$ 27.65 2.41 2.42 0.16 3.13 0.11 3.21 0.015 0.192 0.06 9.03 10.1 0.01 $< 0.01 15.9 - 24.3 77.78 0.05 70, 0.1 1499$ 27.65 2.41 2.42 0.11 2.78 0.03 3.11 0.004 0.05 0.01 90.04 0.05 0.01 $< 0.01 14.27 2.43 77.78 0.05 70, 0.1499$ 24.26 2.40 3.45 0.01 14.27 2.43 77.78 0.03 7.4 1499 24.26 2.40 3.45 0.01 12.71 2.48 0.03 0.01 40.03 0.01 14.27 2.43 77.78 0.03 7.4 1499 24.26 2.40 3.45 0.01 12.71 2.48 0.03 0.01 0.004 0.05 0.04 99.76 16.45 0.07 0.02 0.01 150.5 2.82 0.21 0.001 $- 11497$ 25.7 0.12 1.28 0.03 3.01 0.004 0.05 0.04 99.76 16.45 0.07 0.02 0.01 150.5 2.88 0.27 0.00 $- 11497$ 25.67 0.01 2.41 0.82 2.56 0.01 2.41 0.82 2.56 0.03 0.01 -1.1497 2.56 2.51 0.23 2.51 0.00 0.01 2.51 1.55 2.51 0.00 0.01 17.16 2.58 2.77 0.01 $- 11497$ 22.74 2.59 3.51 0.11 0.43 0.00 3.00 0.05 0.02 99.54 15.98 0.01 0.01 17.16 2.58 0.01 $- 11497$ 22.74 2.59 3.57 0.11 0.43 0.00 3.20 0.09 0.55 0.01 9.50 14.50 0.01 0.01 17.16 2.58 0.01 $- 11497$ 22.74 2.59 3.51 0.12 0.29 0.03 0.02 99.54 15.98 0.04 0.01 17.16 2.58 0.01 $- 11497$ 22.74 2.59 3.50 0.01 0.01 17.16 2.58 1.10 0.01 $- 11497$ 22.74 2.59 2.58 0.21 0.90 0.05 0.02 99.54 15.98 0.04 0.01 17.16 2.58 1.10 0.01 $- 11497$ 22.74 2.91 2.57 0.01 $- 11497$ 22.74 2.91 2.01 0.01 17.16 2.58 1.10 0.01 2.51 1.43 0.01 $- 11497$ 22.74 2.59 2.58 0.01 $- 11497$ 22.74 2.59 2.58 0.01 $- 11497$ 22.74 2.50 2.58 0.11 0.17 0.01 $- 11497$ 22.74 2.50 2.50 0.00 4.50 0.01 2.51 1.55 2.50 0.01 2.50 0.01 $- 11497$ 22.74 2.51 2.50 0.01 2.51 1.50 0.01 $- 11497$ 22.74 2.51 2.50 0.01 2.51 1.50 0.01 $- 11497$ 22.74 2.51 2.50 0.01 2.51 1.50 0.01 $- 11497$ 22.74 2.51 2.50 0.01 2.51 1.50 0.01 $- 11497$ 22.74 2.51 2.50 0.01 2.51 2.51 2.51 2.51 0.51 0.51 2.51 2.51 2.51 0.51 2.51 2.51 2.51 0.51 0.51 2.51 2.51 0.51 0.51 2.50 0.51 2.50 0.51 2.50 0.51 2.50 0.51 2.50 0.51 2.50 0.51 2.50 0.51 2.50 0.51 2.50 0.51 2.50		28.58	1.68	2.50	0.10	4.83	0.21	0.93	0.004	0.105	0.03	98.16	14.78	0.10	0.10	0.02	117.5	182.3	53.65	0.04	K, Q	1.499
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		25.55	1.65	3.49	0.11	5.13	0.17	2.61	0.006	0.057	0.03	16.99	14.75	0.11	0.08	<0.01	107.1	196.1	50.39	0.03	I	1.500
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		26.23	1.77	3.05	0.11	4.93	0.12	2.52	0.019	0.043	0.04	99.07	14.69	0.05	0.06	<0.01	115.4	189.5	54.02	0.05	Ø	1.500
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	27.65 2.41 2.42 0.16 3.13 0.11 3.21 0.015 0.192 0.06 99.53 15.12 0.04 0.05 < 0.01 142.7 224.3 77.78 0.05 Ch, Q 1499 2.48 2.48 2.48 0.11 2.78 0.06 3.12 0.004 0.04 0.134 0.04 93.88 18.19 0.06 0.03 < 0.01 147.4 225.0 75.62 0.03 K 1.498 2.35 2.34 0.12 2.67 0.03 3.01 0.004 0.04 0.038 0.03 0.04 < 0.01 157.3 228.2 78.0 0.03 K 1.498 2.36 2.32.9 2.33 0.12 2.67 0.03 3.01 0.004 0.058 0.03 98.85 13.59 0.03 0.04 < 0.01 157.3 2.28.2 78.0 0.03 C.1. 2.498 2.36 0.04 9.76 16.45 0.07 0.02 < 0.01 168.9 2.56.8 9.2.78 0.01 $ 1.497$ 2.36 1.1 1.66 0.04 3.21 0.009 0.056 0.04 99.76 16.45 0.07 0.02 < 0.01 167.4 2.67 0.03 0.03 0.01 2.01 159.5 2.28.0 82.01 0.01 $ 1.497$ 2.261 2.33 3.12 3.68 0.003 0.03 0.02 0.01 0.01 157.9 2.567 9.302 0.03 $ 1.497$ 2.261 2.39 3.37 0.11 0.43 0.00 3.08 0.009 0.05 0.02 99.94 1.53 0.07 0.02 < 0.01 167.4 261.9 93.02 0.01 $ 1.497$ 2.261 2.97 3.73 0.13 0.11 0.43 0.00 3.08 0.002 0.02 9.94 1.53 0.07 0.02 < 0.01 161.4 3.04 84.97 0.01 $ 1.497$ 2.273 0.06 0.20 0.00 0.05 0.03 0.024 0.02 9.94 1.53 0.07 0.01 171.6 278.7 101.07 0.01 $ 1.497$ 2.273 0.06 0.20 0.00 0.08 0.020 0.02 0.01 80.91 171.6 278.7 101.07 0.01 $ 1.497$ 2.273 0.04 2.23 1.19 0.00 0.00 0.08 0.022 0.01 98.83 0.21 $< 0.01 < 0.01$ 171.6 278.7 101.07 0.01 $ 1.497$ 2.273 0.04 2.23 1.19 0.00 0.02 0.02 0.03 0.024 0.01 < 0.01 171.6 278.7 101.07 0.01 $ 1.497$ 2.273 0.04 2.23 1.19 0.00 0.00 0.08 0.022 0.01 98.83 0.74 0.01 < 0.01 161.4 30.4 84.97 0.00 $ 1.497$ 2.261 2.97 2.21 0.44 0.01 < 0.01 161.4 30.4 2.001 < 0.01 161.4 30.4 2.4 123.12 0.02 0.02 1.99 0.02 0.00 0.02 0.02 $< 0.01 < 0.01 <0.01$ 161.4 30.4 84.97 0.00 $ 1.497$ 2.00 2.21 0.4 0.01 < 0.01 161.4 30.4 84.97 0.00 $ 1.497$ 2.00 2.21 0.44 0.01 $< 0.01 <0.01$ 161.4 30.4 84.97 0.00 $ 1.497$ 2.00 2.21 0.44 0.01 $< 0.01 <0.01$ 161.4 30.4 84.97 0.00 $ 1.497$ 2.00 2.21 0.49 0.01 $< 0.01 <0.01$ 161.4 30.4 84.97 0.00 $ 1.497$ 2.00 2.21 0.01 $< 0.01 <0.01$ 161.4 30.4 84.97 0.00 $ 1.497$ 2.00 2.21 0.44 0.01 $< 0.01 <0.01$ 161.4 30.4 84.97 0.00 $$		25.01	1.99	3.08	0.09	4.28	0.06	2.85	0.004	0.051	0.03	99.20	14.47	0.07	0.03	<0.01	125.9	204.1	65.97	0.05	I	1.498
24.84 2.36 3.16 0.12 3.13 0.06 3.12 0.04 0.134 0.04 98.88 18.19 0.06 0.03 0.01 147.4 235.0 75.62 0.03 K 1.499 24.26 2.49 3.34 0.11 2.78 0.08 3.11 0.004 0.058 0.03 100.17 14.98 0.03 0.01 137.3 228.2 78.80 0.03 K 1.498 23.01 2.29 3.57 0.11 2.67 0.06 3.01 0.04 0.056 0.04 99.66 14.06 0.03 0.01 16.9 25.68 92.78 0.01 -1.497 23.03 23.57 0.11 2.66 0.04 3.21 0.009 0.056 0.04 99.66 14.06 0.03 0.01 16.9 25.8 82.01 0.01 -1.497 23.6 2.261 2.95 3.74 0.14 0.82 0.04 0.057 0.01 99.66 14.06 0.03 0.01 16.01 167.4 261.9 93.02 0.03 -1.497 22.61 2.95 3.74 0.14 0.82 0.04 3.32 0.005 0.02 99.90 14.33 0.07 0.02 0.01 175.9 276.7 97.15 0.01 -1.498 22.61 2.95 3.74 0.14 0.82 0.04 3.32 0.006 0.085 0.02 99.90 14.33 0.07 0.02 0.01 175.6 278.7 0.01 70.01 -1.498 22.74 2.93 3.013 0.13 0.10 0.03 0.04 0.057 0.02 99.90 14.33 0.07 0.02 0.01 175.6 2.97 99.73 0.01 -1.498 22.74 2.93 0.13 0.11 0.43 0.00 3.64 0.02 0.02 99.90 14.33 0.07 0.02 0.01 171.6 278.7 0.01.77 0.01 -1.498 22.74 2.97 3.06 3.01 0.00 3.04 0.02 99.78 18.99 0.01 0.01 16.14 3.04 84.97 0.00 -1.496 20.07 0.242 0.03 10.02 2.345 0.08 0.02 0.01 0.01 16.14 3.04 123.12 0.00 -1.498 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.02 0.05 0.01 98.83 0.78 0.01 0.01 171.6 278.7 0.01 70.01 -0.1498 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.02 2.005 0.01 38.3 0.78 0.01 0.01 16.11 4 30.4 84.9 123.12 0.02 -1.498 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.02 2.005 0.01 38.3 0.78 0.01 0.01 0.01 10.01 -1.14 30.4 123.12 0.02 -1.498 16.86 0.03 0.09 0.10 0.01 -0	24.84 2.36 3.16 0.12 3.13 0.06 3.12 0.004 0.134 0.04 98.88 18.19 0.06 0.03 <0.01 1474 2350 75.62 0.03 K 1499 24.26 24.36 0.11 2.78 0.08 3.11 0.004 0.05 0.04 0.05 173 2.282 78.80 0.03 K 1498 23.49 0.03 2.412 2.45 0.01 1.2.67 0.06 3.01 0.004 0.056 0.04 99.76 16.45 0.01 16.73 2.282 78.80 0.01 - 1497 23.09 2.35 0.11 2.67 0.06 3.01 0.004 0.057 0.01 99.56 14.06 0.01 167.4 261.9 93.02 0.03 - 1497 23.00 2.256 2.35 0.01 1.2.8 0.02 3.65 0.04 0.057 0.01 99.56 14.06 0.03 0.01 167.4 261.9 93.02 0.03 - 1497 23.06 3.31 0.04 0.057 0.01 99.56 14.06 0.03 0.01 1759 2767 97.15 0.01 - 1498 22.66 2.36 0.00 3.36 0.00 3.42 0.00 0.053 0.02 99.54 15.98 0.04 0.01 167.4 261.9 93.02 0.03 - 1497 23.06 3.32 0.33 0.01 167.4 261.9 93.02 0.03 - 1498 22.66 2.33 3.12 3.06 0.03 3.01 0.02 3.45 0.004 0.057 0.01 99.54 15.98 0.04 0.01 167.4 261.9 93.02 0.03 - 1498 22.66 2.33 3.12 3.00 0.00 3.42 0.007 0.02 9.91 43.3 0.01 0.001 175.9 2767 97.15 0.01 - 1498 22.74 2.97 2.73 0.01 0.44 0.02 9.73 0.01 10.41 0.43 0.04 4.497 0.01 - 1498 22.74 2.97 2.73 0.02 3.42 0.007 0.02 9.924 15.98 0.04 -0.01 171.6 2787 10.17 0.01 - 1498 22.74 2.97 2.73 0.04 2.53 11.90 0.00 3.42 0.007 0.224 0.03 10.02 11.4 33.44 123.12 0.007 - 1498 22.74 2.97 2.73 0.04 2.53 11.90 0.00 3.42 0.007 0.22 2.345 0.08 0.02 -0.01 -0.01 175.6 2.92.7 9.73 0.01 - 1497 0.00 - 1498 22.74 2.97 2.31 0.04 2.53 11.90 0.00 0.08 0.002 2.008 0.13 0.01 2.01 -0.01 175.6 2.92.7 9.73 0.01 - 1497 0.00 - 1498 22.74 2.97 2.00 0.00 1.54 0.00 2.001 0.01 176.6 2.92.7 9.73 0.00 - 1498 25.74 0.01 2.01 161.4 30.44 2.43 0.44 2.43 0.00 0.00 2.00 0.00 2.000 2.01 2.001 1.04 - 2.01 -0.01 1.001 1.61.4 30.4 123.12 0.00 - 1498 25.6 0.00 2.20 0.00 0.03 1.04 -0.01 -0.01 2.01 2.01 2.01 2.01 2.01 2.01 2.01		27.65	2.41	2.42	0.16	3.13	0.11	3.21	0.015	0.192	0.06	99.53	15.12	0.04	0.05	<0.01	142.7	224.3	77.78	0.05	Ch, Q	1.499
24.26 2.40 3.45 0.11 2.78 0.08 3.11 0.004 0.058 0.03 100.17 14.98 0.03 0.04 < 0.01 137.3 228.2 78.80 0.03 K 1.498 23.9 23.3 0.12 2.67 0.06 3.01 0.004 0.056 0.04 99.76 16.45 0.07 0.02 < 0.01 16.6.8 22.8. 82.01 0.01 - 1.497 2.73 3.5 0.11 1.66 0.04 3.51 0.009 0.055 0.01 99.60 14.40 0.03 0.01 < 0.01 16.6.8 2.56.8 92.78 0.01 - 1.498 2.74 2.87 3.57 0.12 1.28 0.02 3.55 0.004 0.057 0.01 99.60 14.40 0.03 0.01 < 0.01 16.7.4 26.19 93.02 0.03 - 1.497 2.19 3.12 3.00 0.03 3.7 0.12 1.28 0.00 3.88 0.03 0.01 < 0.01 17.5 2.76 7 0.01 9.50 1.498 2.1430 0.07 0.02 < 0.01 17.5 2.76 7 0.01 9.50 1.498 2.26 7 0.01 2.1437 2.19 0.00 3.88 0.004 0.053 0.02 99.54 15.98 0.04 < 0.01 < 0.01 17.6 2.78 7 10.17 0.01 - 1.496 2.29 3.12 0.01 0.03 0.02 0.01 17.5 2.76 7 0.01 2.41 2.97 2.75 0.01 0.01 2.41 2.97 2.75 0.01 0.03 0.02 0.01 17.6 2.92 7 0.01 - 1.496 2.27 3.06 3.73 0.10 0.03 0.02 9.54 15.98 0.04 < 0.01 < 0.01 17.6 2.78 7 10.07 0.01 - 1.496 2.27 3.0 0.03 0.094 0.02 0.01 17.6 2.92 7 0.97 3.01 - 1.496 2.27 3.0 0.3 0.01 0.001 2.42 0.01 0.01 17.6 2.92 7 0.97 3.01 - 1.496 2.27 3.0 0.3 0.01 2.27 3.0 0.0 0.02 0.01 0.01 2.1 17.6 2.92 7 0.97 0.01 - 1.496 2.27 2.73 0.06 0.20 0.000 0.053 0.02 99.78 18.09 0.21 < 0.01 < 0.01 17.6 2.92 7 0.97 0.01 - 1.496 2.27 2.73 0.06 2.20 0.00 0.05 0.01 9.21 < 0.01 < 0.01 17.6 2.92 7 0.97 0.01 - 1.496 2.27 2.03 0.01 0.02 2.01 17.6 2.92 7 0.97 0.00 - 1.497 2.07 2.01 1.01 7 0.01 1.01 1.01 1.01 1.01 1.01	24.26 2.40 3.45 0.11 2.78 0.08 3.11 0.004 0.058 0.03 100.17 14.98 0.03 0.04 < 0.01 137.3 228.2 78.80 0.03 K 1.498 2.37 2.39 3.33 0.12 2.67 0.06 3.01 0.004 0.056 0.04 9.76 16.45 0.07 0.02 < 0.01 16.89 2.568 9.278 0.01 - 1.497 2.39 3.37 0.11 1.66 0.04 3.35 0.004 0.057 0.01 99.76 16.45 0.07 0.02 < 0.01 16.89 2.568 9.278 0.01 - 1.498 2.261 2.95 3.74 0.14 0.82 0.06 3.85 0.004 0.057 0.01 99.06 14.33 0.07 0.02 < 0.01 175 2.51 9.302 0.03 - 1.497 2.261 2.95 3.74 0.14 0.82 0.06 3.88 0.04 0.057 0.01 99.06 1.168 0.256 0.01 - 1.498 2.266 2.33 3.12 3.68 0.11 0.43 0.00 3.08 0.009 0.055 0.02 99.90 14.33 0.07 0.02 0.01 171.6 2.787 101.07 0.01 - 1.496 2.278 3.31 2.368 0.11 0.43 0.00 3.08 0.009 0.053 0.02 99.90 14.33 0.07 0.02 0.01 171.6 2.787 101.07 0.01 - 1.496 2.273 3.06 3.373 0.13 0.31 0.00 3.094 0.02 99.94 15.58 0.04 $< 0.01 < 0.01 171.6 2.787 101.07 0.01 - 1.496 2.273 3.06 3.373 0.13 0.31 0.020 0.003 0.094 0.02 99.94 15.58 0.04 < 0.01 < 0.01 171.6 2.787 101.07 0.01 - 1.496 2.273 3.06 3.373 0.13 0.31 0.020 0.003 0.094 0.02 99.54 15.98 0.04 < 0.01 < 0.01 171.6 2.787 101.07 0.01 - 1.496 2.273 3.06 3.373 0.13 0.031 0.022 0.003 0.094 0.02 99.54 15.54 0.06 < 0.01 < 0.01 171.6 2.787 101.07 0.01 - 1.496 2.273 3.06 3.373 0.13 0.022 2.038 0.33 0.03 0.094 0.02 9.03 0.094 0.02 9.01 < 0.01 < 0.01 171.6 2.787 101.07 0.01 - 1.496 2.277 2.273 0.06 0.23 0.03 0.094 0.02 9.03 0.024 0.02 9.03 0.01 < 0.01 < 0.01 171.6 2.787 10.077 0.02 - 1.496 2.277 2.273 0.00 0.05 0.00 0.05 0.00 2.008 0.02 0.02 9.234 0.06 < 0.01 < < 0.01 < 0.01 < 0.01 171.6 2.787 0.00 0.00 0.05 0.00 0.058 0.00 0.02 0.00 0.02 0.00 0.001 2.114 3.344 123.12 0.00 - 1.496 2.276 0.279 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.$		24.84	2.36	3.16	0.12	3.13	0.06	3.12	0.004	0.134	0.04	98.88	18.19	0.06	0.03	<0.01	147.4	235.0	75.62	0.03	К	1.499
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		24.26	2.40	3.45	0.11	2.78	0.08	3.11	0.004	0.058	0.03	100.17	14.98	0.03	0.04	<0.01	137.3	228.2	78.80	0.03	K	1.498
23.09 2.92 3.58 0.11 1.66 0.04 3.21 0.009 0.056 0.04 99.76 16.45 0.07 0.02 < 0.01 16.89 256.8 92.78 0.01 - 1.498 22.74 2.85 3.57 0.12 1.28 0.02 3.65 0.004 0.057 0.01 99.60 14.06 0.03 0.01 < 0.01 16.74 261.9 93.02 0.03 - 1.497 22.61 2.95 3.74 0.14 0.82 0.00 $= 3.32$ 0.007 0.02 99.90 14.33 0.07 0.02 < 0.01 175.9 276.7 97.15 0.01 $-$ 1.498 22.61 2.95 3.72 0.01 $= -$ 1.498 22.73 3.12 3.68 0.11 0.43 0.00 $= 3.42$ 0.007 0.05 9.954 15.98 0.04 < 0.01 0.01 171.6 278.7 101.07 0.01 $-$ 1.496 2.197 3.06 3.73 0.17 0.00 $= 3.42$ 0.007 0.054 0.02 99.78 18.09 0.21 0.01 171.6 278.7 101.07 0.01 $-$ 1.496 2.273 3.12 3.06 3.73 0.13 0.31 0.00 $= 3.42$ 0.007 0.02 99.78 18.09 0.21 0.01 161.4 30.04 84.97 0.00 $-$ 1.496 2.273 3.79 2.03 1.78 0.00 $= 0.02$ 0.007 0.24 0.02 99.78 18.09 0.21 0.01 161.4 30.04 84.97 0.00 $-$ 1.496 2.007 3.79 0.03 0.04 0.02 0.003 0.094 0.02 2.34.5 0.00 $< 0.01 << 0.01 161.4 30.04 84.97 0.00 - 1.498 1.68 0.13 0.04 0.02 0.005 0.01 98.83 0.78 < 0.01 << 0.01 < 10.17 0.01 - 1.498 1.68 0.13 0.17 0.00 0.08 0.002 0.003 0.094 0.102 < 0.01 << 0.01 < 10.14 < 0.01 < 10.14 = 1.497 0.00 - 1.78 0.007 0.22 0.03 100.22 2.34.5 0.00 < 0.01 << 0.01 < 10.14 < 30.04 2.53 1.190 0.00 0.08 0.002 0.003 0.940 0.12 < 0.01 << 0.01 < 0.01 < 0.01 < 10.14 < 0.01 < 0.01 < 0.01 < 10.14 < 0.02 0.00 - 1.78 0.007 0.22 < 0.03 0.02 0.005 0.005 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 10.14 < 0.02 0.00 - 1.790 0.00 0.08 0.02 0.003 0.004 0.02 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.02 < 0.00 0.03 0.002 <0.02 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01$	23.09 2.92 3.58 0.11 1.66 0.04 3.21 0.009 0.056 0.04 99.76 16.45 0.07 0.02 $< 0.01 16.89 256.8 92.78 0.01 - 1.498$ 22.61 2.95 3.77 0.12 1.28 0.02 3.65 0.004 0.057 0.01 99.60 14.06 0.03 0.01 $< 0.01 1759 2.61.9 93.02 0.03 - 1.497$ 22.61 2.95 3.74 0.14 0.82 0.00 3.88 0.009 0.063 0.02 99.54 15.98 0.04 $< 0.01 171.6 2.787 101.07 0.01 - 1.496$ 21.97 3.06 3.73 0.13 0.30 0.00 4.66 0.003 0.02 99.54 15.98 0.04 $< 0.01 171.6 2.787 101.07 0.01 - 1.497$ 22.74 2.97 3.73 0.13 0.31 0.00 3.42 0.007 0.054 0.02 99.78 15.98 0.04 $< 0.01 - 6.01 176.6 2.787 101.07 0.01 - 1.496$ 22.74 2.97 3.06 0.13 0.01 4.66 0.003 0.094 0.02 99.78 18.09 0.21 $< 0.01 - 6.01 - 6.01 176.6 2.787 101.07 0.01 - 1.497$ 20.07 3.79 5.98 0.13 0.17 0.06 1.78 0.007 0.242 0.03 100.22 23.45 0.08 0.02 $< 0.01 - 6.01 - 6.01 176.6 2.781 123.12 0.02 - 1.497$ 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.002 0.005 $< 0.01 9.883 0.78 - 6.01 - 6.02 - 1.497 - 1.498$		23.74	2.39	3.33	0.12	2.67	0.06	3.01	0.004	0.064	0.03	98.85	13.59	0.05	0.03	<0.01	150.5	228.0	82.01	0.01	Ι	1.497
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	22.74 2.85 3.57 0.12 1.28 0.02 3.65 0.004 0.057 0.01 99.60 14.06 0.03 0.01 <0.01 167.4 261.9 93.02 0.03 - 1.497 22.61 2.95 3.74 0.14 0.82 0.04 3.32 0.006 0.085 0.02 99.90 14.33 0.07 0.02 <0.01 171.6 278.7 101.07 0.01 - 1.496 2.23 3.12 3.06 3.73 0.17 0.02 3.01 0.02 99.54 15.98 0.04 <0.01 <0.01 171.6 278.7 101.07 0.01 - 1.496 2.297 3.75 3.75 0.17 0.03 0.01 <0.01 1.496 2.297 3.75 <0.01 2.21.97 3.06 3.73 0.13 0.31 0.00 3.42 0.007 0.054 0.02 99.54 15.98 0.04 <0.01 <0.01 171.6 278.7 101.07 0.01 - 1.496 2.297 3.79 0.07 0.31 0.00 3.42 0.007 0.024 0.02 99.78 18.09 0.21 <0.01 171.6 278.7 101.07 0.01 - 1.497 2.007 3.79 0.17 0.05 1.78 0.007 0.24 0.02 99.78 18.09 0.21 <0.01 161.4 300.4 84.97 0.00 - 1.498 2.007 3.79 0.01 2.11.9 0.00 0.08 0.002 0.013 10.02 2.345 0.01 <0.01 161.4 300.4 84.97 0.00 - 1.498 1.499 0.05 1.34 0.00 1.58 0.002 2.008 0.12 <0.01 <0.01 <0.01 161.4 30.4 84.97 0.00 - 1.498 1.499 0.05 1.78 0.001 0.21 <0.01 <0.01 <0.01 161.4 30.4 84.97 0.00 - 1.499 0.05 1.78 0.002 2.008 0.13 98.40 1.04 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01		23.09	2.92	3.58	0.11	1.66	0.04	3.21	0.009	0.056	0.04	99.76	16.45	0.07	0.02	<0.01	168.9	256.8	92.78	0.01	Ι	1.498
22.61 2.95 3.74 0.14 0.82 0.04 3.32 0.006 0.085 0.02 99.90 14.33 0.07 0.02 $< 0.01 175, 9 276, 7 97.15 0.01 - 1.498$ 22.83 3.12 3.68 0.11 0.43 0.00 3.08 0.09 0.063 0.02 99.54 15.98 0.04 $< 0.01 < 0.01 171, 6 278, 7 101.07 0.01 - 1.496$ 21.97 3.06 3.73 0.13 0.31 0.00 3.42 0.007 0.054 0.02 99.78 18.09 0.21 $< 0.01 < 0.01 171, 6 292, 7 99.73 0.01 - 1.497$ 22.74 2.97 2.73 0.06 0.20 0.00 4.66 0.003 0.094 0.02 99.78 18.09 0.21 $< 0.01 < 0.01 161.4 30.4 84.97 0.00 - 1.497$ 20.07 3.79 5.98 0.13 0.17 0.05 1.78 0.007 0.242 0.03 100.22 23.45 0.08 0.02 $< 0.01 < 0.01 161.4 30.4 84.97 0.00 - 1.498$ 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.002 0.005 $< 0.01 98.83 0.78 < 0.01 < 0.01 < 0.01 161.4 334.4 123.12 0.02 - 1.498$ 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.002 0.005 $< 0.01 98.83 0.78 < 0.01 < 0.01 < 0.01 - 0.01$ 37.92 0.21 0.49 0.05 1.34 0.00 1.58 0.002 2.008 0.13 98.40 1.04 $< 0.01 < 0.01 < 0.01 - 0.01$ and for Ca-exchanged samples, H ₂ O - water retention at 47% RH, EGME - EGME retention, f _{CaO} - fraction of CaO left in clay after Co-hexamine exchange, albite, A - anatase, Q - quartz, K - kaolinite, Py - pyrite. tes from the Baltic Basin (Bergström <i>et al.</i> , 1995), ² Miocene hydrothermal clays from Fuzzeradvany, Hungary (Viczián, 1997), ³ Silurian bentonite from SE Poland, from Podhale Basin, Poland (Srodoń <i>et al.</i> , 2006a). ⁵ Carboniferous bentonites from the Upper Silesia Coal Basin, Poland (Srodoń <i>et al.</i> , 2006b). ⁶ Miocene bentonite from the Opper Silesia Coal Basin, Poland (Srodoń <i>et al.</i> , 2006b). ⁶ Miocene bentonite from the Dart (Srodoń <i>et al.</i> , 2006b). ⁶ Miocene bentonite from the toper Silesia Coal Basin, Poland (Srodoń <i>et al.</i> , 2006b). ⁶ Miocene bentonite from the form for the Upper Silesia Coal Basin, Poland (Srodoń <i>et al.</i> , 2006b). ⁶ Miocene bentonite from the toper outer to the Upper Silesia Coal Basin, Poland (Srodoń <i>et al.</i> , 2006b). ⁶ Miocene bentonite from the Upper Silesia Coal Basin, Poland (Srodoń <i>et al.</i> , 2006b). ⁶ Miocene bentonites from the Upper Silesia Coal Basin, Pola	22.61 2.95 3.74 0.14 0.82 0.04 3.32 0.06 0.085 0.02 99.90 14.33 0.07 0.02 <0.01 175.9 276.7 97.15 0.01 - 1.498 22.83 3.12 3.68 0.11 0.43 0.00 3.48 0.09 0.63 0.02 99.54 15.98 0.04 <0.01 171.6 278.7 101.07 0.01 - 1.496 21.97 3.06 3.73 0.13 0.31 0.00 3.42 0.007 0.02 99.54 15.98 0.04 <0.01 171.6 278.7 101.07 0.01 - 1.496 22.7 3.06 3.73 0.13 0.17 0.05 3.17 8.09 0.05 4.02 99.73 15.54 0.06 <0.01 171.6 278.7 101.07 0.01 - 1.496 22.7 3.01 3.01 3.01 0.05 3.02 99.73 0.02 9.27 99.73 0.01 - 1.496 22.07 3.79 5.98 0.13 0.17 0.05 1.78 0.007 0.242 0.03 0.094 0.02 99.78 18.09 0.21 <0.01 161.4 30.4 84.97 0.00 - 1.497 14.98 20.7 3.09 0.01 0.01 2.01 2.01 161.4 334.4 123.12 0.02 - 1.498 16.8 0.13 0.04 2.53 11.90 0.00 0.08 0.002 0.01 98.83 0.78 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.02 <0.00 0.00 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.00 0.000 <0.000 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01		22.74	2.85	3.57	0.12	1.28	0.02	3.65	0.004	0.057	0.01	09.60	14.06	0.03	0.01	<0.01	167.4	261.9	93.02	0.03	Ι	1.497
22.83 3.12 3.68 0.11 0.43 0.00 3.08 0.009 0.063 0.02 99.54 15.98 0.04 <0.01 <0.01 171.6 278.7 101.07 0.01 - 11496 21.97 3.06 3.73 0.13 0.31 0.00 3.42 0.007 0.054 0.02 99.73 15.54 0.06 <0.01 <0.01 178.6 292.7 99.73 0.01 - 11497 20.7 3.79 5.98 0.13 0.17 0.05 1.78 0.003 0.094 0.02 99.78 18.09 0.21 <0.01 161.4 30.4 84.97 0.00 - 11497 20.07 - 11498 1.495 20.7 3.79 5.98 0.13 0.17 0.05 1.78 0.007 0.242 0.03 100.22 23.45 0.08 0.02 <0.01 211.4 334.4 123.12 0.02 - 11498 1.498 1.498 1.5.9 0.01 0.01 <0.01 161.4 30.4 84.97 0.00 - 11498 1.498 1.498 1.5.9 0.01 20.01 <0.01 <0.01 \sim 0.01 20.00 20	22.83 3.12 3.68 0.11 0.43 0.00 3.08 0.009 0.063 0.02 99.54 15.98 0.04 $< 0.01 < 0.01 171.6 278.7 101.07 0.01 - 1.496$ 21.97 3.06 3.73 0.13 0.31 0.00 3.42 0.007 0.054 0.02 98.73 15.54 0.06 $< 0.01 < 0.01 178.6 29.27 99.73 0.01 - 1.497$ 22.74 2.97 2.73 0.06 0.20 0.00 4.66 0.003 0.094 0.02 99.78 18.09 0.21 $< 0.01 < 0.01 161.4 30.04 84.97 0.00 - 1.497$ 26.07 3.79 5.98 0.13 0.17 0.05 1.78 0.007 0.242 0.03 100.22 23.45 0.06 $< 0.01 < 0.01 161.4 30.4 84.97 0.00 - 1.498$ 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.002 0.005 $< 0.01 98.83 0.78 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 37.92 0.21 0.49 0.05 1.34 0.00 1.58 0.002 2.008 0.13 98.40 1.04 < 0.01 < 0.01 < 0.01 < 0.01 and the samples, H2O – water retention at 47% RH, EGME – EGME retention, f_{Ca0} – fraction of CaO left in clay after Co-hexamine exchange, the form the Baltic Basin (Bergström et al., 1995), 2 Miocene hydrothermal clays from Fuzzeradvany, Hungary (Viczián, 1997), 3 Silurian bentonite from SE Poland, f_{C1000000000000000000000000000000000000$		22.61	2.95	3.74	0.14	0.82	0.04	3.32	0.006	0.085	0.02	06.66	14.33	0.07	0.02	<0.01	175.9	276.7	97.15	0.01	Ι	1.498
21.97 3.06 3.73 0.13 0.31 0.00 3.42 0.007 0.054 0.02 98.73 15.54 0.06 <0.01 <0.01 178.6 292.7 99.73 0.01 - 11.496 22.77 2.73 0.06 0.20 0.00 4.66 0.003 0.094 0.02 99.78 18.09 0.21 <0.01 161.4 30.04 84.97 0.00 - 11.497 20.07 2.2.73 1.90 0.00 0.08 0.02 0.01 20.22 23.45 0.08 0.02 <0.01 211.4 334.4 123.12 0.02 - 11.498 1.686 0.13 0.04 2.53 11.90 0.00 0.08 0.005 <0.01 98.83 0.78 <0.01 <0.01 <0.01 20.11 <0.01 20.11 <0.02 - 11.498 1.698 0.13 0.17 0.05 1.78 0.002 0.005 <0.01 98.83 0.78 <0.01 <0.01 0.01 20.11 <0.01 20.11 <0.02 - 11.498 1.698 0.13 0.04 2.53 11.90 0.00 0.08 0.002 0.005 <0.01 98.83 0.78 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.001 <0.01 <0.01 <0.01 <0.01 <0.01 <0.001 <0.01 <0.01	21.97 3.06 3.73 0.13 0.31 0.00 3.42 0.007 0.054 0.02 98.73 15.54 0.06 <0.01 <0.01 178.6 292.7 99.73 0.01 $-$ 1.496 22.77 2.73 0.06 0.20 0.00 4.66 0.003 0.094 0.02 99.78 18.09 0.21 <0.01 161.4 30.04 84.97 0.00 $-$ 1.497 20.07 3.79 5.98 0.13 0.17 0.05 1.78 0.007 0.242 0.03 100.22 23.45 0.08 0.02 <0.01 211.4 334.4 123.12 0.02 $-$ 1.498 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.005 <0.01 98.83 0.78 <0.01 <0.01 <0.01 20.1 $+$ 334.4 123.12 0.02 $-$ 1.498 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.02 0.005 <0.01 98.83 0.78 <0.01 <0.01 <0.01 $-$ 0.01 <0.01 $-$ 1.498 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.002 0.005 <0.01 98.83 0.78 <0.01 <0.01 <0.01 $-$ 0.01 <0.01 $-$ 0.01 <0.01 $-$ 0.01 <0.01 $-$ 0.01 <0.01 $-$ 0.01 $-$		22.83	3.12	3.68	0.11	0.43	0.00	3.08	0.009	0.063	0.02	99.54	15.98	0.04	<0.01	<0.01	171.6	278.7	101.07	0.01	I	1.496
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	22.74 2.97 2.73 0.06 0.20 0.00 4.66 0.003 0.094 0.02 99.78 18.09 0.21 <a -="" 0.00="" 0.002="" 0.007="" 0.01="" 0.02="" 0.03="" 0.04="" 0.05="" 0.08="" 0.13="" 0.17="" 0.242="" 0.78="" 1.497="" 1.498="" 1.78="" 100.22="" 11.90="" 123.12="" 16.86="" 161.4="" 2.53="" 20.07="" 211.4="" 23.45="" 3.79="" 30.4="" 334.4="" 5.98="" 84.97="" 98.83="" <="" <0.01="" <a="" a="" black=""> (0.01 20.11 33.4.4 123.12 0.02 - 1.498 14.98 1.408 1.408 14.408 1.4		21.97	3.06	3.73	0.13	0.31	0.00	3.42	0.007	0.054	0.02	98.73	15.54	0.06	<0.01	<0.01	178.6	292.7	99.73	0.01	Ι	1.496
20.07 3.79 5.98 0.13 0.17 0.05 1.78 0.007 0.242 0.03 100.22 23.45 0.08 0.02 <0.01 211.4 334.4 123.12 0.02 - 1.498 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.005 <0.01 98.83 0.78 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		22.74	2.97	2.73	0.06	0.20	0.00	4.66	0.003	0.094	0.02	99.78	18.09	0.21	<0.01	<0.01	161.4	300.4	84.97	0.00	I	1.497
 16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.002 0.005 <0.01 98.83 0.78 <0.01 <0.01 <0.01 37.92 0.21 0.49 0.05 1.34 0.00 1.58 0.002 2.008 0.13 98.40 1.04 <0.01 <0.01 <0.01 <0.01 ion for Ca-exchanged samples, H₂O – water retention at 47% RH, EGME – EGME retention, f_{CaO} – fraction of CaO left in clay after Co-hexamine exchange, - albite, A – anatase, Q – quartz, K – kaolinite, Py – pyrite. tes from the Baltic Basin (Bergström <i>et al.</i>, 1995), ² Miocene hydrothermal clays from Fuzzeradvany, Hungary (Viczián, 1997), ³ Silurian bentonite from SE Poland, from Podhale Basin. Poland (Srodoń <i>et al.</i>, 2066a). ⁵ Carboniferous bentonites from the Upper Silesia Coal Basin. Poland (Srodoń <i>et al.</i>, 2006a). ⁵ Carboniferous bentonites from the Upper Silesia Coal Basin. Poland (Srodoń <i>et al.</i>, 2006a). ⁵ Carboniferous bentonites from the Upper Silesia Coal Basin. Poland (Srodoń <i>et al.</i>, 2006b). ⁶ Miocene bentonite from 	16.86 0.13 0.04 2.53 11.90 0.00 0.08 0.002 0.005 <0.01 98.83 0.78 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01		20.07	3.79	5.98	0.13	0.17	0.05	1.78	0.007	0.242	0.03	100.22	23.45	0.08	0.02	<0.01	211.4	334.4	123.12	0.02	Ι	1.498
37.92 0.21 0.49 0.05 1.34 0.00 1.58 0.002 2.008 0.13 98.40 1.04 <0.01 <0.01 <0.01 <0.01 ≤0.01 ≤0.01 ≤0.01 ≤0.01 ≤0.01 ±0.00 for Ca-exchange samples, H ₂ O – water retention at 47% RH, EGME – EGME retention, f _{CaO} – fraction of CaO left in clay after Co-hexamine exchange, - albite, A – anatase, Q – quartz, K – kaolinite, Py – pyrite. This from the Baltic Basin (Bergström <i>et al.</i> , 1995), ² Miocene hydrothermal clays from Fuzzeradvany, Hungary (Viczián, 1997), ³ Silurian bentonite from SE Poland, from Podhale Basin. Poland (Srodoń <i>et al.</i> , 2006a). ⁵ Carboniferous bentonites from the Upper Silesia Coal Basin. Poland (Srodoń <i>et al.</i> , 2006a). ⁵ Carboniferous bentonites from the Upper Silesia Coal Basin. Poland (Srodoń <i>et al.</i> , 2006a). ⁵ Carboniferous bentonites from the Upper Silesia Coal Basin. Poland (Srodoń <i>et al.</i> , 2006b). ⁶ Miocene bentonite from	37.92 0.21 0.49 0.05 1.34 0.00 1.58 0.002 2.008 0.13 98.40 1.04 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <		16.86	0.13	0.04	2.53	11.90	0.00	0.08	0.002	0.005 <	0.01	98.83	0.78	<0.01	<0.01	<0.01						
on for Ca-exchanged samples, H ₂ O – water retention at 47% RH, EGME – EGME retention, f _{CaO} – fraction of CaO left in clay after Co-hexamine exchange, - albite, A – anatase, Q – quartz, K – kaolinite, Py – pyrite. tes from the Baltic Basin (Bergström <i>et al.</i> , 1995), ² Miocene hydrothermal clays from Fuzzeradvany, Hungary (Viczián, 1997), ³ Silurian bentonite from SE Poland, from Podhale Basin. Poland (Srodoń <i>et al.</i> , 2006a). ⁵ Carboniferous bentonites from the Upper Silesia Coal Basin. Poland (Srodoń <i>et al.</i> , 2006b). ⁶ Miocene bentonite from	on for Ca-exchanged samples, $H_2O - water retention at 47\%$ RH, EGME – EGME retention, $f_{CaO} - fraction of CaO left in clay after Co-hexamine exchange, - albite, A – anatase, Q – quartz, K – kaolinite, Py – pyrite. tes from the Baltic Basin (Bergström et al., 1995), 2 Miocene hydrothermal clays from Fuzzeradvany, Hungary (Viczián, 1997), 3 Silurian bentonite from SE Poland, from Podhae Basin, Poland (Srodoń et al., 2006a), 5 Carboniferous bentonites from the Upper Silesia Coal Basin, Poland (Środoń et al., 2006b), 6 Miocene bentonite from$		37.92	0.21	0.49	0.05	1.34	0.00	1.58	0.002	2.008	0.13	98.40	1.04	<0.01	<0.01	<0.01						
albite, A – anatase, Q – quartz, K – kaolinite, Py – pyrite. es from the Baltic Basin (Bergström <i>et al.</i> , 1995), ² Miocene hydrothermal clays from Fuzzeradvany, Hungary (Viczián, 1997), ³ Silurian bentonite from SE Poland, rom Podhale Basin. Poland (Srodoń <i>et al.</i> , 2006a). ⁵ Carboniferous bentonites from the Upper Silesia Coal Basin. Poland (Srodoń <i>et al.</i> , 2006b). ⁶ Miocene bentonite from	albite, A – anatase, Q – quartz, K – kaolinite, Py – pyrite. es from the Baltic Basin (Bergström <i>et al.</i> , 1995), ² Miocene hydrothermal clays from Fuzzeradvany, Hungary (Viczián, 1997), ³ Silurian bentonite from SE Poland, rom Podhale Basin, Poland (Środoń <i>et al.</i> , 2006a), ⁵ Carboniferous bentonites from the Upper Silesia Coal Basin, Poland (Środoń <i>et al.</i> , 2006b), ⁶ Miocene bentonite from		in for (Ja-exch	anged a	samples	, H ₂ O	- water re	etention	n at 47'	% RH,	EGME	EGN =	ME retenti	on, $f_{\rm Cac}$	- fr	action	of CaO	left in cl	ay after Co-	-hexami	ine exchange,	
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not collapse entirely at 150°C, all samples were reheated at 250°C and recorded again. At this temperature, the Małe Ciche sample collapsed but did not change the peak positions and shapes of the other samples. The latter set of data was used in the calculations.

The angle-corrected peak breadth (full width at half maximum – FWHM, multiplied by the cosine of the Bragg angle in $^{\circ}\theta$ of that particular peak) increased with increasing *l* (Table 2). Drits *et al.* (2005) demonstrated that this is indicative of the interstratification of 9.98 Å K layers (illite layers) and separate 10.33 Å NH₄⁺-layers (tobellite layers), as opposed to the situation where K⁺ and NH₄⁺ are distributed within the interlayers. This means that the NH₄⁺-bearing I-S should, in fact, be considered as three-component illite-tobellite-smectite.

Using equation 2 from Drits *et al.* (2005), the fractions of NH_4^+ interlayers were calculated from the *d* spacings of the 005 reflections. The results confirm the presence of fixed NH_4^+ for four NH_4^+ -rich samples, and for three of these agree well with the evaluation based on chemistry and modeled expandabilities (Table 2). The sensitivity of this technique was insufficient to detect the small amount of fixed NH_4^+ in sample Nor 27.

The S content from chemical analysis was used to calculate pyrite content and subsequent wt.% Fe₂O₃, which was subtracted from the chemical analysis. These corrections were <0.1% except for sample Den 8, which contained 1.05% pyrite, clearly detectable by XRD (Figure 2). The TiO₂ content is quite scattered (Table 1) and was assigned to anatase, consistent with the XRD data (Table 1, Figure 2). The very stable P content (Table 1) was assumed to be from apatite and the analyses were corrected for %CaO corresponding to a

typical sedimentary apatite composition $(0.55 \text{CaO}/0.40 \text{P}_2 \text{O}_5)$.

Four I-S samples contained measurable admixtures of other minerals. Based on the relative intensities of relevant XRD reflections, the composition of sample Nor 27 was corrected for 1% of Fe-Mg chlorite and 1% of quartz; Silesia 25 for 2% of kaolinite and 1% of quartz; Małe Ciche for 1% of chlorite; and CIC 1/20 for 1.5% of Fe-Mg chlorite and 1% of quartz. The chlorite corrections resulted in removal of traces of Mg originally assigned to I-S interlayer cations. Per analogy, 0.5 and 0.3% of Fe-Mg chlorite were removed from the chemical compositions of samples Swe 151 and Fuzz 3, respectively, which also contained traces of interlayer Mg. An Excel(m) spreadsheet was built, which allowed manipulation of chemical data for all samples simultaneously, and the resulting structural formulae were plotted. The relations of fixed cations per $O_{10}(OH)_2$ (FIX = K⁺+Na⁺+NH₄⁺) and exchangeable cations (EXCH = $2*Ca^{2+}$), critical for this work (Figure 3), were used as a test. Such an assumption about FIX and EXCH, following Srodoń and McCarty (2008), is considered a good approximation, since the samples studied were saturated carefully with Ca²⁺ cations. All the corrections introduced changed the experimental regression only at the third decimal place and improved the R^2 of the regression only at the second decimal place. Introducing 25% Fe²⁺ also had a negligible effect. The trends reported below, which are based on the calculated structural formulae, are therefore, very reliable.

The calculated I-S formulae (Table 3) all have sums of octahedral cations between 1.98 and 2.00, except sample Swe 84 (1.96). After the chlorite corrections, no

Table 2. Peak positions (°20), *d* spacings, peak width at half maximum (FWHM) of K-saturated and heated (250°C) samples, and fixed NH_4^+ as percentages of all interlayers calculated from d_{005} using equation 2 from Drits *et al.* (2005), and calculated from NH_4^+ as a percentage of FIX (Table 3) and %S (high-angle fitting – haf) from Table 5.

	Reflection	°20	d (Å)	FWHM (°2θ)	Cos(°θ)× FWHM	NH_4^+ (XRD)	%NH ₄ ⁺ (chem)
	002	17.68	5.0163	0.70	0.69		
Swe 81	003	26.77	3.3301	0.78	0.76		
5	005	45.33	2.0005	0.99	0.91	8	9
	002	17.69	5.0135	0.58	0.57		
Swe 162	003	26.77	3.3301	0.70	0.68		
5	005	45.34	2.0001	0.90	0.83	7	8
	002	17.71	5.0079	0.64	0.63		
Swe 151	003	26.80	3.3264	0.73	0.71		
~	005	45.38	1.9984	0.94	0.87	5	8
	002	17.64	5.0276	0.71	0.70		
Den 8	003	26.71	3.3374	0.78	0.76		
	005	45.24	2.0043	1.00	0.92	13	7
	002	17.79	4.9856	0.58	0.57		
Nor 27	003	26.86	3.3191	0.61	0.59		
	005	45.49	1.9939	0.73	0.67	0	3



Figure 2. XRD patterns of side-loaded, random preparations of $<0.2 \ \mu m$ fractions illustrating the evolution of tridimensional organization of illite-smectites with decreasing percentage of smectite layers (%S_{XRD}), and the level of contamination by other minerals: Ch – chlorite, A – anatase, Q – quartz, P – pyrite.

Mg was found in excess of the dioctahedral occupancy, except for the reference Cheto montmorillonite sample. Compositional trends in the course of illitization were traced by plotting different components vs. FIX (Figure 3). Scattered linear positive trends were observed for Al^{VI} and NH_4^+ and negative trends for Fe



Figure 3. Chemical evolution during illitization: plots of different components of structural formulae of I-S vs. fixed cations (FIX). Data from Table 3.

TSSA _{Nr} value	in Ta	ible 4.	The $f_{\rm s}$	all spec. >1 for	r Cheto	riace are indicate	e that	othe cov	a iract	selecture	ed for	the I-S	series a	calculat are too	ea rrom H small in t	20 and Ed he case of	this high-cl	n. 700111 harge sme	is une per ctite.	cent allierer	Ice Irom
	Tetrał	redral	Octah	edral				-I	ıterlayer												
Sample name	Si	Al ^{IV}	Al ^{VI}	Fe^{3+}	Mg	Sum VI	Са	Na	К	Mg	$\rm NH_4$	Ø	EXCH	FIX	NH4 as % of FIX	TSSA (H ₂ O) (m ² /g)	%diff from TSSA _{Nr} (%)	$f_{\rm S}({\rm H_2O})$	TSSA (EGME) (m ² /g)	%diff from TSSA _N . (%)	fs (EGME)
Nor 27	3.42	0.58	1.63	0.11	0.26	2.00	0.04	0.03	0.70	0.00	0.02	0.84	0.09	0.75	3	189	25	0.25	200	33	0.26
Fuzz 6	3.42	0.58	1.75	0.02	0.23	2.00	0.05	0.00	0.70	0.00	0.01	0.81	0.11	0.71	1	272	45	0.36	281	50	0.37
Swe 151	3.49	0.51	1.68	0.04	0.27	2.00	0.06	0.01	0.58	0.00	0.06	0.78	0.13	0.65	6	305	30	0.40	353	51	0.46
Swe 162	3.47	0.53	1.70	0.06	0.24	2.00	0.06	0.01	0.57	0.00	0.06	0.77	0.13	0.64	10	295	21	0.39	305	25	0.40
Fuzz 5	3.38	0.62	1.83	0.01	0.14	1.98	0.06	0.00	0.68	0.00	0.01	0.82	0.12	0.69	-	286	43	0.37	291	46	0.38
Swe 81	3.47	0.53	1.72	0.07	0.21	2.00	0.06	0.01	0.55	0.00	0.07	0.75	0.12	0.63	11	283	12	0.37	350	39	0.46
Fuzz 9	3.40	0.60	1.78	0.01	0.21	2.00	0.05	0.00	0.68	0.00	0.01	0.81	0.12	0.69		226	11	0.30	294	45	0.38
Fuzz 3	3.46	0.54	1.73	0.01	0.25	2.00	0.06	0.00	0.65	0.00	0.01	0.79	0.12	0.67	2	271	24	0.35	290	32	0.38
Den 8	3.43	0.57	1.77	0.07	0.15	1.99	0.07	0.01	0.55	0.00	0.06	0.75	0.13	0.62	6	281	6	0.37	328	27	0.43
Zukowice 2	3.64	0.36	1.59	0.07	0.33	1.99	0.09	0.00	0.52	0.00	0.02	0.72	0.18	0.54	3	400	24	0.52	410	27	0.54
Est 62	3.76	0.24	1.46	0.12	0.41	1.99	0.09	0.01	0.49	0.00	0.00	0.68	0.17	0.50	-	419	18	0.55	475	34	0.62
Swe 84	3.78	0.22	1.51	0.12	0.33	1.96	0.09	0.02	0.45	0.00	0.02	0.67	0.18	0.49	4	458	24	0.60	489	33	0.64
Małe Ciche 5	3.42	0.58	1.82	0.05	0.13	2.00	0.12	0.05	0.34	0.00	0.05	0.70	0.25	0.45	12	442	11	0.58	459	15	0.60
Silesia 25	3.59	0.41	1.72	0.04	0.23	2.00	0.11	0.01	0.39	0.00	0.03	0.65	0.22	0.43	7	470	13	0.61	444	7	0.58
Ch3	3.69	0.31	1.56	0.12	0.31	2.00	0.10	0.01	0.40	0.00	0.02	0.64	0.21	0.43	5	428	4	0.56	477	16	0.63
Ch4	3.66	0.34	1.60	0.12	0.28	1.99	0.11	0.01	0.38	0.00	0.02	0.64	0.22	0.41	4	462	8	0.61	461	8	0.60
1M4	3.73	0.27	1.57	0.13	0.28	1.98	0.13	0.01	0.33	0.00	0.01	0.60	0.25	0.35	б	504	5	0.66	497	4	0.65
CIC 1/20	3.62	0.38	1.67	0.13	0.20	2.00	0.15	0.02	0.25	0.00	0.02	0.59	0.31	0.28	5	571	7	0.75	546	2	0.72
Mikołów 27	3.74	0.26	1.57	0.14	0.28	1.99	0.15	0.01	0.24	0.00	0.01	0.56	0.30	0.26	б	590	∞	0.77	572	5	0.75
1Cz2	3.79	0.21	1.55	0.14	0.31	1.99	0.15	0.01	0.21	0.00	0.01	0.54	0.30	0.24	5	549	4-	0.72	555	ς	0.73
2M2	3.81	0.19	1.55	0.14	0.30	1.98	0.15	0.01	0.21	0.00	0.01	0.53	0.30	0.23	4	602	4	0.79	555	-4	0.73
2M3	3.86	0.14	1.52	0.14	0.32	1.98	0.18	0.01	0.13	0.00	0.01	0.51	0.36	0.14	4	676	5	0.89	625	-3	0.82
1Cz3	3.87	0.13	1.51	0.16	0.32	1.99	0.18	0.01	0.10	0.00	0.00	0.47	0.36	0.11	б	670	0	0.88	637	-5	0.84
2M6	3.90	0.10	1.52	0.15	0.33	1.99	0.18	0.02	0.06	0.00	0.01	0.45	0.37	0.08	7	704	-	0.92	673	-	0.88
1Cz5	3.90	0.10	1.54	0.14	0.32	2.00	0.20	0.01	0.03	0.00	0.00	0.44	0.39	0.04	0	686	9	0.90	678	L	0.89
1Cz4	3.92	0.08	1.51	0.15	0.33	1.99	0.19	0.01	0.02	0.00	0.00	0.42	0.39	0.04	0	714	- S	0.94	712	ς	0.94
Wyoming	3.91	0.09	1.53	0.21	0.24	1.98	0.19	0.01	0.02	0.00	0.00	0.39	0.37	0.02		646	-13	0.85	731	-2	0.96
Cheto	3.98	0.02	1.41	0.08	0.51	2.00	0.24	0.01	0.01	0.01	0.01	0.53	0.49	0.03		846	14	1.11	814	10	1.07
Mean															4						

and Mg. The ammonium content, when analyzed as a percentage of substitution for K, ranges from a few percent to >10% (4% on average), but does not follow a clear trend. A good positive correlation exists for AI^{IV} ($R^2 = 0.85$). A strong inverse correlation was found between FIX and EXCH:

$$EXCH = -0.43 \times FIX + 0.41 \qquad R^2 > 0.98 \tag{1}$$

If the relationship is assumed to be valid for the entire I-S series, then extrapolation to theoretical pure smectite (FIX = 0) gives a smectitic charge of 0.41 and to pure illite (EXCH = 0) gives an illitic charge of 0.95, which is close to mica. Does equation 1 imply that these charges are stable in the entire illite-smectite series? In order to understand the meaning of equation 1, the relationship between FIX and EXCH was analyzed theoretically.

Theoretical analysis of illite-smectite parameters

FIX vs. EXCH. Both the FIX and EXCH values depend on the charge of illite (Q_i) and smectite (Q_s) interlayers, respectively, and the fractions of these interlayers in the I-S structure. Both FIX and EXCH refer to bulk illitesmectite, and thus can be considered as the respective layer charges equally distributed (not in a physical but rather in a mathematical sense, during calculation of the structural formula) over all silicate layers in the mixedlayer clay. If the fraction of smectite interlayers is defined as f_s , then the fraction of illite is $1-f_s$, and the following relations apply:

 $FIX = Q_i \times (1 - f_s)$

and

$$\text{EXCH} = Q_{\text{s}} \times f_{\text{s}} \tag{3}$$

(2)

FIX and EXCH are parameters of the bulk I-S, and in a mixed-layer crystal of N silicate layers only N-1interlayers exist. Equations 2 and 3 are therefore true only if the external basal surfaces of a crystal are considered as an extra interlayer. This assumption is implicit in all measurements of TSSA, which, since the work of Dyal and Hendricks (1950), is based on the TSSA of smectite, calculated from the unit-cell dimensions and the molecular weight. The nature of the basal surfaces (smectitic or illitic) strongly affects f_s because the value for N of illite-smectite is a small number, commonly the mean of 5 to 12 according to highresolution transmission electron microscopy (e.g. Środoń et al., 1990) and XRD (e.g. Drits et al., 1997c) measurements. However, the smectitic vs. illitic nature of the external basal surfaces of the mixed-layer crystals is irrelevant for the considerations outlined below.

Solving the above set of equations leads to the analytical form of the relation between FIX and EXCH, analogous to the experimental regression (equation 1):

$$EXCH = -Q_s/Q_i \times FIX + Q_s \tag{4}$$

The relationship is linear only if Q_s and Q_i are stable. Compared to the experimental regression (equation 1), $Q_{\rm s} = 0.41$ and $Q_{\rm s}/Q_{\rm i} = 0.43$, thus $Q_{\rm i} = 0.95$. However the slope of this line is the ratio: $-Q_s/Q_i$, instead of a single value, thus the slope can be preserved if the layer charges are variable but their ratio stays constant. Equations 2 and 3 were used to model this alternative, assuming the layer-charge relations from previous studies described in the Introduction, where Q_s increases during the illitization from 0.41 to 0.63 and Q_i from 0.65 to 0.95. The relation between FIX vs. EXCH for variable charges is not perfectly linear, but it is close (Figure 4). Based on the available experimental data (Figure 3), the variable-charge case cannot be excluded. The deviation from linearity is apparent only if one charge is set as stable and the other as variable (Figure 4).

Determining whether Q_i and Q_s layer charges are stable or variable is impossible using the structural formulae data alone. However, equations 2 and 3 can be used if an independent measurement of f_s is available. The modeled relations between f_s and FIX and EXCH are linear for constant Q_i and Q_s , and concave or convex for variable values (Figure 5). The techniques for measuring f_s are discussed below.

Independent measurements of f_s . One way to obtain an independent estimate of f_s is from the TSSA, which is the sum of all smectitic surfaces in an I-S structure. Thus:

$$f_{\rm s} = {\rm TSSA}/{\rm TSSA}_{\rm smectite}$$
 (5)

 $TSSA_{smectite}$, used as a reference in equation 5, should correspond to the same molecular weight as the measured TSSA because TSSA also depends on the molecular weight (equation 5a in Środoń and McCarty, 2008). It is an approximate calculation, ignoring the edge surfaces, but this simplification introduces <4% error (see below).



Figure 4. Relations between fixed (FIX) and exchangeable (EXCH) cations per $O_{10}(OH)_2$, modeled using equations 2 and 3 for stable and variable Q_i and Q_s .



0.10 0.05 0.00 0.20 0.40 0.60 0.80 1.00Figure 5. Modeled relationships of FIX and EXCH (calculated

Figure 5. Modeled relationships of F1X and EXCH (calculated for stable and variable Q_i and Q_s) with fraction of expandable layers (f_s). The models were tested using f_s values calculated from H₂O- and EGME-retention data (see text for details).

Equation 5 implies that the end-member illite ($f_s = 0$) does not have surfaces adsorbing polar molecules responsible for the sample's TSSA. Theoretically, TSSA = 0 either if the external surfaces of a thin illite crystal do not adsorb polar molecules, or the crystal is so thick that the effect of adsorbing surfaces becomes negligible. In nature the latter alternative applies. This conclusion is based on the observation (*e.g.* the data in this paper) of large CEC and TSSA values for R >0 illite-smectites, entirely devoid of smectite monolayers, *i.e.* composed entirely of thin illite fundamental particles (<35%S by XRD: *cf.* figure 12 in Środoń *et al.*, 2000).

Another opportunity is offered by the fundamental particle-thickness measurements. A fundamental particle, the term used here *sensu* Nadeau *et al.* (1984), is the finest non-swelling 'building block' of a mixed-layer I-S crystal, *i.e.* a smectite monolayer or a set of illite layers. A simple geometrical analysis (Środoń *et al.*, 1992) indicates that the mean fundamental particle thickness, expressed as the mean number of layers (N) of the whole population of illite and smectite layers, is:

$$N = 1/f_{\rm s} \tag{6}$$

Such f_s is equivalent to $\% S_{MAX}/100$, defined by Środoń *et al.* (1992). Equation 6 is based on the

conclusion that all basal surfaces of fundamental particles, including the mixed-layer crystal edges, are smectitic, *i.e.* they hold exchangeable cations and water. The reasoning for this conclusion has been given above (large CEC and TSSA values of samples consisting entirely of illite fundamental particles).

N, if measured (*e.g.* by electron microscopy), can be used to obtain f_s for the tests based on equations 2 and 3. Combining equations 6 and 2 leads to:

$$N = Q_i / (Q_i - FIX) \tag{7}$$

Being related to equation 6, this formula also relies on the concept of smectitic surfaces of illite crystals. Equation 7 implies that, when FIX approaches Q_i , Nbecomes infinitely large. This explains why clay-sized illites with FIX approaching the end-member value are not available.

The third opportunity to measure f_s is by modeling the X-ray diffraction effects from mixed-layer crystals, as the percentage of smectite layers is one of the key results sought in such modeling (*e.g.* Moore and Reynolds, 1997; Drits *et al.*, 2004).

The approach presented below is based on the TSSA measurements from H_2O and EGME sorption, supported by the CEC data. Problems inherent in the XRD pattern modeling approach are also discussed.

Experimental verification of the model using the TSSA measurements

The TSSA value was calculated from the adsorbed masses (retentions) of water and EGME, using water and EGME coverages (mg/m^2) established from the retention and theoretical surface areas of reference smectites (Środoń and McCarty, 2008). Based on the retention for the most smectitic samples (1Cz5 and 1Cz4: Table 1), the Wyoming sample coverage was used for EGME (0.41 mg/m^2) and intermediate coverage (0.25 mg/m^2) was used for water. The TSSA values calculated by this approach reveal a good linear correlation (Table 3), though they do not extrapolate to 0 for pure illite. f_s was calculated both from H₂O and EGME data using equation 5 (Table 3). The TSSA value of a smectite sample with the same Fe content as a given I-S sample, needed in equation 5, was calculated using the experimental regression of Środoń and McCarty (2008) from the Fe contents (Table 3).

The relationships of the experimental f_s values with FIX and EXCH are similar (Figure 5). For R0 I-S the model of stable Q_i and Q_s is followed. The data deviate from the model, but in the opposite direction from that predicted by the variable Q_i and Q_s model, and for the most illitic samples they fall again on the stable Q trend lines.

This type of deviation may indicate that the smectitic coverages given above may not apply to R>0 clays, but that greater values should be used. The greatest deviations in Figure 5 appear to correspond to the

largest AI^{IV} value in Figure 3, and suggest therefore that the extensive tetrahedral substitution (the layer charge localized over Al-Si substitution sites instead of a random-charge distribution) corresponds to greater values for H₂O and EGME coverage.

The above conclusion was verified using an independent measurement of CEC. Water and EGME retention and CEC correspond to the same surface, thus their ratio should be stable if the liquid coverage and the smectitic layer charge stay constant. Figure 6 presents the ratios of water or EGME retention and CECcorr (values corrected for Ca left on clay after Co-hexamine treatment: see below for details), plotted against FIX, which is used as the measure of the extent of illitization. Both ratios stay constant up to FIX = 0.4, and then both increase significantly. This increase could be due to a smaller smectitic layer charge, which is unlikely, or greater liquid coverage, which is feasible. In the range of stable ratios, the TSSA and f_s values measured from water and EGME retention are reliable, and they support the stable-charge model (Figure 5).

Stable Q_i and Q_s values are the best explanation for the experimental data shown in Figure 3e and this allows use of equations 2, 3, 5, and 7 to calculate f_s , TSSA, and N from structural formulae data. The results are presented below.

Illite-smectite parameters calculated from structural formulae

The f_s values obtained from EXCH (equation 3) and FIX (equation 2) are very close (Table 4), except for sample Małe Ciche, which is characterized by an elevated EXCH value due to its large Ca content, probably the result of incomplete dialysis, because the elevated value is not consistent with the CEC (Table 1). f_s based on FIX is therefore considered to be most reliable and is used in further calculations.

The mean particle thickness, N, calculated from f_s (equation 6), allows estimation of the fundamental particle radius (r), based on the regression of Środoń *et al.* (2000, figure 7):

$$r\left(\frac{7728 - 18368 \times N_i + 10988 \times N_i^2}{\pi}\right)^{0.5}$$
(8)

where N_i is the mean number of layers in illite fundamental particles. N_i approaches N for N>2 (table 1 of Środoń *et al.*, 2000), so in this range N can be used in equation 8 as a good approximation of N_i . The r calculated for N = 2 was accepted as representative of the more smectitic samples (Table 4), because r does not vary significantly in this compositional range (Środoń *et al.*, 2000).

Knowing N and r permits calculation of the TSSA that accounts for crystal edges (TSSA_{Nr}) from equation 1 of Środoń and McCarty (2008):

$$\mathrm{TSSA}_{Nr} = \frac{2000}{\rho_{\mathrm{IS}}} \times \left(\frac{1}{N^* t_{\mathrm{s}}} + \frac{1}{r}\right) \tag{9}$$

where ρ_{IS} is the density of dry illite-smectite and t_s is the thickness of the silicate layer which varies from 0.96 nm, the value for fully dehydrated smectite (Srodoń and McCarty, 2008), to 0.998 nm, the most common value for illite (Drits *et al.*, 1997a). The mean t_s value $(t_s = 0.96f_s + 0.998(1 - f_s))$ was used, even though the effect of the exact value of t_s on TSSA is negligible. The ρ_{IS} value was calculated from the molecular weight (MW) obtained from the structural formula and the unitcell parameters based on the unit-cell parameter b obtained from d_{06} and the mean t_s (cf. Środoń and McCarty, 2008). The effect of r on TSSA is small, because r is large compared to N; if edges are ignored, *i.e.* r is infinitely large in equation 9, the resulting $TSSA_N$ is only 2–3% smaller (Table 4). The calculation of TSSA by equation 9 is considered most accurate and used as the reference throughout this study.

An alternative calculation of TSSA from f_s is possible via equation 5, if the TSSA of pure smectite of the same molecular weight as the investigated sample is known. Such a value for TSSA can be obtained from an experimental regression relating TSSA_{Nr} to the Fe content of smectite (Srodoń and McCarty, 2008). The resulting TSSA values (Table 4) are identical to the $TSSA_{Nr}$ values for smectitic samples and are up to 4% greater for illitic samples. This systematic discrepancy reflects the approximate character of the calculation via equation 5, which assumes that TSSA corresponds only to basal smectitic surfaces of fundamental particles of I-S and the edge surfaces are ignored. This assumption works well for the smectitic end of the I-S series; but at the illitic end, the contribution of the edge surfaces becomes relatively more important because of fewer basal smectitic surfaces. For this reason the TSSA of I-S is overestimated when calculated using the reference TSSA of smectite. This calculation is useful as it proves that the overestimation of f_s and TSSA for the illitic I-S samples, calculated from EGME and H₂O data (Table 3), is much greater than expected from the approximate character of equation 5. This supports the interpretation presented above.

Illite-smectite parameters calculated from CEC and from water- and EGME-retention

As demonstrated above, water- and EGME-retention are not optimum measurements for calculating TSSA and f_s of I-S, because of the excess retention in R>0 I-S. The CEC is an alternative, because it is directly related to EXCH (Środoń and McCarty, 2008). In order to use CEC measurements for TSSA and f_s calculations, the measured values must be corrected for Ca remaining in the sample after Co-hexamine exchange and for the residual water in the sample after heating at 200°C

				Table 4.	Illite-sme	ectite paramete	ers calcula	ted from s	tructural fo	ormulae.				
Sample name	$f_{\rm s}$ from	$f_{\rm s}$ from	% diff	N from	r	$b \ {\rm from} \ d_{06}$	Δ	MM	Density	$TSSA_{Nr}$	$TSSA_N$	%diff from	TSSA from	%diff from
	FACI	VLI		VII	(uu)	(uu)	(nm ³)	(g/mole)	(g/cm^3)	(m^2/g)	(m^2/g)	(%)	(m ² /g)	(%)
Nor 27	0.21	0.21	4	4.86	238	0.9005	0.4636	783.8	2.808	151	148	-2	157	4
Fuzz 6	0.26	0.25	1	3.93	183	0.8992	0.4613	777.8	2.800	188	184	-2	195	4
Swe 151	0.32	0.31	1	3.19	139	0.9005	0.4616	770.8	2.772	234	229	-2	240	2
Swe 162	0.31	0.33	9-	3.06	132	0.8997	0.4606	770.5	2.778	244	239	-2	250	2
Fuzz 5	0.30	0.27	11	3.70	169	0.8981	0.4600	776.5	2.803	200	195	-2	207	4
Swe 81	0.29	0.34	-14	2.98	127	0.8997	0.4604	769.3	2.775	252	246	-2	257	2
Fuzz 9	0.29	0.28	5	3.63	165	0.8984	0.4602	776.6	2.802	203	199	-2	211	4
Fuzz 3	0.30	0.30	2	3.39	151	0.8987	0.4601	774.7	2.796	219	214	-2	226	ю
Den 8	0.32	0.34	-6	2.90	122	0.8989	0.4595	770.1	2.783	258	252	-2	264	2
Zukowice 2	0.43	0.43	-1	2.33	88	0.8999	0.4590	769.1	2.782	323	315	-3	329	2
Est 62	0.42	0.47	-10	2.12	76	0.8999	0.4583	770.2	2.791	354	345	-3	360	1
Swe 84	0.44	0.49	6	2.05	72	0.9008	0.4588	766.0	2.772	369	359	-3	372	1
Małe Ciche 5	0.62	0.53	17	1.90	63	0.8981	0.4555	760.2	2.771	399	388	-3	402	1
Silesia 25	0.54	0.55	-1	1.83	63	0.8992	0.4562	760.1	2.767	416	404	-3	418	1
Ch3	0.51	0.55	L	1.83	63	0.8999	0.4570	764.5	2.778	413	402	-3	416	1
Ch4	0.55	0.56	- 0	1.77	63	0.8997	0.4564	763.9	2.780	427	416	- 1	431	1
1M4	0.62	0.63	-2	1.58	63	0.8989	0.4544	761.3	2.782	478	466	-2	481	1
CIC 1/20	0.75	0.70	9	1.42	63	0.8992	0.4533	758.3	2.778	534	522	-2	537	1
Mikołów 27	0.73	0.72	1	1.39	63	0.8992	0.4531	757.8	2.777	547	535	-2	549	0
1Cz2	0.73	0.75	- 0	1.33	63	0.8989	0.4523	755.1	2.773	571	560	-2	573	0
2M2	0.74	0.76	- v	1.32	63	0.8984	0.4516	754.4	2.774	577	566	-2	579	0
2M3	0.89	0.85	S	1.18	63	0.8989	0.4506	750.9	2.768	646	635	-2	646	0
1Cz3	0.88	0.88	0	1.14	63	0.8981	0.4492	750.1	2.773	670	658	-2	670	0
2M6	0.90	0.91	-1	1.10	63	0.8987	0.4492	747.0	2.762	697	686	-2	694	0
1Cz5	0.95	0.95	0	1.05	63	0.8978	0.4476	745.1	2.764	728	717	-2	726	0
1Cz4	0.94	0.96	-2	1.04	63	0.8978	0.4475	745.2	2.765	733	722	-2	730	0
Wyoming	0.91	0.98	L	1.02	63	0.8981	0.4475	746.4	2.770	746	734	-2	741	-1
Cheto	1.21	0.96	25	1.04	63	0.8987	0.4483	743.4	2.754	740	729	-2	737	0
$f_{\rm s}$ – fraction of s	mectitic laye	$\frac{1}{100} N - m$	ean numbe	r of layers	in fundan	nental particle	s, r mean	particle rac	fius, $V - \eta$	unit-cell vo	lume, TSS	A _{Nr} and TSS ₁	$A_N - ext{total spec}$	cific surface
area rrom equatic	an os) c un	KI TOT DELAL	IS).											

(Srodoń and McCarty, 2008). The assumption that the trivalent Co-hexamine cation substitutes all exchangeable cations is a good approximation for routine work, but for this more sensitive study, the residual Ca must be considered. The first correction was made by multiplying the measured CEC by $1+f_{CaO}$, where f_{CaO} is the ratio between the residual CaO and the total CaO measured on the Ca-sample; both CaO values corrected for the CaO assigned to apatite (Table 1). This ratio varies between 1 and 6%, but in general increases from 2 to 4% with advancing illitization. This trend suggests that bonding forces for divalent Ca are stronger than for trivalent Co-hexamine cations in some sites, perhaps as a result of local charge concentration (see below). The CEC values corrected in this manner (CECcorr in Table 5) were used in Figure 6.

The excess water correction for CEC is based on the 6 wt.% of molecular water remaining in pure Casmectites after heating at 200°C (tables 3 and 4 in Środoń and McCarty, 2008). In more illitic samples, this water is assumed to decrease in proportion to the decreasing smectite content. The CEC is assumed to vary between 0 and 100 meq/100 g and is used in the correction calculation as a measure of smectite content. Thus the second correction (CEC_{corr2} in Table 5) is made by multiplying the CEC_{corr} by (1 + CEC × 0.06/100).

The CEC measured with Co-hexamine and corrected as shown above was compared with CEC calculated from EXCH using equation 10 of Środoń and McCarty (2008). A linear correlation with $R^2 = 0.99$ and a slight systematic deviation was observed.

Values for TSSA, f_s , and N (via equation 6) can be calculated from CEC_{corr2} when Q_s is known. TSSA was calculated (Table 5) using equation 11 of Środoń and McCarty (2008) and f_s by combining equation 3 of the present study with the equation 10 of Środoń and McCarty (2008). For R0 I-S, the results of CEC-based calculations are of similar accuracy to H₂O- and EGMEbased calculations (Table 3 and 4), but for R>0 I-S the CEC calculations are more accurate. No systematic difference appears between the f_s values calculated from CEC and from EXCH or FIX (Tables 4, 5).



Figure 6. Evolution of the ratios of H_2O and EGME retention (mg/g) to CEC (meq/100 g) in the course of illitization, expressed by the amount of fixed cations (FIX).

The CEC-based calculations of TSSA and f_s , performed above using theoretical formulae, can also be achieved by direct experimental regressions established from the accumulated data (Figure 7). First, CEC_{corr2} is calculated from CEC_{meas} (Figure 7a) and is plotted *vs.* TSSA_{Nr} and f_s from FIX (Figure 7b,c). The results of employing the regressions from Figure 7 are presented in Table 5. The mean relative measurement error is ±4%. Table 5 also shows analogous calculations of TSSA, based on the experimental regression of TSSA_{Nr} (from Table 4) *vs.* water and EGME retention (from Table 1). These regressions are polynomial (Figure 7d,e), and, as expected, the errors of such calculations are greater than if using CEC, especially for R >0 I-S.

XRD determination of % smectite layers and of tridimensional organization

The percentage of smectite layers in I-S ($\% S_{\text{XRD}}$) was evaluated by XRD from oriented, glycolated preparations using the peak-position techniques of Środoń (1980; the peaks in the $42-48^{\circ}2\theta$ region) and of Dudek and Srodoń (1996; the peaks in 15-27°20 region), based on the NEWMOD modeling program (Reynolds, 1985), and by whole-pattern modeling using the SYBILLA program (Chevron proprietary software), which is a more user-friendly version of the original program by Drits and Sakharov (1976). Both programs allow for detailed modeling of mixed-layered minerals in terms of the nature and the proportions of the layer types and their structural and probability parameters (more details and examples in Drits et al., 1997b; Moore and Reynolds, 1997; Sakharov et al., 1999; Drits et al., 2004; Aplin et al., 2006; McCarty et al., 2008).

In the past, SYBILLA and the program by Drits and Sakharov (1976) have mainly been used to qualitatively and quantitatively model multiphase clay assemblages. For this purpose obtaining a close fit between the calculated and the experimental intensities over the entire recorded angular range is necessary. In the current study, however, the purpose was to evaluate the $\% S_{\rm XRD}$ and T (the mean number of 2:1 layers in the mixed-layer crystals) in the predominantly mono-phase I-S samples, which required a different approach and to allow for some simplifications. The 'whole-pattern fitting' (wpf) approach was applied originally, but the result was that the higher-angle reflections and the lower-angle reflections could not be reconciled into one overall satisfactory model but at best into a 'compromise' fit (Figure 8a). Such a fit required an unrealistically large T value (see below) to reasonably match the peak positions of the lower-angle reflections as they were displaced towards smaller angles with decreasing T values, because positions of broader peaks are affected more by the steep LpG^2 at smaller angles (cf. Drits et al., 1998). The compromise fit could not model precisely the shape of the $26-27^{\circ}2\theta$ reflection, which is the illite-

able 5. CEC rd from regr	values correct ession equatic	ted for Ca lef ons relating 7	ft in the clay TSSA _N , with	after Co-hexa CEC _{corr2} , H ₂	unine treatm	nent (CEC _{corr} and EGME	r) and for H ₂ retention.	O present in	the clay at	200°C (CEC.	_{orr2}). Calcula	tion of TSSA	, and $f_{\rm s}$ directly	r from CEC
ample name	CEC _{corr}	CEC _{corr2}	TSSA from CEC	%diff from f	from CEC	%diff from f from EIV	TSSA	%diff from Tec A	$f_{\rm s}$	%diff from	TSSA (H O 5000)	%diff from TSSA	TSSA	%diff from
	(meq/100 g)	(meq/100 g)	(m ² /g)	-///WWC1 (%)		7s num 11x (%)	(m^2/g)			7s num rix (%)	(m^2/g)	1900 (%)	(m ² /g)	-//V-/
or 27	17.07	17.25	119	-21	0.16	-20	153	1	0.21	1	148	-2	126	-16
azz 6	26.92	27.35	188	0	0.26	2	219	17	0.29	16	221	18	199	9
we 151	28.14	28.61	197	-16	0.27	-14	227	- 1	0.30	 -	251	7	273	16
we 162	36.17	36.79	253	б	0.35	9	233	-5	0.31	-5	242	-1	223	6

Sample name	CECcorr	CEC _{corr2}	TSSA from CEC	%diff from TSSA _N :	fs from CEC	%diff from fs from FIX	TSSA (CEC regr)	%diff from TSSA _M .	fs (CEC regr)	%diff from f _s from FIX	TSSA (H,O regr)	%diff from TSSA _{Nr}	TSSA (EGME regr)	%diff from TSSA _N :
	(meq/100 g)	(meq/100 g)	(m ² /g)	(%)		(%)	(m ² /g)	(%)) ,	(%)	(m ² /g)	(%)	(m ² /g)	(%)
Nor 27	17.07	17.25	119	-21	0.16	-20	153	1	0.21	1	148	-2	126	-16
Fuzz 6	26.92	27.35	188	0	0.26	2	219	17	0.29	16	221	18	199	9
Swe 151	28.14	28.61	197	-16	0.27	-14	227	-3	0.30	-3	251	7	273	16
Swe 162	36.17	36.79	253	ю	0.35	9	233	-5	0.31	-5	242	-1	223	-9
Fuzz 5	29.45	29.95	205	ŝ	0.28	5	233	16	0.31	15	234	17	209	4
Swe 81	31.38	31.94	219	-13	0.30	-11	242	-4	0.32	-4	230	-8	270	7
Fuzz 9	26.46	26.87	184	-10	0.25	-8	213	5	0.29	4	180	-12	212	4
Fuzz 3	29.40	29.92	205	9-	0.28	-4	238	6	0.32	8	219	0	207	-5
Den 8	32.06	32.64	224	-13	0.31	-11	246	-5	0.3	-5	229	-11	246	-4
Zukowice 2	40.05	41.00	282	-13	0.38	-11	308	-5	0.41	-5	346	7	338	5
Est 62	48.92	50.28	345	-3	0.47	0	351		0.4	-2	366	б	419	18
Swe 84	46.50	47.74	329	-11	0.45	6-	340	-8	0.45	-8	409	11	437	18
Małe Ciche 5	58.42	60.37	413	С	0.56	7	416	4	0.55	4	392	-2	398	0
Silesia 25	55.91	57.71	396	-5	0.53	-2	402	-3	0.53	-3	423	2	379	-6
Ch3	52.23	53.81	370	-11	0.50	-8	380	-8	0.5	-8	377	6	422	2
Ch4	55.45	57.24	393	-8	0.53	-6	405	-5	0.5	9-	413	-3	401	9-
IM4	68.98	71.71	491	3	0.67	5	485	2	0.64	1	461	-3	447	9-
CIC 1/20	80.38	84.13	577	8	0.78	10	565	9	0.74	5	542	1	515	4-
Mikołów 27	79.40	83.00	569	4	0.77	9	551	1	0.72	0	565	б	552	-
1Cz2	81.43	85.28	584	2	0.79	4	572	0	0.75	0	515	-10	528	-8
2M2	83.02	87.11	596	ŝ	0.80	5	594	б	0.78	2	581	1	527	6-
2M3	93.91	99.14	679	5	0.91	7	667	б	0.87	ю	677	5	632	-2
1Cz3	96.17	101.54	695	4	0.93	9	668	0	0.87		699	0	651	
2M6	98.56	104.31	714	2	0.95	4	696	0	0.91	0	715	ю	40 <i>L</i>	2
1Cz5	102.47	108.68	743	2	0.99	4	723		0.9		691	-5	717	-2
1Cz4	101.13	107.18	733	0	0.97	2	714	-3	0.9	-3	730	0	774	9
Mean				7		7		4		4		9		7



Figure 7. Experimental regressions, based on data from Tables 1, 3, and 4, used to correct measured CEC (a); to calculate $TSSA_{Nr}$ (b) and f_s (c) from such corrected CEC; and to calculate $TSSA_{Nr}$ from water (d) and EGME retention (e).

smectite peak most strongly controlled by *T* (Drits *et al.*, 1997c).

To overcome this problem the shape of the illitesmectite reflection at $26-27^{\circ}2\theta$ was chosen to model T accurately. The precise evaluation of $\%S_{\text{XRD}}$ was based on a close fit of peak positions and shapes for all reflections $>26^{\circ}2\theta$, allowing for a worse fit at smaller angles (Figure 8b). In this approach the most important parameters to be modeled precisely were: $\% S_{\text{XRD}}$, T, the junction probabilities of R>0 I-S, smectite d spacing (d_s) and its fluctuation (δd_s), and illite d spacing (d_i) and its fluctuation (δd_i). The last two variables were found to change from the default values 9.98 and 0 only in the case of highly illitic, ammonium-rich samples. Illite layer Fe and K contents and smectite layer Fe, Ca, water, and glycol contents were unchanged from their approximated values in the 'compromise' fit, as they only influence absolute intensities and not peak positions or peak shapes and thus are unimportant in determining $\%S_{\rm XRD}$. For this reason the K content was actually left unchanged from its default value of 0.85 atoms of K per half unit cell. The approximated Fe contents were found to be very close to the Fe contents evident from the structural formulae calculations (on average within 0.08 atoms of Fe per half unit cell). The actual Fe- and K-content values from the structural formulae were used as fixed parameters for a few samples but no measurable differences in output values for $\%S_{\rm XRD}$ and T were observed.

Most attention was paid to obtaining a good fit for the glycolated state as the expandable layers were found to exhibit an heterogeneous swelling in the air-dry state. The presence of the tobellite layers was ignored and instead a larger illite d spacing was used as compensation when necessary, because the *SYBILLA* program does not support illite-tobellite-smectite mixed-layered struc-



Figure 8. Examples of *SYBILLA* models and experimental XRD patterns of glycolated, Ca^{2+} -saturated I-S. Comparison of two models for sample CIC 1/20 (chlorite peaks not modeled): (a) 'compromise fit' based on the entire angular range; (b) 'high-angle fit' employing peaks >26°2 θ c) examples of 'high-angle fits' for samples with different layer compositions. The *d* values for the peaks are shown in Å. Key parameters used in the models are listed in the figures: R (Reichweite), d_s and d_i (smectite and illite layer thicknesses, respectively), δd_s and δd_i (fluctuation of smectite and illite layer thicknesses), and *T* (mean thickness of the mixed-layer crystals). In (a) and (b) the scale of the patterns is increased ×4 at 8.25°2 θ for clearer presentation.

tures for R > 1 (and samples with R > 1 are those with the most NH₄⁺ content). Given the relatively small contribution of tobellite layers (4% of FIX on average), the impact of this simplification on the $\%S_{\rm XRD}$ determined is negligible. Furthermore, it was decided to use only two laver types (illite and smectite) to model the patterns, as initial trials showed that the use of a third layer type (vermiculite) had a very limited impact on improving the fits (very small percentages of this component) and only complicated the modeling process, especially for R>0 structures. The modeled total percentage of expandable layers did not change substantially. The results from Inoue et al. (2005), obtained for hydrothermally altered volcanics, and from Lindgreen et al. (2000) for shales, also show that in glycolated Ca²⁺ samples, such vermiculitic layers, if present, occur only in small quantities (0-5%). Finally, satisfactory fit could also be obtained using just one I-S phase.

Table 6 lists the results of the *NEWMOD*- and *SYBILLA*-based analyses. Figure 8 compares, for sample CIC 1/20, the compromise fit (a) to the fit based on the larger-angle reflections (b). For all samples, two such fits were modeled and compared. The differences in $\%S_{\rm XRD}$ were generally found to be 2% absolute or less, indicating that this number is very robust (Table 6). The differences in all other parameters used were also small, except for a substantial difference in *T* (Table 6). *SYBILLA* fits obtained by the large-angle fitting approach are shown (Figure 8c) for a very smectitic sample (1Cz5) and a very illitic sample (Swe 151).

The tridimensional structure of the investigated set of samples evolves with illitization (Figure 2). Down to $50\% S_{\rm XRD}$, the XRD characteristics are essentially turbostratic. At ~ $30\% S_{\rm XRD}$, the beginning of 1*M* organization, both in *tv* (Ch3) and *cv* (Ch4) versions, becomes visible. At ~ $15\% S_{\rm XRD}$, 1*Mtv* (Fuzz 9), 1*Mcv* (Swe 162), and 1*Md* (Den 8) polytypic varieties were observed. The evolution in the $36-38^{\circ}2\theta$ range indicates that $n \times 120^{\circ}$ rotations are dominant (*cf.* Moore and Reynolds, 1997).

fs compared to %S_{XRD}

Plots of f_s (from Table 4) vs. $\% S_{\rm XRD}$ data sets from Table 6 (Figure 9) are very similar: in most cases XRD underestimates the smectite layer content calculated from chemistry (f_s), with the largest differences at intermediate and small values for f_s . The underestimation is greatest for measurements based on the peaks in the 15–27°20 region, intermediate for the peaks in 42–48°20 region, and smallest for the *SYBILLA* models.

The general shape of the plot in Figure 9 can be attributed to the effect of the small thickness of illite-smectite crystals: computer models do not account for the external surfaces of illite-smectite crystals. Assuming that these surfaces are smectitic, it follows that the XRD measurements underestimate the smectite content (Środoń *et al.*, 1992), and that this under-

estimation should be greatest for the most illitic compositions (*cf.* Środoń, 1999). On the other hand, if the mixed-layer crystal edges were illitic (at least those edges which have the neighboring illitic interlayer), then for illite no difference would be observed between the XRD estimate and f_s , and for more smectitic compositions the XRD numbers would be close to f_s . This reasoning does not rely on the fundamental particle concept but just on the properties of the mixed-layer crystals (Figure 10). It follows that the data presented in Figure 9 can be considered as proof of the smectitic nature of mixed-layer crystal edges.

In order to verify the conclusion above quantitatively, the experimental relationship between the mean number of layers in the fundamental particles (N) and in the mixed-layer crystals (T) was established using wholly independent data: N measured by TEM (Środoń *et al.*, 2000) and T measured by the modified Scherrer equation (Drits *et al.*, 1997c) and by the Bertaut-Warren-Averbach technique (Drits *et al.*, 1998):

$$T = 0.763 \times N + 4.113 \quad \mathbf{R}^2 = 0.89 \tag{10}$$

Then *N* values from Table 4 were used to calculate *T* (referred to as '*T* from equation 10' in Table 7), and from these two values the theoretical value of $\%S_{\text{XRD}}$ ($\%S_{\text{XRD}}$ theor) was calculated applying the smectitic crystal-edge assumption (equation 9 of Środoń *et al.*, 1992) and plotted in Figure 9 vs. f_s from Table 4. The plot demonstrates that most of the underestimation has been explained. In the intermediate range of f_s , the $\%S_{\text{XRD}}$ is even smaller than expected from the model. This discrepancy deserves further study. Equation 10 gave *T* values quite close to the values modeled in *SYBILLA* by the large-angle fitting approach (compare *T* from equation 10 in Table 7 with *T* (haf) in Table 6).

Equation 9 of Środoń *et al.* (1992) was also applied differently to calculate T using N from Table 4 and $\%S_{\text{XRD}}$ from Table 6. Considering how sensitive this calculation is to small errors in $\%S_{\text{XRD}}$ (especially for



Figure 9. Fraction of smectitic layers (f_s) calculated from FIX vs. percent expandable layers measured by two XRD peak-position techniques and by *SYBILLA* modeling (from Table 6). This relationship is modeled using theoretical $\% S_{\rm XRD}$ values calculated by rearranged equation 10 of Środoń *et al.* (1992) from the thickness of the fundamental particles (*N* in Table 4) and of the mixed-layer crystals (*T* in Table 6).

Table 6. XRL peak-position fitting (haf)). Reichweite (F	data fro method Column: (), glycc	of Dud of Dud s 16 and al smecti	ted prep ek and 5 17 com te layer	arations Srodoń (pare mea thicknes	(columr 1996, cc in numb is (d _s) a	ls $1-11$) blumn 12 er of lay nd its m	. Mixed-J 2), Δ2 m ers in mix ean fluct	layer pea ethod of xed-layer uation (i	tks are id Šrodoń r crystals Šds), illite	entified by (1980, colu (<i>T</i>) used ir ? layer thic	number an mun 13), an t wpf and t kness (d_i)	d type c nd <i>SYBI</i> naf mode and its	of treatmo LLA moo cling. Co mean flu	ent (air- deling (lumns 1 letuation	dry νs. et column 1 8–22 prc ι (δd _i).	hylene g 4: whole wide par	ycol). Ex pattern ameters u	rpandibili fitting; c sed in SJ	ty calcul olumn 1: BILLA P	ations by 5: high-a laf mode	y the ingle ling:
Sample	2 AIR	1 GLY	2 GLY	3 GLY	4 GLY	5 GLY	6 GLY	7 GLY	8 GLY	A2=8GLY- 7GLY	%5 (4/5)	%S (Δ2)	%S%	%S (haf)	T (wpf)	T (haf)	Я	ds	δd_s	\mathbf{d}_i	$\delta \mathbf{d}_i$
Column no.	1 (°20)	2 (°20)	3 (°20)	4 (°20)	6 (°20)	7 (°20)	8 (°20)	9 (020)	10 (°20)	11=10-9 (°2 ⁰)	12	13	14	15	16	17	18	19 (Å)	20 (Å)	21 (Å)	22 (Å)
Nor 27	8.55		8.28	8.92	17.58	26.76	35.22	45.26			7		8	8	11.12	10.57	R3	16.77	0.29	9.98	0.10
Swe 151	8.20		7.75	9.20	17.30	26.75	34.65	44.95	46.15	1.20	13	14	16	16	10.28	8.83	R3	16.76	0.33	9.69	0.10
Swe 162	8.10		7.75	9.25	17.25	26.70	34.65	44.80	46.25	1.45	13	16	16	16	9.99	8.54	R3	16.80	0.30	10.00	
Swe 81	8.10		7.65	9.15	17.20	26.65	34.55	44.70	46.15	1.45	14	16	17	16	9.70	8.54	R3	16.82	0.28	10.01	0.10
Fuzz 9	8.10		7.80	9.25	17.20	26.65	34.70	44.75	46.20	1.45	14	16	19	19	10.28	10.28	R3	16.79	0.32	10.00	
Den 8 Z I · · ·	8.15		7.46	9.16	17.08	26.62	34.42	44.62	46.00	1.38	16	15	17	18	9.23	8.25	R3	16.79	0.29	10.03	0.10
Lukowice 2 Fet 67	7.45	2.6U	66.0 68.9	00.6 9.45	1/.00	26.75 26.75	34.00 33 80	44.60 44.50	46.90	2.40 2.40	57 86	87 7	34 34	34 24	9.41 0.41	10.0	7 22 2 22	16.70 16.74	0.34 0.34	9.98 9.98	
Swe 84	7.50	2.65	6.75	9.50	16.85	26.75	33.80	44.40	47.10	2.70	28	32	34	35	9.99	5.64	R2	16.77	0.32	9.98	
Małe Ciche 5	7.45	2.90	6.75	9.65	16.75	26.70	33.75	44.25	47.20	2.95	30	36	38	40	7.09	7.09	\mathbb{R}^2	16.70	0.30	10.02	
Silesia 25	7.30	3.15	6.70	9.70	16.70	26.65	33.55	44.15	47.35	3.20	35	41	40	42	8.83	6.80	R2	16.74	0.22	9.98	
Ch3	7.50	2.95	6.75	9.60	16.75	26.70	33.65	44.30	47.05	2.75	30	33	36	38	9.12	6.22	R2 (R1)	16.78	0.32	9.98	
Ch4	7.45	3.00	6.60	9.75	16.70	26.70	33.50	44.20	47.15	2.95	35	36	40	41	9.70	6.80	R1	16.78	0.25	9.98	
1M4	7.10	3.15	5.90	9.90	16.40	26.60	33.10	43.90	47.40	3.50	51	48	53	56	8.54	6.51	R1	16.80	0.30	9.98	
CIC 1/20	6.45		5.30	10.00	16.25	26.60	32.15	43.80	47.80	4.00	50	53	62	62	8.54	5.93	R0	16.77	0.27	9.98	
Mikołów 27	6.20		5.35	10.00	16.25	26.60	31.90	43.70	47.70	4.00	50	53	68	67	7.09	5.06	$\mathbb{R}0$	16.79	0.32	9.98	
1Cz2	6.35		5.35	10.02	16.20	26.65	32.05	43.55	48.15	4.60	58	63	70	71	7.96	5.93	$\mathbb{R}0$	16.77	0.23	9.98	
2M2	6.20		5.30	10.15	16.10	26.55	31.90	43.50	48.15	4.65	60	64	73	73	9.70	5.64	$\mathbb{R}0$	16.80	0.25	9.98	
2M3	6.15		5.25	10.30	15.95	26.50	31.85	43.20	48.35	5.15	75	80	83	84	9.41	5.64	R0	16.83	0.24	9.98	
1Cz3	6.15		5.25	10.35	15.90	26.50	31.85	43.10	48.45	5.35	80	88	87	88	8.04	5.93	$\mathbb{R}0$	16.83	0.22	9.98	
2M6	6.10		5.20	10.35	15.85	26.50	31.80	43.05	48.50	5.45	88	92	92	93	6.80	5.06	$\mathbb{R}0$	16.83	0.24	9.98	
1Cz5	5.90		5.20	10.40	15.78	26.44	31.84	42.98	48.58	5.60	96	98	98	98	7.09	5.64	$\mathbb{R}0$	16.85	0.23	9.98	
1Cz4	5.90		5.24	10.40	15.82	26.50	31.82	42.98	48.58	5.60	67	98	100	66	7.38	5.06	$\mathbb{R}0$	16.75	0.23	9.98	
Wyoming	6.10		5.20	10.38	15.72	26.34	31.72	42.72	48.40	5.68	67	100	96	96	7.38	5.64	R0	16.83	0.24	9.98	
Cheto	5.85		5.25	10.45	15.85	26.60	31.95	43.10	48.85	5.75	66	100	100	100	5.35	4.19	R0	16.74	0.24	9.98	



Figure 10. Calculation of layer compositions of illite-smectite mixed-layer crystals under different assumptions about the nature of crystal basal surfaces. S_{NEWMOD} – surfaces ignored; f_s (il) – illitic or smectitic surface, depending on the nature of the closest interlayer; f_s (sm) – surfaces always smectitic. S_{NEWMOD} vs. f_s (sm) model explains the data presented in Figure 9.

large $\%S_{\text{XRD}}$ values), in the reliable, highly illitic range, the results are consistent with the calculations based on equation 10 (Table 7).

The small but systematic differences between the measurements of S_{XRD} are understandable artifacts of the modeling techniques. The *NEWMOD* computer program does not account for external crystal surfaces, and thus strongly underestimates S_{XRD} , as I-S crystals are very thin (Srodoń *et al.*, 1990, 1992). The algorithms of Drits and Sakharov (1976) include one crystal edge in the calculation, treating it either as smectitic or illitic; thus they also underestimate the smectite content, but to a lesser extent. This difference in models can explain why S_{XRD} values from *SYBILLA* are generally greater than those from *NEWMOD*-based techniques.

The difference between the two NEWMOD-based techniques can be traced to the use of the $15.5-17.5^{\circ}2\theta$ reflection in one of them. This peak, when modeled, is quite asymmetric, while in the experimental patterns it is much more symmetric (Figure 8). The strong asymmetry of the modeled reflection is interpreted here as being the result of a simplified structural factor function selected for the model (cf. discussion by Drits et al., 1998, concerning the illite 001 peak). Perhaps such simplification can displace the maximum of the peak toward lower angles from the position of the interference function. Judging from the more symmetric peaks of the experimental patterns, in natural samples this effect is much smaller due to the natural chemical heterogeneity of I-S, resulting in variability of the structure factors. As a result, for a given $\% S_{\text{XRD}}$, the peak position of a natural sample is displaced toward a more illitic composition with respect to the modeled peak, which was used for the calibration. This effect of the use of simplified structure factors by the computer models forced us to use the high-angle fitting approach, as it is displacing peak maxima in 001 and 002 illite ranges.

The selected XRD peak positions from Table 6 were plotted vs. f_s from Table 4 (Figure 11). If the angular distance between end-member reflections of illite and smectite is <2.5°2 θ , the corresponding mixed-reflection positions or their angular distance ($\Delta 2$) are related to f_s by linear equations (Figure 11a,c,e,f). For more distant end-member reflections, this relationship was more complex (Figure 11b,d). The experimental regressions (Figure 11) can be used for measuring f_s from the XRD data. The regressions in Figure 11b,d are applicable only to R>0 I-S (*cf.* Środoń, 1984). Calculations of f_s using the experimental regressions are presented in Table 7. The errors are random, thus averaging results produces the most accurate numbers. Sample Fuzz 9 gives the largest error, probably due to the crystal-size effect. This is the only hydrothermal sample in the set and its crystal size is much larger (Table 6).

The linear regressions in Figure 11 extrapolate to positions characterizing discrete end-member illite (9.98 Å) not at $f_s = 0$ but at ~0.10-0.15, equivalent to N = 7-10 (equation 6). This seems to indicate that beginning from this level of N, illite fundamental particles exist independently, *i.e.* their tendency to associate into mixed-layer crystals disappears (N = T), and all exchange cations still present in such clays come from the external surfaces of illite crystals.

Chemical composition of the end-member minerals

The trends from Figure 3, when extrapolated to FIX = 0.95, yield an average composition of end-member illite close to intermediate between muscovite and phengite:

The end-member smectite composition obtained by extrapolation to FIX = 0 is a montmorillonite intermediate between Wyoming and Cheto:

The interlayer and the tetrahedral sheet compositions in these formulae are more reliable than the octahedralsheet composition, the latter extrapolated from data which are quite scattered (Figure 3). Such scatter was attributed by Ylagan *et al.* (2000) and Inoue *et al.* (2004) to the chemical composition of the reacting solutions.

ulated from experime	%diff $f_{\rm s}$ %d
rs (f _s) calc	$f_{ m s}$
ctitic layer	%diff
s of sme	$f_{ m s}$
und fraction	%diff
letails) a	$f_{\rm s}$
text for d	%diff
ues (see	$f_{\rm s}$
ent techniq	%diff
y differe	$f_{\rm s}$
alculated 0	%diff
uls (7) c.	<i>f</i> _s (2
1-layer crysta	T (from
the mixed	Т
Table 7. Mean thickness of 1 regressions (Figure 10).	T (from

Table 7. Mea regressions (]	an thickness of Figure 10).	the mixed-l	ayer crysti	als (T) ca	ilculated i	by differei	nt technic	aes) sent	text for d	letails) and	l fraction	is of sme	ctitic laye	rs (f _s) cal	lculated fr	om expei	
	T (from equation 10)	T (from %S SYBILLA)	T (from %S $\Delta 2$)	f _s (2 GLY)	%diff from $f_{\rm s}$ (FIX)	$f_{\rm s}$ (3 GLY)	%diff from $f_{\rm s}$ (FIX)	$f_{\rm s}$ (4 GLY)	%diff from $f_{\rm s}$ (FIX)	$f_{\rm s}$ (6 GLY)	%diff from $f_{\rm s}$ (FIX)	(7 GLY)	%diff from $f_{\rm s}$ (FIX)	$f_{\rm s}^{\rm s}$ ($\Delta 2$)	%diff from $f_{\rm s}$ (FIX)	fs (mean)	%diff from $f_{\rm s}$ (FIX)
Nor 27	7.82	7.31	6.85	0.19	6	0.17	-15	0.17	-18	0.16	-22	0.19	6			0.18	-15
Swe 151	6.55	5.48	4.96	0.30	-5	0.32	-	0.29	-8	0.29	9-	0.29	-8	0.29	6-	0.30	9-
Swe 162	6.45	5.04	5.04	0.30	6-	0.34	5	0.31	-5	0.29	-10	0.34	4	0.32	-	0.33	-3
Swe 81	6.38	5.00	4.77	0.32	-5	0.29	-13	0.33	-2	0.32	9-	0.37	11	0.32	-4	0.33	-3
Fuzz 9	6.89	9.50	7.29	0.29	4	0.34	24	0.33	20	0.28	2	0.36	29	0.32	17	0.34	16
Den 8	6.33	4.75	4.36	0.36	4	0.30	-14	0.38	11	0.35	1	0.40	16	0.31	-10	0.35	1
Zukowice 2	5.89	5.75	4.80	0.46	8	0.47	6	0.42	-3	0.44	б	0.41	9-	0.46	8	0.44	б
Est 62	5.73	5.01	3.75	0.48	З	0.44	9-	0.48	7	0.49	4	0.44	L	0.46	-2	0.46	-
Swe 84	5.68	4.47	4.05	0.51	4	0.47	-4	0.48	-	0.49	-	0.47	-3	0.51	4	0.48	0
Małe Ciche 5	5.57	4.26	3.87	0.51	-4	0.55	4	0.52	0	0.50	-4	0.52		0.54	Э	0.53	0
Silesia 25	5.51	4.10	4.33	0.52	9-	0.57	5	0.55	0	0.55	0	0.56	2	0.58	9	0.56	-
Ch3	5.51	3.22	3.11	0.51	L—	0.52	-5	0.52	4	0.53	4-	0.51	L	0.51	9-	0.52	-5
Ch4	5.47	3.64	3.13	0.54	-5	0.60	9	0.55	-3	0.5		0.54	-5	0.54	-4	0.56	-2
1M4	5.32	4.62	3.43			0.67	7	0.67	7			0.64	1	0.62		0.65	б
CIC 1/20	5.20	4.49	2.69			0.72	Э	0.74	5			0.67	-5	0.70		0.71	0
Mikołów 27	5.17	7.72	2.45			0.72	0	0.74	2			0.70	-2	0.70	- G	0.72	-
1Cz2	5.13	5.73	3.02			0.73	-2	0.76	-			0.75	0	0.79	5	0.76	-
2M2	5.12	8.93	2.99			0.80	S	0.80	9			0.77	-	0.79	4	0.79	4
2M3	5.01	9.32	4.15			0.88	б	0.87	7			0.87	б	0.87	2	0.87	б
1Cz3	4.98	12.47	281.05			0.90	2	0.89	1			0.90	ы	0.90	2	0.90	7
2M6	4.95	-10.08	-10.08			0.90	-1	0.91	0			0.92	1	0.91	0	0.91	0
1Cz5	4.91	-0.73	-0.73			0.93	-3	0.94	-			0.94	-	0.93	-2	0.94	-2
Cheto	4.91	-77.75	-0.97			0.93	-3	0.9	4-			0.94	-2	0.93	- S	0.9	-3
1Cz4	4.89	00.00	0.00			0.92	9-	0.96	-			1.03	5	0.95	-3	0.96	-
Wyoming	4.90	0.00	0.00			0.95	-	0.91	9			06.0	9	0.96	-1	0.93	4-



Figure 11. Plots of selected XRD peak positions or angular distances between selected peaks (data from Table 6) vs. f_s from Table 4. These experimental regressions can be used for measuring f_s from the XRD data. The theoretical positions of end-member illite reflections ($d_{001} = 9.98$ Å) are marked by squares.

SUMMARY AND CONCLUSIONS

The major result of this study, *i.e.* evidence of the stability of the charge of illite and smectite layers in the course of illitization, confirms the results of Środoń *et al.* (1992) and Ylagan *et al.* (2000). The evaluation of the smectitic charge is very similar in all three papers. The recognition of an illitic charge so close to that of mica is the result of accounting for fixed ammonium, which was not analyzed in the previous studies, and of the application of the FIX *vs.* EXCH plot instead of plotting FIX *vs.* electron microscopy-based data. If these new results are accepted, several consequences are apparent.

From a general perspective the most important conclusion is that illite is a mineral species closer to mica than previously thought, with a composition intermediate between muscovite and phengite: 95% of the fixed cation positions are occupied. The external surfaces of illite fundamental particles have smectitic charges and hold exchangeable hydrated cations and tightly bound water molecules, which can be expelled only by heating to temperatures of >200°C. The distinction between illite and I-S could be based on the fundamental particle thickness: at N = 7-10 their

tendency to associate into mixed-layer crystals seems to disappear (N = T; XRD peak positions correspond to pure illite).

More specific conclusions are:

(1) FIX can be used to calculate all essential parameters of I-S (equations 5, 6, 7, 9, 10).

(2) The CEC can be used also to calculate these parameters *via* experimental regressions (Figure 7). In the case of I-S, the evaluation of TSSA from CEC is more accurate than from H_2O or EGME retention (unlike pure smectites: Środoń and McCarty, 2008).

(3) XRD expandability measurements based on peakposition techniques or modeled by *SYBILLA* are close to each other. Minor systematic differences between these measurements have been detected and explained. They all heavily underestimate f_s (Figure 9); a feature attributed to the limited thickness of the mixed-layer crystals, the smectitic nature of their external surfaces, and the definition of expandability in the models of the diffraction effects. However, the correct f_s values can be measured quite accurately from peak-position data *via* experimental regressions (Figure 11), and all other parameters can be calculated from f_s (equations 5, 6, 9, 10).

(4) Illite interlayers seem to contain insufficient vacancies to accommodate molecular water released by illites on heating to >300°C, as assumed by Slonimskaya et al. (1978), Loucks (1991), and Drits and McCarty (2007). Środoń and McCarty (2008) demonstrated that pure smectites, devoid of any contracted layers, contain stable amounts of tightly bound water molecules, corresponding to ~1.3% of the mass of dry smectite. The illites studied by Slonimskaya et al. (1978) and Drits and McCarty (2007) have FIX = 0.74; thus $f_s = 0.22$ (equation 7) and N = 4.52 (equation 6). Such an amount of smectitic surface corresponds to ~0.29% of tightly bound H₂O, close to the 0.35-0.37% measured by Drits and McCarty (2007). According to the results of this study, such illite can have a maximum of 0.05 vacancies/ $O_{10}(OH)_2$, which could accommodate up to only 0.18% H₂O. Thus, at least half of the measured, tightly bound water must come from the external, smectitic surfaces of illite crystals. This interpretation explains why the hightemperature dehydration is so easily reversible, as demonstrated by Drits and McCarty (2007) for illites, and by Srodoń and McCarty (2008) for smectites.

(5) A stable charge of smectitic layers is an intriguing finding, given a broad charge variability of pure smectites. Either these data support the claim of Sato et al. (1996) that smectites evolve chemically before the onset of illitization, or they reflect the restricted chemical composition of parent pyroclastic materials of bentonites (acidic glasses). This alternative deserves further investigation, crucial for the application of a 0.41 smectitic charge to I-S of different origins. Despite its stable charge, the smectitic interlayer properties are evolving, as demonstrated by the greater coverages of H₂O and EGME, as well as the more strongly held Ca in more illitic samples. Such features probably reflect an increasing share of tetrahedral substitution in smectitic charges and changes in charge distribution. Smectitic charge is delocalized and occurs as a 'charge field' provided by a distant octahedral substitution, with exchangeable cations distributed at equal distances one from each other. Tetrahedral substitution provides the charge sites located over the Al-Si substitution sites. In the case of Ca saturation of the tetrahedral-dominated surface layer charge, the divalent cation cannot simultaneously satisfy two strong monovalent negative charge sites which are located at a distance from each other. This provides excess positive charge in one spot and excess negative charge in another. Water is needed, therefore, to distribute charge among charge-saturated/ undersaturated spots. This mechanism can make water adsorption in illitic phases different from that in smectitic I-S. Under the experimental conditions of the present study (Ca²⁺, ethylene glycol, 47% RH), this evolution did not result in the evolving XRD characteristics (from smectitic to vermiculitic).

The present study resulted in an improved technique for measuring TSSA and CEC values. The technique applied which uses sequential H_2O and EGME sorption and CEC measurement has the advantage of using only one sample split, and of referring all measurements to the same sample weight at 200°C, which limits the errors related to weighing and to the tightly bound water content. The Co-hexamine technique of Bardon *et al.* (1983) requires correction for Ca²⁺ not exchanged by this procedure, the amount of which increases for more illitic minerals (Table 1).

The study confirmed earlier reports of ammonium in I-S from bentonites (Nadeau and Bain, 1986; Środoń *et al.*, 2006b). On average 4% of ammonium in the fixed cations population (up to 12%) was measured. As bentonite layers have no source of ammonium ions (in contrast to shales), such fixed ammonium represents a record of ammonium migration throughout the rocks, a phenomenon directly related to oil and gas generation.

It should be stressed that the findings of this paper result from studying altered pyroclastics, a specific rock type, offering the opportunity to separate mono-mineral illite-smectite. Further studies will verify if these characteristics apply to illite-smectite in common sedimentary rocks.

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