INVESTIGATION OF THE CLAY FRACTION (<2 μm) OF THE CLAY MINERALS SOCIETY REFERENCE CLAYS

CHRISTOPH VOGT[1,*], JÖRN LAUTERJUNG[2] AND REINHARD X. FISCHER[1]

[1] FB Geowissenschaften/Geo Sciences, Universität Bremen, Post Box 330440, D-28334 Bremen, Germany
[2] GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany

Abstract—We studied a set of 15 reference clays from The Clay Minerals Society (CMS) Source Clays repository. Our aim was to use them as reference materials in our version of the QUAX mineral database. The QUAX software (Quantitative Phase-Analysis with X-ray Powder Diffraction) has been used successfully at the KTB site (German Continental Deep Drilling) to determine mineral assemblages quickly, in an automatic fashion, on a large number of samples (~40,000). It was also applied to Quaternary marine sediments of the Japan Sea. Our current research focuses on marine and lacrustrine sediments from the Arctic Ocean and Siberia.

QUAX is a full-pattern method using a reference materials database. The quality of a particular quantification depends on the availability of the relevant mineral phases in the database. Our aim is to extend and improve the database continuously with new data from our current projects, particularly from clay and feldspar minerals.

A reference material in the QUAX software must be monomineralic. Before X-ray diffraction (XRD) patterns of CMS clays could be added to the database, quantification of any impurities was necessary. After measuring the bulk material by XRD, the <2 μm fraction was separated because we assumed it would contain the smallest amount of impurities. Here we present grain-size data, XRD data and X-ray fluorescence (XRF) data for this clay-sized fraction. The results of chemical and mineralogical preparation techniques and (elemental) analysis methods were combined. For XRD, random and oriented clay-aggregate samples as well as pressed pellets for QUAX analysis were prepared. Semi-quantitative clay mineral determinations were run for comparison.

Key Words—Arctic Ocean, Clay Minerals Society (CMS), Source Clays Repository, Marine Geology, Quantitative Phase Analysis, Reference Clays, XRD, XRF.

INTRODUCTION

X-ray diffraction of fined-grained sediments is one of the most common methods used to reconstruct the mode of sediment transport and sedimentary environments. Specific information on the clay mineral content of a sediment sample is useful in various ways for marine geology or paleo-oceanography. Sediment fluxes and sedimentation budgets are very important for the reconstruction of the regional or even global history. Large mathematical models of a specific river-drainage basin or global and atmospheric changes use these data as input or boundary parameters.

We investigated the mineral assemblages of young and poorly-crystalline marine sediments from the Eurasian Basin and adjacent Siberian shelves of the Arctic Ocean. The samples were mainly physically-eroded fine-grained material that was transported by rivers and glaciers to the extensive shelf regions, the major primary dumping site. The material from the shelves was redistributed by sea ice, icebergs, and gravitational transport into the central Arctic Ocean. The mineral assemblages of the fine-grained material consists of >50 wt.% phyllosilicates. In the coarser fractions, feldspars and quartz are the main components.

A detailed reconstruction of transport pathways and sedimentary environments has to be based on a precise determination of the sediment composition. Therefore, we are interested in improvements in the quantitative determination of mineral content, in particular of materials rich in phyllosilicates. Their quantification is still a crucial component in the characterization of sediments (Moore and Reynolds, 1997). Various methods of preparation and measurement of the samples, as well as analysis and interpretation of diffraction data have resulted in a range of values for the mineral content of the same standard samples. Semi-quantitative calculations, such as the traditional empirically-determined and typically only regionally-applied correction factors (*e.g.* Biscaye, 1965) are still used extensively as well as sophisticated expert systems (*e.g.* Plançon and Drits, 2000). A 'Round Robin' laboratory comparison in Germany and Austria of various XRD (including Rietveld analysis), geochemical, and infrared (IR) spectroscopy methods resulted in extremely large deviations between splits of the same sample, even in the qualitative determination of single clay minerals or clay mineral groups (Ottner *et al.*, 2000).

The accuracy of the determinations was far outside the range of values recommended by Moore and Reynolds (1997) with a standard deviation of ±10% for main components constituting >20 wt.% of the sample

* E-mail address of corresponding author:
cvogt@uni-bremen.de

and ±20% for minor components. The difficulties in quantitative analyses using XRD methods, in particular Rietveld analysis, originate primarily from two causes. The first is the variable chemical composition, which influences selective peak intensities, the second is disorder effects, which cause decreased intensity and broadening of peaks (diffuse diffraction; *c.f.* Reynolds and Walker, 1993; Bergmann and Kleeberg, 1998).

An investigation of thousands of samples from surface sediments and sediment cores becomes extremely time consuming and virtually impracticable if complicated preparation techniques have to be applied (grain-size separation, heating, multiple scanning, dissolution of organic components, *etc.*). Therefore we use QUAX, a full-pattern analysis program, for quantitative phase analysis with XRD (Emmermann and Lauterjung, 1990), developed to investigate borehole cuttings and core samples in the German Continental Deep Drilling Project (Kontinentales Tiefbohrprogramm, KTB). At the KTB, ~40,000 ground bulk samples have been investigated so far. An initial study of Quaternary sediments from the Japan Sea with QUAX was performed by Dersch and Stein (1994). The bulk mineral composition of surface sediments of the Eurasian Basin of the Arctic Ocean was quantified by Vogt (1996).

QUAX uses a structured database of pure mineral phases. The quality of the analysis depends on the availability of as many different pure or nearly pure mineral measurements as possible. Since the chemical composition of some minerals, particularly feldspars and phyllosilicates, is extremely variable, QUAX needs reference data for various members in the solid-solution series for proper identification and quantification. Grouping of minerals helps to organize the database and facilitates the search.

For detailed investigation of the Quaternary sediments of the Arctic Ocean, the QUAX database had to be adapted to the potentially high abundance of phyllosilicates and also feldspar. Therefore, we searched for additional material to be integrated into the database. The collection of the Geosciences Department in Bremen and samples from colleagues provided natural materials or XRD measurements. Many XRD measurements of feldspar, mica, illites, montmorillonites, kaolinites and chlorites of different origin and chemistry were incorporated in the database. To extend the capabilities of QUAX for clay minerals, we obtained the whole set of materials from the CMS repository and report here the XRD, XRF and grain-size data from 15 of them: two kaolinites (low-defect and high-defect), the chlorite ripidolite, two natural and one synthetic illite-smectite mixed-layer clays, one illite, the smectites hectorite, beidellite and saponite, and various montmorillonites, as well as palygorskite (attapulgite) and sepiolite. The reference minerals data handbook (van Olphen and Fripiat, 1973) and the website for minerals from the CMS repository (Clay Minerals Society, 2000)

report that these materials possess several impurities. Many studies, however, (*e.g.* Jasmund and Lagaly, 1993; Köster *et al.*, 1999; Keeling *et al.,* 2000) recognized that the clay fractions (<2 µm or even smaller) of the CMS and other nearly monomineralic clay materials contain fewer impurities than the bulk matter. Based on their findings, we chose to study the clay fraction of the CMS source clays to obtain the purest fraction, to be incorporated into the database.

MATERIALS AND METHODS

Approximately 30 mg of the ground sample were examined for carbonate, organic C and N using a Heraeus CHN-elemental-analyser at the Alfred Wegener Institute (AWI, Bremerhaven). Carbonate contents were calculated as $CaCO_3(\%)$ = (total carbon–total organic carbon) $\times$ 8.333. The C and N measurements have standard deviations of 0.06 wt.% and 0.02 wt.%, respectively, determined by permanent repetition of internal and external standard sample measurements (*c.f.* Stax 1994; Knies and Stein, 1998). Schubert and Calvert (2001) give a precision of ±1.2% for C and ±2.7% for N, for the same instrument.

One subsample (~3 g) of the dried bulk sample was used for the evaluation of bulk mineral content by means of XRD measurements of a pressed pellet with a Philips PW 3020 diffractometer at the AWI, equipped with Co radiation, automatic divergence slit (ADS), graphite monochromator, and automatic sample changer (Figure 1). Selected single peaks for bulk and clay mineralogy and data collection parameters are given in Table 1. Individual mineral contents were expressed as percentages of bulk material.

A second split of the original sample was treated with 3−10% H_2O_2 to oxidize organic matter. The material was separated into coarse (>2 µm) and clay fractions (<2 µm) by the Atterberg settling tubes method (according to Stoke's law; Müller, 1967).

The separated clay fraction was homogenized by careful grinding with mortar and pestle. This powder was used in three procedures: (1) in the XRD measurements as random powder and oriented pressed pellets (the latter being a prerequisite for the QUAX determination, the preparation in aluminum rings has been adapted from XRF sample treatment; Emmermann and Lauterjung 1990); (2) for the Hereaus CHN elemental analysis at the AWI to determine the carbonate content; and (3) for XRF analysis using a Philips 1404 XRF spectrometer with Rh tube at the Institute of Mineralogy, University of Mainz; the standard deviation for major components is between ±0.11% (Fe_2O_3) and 0.88% (MnO) (Groschopf, 1997).

Quantitative phase analysis

Quantification was carried out using the QUAX software package (Figure 2; Emmermann and
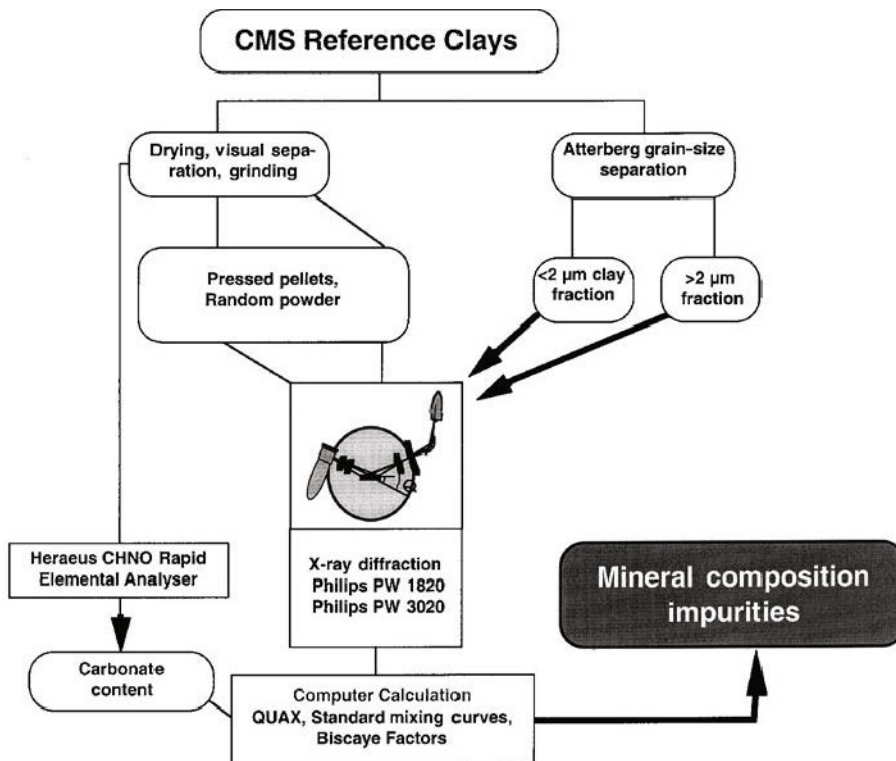
Figure 1. Preparation, measurements and computation methods used.

Lauterjung, 1990). The standard deviation for bulk mineral determination is ±2% for quartz and ±1% for the carbonates (Vogt, 1997). For feldspar and clay minerals the standard deviation currently ranges ±5−10%. These standard deviations have been determined by investigating 15 mixtures of two minerals of commercially-available pure phases. An example would be a quartz/kaolinite-mixing curve with 10% steps (*e.g.*

Table 1. (a) XRD operational parameters for bulk and clay mineral analysis. (b) XRD peaks (Å) used for the semiquantitative determination and standard mixing curve tests.

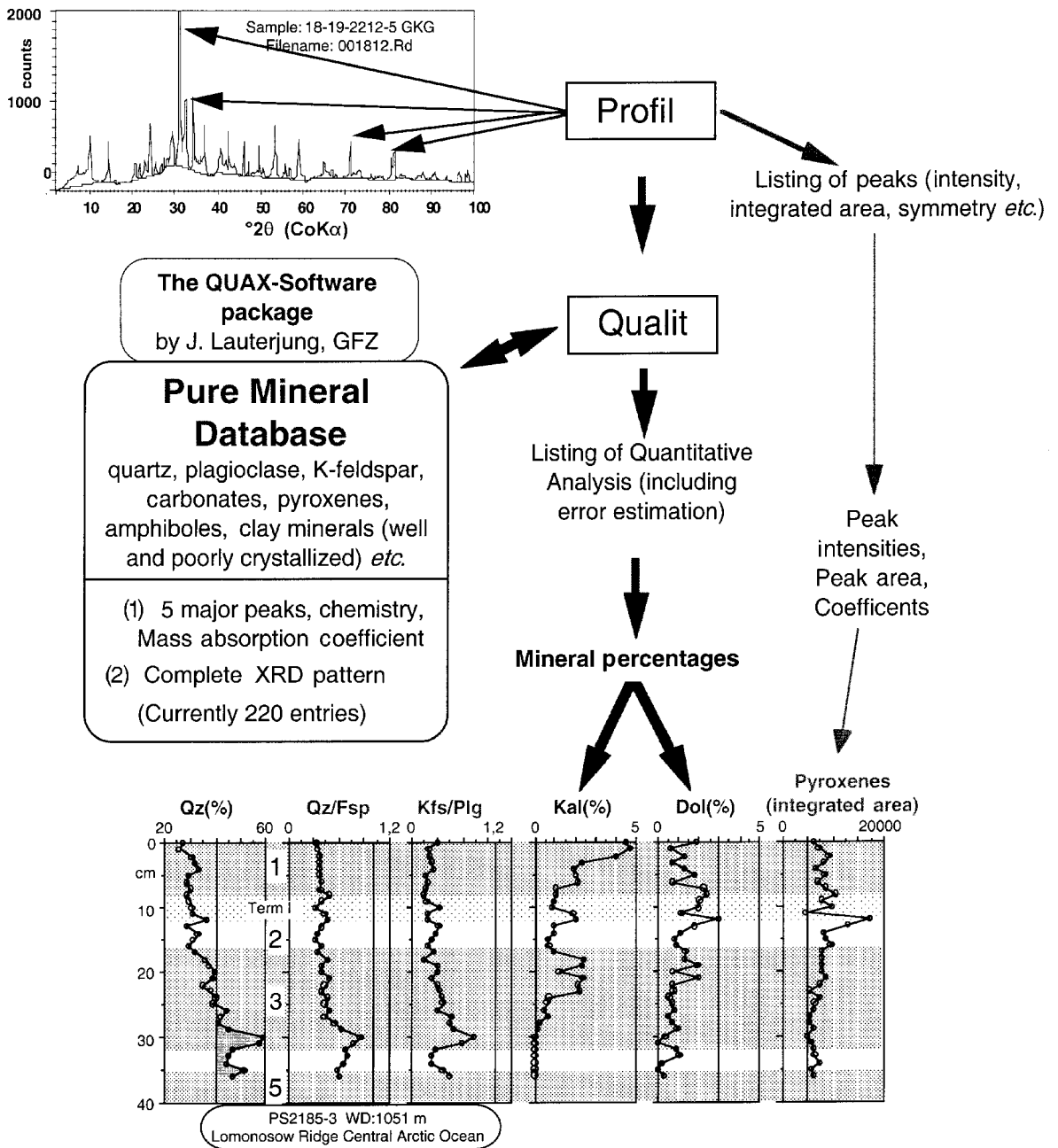| Measurement (CoKα radiation)	Sample preparation	Range (°2θ)	Stepsize (°2θ)	Count time/step (s)
(a)				
Bulk sample	Pressed pellets	2−100	0.02	1
Clay fraction >18 h glycolation slow scan	Oriented clay aggregates	2−40 28.5−30.5	0.02 0.005	1 2
(b)				
Peak positions of non-clay minerals (Å)	Quartz	3.34, 4.26		
	K-feldpar	3.24		
	Plagioclase	3.18		
	Calcite	3.035		
	Dolomite	2.89		
	Pyroxenes	3.0–2.91		
Basal clay mineral group peaks (Å) for determination after Biscaye (1965)	Smectite	17 glycolated		
	Illite	10		
	Kaolinite	7, 3.58		
	Chlorite	7, 3.54		

Figure 2. Structure, working scheme and results from the QUAX software. Peaks are recognized and characterized by the software module PROFIL. The results of PROFIL are compared with the database content. Results of the quantification with QUALIT are combined to a depth record. A sediment core from the central Arctic Ocean is shown with glacial/interglacial changes in mineral composition. (Grey shades mark interglacial or warmer periods of the youngest Quaternary, the last ~140.000 years. Marine Isotope Stages 1−5 and the Termination I are indicated according to Nørgaard-Pedersen *et al.,* 1998).

10:90; 20:80.... quartz: kaolinite). We also investigated several two-phase mixtures of clay minerals. The peak area intensities and ratios of several peaks have also been used to cross check the QUAX results.

A final step in improving and checking the quality of determination was the analysis of eight six-phase materials of quartz, plagioclase, K-feldspar, illite,

kaolinite and montmorillonite with various amounts. For these six minerals, the standard deviation was 1.4% for quartz, 2.7% for the feldspars, 1.6% for kaolinite, 3% for montmorillonite and 4.8% for illite (Vogt *et al.,* 2000).

Our latest check on the quality of QUAX determination involved two materials described by Ottner *et al.*

Table 2. Impurities (wt.%) in the clay fraction (<2 μm) of the CMS reference clays for the QUAX method.

Mineral	CMS no.	Quartz	Plagio-clase	K-feldspar	Calcite	Dolomite	Kaolinite	Chlorite	Clino-pyroxene	Ortho-pyroxene	Total
Illite	IMt-2	3.3	1.5	4.6	0.1	0.1	0.7	0.2	0.2	0.0	10.7
Mixed layer	ISMt-2	1.3	3.7	1.7	0.0	0.0	0.7	0.0	0.0	0.0	7.4
Mixed layer2	ISCz-1	0.7	5.5	2.3	0.2	0.0	0.2	1.2	0.0	0.0	10.1
Cheto (Mont)	SAz-1	0.2	0.3	0.8	0.4	0.2	1.2	0.4	0.7	0.2	4.4
Otay (Mont)	SCa-3	0.0	0.6	0.0	0.4	0.1	0.0	0.0	0.3	0.0	1.4
Gonz (Mont)	STx-1	0.1	0.6	0.9	0.5	0.1	2.1	0.4	0.8	0.0	5.4
Na-mont.	SWy-2	5.2	0.1	0.0	0.4	0.2	1.3	0.2	4.4	1.4	13.3
Hectorite	SHCa-1	0.2	0.6	1.2	0.4	0.1	2.7	0.0	0.0	0.0	5.2
Beidellite	SBCa-1	0.5	3.0	1.7	0.7	0.2	11.1	0.9	0.0	0.0	18.1
Saponite	SapCa-2	0.1	0.8	4.0	0.4	1.9	1.5	0.3	1.3	0.0	10.2
Palygorskite	PFl-1	1.7	2.5	5.8	0.1	0.0	1.7	0.0	0.5	0.0	12.2
Sepiolite	SepSp-1	0.0	5.7	1.5	0.1	0.0	2.7	0.1	0.0	0.2	10.2

							Illite/mixed ed-layer	Montmo-rillonite			
Kaolinite	KGa-1b	0.5	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7
Kaolinite	KGa-2	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	1.2
Ripidolite	CCa-2	0.0	0.0	0.0	0.0	0.0	8.8	0.0	0.0	0.0	8.8

(2000). We found very small deviations (1−2 wt.%) from the most probable content of non-clay minerals and 3−7 wt.% deviations of the content of specific clay minerals (Vogt *et al.*, 2001). For this latest study, QUAX included all the CMS reference clays being discussed in this paper. Although this latest test of QUAX gave very promising results, perfectly satisfactory for provenance and paleo-oceanographic studies, our aim is to reduce the error values by adding as many XRD patterns as possible to the database, especially for poorly-crystallized materials. Mineral weight fractions in Tables 2−5 are given with the first digit after the decimal point to include fractions <1 wt.%.

Semi-quantitative determination of clay mineral contents

To compare the data with a standard technique of marine geology — a major part of our current research project — the clay mineral assemblage from the CMS clays was also determined by standard preparation (oriented clay-aggregate samples) and analysis techniques as outlined by Ehrmann *et al.* (1992) and Petschick *et al.* (1996). Only CMS clays with known expandable clay components were investigated (see Table 4). The peak areas of the most prominent basal reflection representing a certain clay mineral group (Table 1) were calculated and transformed into relative clay mineral percentages by means of Biscaye empirical factors (Biscaye, 1965). This is based on the assumption that the clay fraction consists only of the four clay mineral groups smectite, illite, kaolinite and chlorite. Kaolinite and chlorite differentiation is based on the slow-scan method and the peak intensity ratio of the 3.58 and 3.54 Å peaks applied to the coupled 7 Å peaks

(Biscaye, 1964). For Arctic Ocean sediments, careful preparation allows a reproducibility of the semi-quantitative determination from multiple specimens of the same sample of ±3% (Vogt, 1997).

RESULTS

Bulk fraction mineral composition and comparison of QUAX quantification to published data

We began our study of the CMS materials with the bulk sample. Our QUAX determinations of the bulk fraction composition closely resembled published data (*e.g.* 27 wt.% calcite in the bulk content of hectorite SHCa-1 and 4 wt.% quartz in the illite IMt-2; *c.f.* van Olphen and Fripiat, 1973). These data and an investigation of some of the latest additions to the CMS source clays repository gave us additional confidence in the QUAX determination. For the fairly new CMS nontronites NAu-1 and NAu-2, we calculated similar but slightly higher impurity levels in the bulk sample compared to those presented by Keeling *et al.* (2000). The results of QUAX are for the bulk sample NAu-1 (in wt.%): 79% nontronites/montmorillonites, 1% quartz, 12% kaolinite, 6% biotite, 1% talc, 0.4% goethite with traces of plagioclase, K-feldspar, gypsum, apatite, amphibole, chloritoid and zircon, and for the bulk sample NAu-2: 85% nontronites/montmorillonites, 0.6% quartz, 4% plagioclase, 3% K-feldspar, 3.5% talc, 2% biotite/illite, 1% amphibole, 0.3% carbonates (calcite, dolomite, siderite) and traces of apatite, garnet, sillimanite, goethite and zircon.

For the QUAX database, the full diffraction pattern of a (nearly) monomineralic sample is needed and materials with larger amounts of impurities like the bulk

Table 3. Single run of QUAX quantification of mineral contents of the clay fraction of Na-montmorillonite (SWy-2). Reference standards and peaks of standards used for the determination.

Recognized minerals				Kaolinite	Smectite Geisenheim	Montmorillonite Mösburg	Augite	Quartz	Saponite	Montmorillonite
QUAX quantification (wt.%)				0.5	22.3	48.6	4.7	5.0	10.9	8.4
Peak no.	d-value (Å)	Integrated Intensity	Calculated Intensity	Intensity (%) of maximum intensity (Reference Material)						
1	14.524	67743	67759	0	100	100	0	0	100	100
2	5.057	999	1414	0	2	3	0	0	0	6
3	4.966	1274	945	0	1	2	0	0	0	5
4	4.901	1883	1411	0	2	1	0	0	0	14
5	4.850	1083	683	0	0	0	0	0	7	0
6	4.802	1085	1008	0	2	0	0	0	0	5
7	4.747	380	524	0	1	1	0	0	0	2
8	4.477	8737	7528	0	2	31	7	0	0	26
9	4.348	2999	2421	100	1	7	0	0	0	19
10	4.253	3906	3620	0	1	8	0	18	0	34
11	4.146	528	725	8	0	2	0	0	0	5
12	4.080	439	1273	0	1	5	0	0	0	2
13	3.987	377	870	0	0	4	0	0	0	3
14	3.663	1184	1981	0	1	4	0	0	9	0
15	3.618	448	285	0	0	1	0	0	0	0
16	3.589	319	830	31	1	3	0	0	0	0
17	3.337	8586	8898	0	1	6	5	100	0	84
18	3.075	331	1357	0	0	3	0	0	0	29
19	3.056	546	784	0	0	2	0	0	0	14
20	3.031	846	567	0	0	1	0	0	0	11
21	3.011	1071	834	0	0	2	0	0	0	13
22	2.989	1879	2148	0	3	1	82	0	0	0
23	2.967	1966	1698	0	1	1	100	0	0	4
24	2.933	3432	2906	0	1	1	0	0	23	4
25	2.908	1776	956	0	1	1	41	0	0	3
26	2.881	783	295	0	0	0	0	0	0	2
27	2.587	619	1068	0	0	4	0	0	3	0
28	2.572	1154	1554	5	0	5	34	0	0	8
29	2.549	3826	3935	0	4	7	48	0	2	15
30	2.530	2188	2059	4	1	7	0	0	0	11
31	2.512	2053	2072	0	1	4	49	0	2	10
32	2.489	2498	2320	5	2	7	0	0	0	14
33	2.467	1494	1513	0	1	2	2	9	1	5
34	2.454	2789	2025	0	1	5	0	0	1	22
35	2.411	839	1321	0	1	3	0	0	1	6
36	2.382	759	1091	4	1	3	0	0	1	8
37	2.358	278	702	0	1	2	0	0	0	2
38	2.336	248	173	10	0	0	0	0	1	2
39	2.279	528	803	6	0	0	0	8	2	8
40	2.129	588	680	0	0	0	20	6	0	7
41	1.984	753	524	0	0	0	6	4	0	3
42	1.819	1357	1106	0	0	0	3	16	0	11
43	1.697	945	1485	0	1	4	0	0	0	6
44	1.687	1084	318	0	0	1	0	0	0	4
45	1.674	1907	1125	0	0	3	10	5	0	10
46	1.659	711	697	3	0	1	0	2	0	6
47	1.543	1055	1337	0	0	0	58	12	0	7
48	1.497	5950	5101	0	4	16	0	0	0	26
49	1.374	1769	1241	0	0	0	0	15	0	18
50	1.289	3382	2041	0	1	6	0	3	0	19
51	1.282	359	558	0	0	1	13	0	0	8
52	1.247	1025	341	0	0	1	0	0	0	5

Table 4. XRF data (wt.%) of the clay fractions of the CMS reference materials compared with the CMS data of the bulk fraction (van Olphen and Fripiat, 1973; Clay Minerals Society, 2000), and mean values of different clay fraction grain-sizes of Newman and Brown (1987) and Weaver and Pollard (1973).

Mineral	CMS no.	SiO$_2$ %	Al$_2$O$_3$ %	Fe$_2$O$_3$ %	MnO %	MgO %	CaO %	Na$_2$O %	K$_2$O %	TiO$_2$ %	P$_2$O$_5$ %	Cr$_2$O$_3$ %	NiO %	LOI %	Total %
Illite	**IMt-2**	**50.73**	**22.37**	**7.43**	**0.04**	**2.103**	**0.05**	**b.d.**	**7.92**	**0.73**	**0.08**	**0.023**	**0.01**	**8.02**	**100.34**
CMS data		49.30	24.25	7.50	0.03	2.56	0.43	0.00	7.83	0.55	0.08			8.02	100.55
Newman and Brown (Mean of 7)		54.41	22.64	6.61	0.00	3.26	0.86	0.09	7.16	0.79				7.72	103.54
Mixed-layer	**ISMt-2**	**50.65**	**25.69**	**1.94**	**0.01**	**3.14**	**0.21**	**0.08**	**4.84**	**0.15**	**0.03**	**b.d.**	**0.0009**	**13.66**	**100.39**
CMS data		51.20	26.30	1.50	0.01	2.41	1.40	0.04	4.74	0.17	0.05			12.60	100.42
Newman and Brown (Mean of 4)		55.47	29.78	2.85		1.91	1.16	1.74	3.46	0.28				4.49	101.14
Mixed-layer 2	**ISCz-1**	**51.01**	**25.98**	**1.32**	**0.01**	**3.73**	**0**	**b.d.**	**5.78**	**0.12**	**0.02**	**0.002**	**0.0012**	**12.29**	**100.22**
CMS data		51.60	25.60	1.12	0.04	2.46	0.67	0.32	5.36	0.04	0.04			10.20	97.45
Newman and Brown (Mean of 4)		54.35	17.77	9.20		4.51	0.74	0.99	4.72	0.36				10.46	103.10
Cheto (Mont)	**SAz-1**	**52.5**	**15.15**	**1.43**	**0.07**	**7.44**	**0.18**	**b.d.**	**0.05**	**0.2**	**0.01**	**b.d.**	**0.0008**	**23.61**	**100.64**
CMS data		60.40	17.60	1.43	0.10	6.46	2.82	0.06	0.19	0.24	0.02			9.91	99.23
Weaver and Pollard (Mean of 7)		62.33	20.25	1.70		5.79	0.88	0.18	0.04	0.07				7.78	99.02
Otay (Mont)	**SCa-3**	**51.72**	**14.93**	**1.26**	**0.04**	**8.19**	**0.05**	**b.d.**	**0.07**	**0.19**	**0.01**	**b.d.**	**0.0017**	**24.23**	**100.67**
CMS data		52.80	15.70	1.10	0.03	7.98	0.95	0.92	0.03	0.18	0.02			21.20	100.91
Newman and Brown data		62.58	18.44	1.20	0.01	7.30	0.08	3.40	0.02	0.14				6.47	99.64
Gonz (Mont)	**STx-1**	**62.16**	**14.45**	**0.58**	**0.01**	**4.57**	**0.12**	**b.d.**	**0.04**	**0.22**	**0.02**	**b.d.**	**0.0004**	**18.33**	**100.48**
CMS data		70.10	16.00	0.70	0.01	3.69	1.59	0.27	0.08	0.22	0.03			3.48	96.16
Newman and Brown (Mean of 6)		57.37	19.95	4.44	0.02	2.91	0.2	2.98	0.01	0.19				6.02	94.09
Na-mont	**SWy-2**	**57.34**	**17.89**	**3.73**	**0.01**	**3.91**	**0.05**	**b.d.**	**0.12**	**0.11**	**0.02**	**b.d.**	**0.001**	**17.38**	**100.56**
CMS data		62.90	19.60	3.40	0.01	3.05	1.68	1.53	0.53	0.09	0.05			6.06	98.90
Weaver and Pollard (Mean of 9)		61.23	23.78	4.70		1.74	0.25	0.36	0.47	0.35				6.52	99.40
Hectorite	**SHCa-1**	**52.13**	**15.17**	**1.4**	**0.07**	**7.54**	**0.12**	**b.d.**	**0.05**	**0.2**	**0.01**	**b.d.**	**0.0009**	**24.17**	**100.86**
CMS data		34.70	0.69	0.30	0.01	15.30	23.40	1.26	0.13	0.04	0.01			21.80	97.64
Newman and Brown (Mean of 4)		58.55	0.39	0.20	0.05	26.60	0.46	1.69	0.15	0.01				13.57	101.67
Beidellite	**SBCa-1**	**47.86**	**28.25**	**1.86**	**0.01**	**2.63**	**0.02**	**b.d.**	**1.33**	**0.63**	**0.04**	**0.0009**	**0.0013**	**17.59**	**100.21**
CMS data		46.45	27.95	2.13	0.08	0.94	1.01	0.00	0.72	0.52	0.11			20.25	100.16
Newman and Brown (Mean of 3)		59.70	31.24	0.37		1.72	0.75	2.68	0.64	0.09				3.23	100.42
Saponite	**SapCa-2**	**47.5**	**4.27**	**0.93**	**0.02**	**27.41**	**0.14**	**b.d.**	**0.02**	**0.04**	**0**	**0.0013**	**0.0005**	**20.49**	**100.79**
CMS data		47.90	4.17	0.67	0.05	26.10	0.90	2.73	0.39	0.03				12.60	95.54
Newman and Brown (Mean of 8)		47.74	6.51	6.00	0.04	27.04	2.22	0.11	0.04	0.11				7.66	97.47
Palygorskite	**PFl-1**	**54.09**	**9.91**	**3.42**	**0.03**	**10.32**	**1.38**	**b.d.**	**0.51**	**0.42**	**0.88**	**0.0227**	**0.0031**	**19.97**	**100.98**
CMS data		60.90	10.40	3.00	0.06	10.20	1.98	0.06	0.80	0.49	0.80			10.31	99.00
Newman and Brown (Mean of 6)		55.08	8.32	2.10	0.11	11.56	0.79	0.07	0.25	0.30				21.30	99.87
Sepiolite	**SepSp-1**	**54.43**	**1.5**	**0.44**	**0.01**	**22.83**	**0.06**	**b.d.**	**0.14**	**0.05**	**0.04**	**0.0028**	**0.0008**	**21.08**	**100.58**
CMS data		52.90	2.56	1.27	0.13	23.60	0.00	0.00	0.05	0.00	0.01			20.80	101.32
Newman and Brown (Mean of 5)		53.64	0.59	1.4	1.21	22.53	0.37	0.08	0.01	0				19.98	99.81

LOI: Loss on ignition
b.d. below detection limits.

Table 5. Comparison of clay mineral contents (%) determination according to Biscaye (1965) and QUAX. The clay minerals content of QUAX was normalized to 100% and the clay mineral contents were summed for the four different clay mineral groups as described by Biscaye (1965).

CMS Clay	Smectite	Illite	Kaolinite	Chlorite	Quartz	Fsp/MoS$_2$	Calcite	Dolomite	Pyx/MoS$_2$
Beidellite	52.7	1	29	18	1.7	0.46	0.06	0.7	0.03
based on QUAX	87.1	0	11.9	1					
Hectorite	81.9	8	5	5	0.4	0.04	0.04	0.3	0.57
based on QUAX	97.1	0	2.9	0					
Saponite	98.4	1.2	0.4	0	2.4	0.00	0.02	1.8	0.47
based on QUAX	98	0	1.8	0.2					
Otay (Mont)	94.9	5	0	0	0.7	0.56	0.02	0.4	0.20
Cheto (Mont)	96.6	3	0	0	1.1	0.00	0.00	0.4	0.10
ISMt-2(60/40Mix)	1.2	94	5	0	0.5	0.01	0.04	0.1	0.13
ISCz-1(70/30Mix)	0.3	98	0	0	0.2	0.05	0.13	0.1	0.08
Sepiolite	0	99	1	0	0.2	0.03	0.10	0.0	0.02

Fsp/MoS$_2$ and Pyx(Pyroxene)/MoS$_2$ are ratios of the sum of integrated peak areas of mineral peaks to the integrated peak area of the MoS$_2$ peak at a d-value of 6.15 Å (*cf.* Table 1).

material of NAu-1 and NAu-2 cannot be used. Therefore, we focused our studies on the <2 µm clay fractions, which we assumed to contain fewer impurities.

Grain-size of the CMS source clays

The proportion of clay-sized particles in the CMS source clay samples studied varied from 1.2 wt.% in ripidolite CCa-2 to >80 wt.% in illite IMt-2 and Na-montmorillonite SWy-2 (Figure 3). Our value of ~40% clay fraction for ISMt-2 is lower than the corresponding values of Jasmund and Lagaly (1993) of ~65 wt.% (sum of the fractions 0.06−0.2, 0.2−0.6 and 0.6−2 µm in their diagram on page 12). This could be related to differences in the CMS clays ISMt-1 and ISMt-2 and/or differences in separation techniques. For

the settling-tube separation technique used, Melles (1991) reported that despite ultrasonic treatment and the use of Na hexametaphospate as a dispersant, up to 8% of the clay-sized particles may remain with the coarser fraction due to their strong aggregation into clumps with sinking velocities similar to sand- and silt-size particles. There are no indications that the aggregates are mineralogically different from the separated clay fraction. In a study of Arctic Ocean sediments, using this standard separation technique, most of the clay mineral content in the silt fraction (2−63 µm) was attributed to these aggregates (Vogt, 1997). They largely match the composition of the clay fraction of the same sample with addition of some coarser size phyllosilicate clay minerals (*i.e.* micas and chlorites).
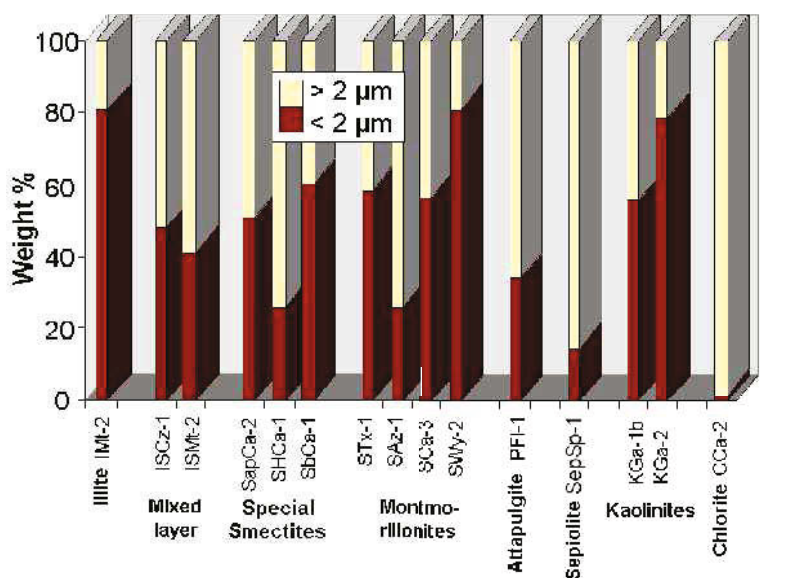

Figure 3. Grain-size contents of CMS reference materials.

The clay fraction phase composition

QUAX results on the major impurities are listed in Table 2. Traces of other minerals have also been found but not quantified (*e.g.* anatase in both kaolinites, or barite in sepiolite and Ca-montmorillonite). All CMS reference materials possess minor to significant amounts of impurities in the clay fraction. This is not surprising, as (among others) Jasmund and Lagaly (1993) for the CMS reference material ISMt-1 and, recently, Köster *et al.* (1999) and Keeling *et al.* (2000) for several Fe-rich smectites and nontronites, have shown that only the <0.2 µm fraction can be regarded as consisting purely of the clay mineral (see also Chipera and Bish, 2001). However, fractionation of the <0.2 µm size-fraction is time consuming and therefore impractical for all samples. Sample preparation as pressed pellets for the QUAX measurements requires a minimum of 3 g of sample material (Emmermann and Lauterjung, 1990; Vogt, 1997). Even more material was needed for the standard mixing curves to test the effectiveness of the QUAX quantitative determinations. Therefore, the focus of our study was to pinpoint the amount of impurities in the <2 µm clay fraction, and then decide whether the sample was acceptable for the QUAX database.

By confining the studies to the <2 µm size-fraction the proportion of impurities is much reduced in comparison to the bulk samples (Tables 2—5). An example is the low carbonate content of hectorite (CMS SHCa-1; Table 2). Unfortunately, there are still clay-sized fractions with too many impurities. In the clay fraction of beidellite SBCa-

1, we determined >11% kaolinite (Table 2). In the XRD pattern of the glycolated and oriented sample, the basal reflections of kaolinite or at least 7 Å minerals are obvious (Figure 4). QUAX also calculated a minor amount of chlorite. A slow scan of the oriented clay fraction sample shows the coupled peaks at 3.58 and 3.54 Å (Figure 4), and QUAX also decomposed the 7 Å peaks for the quantification. The almost total absence of a 4.72 Å peak might be an indicator of the particular chemistry of the chlorite (Fe-rich? Figure 4). Although QUAX already contained several full patterns of different chlorites (Fe- and Mg-rich and different symmetries), the exact quantification of chlorite in the beidellite might be hampered by the lack of the particular pure mineral chlorite XRD pattern in the database.

Currently, in many investigations of marine sediments, only four different clay mineral groups are distinguished for sediment provenance studies, as proposed by Biscaye (1965). This concept is widely used because the data are comparable to former investigations and because semi-quantification is easy to apply. For many marine investigations, knowing the changes in the source region of the terrestrial material is sufficient. Therefore, the occurrence of different clay minerals of the same clay mineral group would not pose any difficulty for comparison with other marine investigations. We would use the sum of these minerals for the paleo-oceanographic reconstruction (*e.g.* montmorillonites, smectites and mixed-layer clays all belong to one group: the expandable minerals or 'smectite' group in the Biscaye concept). Kaolinite and chlorite are
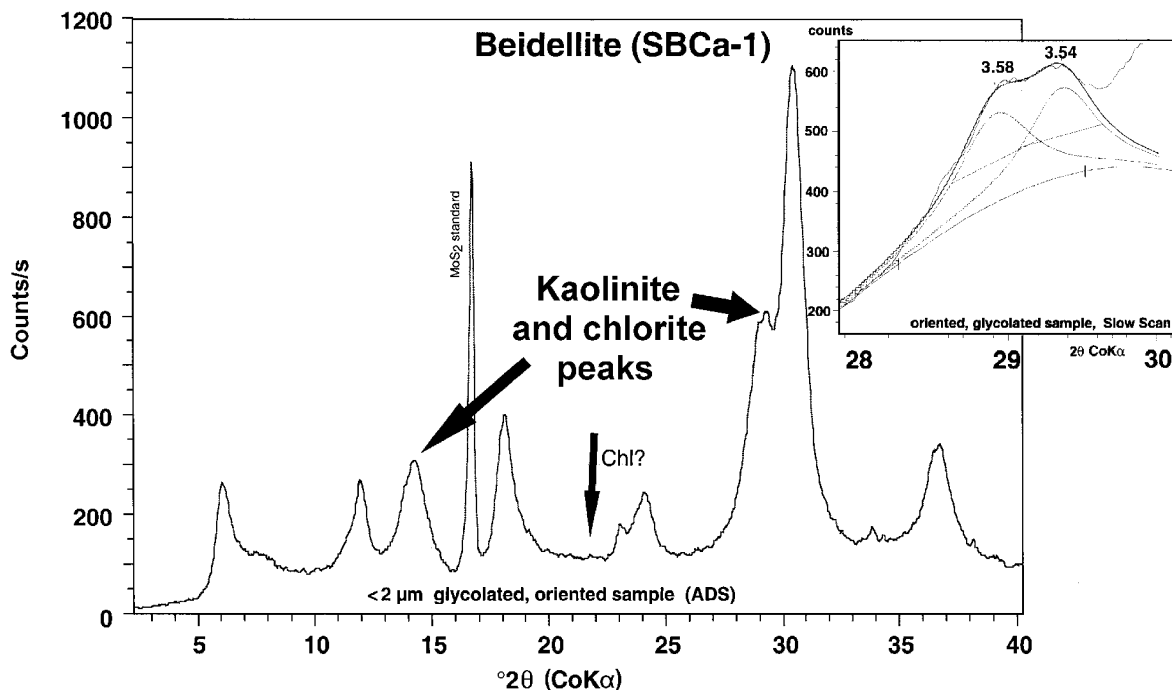

Figure 4. XRD pattern of the glycolated, Mg-saturated, oriented clay fraction of beidellite (CMS SBCa-1). Measurements according to Petschick *et al.* (1996). Inset shows the slow scan and the deconvoluted peak doublet of kaolinite (3.58 Å) and chlorite (3.54 Å).

two of the other three clay mineral groups in the Biscaye-type investigation (see the section on material and methods). If the impurities in the beidellite SBCa-1 were montmorillonites or expandable mixed-layer clays, SBCa-1 would still be acceptable as a QUAX reference material for paleo-oceanographic investigations. But the major impurities are kaolinite and chlorite. Thus, we cannot include the clay fraction of the beidellite SBCa-1 in our database of QUAX.

Another example is the pyroxene content in the clay fraction of the CMS clay SWy-2, a Na-montmorillonite. QUAX recognized 15 peaks to be diagnostic for the pyroxene standard augite (Table 3), of which the ones at 2.989 and 2.908 Å are the most prominent in Figure 5. In Table 3 we also demonstrate the way in which QUAX processes an unknown measurement (*c.f.* Emmermann and Lauterjung, 1990). In a first step, peaks are recognized and the *d*-values are determined. The integrated intensities of the peaks are computed. The list of peaks is then compared to the list of most prominent mineral peaks (of the pure minerals) in the database. The most prominent minerals in the sample are listed according to their decreasing probability. Based on this list the full pattern of the reference minerals are used to compute an XRD pattern matching as closely as possible to the observed intensities. After the most abundant minerals have been processed, the residual intensities are assigned to less abundant minerals.

In Table 3, the reference mineral augite is one of these minor minerals. None of the 15 peaks QUAX uses for the recognition of this augite is exclusively an augite peak, but all had residual intensities after calculations with the more probable minerals, the montmorillonites, smectites and quartz. After the fourth iteration, QUAX found this pyroxene which was masked by the overwhelming content of the clay minerals. The final

quantification of mineral content involves the mass attenuation coefficients of the reference minerals in the database and a calculation through a 5—10 fold overestimated system of linear equations (Emmermann and Lauterjung, 1990). This system can be tested statistically for significance, correlations and goodness of fit for the calculated mineralogical composition. At this point, tight probability margins are used. After all these restrictions, augite was recognized. Together with the 5.2% quartz content and traces of kaolinite (Table 2), it is difficult to incorporate this material into the QUAX database. The XRD pattern of the oriented and glycolated sample (Figure 5) indicates the presence of these impurities.

The clay fraction of sepiolite (SepSp-1) contains ~5% plagioclase, 1.5% K-feldspar, and 2.5% kaolinite (Table 2). Both feldspar groups are clearly recognizable by their dominant X-ray peaks. As for the other CMS samples with significant amounts of impurities, the clay fraction needs to undergo further fractionation before being adopted in the QUAX database.

While the clay fractions of the kaolinites are very pure with very small amounts of quartz and plagioclase, the clay fraction of ripidolite contains ~9% of an illite-smectite mixed-layer clay mineral. According to the QUAX quantification, the clay fraction of the palygorskite PFl-1 contains ~12% smectites in addition to the impurities listed in Table 2. Chipera and Bish (2001) found a similar amount of smectite in their <2 μm fraction of PFl-1 (~10%). As we currently use QUAX for paleo-oceanographic applications, this amount would not be critical, as outlined above ('Biscaye-like' investigation of clay contents). The palygorskite content would be reported together with smectites and mixed-layer clay minerals, but the total of the listed impurities in the clay fraction of palygorskite already exceeds 10%.
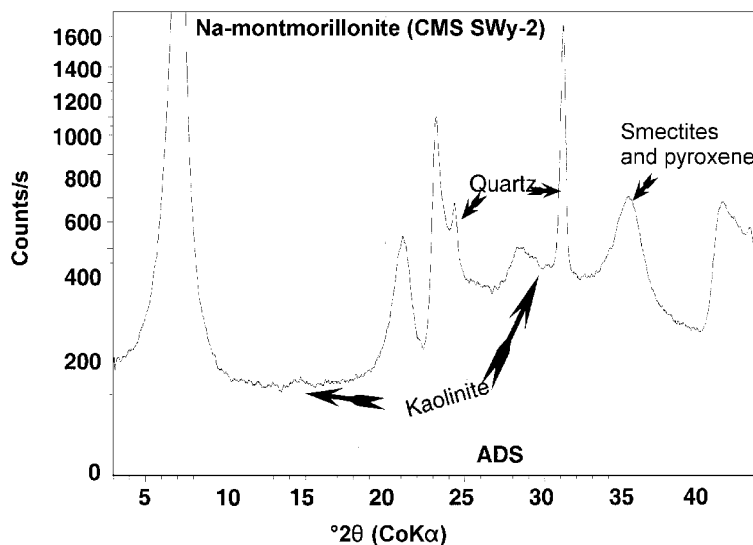

Figure 5. XRD pattern of the glycolated, Mg-saturated, oriented, clay fraction of the Na-rich montmorillonite (CMS SWy-2). Measurement according to Petschick *et al.* (1996).

Therefore, the clay fraction XRD pattern of palygorskite was not included in the QUAX reference database and further processing was needed.

X-RAY FLUORESCENCE

The results from our XRF analyses for the clay-sized fraction of 12 CMS clays with recognized impurities are comparable to the chemical data in various reference collections for clay minerals (Table 4, *e.g.* Weaver and Pollard, 1973; Newman and Brown, 1987; Jasmund and Lagaly, 1993). It is obvious that a significant reduction in the level of impurities was achieved by using only the clay fraction. The low CaO content in the <2 μm fraction of hectorite (SHCa-1) demonstrates the greatly diminished calcite content compared to the sample of the raw material (*c.f.* van Olphen and Fripiat, 1973). The results are somewhat restricted as the XRF Na_2O values were close to the detection limits and consequently not reported. For comparison with the mean values of Newman and Brown (1987) and Weaver and Pollard (1973), one has to bear in mind the differences in the preparation of the samples before the measurement. Our values are from the sample without previous drying or heating. Instead, the loss on ignition was determined (Table 4). Some of the other data are based on heating or drying before determination of the chemical composition (*e.g.* Table 1.15, on page 50 of Newman and Brown, 1987). Additionally, different grain-sizes of the fine fractions were investigated.

Together with the published data, major element contents clearly show impurities in the clay fraction of the CMS clays. Here are two examples from Table 4. The K_2O content in beidellite is greater than the published data (1.33 to 0.72 and 0.64 wt.%), supporting the XRD determination of a K-bearing phase, such as K-feldspar (Table 2). The second example is the MgO content in the Na-montmorillonite (SWy-2) that is doubled when compared to the mean of the Newman and Brown (1987) data (Table 4). This could support the XRD determination of abundant pyroxenes in the Na-montmorillonite.

The greatest deviation between the published and our data is observed for hectorite: the Al_2O_3 content in our measurement is much bigger (Table 4). The QUAX analysis recognized 4.5 wt.% plagioclase, K-feldspar and kaolinite (Table 2). Based on published and measured chemical data for the composition of our plagioclase, K-feldspar and kaolinite reference materials, those minerals could account for ~2−3 wt.% of the additional Al_2O_3 in our analyzed hectorite clay fraction (Table 4). Therefore, the clay fraction of hectorite might contain other expandable minerals such as montmorillonites or mixed-layer clays causing an increased Al_2O_3 content. A detailed investigation of the hectorite material is beyond the scope of this study. The increased Al_2O_3 content is coupled with reduced MgO values.

QUANTITATIVE DETERMINATION *VS.* SEMIQUANTITATIVE METHODS

Sedimentary clay mineral assemblages are very often determined by the semi-quantitative method proposed by Biscaye (1965) and the sample preparation method described in detail by Petschick *et al.* (1996). Using these methods involves too many assumptions (*e.g.* the whole clay fraction consists of clay minerals) and contains too many sources of error (*e.g.* for the separation by settling tube or centrifuge) to calculate sediment or mineral fluxes. The empirically-deduced coefficients for the single basal peaks are internally and externally consistent for clay mineral-group investigations of oceans all over the world, but do not reflect different assemblages of the compositionally-variable clay minerals, such as the chlorite group with Fe-rich and Fe-poor phases. Nevertheless, it has served the marine geology community well for more than 30 years while other processes for the rapid investigation of clay mineral assemblages, such as the method proposed by Glass (*c.f.* Hughes *et al.*, 1994), have barely made an impact on marine geology.

In Table 5 the QUAX-determined clay minerals content of three of eight clay fractions of the investigated CMS clays is compared with data based on Biscaye factors. The amount of clay minerals from the QUAX investigation must be normalized to 100% and combined into the four clay mineral groups used by Biscaye (1965). Some of the samples have produced a very similar content for the four different clay mineral groups, but some did not. The example in which our values differ most is beidellite. The Biscaye factors led to much larger kaolinite and chlorite contents than recognized by the QUAX analysis (Table 5).

Tabulated quartz and carbonate mineral contents are based on standard mixing curves and integrated peak-area intensities for the oriented samples (Table 5). Ratios of the integrated peak intensity of quartz, feldspar, carbonate and pyroxene *vs.* the integrated peak intensity of MoS_2 as an internal standard also support the quantification for these minerals by QUAX (compare Tables 5 and 2).

CONCLUSIONS

The clay-sized fraction of the CMS reference materials contain minor to significant amounts of impurities. Some of the CMS reference materials could only be incorporated into the QUAX database after extensive treatment. The reference clays added to the database improved the performance of the QUAX quantification procedure significantly. The bulk mineralogical composition of Arctic Ocean sediments can now be investigated with more precision, leading, for example, to detailed maps of the distribution of clay minerals in surface sediments (Figure 6). A widely-used
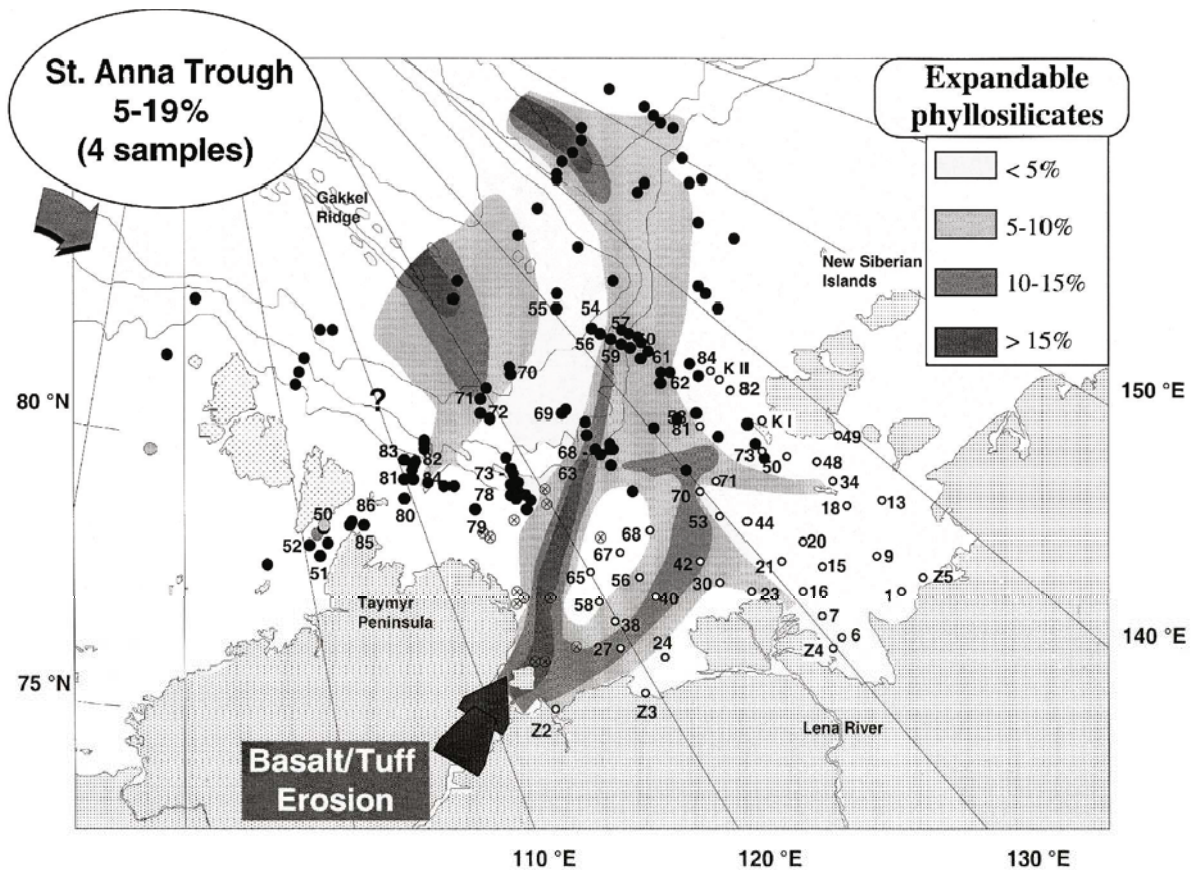
Figure 6. Map of the Laptev Sea, Siberia. Distribution of surface samples recovered by *RV Polarstern* and Russian research vessels under the auspices of the German Polar Research Programs at the Alfred Wegener Institute, Bremerhaven and Potsdam, and the Laptev Sea Project (Stein *et al.*, 1996; Kassens *et al.,* 1999). Expandable clay minerals content in the bulk sediment (mainly nontronites and smectites in the western region and montmorillonites in the eastern region): ○ Sample locations of the Transdrift I expedition in 1993 with *RV Ivan Kireyev*: ● sampling location sets ARK-IX/4 and ARK-XI/1 from cruises of *RV Polarstern* 1993 and 1995, respectively. ⊗ Additional surface samples from the Laptev Sea Project provided by T. Müller-Lupp (GEOMAR, Kiel). Different shades of gray for the sampling locations in the eastern Kara Sea and the Vilkitsky Strait are related to mineral contents, as in the map legend. All other contents are <5%.

semi-quantitative determination of the clay mineral composition of the clay-sized fraction (Biscaye, 1965) was compared to the QUAX records and the differences reported in Table 5. While the calculation of mineral contents of sediments and, in particular clay mineral flux data, is biased by the inconsistency of semi-quantitative clay mineral determination, by the various preparation techniques, and by grain size separation techniques, a QUAX analysis of the bulk sediment is one way to improve the calculations of flux rates, the most important input for paleo-oceanographic reconstructions. The more precise data on the impurities of CMS clays will help in further studies.

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