

DETERMINATION OF EXCHANGEABLE CALCIUM OF CALCAREOUS AND GYPSIFEROUS BENTONITES

REINER DOHRMANN^{1,*} AND STEPHAN KAUFHOLD²

¹ Bundesanstalt für Geowissenschaften und Rohstoffe (BGR)/Landesamt für Bergbau, Energie und Geologie (LBEG),
Stilleweg 2, D-30655 Hannover, Germany

² Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Stilleweg 2, D-30655 Hannover, Germany

Abstract—The aim of the present study was to find methodological tools to obtain reasonable results for exchangeable Ca^{2+} of gypsiferous bentonites. Cation exchange capacity (CEC) is an important property of clays. Numerous methods for calculating CEC and exchangeable cations exist; determination of exchangeable Ca^{2+} fails, however, when gypsiferous clays are examined because gypsum is dissolved throughout the exchange experiment, which in turn increases measurable Ca^{2+} concentrations. Several new methods ($\text{AgTU}_{\text{calcite}}$, $\text{CoHex}_{\text{calcite}}$, and $\text{Cu-trien}_{5 \times \text{calcite}}$) have been developed to overcome a similar problem occurring with calcite by using exchange solutions saturated with respect to calcite prior to the experiment. In the present study these three solutions were also pre-treated with gypsum and labeled $\text{AgTU}_{\text{CcGp}}$, $\text{CoHex}_{\text{CcGp}}$, and $\text{Cu-trien}_{5 \times \text{CcGp}}$. The special solutions were applied first to a gypsum- and calcite-free bentonite with known reference values for exchangeable Ca^{2+} . The resulting exchangeable Ca^{2+} values obtained did not match with reference values. The solutions were then applied to natural calcareous and gypsiferous bentonites but only the proposed $\text{AgTU}_{\text{CcGp}}$ test method was successful. The performance of $\text{AgTU}_{\text{CcGp}}$ was relatively poor when applied to calcareous non-gypsiferous bentonites, the third group of test materials. Reasonable values for exchangeable Ca^{2+} of gypsiferous clays were obtained using a combination of two separate results: (1) calcite saturation of exchange solution (e.g. $\text{Cu-trien}_{5 \times \text{calcite}}$) and (2) quantification of gypsum with suitable mineralogical methods. Result 1 eliminates errors caused by calcite dissolution though it is still incorrect because it contains significant amounts of Ca^{2+} from gypsum dissolution. After proving that gypsum was completely dissolved during the exchange experiment, result 2 was used to subtract the theoretical Ca^{2+} portion of gypsum from result 1. The initial concentration of gypsum of the samples studied was <1 wt.%, typical of many commercial bentonites. Using this combined procedure the sum of exchangeable cations is very close to the CEC, though it still exceeds the CEC by, on average, 3%, which is a satisfactory improvement. The resulting exchangeable Ca^{2+} values can be considered as operationally correct using this approach. Ca^{2+} saturation (Ca/CEC in %) of seven gypsiferous bentonites ranges from 1 to 69%.

Key Words— $\text{AgTU}_{\text{CcGp}}$ Method, Bentonites, Gypsiferous Clays, CEC, $\text{CoHex}_{\text{CcGp}}$ Method, $\text{Cu-trien}_{5 \times \text{CcGp}}$ Method, Exchangeable Calcium.

INTRODUCTION

The performance of clays in natural and geotechnical processes with respect to swelling and sorption processes, for example, is determined by their ability to exchange cations. In particular, the extent of swelling and shrinking upon addition or loss of water by swelling clays such as bentonites is controlled by the proportion of mono- to bivalent cations. In any clay or soil such cations can be measured using cation exchange capacity (CEC) methods which also extract more or less readily soluble minerals such as halite, gypsum, or calcite that are typically present, such as in saline soils (Rhoades, 1996) and clay formations (OECD, 2009).

Exchangeable cation results proved to be erroneous if such partly soluble minerals are present because they react with the exchange solutions during the CEC experiment: “The accurate determination of exchangeable cations in saline and calcareous soils is clearly compromised because of this problem of quantitatively separating soluble or sparingly soluble from exchangeable cations during the extraction procedure by any method” (Sumner and Miller, 1996). Several CEC methods have been developed to measure or calculate the actual exchange population of calcareous and gypsiferous clays (e.g. Hissink, 1923; Tobia and Milad, 1956; Bascomb, 1964; Neal, 1977; Deller, 1981); all of the approaches failed. Dohrmann and Kaufhold (2009) summarized the possibilities and limitations of methodological approaches to overcome the problem. The weaknesses, however, of the simplest approach for correction of ‘inflated exchangeable’ Ca^{2+} values were not discussed: why is a simple subtraction misleading for calcareous, gypsiferous, and saline clays? The simplest approach would be a subtraction of the measured

* E-mail address of corresponding author:
reiner.dohrmann@lbeg.niedersachsen.de
DOI: 10.1346/CCMN.2010.0580108

exchangeable cations Na^+ , K^+ , and Mg^{2+} from the CEC to give 'corrected exchangeable' Ca^{2+} in the following way:

$$\text{CEC} - \text{Na}_{\text{exc}}^+ - \text{K}_{\text{exc}}^+ - \text{Mg}_{\text{exc}}^{2+} = \text{Ca}_{\text{exc}}^{2+} \quad (1)$$

with Na_{exc}^+ = exchangeable Na^+ , K_{exc}^+ = exchangeable K^+ , $\text{Mg}_{\text{exc}}^{2+}$ = exchangeable Mg^{2+} , and $\text{Ca}_{\text{exc}}^{2+}$ = exchangeable Ca^{2+} . Because gypsiferous or calcareous clays may contain soluble salts (*e.g.* NaCl) in the form of minerals or electrolyte-rich pore fluids, such an approach will be misleading. Two typical examples from soil-science and engineered-barrier studies are reported here: Florea and Al-Joumaa (1998) reported on the genesis and classification of gypsiferous soils from Syria and suggested that direct determination of all cations was impossible and calculated the sum of $\text{Ca}_{\text{exc}}^{2+} + \text{Mg}_{\text{exc}}^{2+}$ by subtraction of Na_{exc}^+ and K_{exc}^+ from the CEC. Most soils were dominated almost entirely by bivalent cation. In one profile (P21, south of Abu Hammad) however, Na^+ -saturation reached values of 17–28% of all exchange sites although the samples contained both calcite (22–33 wt.%) and gypsum (2–25 wt.%). The 'Na⁺ saturation' was caused by the presence of soluble NaCl salts and represents a mixture of Na_{exc}^+ and sodium from dissolution of soluble salts (Na_{dis}^+).

Kaufhold and Dohrmann (2008) performed colloidal detachment experiments on bentonites and proved the presence of significant amounts of dissolved chloride (mainly related to Na_{dis}^+) in the pore water of 13 of 38 samples. If a simple subtraction calculation were applied to one of the 13 electrolyte-rich samples, the resulting $\text{Ca}_{\text{exc}}^{2+}$ values would be systematically underestimated and the error would be scarcely identified:

$$\text{CEC} - (\text{Na}_{\text{exc}}^+ + \text{Na}_{\text{dis}}^+) - \text{K}_{\text{exc}}^+ - \text{Mg}_{\text{exc}}^{2+} = \text{Ca}_{\text{exc}}^{2+} \quad (2)$$

The larger the Na_{dis}^+ , the less $\text{Ca}_{\text{exc}}^{2+}$ is obtained. If Na_{dis}^+ is not identified the underestimation of $\text{Ca}_{\text{exc}}^{2+}$ cannot be identified as long as $\text{Na}_{\text{dis}}^+ \leq \text{Ca}_{\text{exc}}^{2+}$. The error becomes apparent if Na_{dis}^+ exceeds $\text{Ca}_{\text{exc}}^{2+}$, resulting in negative $\text{Ca}_{\text{exc}}^{2+}$ values. The subtraction method described is, therefore, insufficient. One must distinguish between Na_{exc}^+ and Na_{dis}^+ and that distinction requires operationally correct $\text{Ca}_{\text{exc}}^{2+}$ values.

Why is an initial washing procedure misleading for such clays? A typical pre-treatment for removal of soluble minerals or electrolyte-rich pore water of clays is a simple washing procedure using deionized water, followed by centrifugation or dialysis. Such treatment is not suitable for preparing a clay which should be examined in order to describe the actual exchange population of the clay sample because the initial exchange population will be modified during any washing procedure. Cation exchange is a very quick and, at least for natural cations such as Na^+ or Ca^{2+} , reproducible process. If the samples were washed with deionized water then gypsum and/or calcite would be (at least partly) dissolved immediately, leading to an

increased Ca^{2+} concentration and instantaneously to a cation exchange competition in a way that monovalent cations and Mg^{2+} would be desorbed and Ca^{2+} would be adsorbed. All desorbed cations would be removed together with the washing solution. The final product would be clay that would have a modified exchange population. The extent of such a modification depends on the washing techniques and the composition of the samples. Dohrmann (2006d) reported significant changes when ammonium-saturated calcareous clays were subjected to such a washing procedure. With increasing calcite content the $\text{NH}_4^+:\text{Ca}^{2+}$ ratio decreased to ~0.5 for a clay with 15 wt.% calcite although the aim of the washing process was removal of excess ammonium acetate solution which was used to prepare the homoionic NH_4^+ clays.

What other options exist? The first successful method for determining operationally correct $\text{Ca}_{\text{exc}}^{2+}$ of calcareous clays is based on a silver-thiourea complex (AgTU) (Dohrmann, 2006c) where the exchange solution was saturated with calcite before the CEC experiment ($\text{AgTU}_{\text{calcite}}$). During the exchange procedure, $\text{Ca}_{\text{exc}}^{2+}$ was exchanged for silver-thiourea index cations and further dissolution of calcite of a given calcareous sample was largely (97%) prevented.

Dohrmann and Kaufhold (2009) proposed three new methods which are less laborious than $\text{AgTU}_{\text{calcite}}$ and concluded that all three ($\text{Cu-trien}_{\text{calcite}}$, $\text{CoHex}_{\text{calcite}}$, and $\text{Cu-trien}_{5 \times \text{calcite}}$) allowed the determination of operationally correct $\text{Ca}_{\text{exc}}^{2+}$ but fail if gypsum is present. The same holds true for the $\text{AgTU}_{\text{calcite}}$ method (Dohrmann, 2006c).

How could a method for detecting $\text{Ca}_{\text{exc}}^{2+}$ of gypsiferous clays be designed? In the present study, three different exchange solutions ($\text{AgTU}_{\text{calcite}}$, $\text{CoHex}_{\text{calcite}}$, and $\text{Cu-trien}_{5 \times \text{calcite}}$) were treated with gypsum to prevent further gypsum dissolution during contact with gypsiferous clay. The methods are termed $\text{AgTU}_{\text{calcite}+\text{gypsum}}$ ($\text{AgTU}_{\text{CcGp}}$), $\text{Cu-trien}_{5 \times \text{calcite}+\text{gypsum}}$ ($\text{Cu-trien}_{5 \times \text{CcGp}}$), and $\text{CoHex}_{\text{calcite}+\text{gypsum}}$ ($\text{CoHex}_{\text{CcGp}}$). Furthermore, a correction procedure was developed, based on measured exchangeable cations and quantitative mineral analysis.

MATERIALS AND METHODS

Samples used for the development of the CEC test methods

Pure, fine-grained natural calcite (originally cm–dm sized clear crystals from an unknown location), pure, fine-grained gypsum (Poland), and a non-gypsiferous and non-calcareous bentonite (<2 mm, Milos, Greece) were used to evaluate the suitability of gypsum saturation experiments of the exchange solutions. The quantitative mineralogical composition and layer-charge density of the Milos bentonite (SP-4) was described by Dohrmann (2006b) and the exchangeable cations and

CEC (107 meq/100 g using $\text{Cu-trien}_{5 \times \text{calcite}}$) by Dohrmann and Kaufhold (2009). Artificial mixtures (Table 1) of this bentonite with (1) gypsum (10–50 wt.%) and (2) calcite + gypsum (10 and 20 wt.%, respectively) were produced by weighing the materials directly into centrifuge tubes.

Samples used for the application assessment of the test methods

The new exchange solutions $\text{AgTU}_{\text{CcGp}}$, $\text{Cu-trien}_{\text{CcGp}}$, and $\text{CoHex}_{\text{CcGp}}$ were tested using a set of (1) three calcareous, gypsum-free bentonites, and (2) three calcareous and gypsiferous bentonites (Table 1) with small gypsum contents (<1 wt.%) which were characterized by Ufer *et al.* (2008) for quantitative mineralogical composition, by Dohrmann and Kaufhold (2009) for CEC and exchangeable cations, and by Kaufhold and Dohrmann (2008) for anionic composition of aqueous extracts.

Samples used for evaluation of the correction procedure for $\text{Ca}_{\text{exc}}^{2+}$

A correction procedure for $\text{Ca}_{\text{exc}}^{2+}$ was developed in the present study which is based on measured exchangeable cations and quantitative mineral analysis. To evaluate the procedure, four additional gypsiferous bentonites (Table 1) were chosen. The samples were characterized in the same way as the samples used for the application assessment of the test methods. Gypsum concentrations ranged from 0.2 to 0.8 wt.% and the

Table 1. Concentration (wt.%) of calcite and gypsum in artificial mixtures with bentonite and in natural bentonites.

Sample	Calcite	Gypsum
Samples used for development of test methods		
Milos bentonite SP-4		
SP-4 + 10% gypsum		10.0
SP-4 + 20% gypsum		20.0
SP-4 + 50% gypsum		50.0
SP-4 + 10% calcite + 10% gypsum	10.0	10.0
SP-4 + 20% calcite + 20% gypsum	20.0	20.0
Samples used for evaluation of test methods		
B01	0.9	
B05	5.4	0.8
B07	1.3	
B08	0.9	0.3
B09	8.0	0.3
B10	0.6	
Samples used for evaluation of correction procedure for exchangeable Ca^{2+}		
B12	0.9	0.3
B16		0.4
B20	0.4	0.6
B27	0.7	0.2

average statistical error calculated by the Rietveld software BGMN (Bergmann, 1998) was 0.07 wt.% (1σ).

The reaction products of bentonites after 2 h of exchange with $\text{Cu-trien}_{5 \times \text{calcite}}$ were controlled for any possible remaining gypsum using X-ray powder diffraction (XRD). The analyses were performed after centrifugation of the slurry, decantation of the clear supernatant, drying of this material at 60°C, and homogenization. No further washing was applied to avoid gypsum dissolution. The XRD analysis was performed on a Seifert 3003 TT using Co radiation, variable primary slit, 10 mm radiated sample length, diffracted-beam graphite monochromator, and scintillation counter. Measuring conditions were 30 s/step, step size of 0.02°, and range of 10–17°2 θ .

Correction procedure for water content

The bentonites were oven dried at 60°C. In parallel drying analyses, the water loss up to 105°C (oven drying for 4 days) was determined. The difference between 60°C and 105°C represented the mass of adsorbed water and was used to recalculate the mass in each experiment in a way that all results were referred to 105°C dry mass. Pure calcite and gypsum were air dried and no correction for water content was performed.

Preparation of exchange solutions

(A) *Silver-thiourea method with calcite and gypsum saturation: $\text{AgTU}_{\text{CcGp}}$.* 10 g of fine-grained gypsum was added to 2 L of $\text{AgTU}_{\text{calcite}}$ solution in a beaker which was prepared as described by Dohrmann (2006c). This mixture was placed in an ultrasonic bath for 30 min. To minimize temperature effects on gypsum solubility the solution was stirred for another 30 min with a magnetic stirrer. After switching off the stirrer, gypsum which was not dissolved was allowed to settle overnight.

The laborious washing procedure which is required to avoid inflated CEC values caused by excess adsorption of AgTU cations was not performed because the focus of the study was to develop a method for improved $\text{Ca}_{\text{exc}}^{2+}$ determination. The $\text{AgTU}_{\text{CcGp}}$ CEC data are, therefore, not reported.

(B) *Cu(II)triethylenetetramine with calcite and gypsum saturation: $\text{Cu-trien}_{5 \times \text{CcGp}}$.* 10 g of fine-grained gypsum was added to 2 L of $\text{Cu-trien}_{5 \times \text{calcite}}$ solution in a beaker which was prepared as described by Dohrmann and Kaufhold (2009). Gypsum saturation was performed exactly as described in procedure A.

(C) *Co(III)hexamine with calcite and gypsum saturation: $\text{CoHex}_{\text{CcGp}}$.* 10 g of fine-grained gypsum was added to 2 L of $\text{CoHex}_{\text{calcite}}$ solution in a beaker which was prepared as described by Dohrmann and Kaufhold (2009). Gypsum saturation was performed exactly as described in procedure A.

Exchange experiments and determination of cation concentrations

Exchange experiments and elemental analysis were performed in a thermo-constant laboratory (23°C) as follows. First, samples were weighed into centrifuge tubes. Depending on the concentration and valence of the index cations the following sample masses were used: 200 and 300 mg for AgTU_{CcGp} (A), 400 and 600 mg for Cu-trien_{5 × CcGp} (B), and 800 and 1200 mg for CoHex_{CcGp} (C). Subsequently, 50.0 mL of exchange solution A, B, or C was added to samples in centrifuge tubes. The resulting slurries were shaken end-over-end for 2 h followed by centrifugation. Aliquots of the clear supernatant were diluted (1:10–1:50) using HNO₃ solution, followed by inductively coupled plasma (ICP) analysis of exchangeable cations and index cations. AgTU_{CcGp} (A) contains a 0.1 M ammonium acetate buffer. Dilution of 1:50 was chosen for AgTU_{CcGp} (A) because the total electrolyte concentration of that solution is much greater than in the other two. Two blanks (whole experiment but without addition of sample) were added to each series of experiments to serve as a control for the index cation concentration.

The precision of the dilution was measured using a 100.0 mg/L Cu standard in duplicate. The differences between the measured concentrations of this 100.0 mg/L Cu standard and the nominal concentration were quantified. The inductively coupled plasma results of all the samples were corrected if the deviation exceeded 1.5%.

An additional correction was necessary for the calculation of Ca_{exc}²⁺. Here the Ca²⁺ concentration of the blank (~500–1100 mg/L Ca²⁺ depending on the method used) had to be subtracted because it contained the initial Ca²⁺ loading which stems from treatment with calcite and gypsum. Including a control for the Ca²⁺ concentrations of the blank solutions with each new measurement series and use of these values for the correction procedure is recommended.

Quantitative criteria for evaluation of CEC and exchangeable cation data

For comparison of measured and reference results, criteria had to be defined to assess those differences which can be accepted. Dohrmann and Kaufhold (2009) reported the statistical errors between different methods (CoHex_{calcite} vs. Cu-trien_{5 × calcite}) using the same samples in the same laboratory and listed the individual errors for CEC and for all exchangeable cations. The errors ($\pm 3\sigma$) increased with the measured ranges from K_{exc}⁺ over Mg_{exc}²⁺, Ca_{exc}²⁺, Na_{exc}⁺, and the CEC. If a large range is considered, such as for Na⁺ (0–70 meq/100 g), the absolute error was smaller for the lower concentrations. For 0–10/10–25/25–70 meq/100 g Na_{exc}⁺ the errors were $\pm 0.2/1.3/3.9$ meq/100 g, whereas the overall error for the whole range was ± 2.8 meq/100 g. The errors were unknown for the test methods which required estimation of reasonable ranges so $\pm 10\%$ (relative)

difference for values >2 meq/100 g and ± 0.5 meq/100 g for smaller values were chosen. Data that differed by more than these ranges were assessed as non-reliable and are marked in italics (Tables 2–4). The parameter ‘sum of exchangeable cations’ was also assessed as non-reliable if at least one of the exchangeable cations was assessed as non-reliable.

RESULTS AND DISCUSSION

In the present study, the Cu-trien_{5 × calcite} data of all bentonite samples used were taken from Dohrmann and Kaufhold (2009). These data were considered as reference values because that was the best method tested in that study.

Development of the test methods

Evaluation of CEC test methods can be performed by comparing experimental results with reference values using standard materials (Milos bentonite SP-4 in this case). In addition, the results of artificial mixtures of this bentonite with gypsum \pm calcite can be compared with the same reference values of the pure bentonite assuming that calcite and gypsum have, in principle, no detectable quantities of exchangeable cations and CEC (Table 2).

The results of these mixtures were hence calculated in a way that only the bentonite mass was considered because bentonite was the only component of the admixtures that had a realistic contribution to CEC and exchangeable cation values. Using this simplification, reference values were unchanged which allowed fast comparison between the theoretical and the measured results and a circuitous recalculation of theoretical reference values of each mixture was avoided.

The results show that only one data set was entirely identical (within $\pm 10\%$ relative difference) to the reference values (Table 2): Cu-trien_{5 × CcGp} (B) in combination with pure bentonite SP-4 (0.6 g sample mass). The results of all other experiments differed in the case of at least of one parameter by $>10\%$ from the reference values. The most critical parameter was Ca_{exc}²⁺. For Cu-trien_{5 × CcGp} (B) and CoHex_{CcGp} (C), the results were systematically too low, ranging from 9–33 meq/100 g and 1–31 meq/100 g, respectively, instead of ~ 37 meq/100 g. For these two methods, all other parameters were close to the reference values; the CEC, however, was slightly but systematically smaller by 3% for Cu-trien_{5 × CcGp} (B) and greater by 5% for CoHex_{CcGp} (C). Although large quantities of dissolved Ca²⁺ were present in the exchange solutions, the selectivities of the exchange complexes were still great enough to assure ‘complete’ cation exchange (*i.e.* close to 100%) by the index cations. The results were more differentiated using the AgTU_{CcGp} (A) method. In four of 12 experiments, reasonable Ca_{exc}²⁺ values were recorded. In three experiments Ca_{exc}²⁺ results were significantly ($>10\%$) greater and in five experiments

$\text{Ca}_{\text{exc}}^{2+}$ results were smaller than the reference values. The overall range was 25–59 meq/100 g $\text{Ca}_{\text{exc}}^{2+}$. Most $\text{Na}_{\text{exc}}^{+}$ and $\text{K}_{\text{exc}}^{+}$ and some $\text{Mg}_{\text{exc}}^{2+}$ results were smaller than required, though this deviation cannot be explained.

Systematic deviation and scattering of $\text{Ca}_{\text{exc}}^{2+}$ values

For all test methods, $\text{Ca}_{\text{exc}}^{2+}$ showed relatively large errors that may result from two sources.

Table 2. Results of saturation tests of exchange solution with calcite and gypsum for bentonite SP-4 and admixtures thereof with calcite and/or gypsum. Results were recalculated in a way that only the bentonite sample mass was considered.

Sample	Bentonite —— Mass (g) ——	Calcite ——	Gypsum ——	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Sum	CEC	Sum-CEC
				(meq/100 g)						
Cu-trien ₅ × calcite reference values										
SP-4	0.400			24.2	1.4	46.2	37.2	109.2	109	0.7
SP-4	0.601			24.6	1.5	46.1	37.1	109.4	106	3.4
AgTU _{CcGp} (A)										
SP-4	0.201			24.5	−0.5	50.7	50.2	124.9	n.a.	n.a.
SP-4	0.300			23.5	0.4	50.5	33.5	107.9	n.a.	n.a.
SP-4 + 10 % gypsum	0.200		0.021	21.7	0.2	45.4	33.1	100.4	n.a.	n.a.
SP-4 + 10 % gypsum	0.301		0.030	21.7	0.6	45.2	26.3	93.8	n.a.	n.a.
SP-4 + 20 % gypsum	0.201		0.040	19.4	0.2	41.6	36.1	97.3	n.a.	n.a.
SP-4 + 20 % gypsum	0.301		0.060	19.9	0.9	41.6	27.9	90.3	n.a.	n.a.
SP-4 + 50 % gypsum	0.200		0.100	15.9	0.2	33.6	29.0	78.7	n.a.	n.a.
SP-4 + 50 % gypsum	0.300		0.151	15.9	0.4	33.6	25.4	75.3	n.a.	n.a.
SP-4 + 10 % calcite + 10 % gypsum	0.200	0.020	0.020	19.9	0.2	42.0	59.0	121.1	n.a.	n.a.
SP-4 + 10 % calcite + 10 % gypsum	0.300	0.030	0.030	19.9	0.7	42.0	35.6	98.2	n.a.	n.a.
SP-4 + 20 % calcite + 20 % gypsum	0.201	0.040	0.040	17.0	0.4	35.6	45.5	98.5	n.a.	n.a.
SP-4 + 20 % calcite + 20 % gypsum	0.300	0.060	0.060	17.1	0.6	35.9	37.0	90.6	n.a.	n.a.
CoHex _{CcGp} (C)										
SP-4	0.801			24.3	1.5	48.5	30.7	105.0	113	−8.4
SP-4	1.201			23.9	1.5	47.5	30.9	103.8	110	−5.8
SP-4 + 10 % gypsum	0.720		0.080	24.4	1.5	48.6	11.7	86.2	114	−27.3
SP-4 + 10 % gypsum	1.081		0.120	24.5	1.5	48.1	4.5	78.6	109	−30.6
SP-4 + 20 % gypsum	0.640		0.160	24.8	1.5	48.6	7.0	81.9	109	−26.8
SP-4 + 20 % gypsum	0.960		0.240	24.2	1.5	48.4	1.1	75.2	111	−36.2
SP-4 + 50 % gypsum	0.400		0.400	24.6	1.6	48.9	4.7	79.8	116	−36.3
SP-4 + 50 % gypsum	0.600		0.600	24.9	1.5	48.9	5.2	80.5	112	−31.7
SP-4 + 10 % calcite + 10 % gypsum	0.640	0.080	0.080	24.6	1.5	48.7	16.7	91.5	116	−24.1
SP-4 + 10 % calcite + 10 % gypsum	0.961	0.120	0.120	24.3	1.5	48.2	9.0	83.0	113	−29.6
SP-4 + 20 % calcite + 20 % gypsum	0.480	0.160	0.160	24.0	1.5	48.8	12.2	86.5	116	−29.5
SP-4 + 20 % calcite + 20 % gypsum	0.720	0.240	0.240	24.4	1.5	48.5	5.9	80.3	116	−35.2
Cu-trien ₅ × CcGp (B)										
SP-4	0.400			24.9	1.5	47.0	32.8	106	105	1.2
SP-4	0.600			24.5	1.4	46.8	34.6	107	103	4.0
SP-4 + 10 % gypsum	0.361		0.040	24.8	1.4	47.5	12.9	87	104	−17.5
SP-4 + 10 % gypsum	0.541		0.060	24.1	1.4	46.8	12.6	85	105	−20.2
SP-4 + 20 % gypsum	0.320		0.080	24.1	1.3	46.7	9.4	82	105	−23.3
SP-4 + 20 % gypsum	0.481		0.120	24.3	1.4	47.3	10.2	83	103	−19.3
SP-4 + 50 % gypsum	0.200		0.200	24.0	1.2	48.0	21.8	95	102	−6.6
SP-4 + 50 % gypsum	0.300		0.300	24.5	1.3	47.3	14.5	88	102	−14.4
SP-4 + 10 % calcite + 10 % gypsum	0.321	0.040	0.040	23.8	1.4	46.7	21.3	93	105	−11.5
SP-4 + 10 % calcite + 10 % gypsum	0.480	0.060	0.060	23.6	1.4	46.8	19.9	92	103	−11.6
SP-4 + 20 % calcite + 20 % gypsum	0.241	0.080	0.080	23.6	1.2	47.4	13.6	86	107	−20.7
SP-4 + 20 % calcite + 20 % gypsum	0.361	0.120	0.120	23.7	1.3	46.6	12.9	85	107	−22.0

The reference values (Cu-trien₅ × calcite data taken from Dohrmann and Kaufhold, 2009) are shown in the first two rows. Non-reliable data are marked in italics. Negative exchangeable cation concentrations are reported to demonstrate how critical calculation of exchangeable cations is in such electrolyte-rich solutions; physicochemically, these negative concentrations have no meaning.

n.a. = not analyzed.

Sum = sum of exchangeable cations.

(1) *Scattering*. Calcite and particularly gypsum saturation of exchange solutions yielded very large initial Ca^{2+} concentrations of the exchange solutions (~500–1100 mg/L). The $\text{Ca}_{\text{exc}}^{2+}$ which was desorbed during the exchange experiment made up only 1–160 mg/L. In theory, scattering of *e.g.* 1% in ICP analysis of $\text{AgTU}_{\text{CcGp}}$ (A) solution would cause an error of ~5–8 meq/100 g depending on the sample mass. In $\text{CoHex}_{\text{CcGp}}$ (C) and $\text{Cu-trien}_{5 \times \text{CcGp}}$ (B) solutions, greater sample masses were applied which of course reduced the effect of the hypothetically assumed

scattering of ICP results on calculated meq/100 g values. Scattering of 1% would then have resulted in errors of 2–4 meq/100 g. This effect was significantly larger for the exchange solutions tested in the present study than in the case of only calcite-saturated exchange solutions such as $\text{Cu-trien}_{5 \times \text{calcite}}$. The initial Ca^{2+} concentration of $\text{Cu-trien}_{5 \times \text{calcite}}$ accounted for ~10 mg/L which is at least 50 times less than in $\text{Cu-trien}_{5 \times \text{CcGp}}$ (B).

(2) *Systematic errors*. Conceivably, the precipitation of sulfates may have occurred as a result of reactions of the

Table 3. Results of saturation tests of exchange solution with calcite and gypsum for three calcareous and gypsum-free bentonites.

Sample	Bentonite Mass (g)	Calcite – (Wt.%) –	Gypsum	Na^+	K^+	Mg^{2+}	Ca^{2+} (meq/100 g)	Sum	CEC	Sum-CEC
$\text{Cu-trien}_{5 \times \text{calcite}}$ reference values										
B01	0.400	0.9		14.9	1.7	42.6	34.1	93.3	93.0	0.3
B01	0.600	0.9		14.9	1.6	42.3	34.2	93.0	92.3	0.7
$\text{AgTU}_{\text{CcGp}}$										
B01	0.200	0.9		14.4	0.9	46.1	48.5	109.9	n.a.	n.a.
B01	0.300	0.9		14.6	0.8	46.2	50.0	111.6	n.a.	n.a.
$\text{CoHex}_{\text{CcGp}}$										
B01	0.800	0.9		14.8	1.7	44.2	30.4	91.1	102.4	-11.3
B01	1.200	0.9		14.4	1.7	43.6	29.4	89.1	98.8	-9.7
$\text{Cu-trien}_{5 \times \text{CcGp}}$										
B01	0.400	0.9		14.4	1.5	42.4	30.3	88.6	91.7	-3.1
B01	0.600	0.9		14.0	1.6	42.5	27.2	85.3	89.7	-4.4
$\text{Cu-trien}_{5 \times \text{calcite}}$ reference values										
B07	0.401	1.3		62.1	4.2	3.1	21.7	91.1	89.3	1.8
B07	0.600	1.3		60.9	4.1	3.0	21.8	89.8	89.3	0.5
$\text{AgTU}_{\text{CcGp}}$										
B07	0.201	1.3		62.5	4.4	5.1	33.5	105.5	n.a.	n.a.
B07	0.300	1.3		61.2	4.2	4.9	26.6	96.9	n.a.	n.a.
$\text{CoHex}_{\text{CcGp}}$										
B07	0.800	1.3		59.5	4.4	4.6	15.3	83.8	95.6	-11.8
B07	1.201	1.3		60.1	4.3	4.3	13.5	82.2	91.3	-9.1
$\text{Cu-trien}_{5 \times \text{CcGp}}$										
B07	0.401	1.3		59.0	4.2	3.7	11.3	78.2	88.1	-9.9
B07	0.601	1.3		57.2	4.1	3.5	16.3	81.1	85.7	-4.6
$\text{Cu-trien}_{5 \times \text{calcite}}$ reference values										
B10	0.401	0.6		26.8	1.6	20.3	42.2	90.9	91.1	-0.2
B10	0.600	0.6		26.7	1.5	20.1	42.0	90.3	90.1	0.2
$\text{AgTU}_{\text{CcGp}}$										
B10	0.200	0.6		26.4	1.5	21.8	47.3	97.0	n.a.	n.a.
B10	0.301	0.6		27.3	1.9	21.9	44.4	95.5	n.a.	n.a.
$\text{CoHex}_{\text{CcGp}}$										
B10	0.800	0.6		26.8	1.7	21.2	37.2	86.9	95.2	-8.3
B10	1.200	0.6		25.8	1.6	20.9	35.9	84.2	90.3	-6.1
$\text{Cu-trien}_{5 \times \text{CcGp}}$										
B10	0.401	0.6		25.6	1.4	20.9	38.5	86.4	85.4	1.0
B10	0.601	0.6		24.9	1.4	20.6	33.4	80.3	85.5	-5.2

The reference values ($\text{Cu-trien}_{5 \times \text{calcite}}$ data taken from Dohrmann and Kaufhold, 2009) of each sample are shown in the first two rows. Non-reliable data are marked in italics. n.a. = not analyzed.

Ca²⁺- and SO₄²⁻-rich exchange solutions with the samples resulted in degraded Ca²⁺ concentrations, and the added during exchange experiments. This should have resulting Ca_{exc}²⁺ values would have been too small. This

Table 4. Results of saturation tests of exchange solution with calcite and gypsum for three calcareous and gypsiferous bentonites.

Sample	Bentonite mass (g)	Calcite – (Wt.%) –	Gypsum –	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺ (meq/100 g)	Sum	CEC	Sum-CEC
Cu-trien ₅ × calcite reference values (erroneous for exchangeable Ca ²⁺)										
B05	0.400	5.4	0.8	12.9	2.2	34.3	50.9	100.3	88.5	11.8
B05	0.600	5.4	0.8	12.7	2.2	33.4	50.4	98.7	89.8	8.9
Combination of Cu-trien ₅ × calcite and correction for gypsum content										
B05				12.8	2.2	33.9	41	90	89.2	1
AgTU _{CcGp}										
B05	0.200	5.4	0.8	12.1	1.5	36.4	46.3	96.3	n.a.	n.a.
B05	0.300	5.4	0.8	12.8	2.1	36.0	43.5	94.4	n.a.	n.a.
CoHex _{CcGp}										
B05	0.801	5.4	0.8	12.8	2.3	34.9	35.2	85.2	90.8	-5.6
B05	1.200	5.4	0.8	12.6	2.2	34.5	31.8	81.1	89.5	-8.4
Cu-trien ₅ × CcGp										
B05	0.401	5.4	0.8	12.4	2.2	34.5	30.8	79.9	88.4	-8.5
B05	0.601	5.4	0.8	12.2	2.1	34.0	33.5	81.8	86.4	-4.6
Cu-trien ₅ × calcite reference values (erroneous for exchangeable Ca ²⁺)										
B08	0.405	0.9	0.3	66.7	0.3	0.5	4.3	71.8	70.4	1.4
B08	0.600	0.9	0.3	65.4	0.3	0.4	4.1	70.2	63.8	6.4
Combination of Cu-trien ₅ × calcite and correction for gypsum content										
B08				66.1	0.3	0.5	1	68	67.1	1
AgTU _{CcGp}										
B08	0.200	0.9	0.3	67.4	0.5	0.9	2.0	70.8	n.a.	n.a.
B08	0.300	0.9	0.3	67.4	0.6	0.9	1.4	70.3	n.a.	n.a.
CoHex _{CcGp}										
B08	0.800	0.9	0.3	65.7	0.4	0.8	-4.1	62.8	60.1	2.7
B08	1.200	0.9	0.3	65.4	0.4	0.8	-5.8	60.8	58.2	2.6
Cu-trien ₅ × CcGp										
B08	0.401	0.9	0.3	61.8	0.2	0.6	-1.8	60.8	63.5	-2.7
B08	0.601	0.9	0.3	63.6	0.2	0.6	2.0	66.4	60.9	5.5
Cu-trien ₅ × calcite reference values (erroneous for exchangeable Ca ²⁺)										
B09	0.400	8.0	0.3	60.2	0.3	1.2	11.5	73.2	66.4	6.8
B09	0.601	8.0	0.3	59.4	0.3	1.2	11.0	71.9	66.8	5.1
Combination of Cu-trien ₅ × calcite and correction for gypsum content										
B09				59.8	0.3	1.2	8	69	66.6	2
AgTU _{CcGp}										
B09	0.201	8.0	0.3	62.1	0.5	1.9	8.2	72.7	n.a.	n.a.
B09	0.301	8.0	0.3	61.8	0.6	1.8	5.5	69.7	n.a.	n.a.
CoHex _{CcGp}										
B09	0.800	8.0	0.3	60.9	0.4	1.8	-1.8	61.3	58.3	3.0
B09	1.201	8.0	0.3	60.0	0.4	1.7	-3.1	59.0	59.3	-0.3
Cu-trien ₅ × CcGp										
B09	0.400	8.0	0.3	58.9	0.1	1.7	-4.9	55.8	60.7	-4.9
B09	0.600	8.0	0.3	58.1	0.1	1.5	4.1	63.8	60.3	3.5

The reference values (Cu-trien₅ × calcite data taken from Dohrmann and Kaufhold, 2009) of each sample are shown in the first two rows. Exchangeable Ca²⁺ reference values have been further corrected for gypsum dissolution based on gypsum content (third row of data); data in this row is used to evaluate plausibility. Due to increased uncertainty of these exchangeable Ca²⁺ values, the plausibility interval was increased by a factor of 2 for values of <2 meq/100 g. Non-reliable data are marked in italics. Negative exchangeable cation concentrations are reported to demonstrate how critical calculation of exchangeable cations is in such electrolyte-rich solutions; physicochemically, these negative concentrations have no meaning. n.a. = not analyzed.

hypothesis could be used to explain the poor quality of Cu-trien₅ × CcGp (B) and CoHex_{CcGp} (C) Ca²⁺_{exc} data (too small) reported above.

Application assessment of the test methods

After the assessment of the test methods with pure non-calcareous and non-gypsiferous bentonite and admixtures of this bentonite with calcite and gypsum, six other bentonites of natural origin were analyzed using the three test methods. Three of these bentonites contained only calcite and the other three bentonites contained both calcite and gypsum (Table 1). In the present paper these bentonites were treated separately because the reference values (Table 3) for non-gypsiferous calcareous bentonites were considered to be correct whereas the Ca²⁺_{exc} reference values of gypsiferous bentonites were clearly incorrect because of gypsum dissolution (Ca²⁺_{dis}).

Calcareous bentonites

None of the CEC approaches enabled reliable recovery of the reference values of the three calcareous but gypsum-free bentonites for Ca²⁺_{exc} (Table 3). In some experiments, Ca²⁺_{exc} data fell within a ±10% difference window, but reproducibility was poor. Only two of 18 values differed by <10% (relative). In most cases the other exchangeable cations – Na⁺_{exc}, K⁺_{exc}, and Mg²⁺_{exc} – as well as the CEC fit within the ranges defined as reasonable.

Calcareous and gypsiferous bentonites

Assessment of the correctness of the Ca²⁺_{exc} results in comparison with any of the applied test or reference methods was complex because even the reference data from Cu-trien₅ × calcite were systematically erroneous. In calcite-saturated exchange solutions gypsum was still soluble (= Ca²⁺_{exc-inflated}). Accordingly, it was first necessary to correct the Ca²⁺_{exc-inflated} reference values for Ca²⁺_{dis} contribution by gypsum: Ca²⁺_{exc-inflated} – Ca²⁺_{dis} = Ca²⁺_{exc}.

Correction of Ca²⁺_{exc-inflated} reference values for Ca²⁺_{dis} contribution by gypsum

Gypsum concentrations of the bentonites studied were known from XRD Rietveld analyses (Ufer *et al.*, 2008) and correlated (R² = 0.82, n = 7) well with sulfate-extraction data (Kaufhold and Dohrmann, 2008). The gypsum contents could be used to calculate the theoretical Ca²⁺_{dis} value caused by gypsum dissolution: 1 wt.% gypsum ≅ 11.8 meq/100 g Ca²⁺_{dis}. Cu-trien₅ × calcite gave Ca²⁺_{exc-inflated} values for samples B05 (0.8 wt.% gypsum), B08, and B09 (0.3 wt.% gypsum each). Accordingly Ca²⁺_{dis} was calculated to give 9.4 meq/100 g, (B05) and 3.5 meq/100 g (B08 and B09), respectively, values which were then used for correlation of Ca²⁺_{dis} values. The corrected Ca²⁺_{exc} values are reported in the rows below the Cu-trien₅ × calcite reference values and labeled: 'Combination of Cu-trien₅ × calcite and correction for gypsum content' (Table 4).

The corrected reference values for Ca²⁺_{exc} had to be checked for plausibility. The most efficient test is the comparison of the sum of exchangeable cations and the CEC. If (1) these parameters are identical (within a few percent); (2) XRD analysis of the reacted samples proves the absence of gypsum; (3) the CEC fits with mineralogical composition as described by Dohrmann (2006a); and (4) no excess anions (in this case other than sulfate) occur in large quantities such as in extracts of saline or alkaline soils, then the data can be assumed to be at least a reasonable measure of the actual exchange population. The results of the correction procedure showed that for each sample (1) the CEC correlated well with the sum of exchangeable cations (Figure 1). (2) The absence of gypsum was proven in the reacted samples. (3) The smectite content (89, 63, and 59 wt.% for B05, B08, and B09, respectively) correlated well with the CEC. The correlation was more a qualitative indication because differences in layer-charge densities of the different smectites present in the different bentonites were not taken into account. (4) The fourth important criterion, however, was also fulfilled because chloride concentrations of these three bentonites were negligible (Kaufhold *et al.*, 2008).

The real advantage of these corrections was evident when corrected data were compared with data using an inappropriate method such as Cu-trien without any pretreatment of the exchange solution to avoid calcite and gypsum dissolution. As expected, the resulting sum of exchangeable cations (Figure 1, open circles, data from Kaufhold *et al.*, 2008) were affected by Ca²⁺_{exc-inflated} values: for B05/B08/B09 they were 67/16/31 meq/100 g instead of 41/1/8 meq/100 g, which were considered as reasonable after all corrections were applied in the present study.

Evaluation of correction procedure for Ca²⁺_{exc}

The correction procedure for Ca²⁺_{exc} was also applied to four other gypsiferous bentonites which were not included in the comparison of the test methods (B12, B16, B20, and B27, see Table 1). After correction, the sum of exchangeable cations also correlated well with the CEC; only one sample (B12) had an inflated sum of exchangeable cations which could be explained by a significant excess of chloride (Kaufhold and Dohrmann, 2008). The other three bentonites (B16, B20, and B27) had negligible chloride concentrations. Although all but one (B12) sample showed a good correlation between the CEC and the sum of exchangeable cations (all data are located on the y = x line within analytical error), the sum of exchangeable cations is systematically too large (on average 2.2 meq/100 g, *i.e.* 3% of the CEC; B12 is not considered here). The difference refers to a theoretical gypsum content of 0.2 wt.% which is as large as the unsystematic scattering of the Rietveld quantification of gypsum of the seven bentonites studied: ±0.2 wt.% (3σ). Based on the data in the present study, it is still unclear whether the systematic

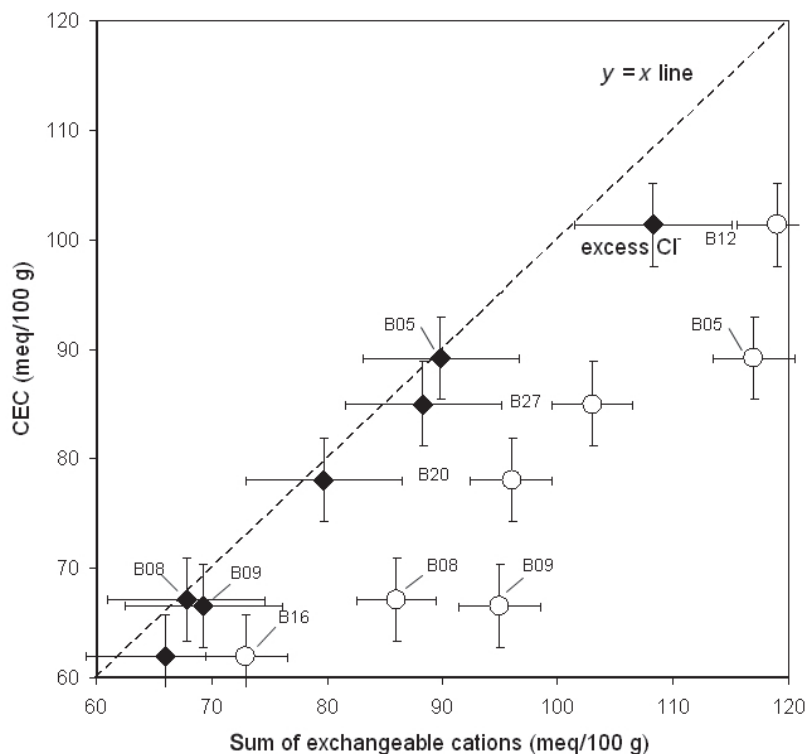


Figure 1. Correlation of the CEC reference data with the sum of exchangeable cations using (1) corrected Ca^{2+} reference values as described in the text (filled diamonds) and (2) an inappropriate method such as Cu-trien (open circles) without any pre-treatment. Error bars (3σ) are based on Dohrmann and Kaufhold (2009). For method 1 the scattering of the gypsum quantification was added (± 2.3 meq/100 g (3σ)) caused by the calculated error of the Rietveld quantification (± 0.2 wt.% (3σ , $n = 7$)).

difference accounting for 2.2 meq/100 g is caused by errors in the Rietveld method or by the exchange procedure, or both.

Evaluation of exchangeable cation and CEC results of test methods using gypsiferous bentonites

The results of the three test methods with calcite and gypsum saturation were evaluated based on the corrected $\text{Ca}_{\text{exc}}^{2+}$ values. In contrast to the artificial mixtures where the $\text{AgTU}_{\text{CcGp}}$ (A) test method failed, the directly measured $\text{AgTU}_{\text{CcGp}}$ (A) Ca^{2+} data of the gypsiferous bentonites were nearly identical to the corrected $\text{Ca}_{\text{exc}}^{2+}$ values; four of six experiments correlated well with the corrected reference values, and the two which failed were relatively close to the $\pm 10\%$ criterion. $\text{CoHex}_{\text{CcGp}}$ (C) failed completely and $\text{Cu-trien}_{5 \times \text{calcite}}$ failed in five of six experiments. Apart from minor deviations of $\text{Mg}_{\text{exc}}^{2+}$ (B09), all other exchangeable cations correlated well with reference data. The CEC results were systematically smaller (by $\sim 10\%$) than the average reference CEC values, the reason for which is unclear.

Correction of $\text{Na}_{\text{exc}}^{+}$ of gypsiferous bentonites using corrected $\text{Ca}_{\text{exc}}^{2+}$

For bentonite B12, a value of 52 meq/100 g of $\text{Na}_{\text{exc}}^{+}$ -inflated was determined and inflation of the $\text{Na}_{\text{exc}}^{+}$

value was caused by the presence of chloride (Figure 1). Using $\text{Ca}_{\text{exc}}^{2+}$ which was corrected for $\text{Ca}_{\text{dis}}^{2+}$ (gypsum dissolution), $\text{Na}_{\text{exc}}^{+}$ could be calculated as 46 meq/100 g by subtraction of $\text{Ca}_{\text{exc}}^{2+}$, $\text{Mg}_{\text{exc}}^{2+}$, and $\text{K}_{\text{exc}}^{+}$ from the CEC. The precision of this doubly corrected $\text{Na}_{\text{exc}}^{+}$ value was of course much less than typically measured $\text{Na}_{\text{exc}}^{+}$ of bentonite free of excess chloride. In general, $\text{Mg}_{\text{exc}}^{2+}$ might also be possibly inflated by chloride but, in the case of the bentonites used in the present study, the chloride-rich samples were largely dominated by $\text{Na}_{\text{exc}}^{+}$.

CONCLUSIONS

The results of this study indicate that none of the three test methods applied provided reasonable $\text{Ca}_{\text{exc}}^{2+}$ values of calcareous and gypsiferous clays. The proposed test method $\text{AgTU}_{\text{CcGp}}$ (A) could be applied successfully for the selected gypsiferous bentonites but not for gypsum-free calcareous bentonites. Still to be proven, however, is whether this method gives reliable values for more heterogeneous samples from other natural clays and soils. The most reliable $\text{Ca}_{\text{exc}}^{2+}$ values of non-saline calcareous and gypsiferous bentonites were obtained by a combination of two different results: (1) calcite saturation of exchange solution (e.g. $\text{Cu-trien}_{5 \times \text{calcite}}$) and (2) quantification of gypsum using XRD (Rietveld method). A correction of

$\text{Ca}_{\text{exc}}^{2+}$ -inflated by subtraction of $\text{Ca}_{\text{dis}}^{2+}$ caused by gypsum dissolution followed and the resulting $\text{Ca}_{\text{exc}}^{2+}$ values could be considered as operationally correct and the resulting $\text{Ca}_{\text{exc}}^{2+}$ saturation (Ca/CEC in %) of the seven gypsiferous bentonites ranged from 1 to 69%.

ACKNOWLEDGMENTS

The authors are grateful to Natascha Schleunig and Wolfgang Glatte for their analytical work. Comments and suggestions by George Christidis and Bruno Lanson were valuable and helped to improve the manuscript.

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(Received 11 May 2009; revised 9 September 2009; Ms. 316; A.E. B. Lanson)