

## **Smectite clay identification and quantification as an indicator of basic igneous rock durability**

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### Abstract

Basic igneous rocks are one of the most used road building materials in South Africa in terms of the aerial extent of their use mainly because approximately 57% of South Africa's surface consists of lithologies with poor road construction material properties rendering the localized Karoo dolerite intrusions the best construction materials available for many road construction projects. Historically examples of such materials with poor durability have been reported and investigated by many authors and current South Africa specifications specifically require consideration of this potential phenomenon. There is however still the need for an accurate, reasonably quick and inexpensive method of determining the durability of materials to identify the variations in durability within any one source of aggregate. The smectite clay content of has been proposed for this task but in recent studies the quantification of the clay mineral contents of typical Karoo basic igneous rock aggregates was problematic. Published works have commonly discussed reasons why quantitative X-ray diffraction analyses of clays and some of the techniques developed to qualify and quantify the clays using X-ray diffraction are problematic. Resent attempts to quantify clay mineralogy as an indication of basic igneous rock aggregate durability proved inconclusive and lead to a comparative study being done on X-ray diffraction results obtained using different techniques and by different laboratories. The findings confirmed what literature suggested and also revealed that proposed specifications based on smectite contents are not feasible due to quantification accuracy exceeding some of the proposed limits.

### Keywords

X-ray diffraction, point counting, smectite, clay identification, aggregate durability.

## **1. Introduction**

Basic igneous rocks are one of the most used road building materials in South Africa in terms of the aerial extent of their use (Netterberg 1994). This is mainly because approximately 57% of South Africa's surface consists of lithologies belonging to the Karoo Supergroup main basin within which sedimentary rocks (tillite, mudrock/shale and sandstone) with poor road construction material properties are predominant. Localized Karoo dolerite intrusions are therefore the best construction materials available for many road construction projects in such areas. Numerous occurrences of Karoo basic igneous rocks with poor durability have, however, also been reported. Research on this topic has been extensive (Orr (1979), Weinert (1980), Haskins and Bell (1995), Dunlevey and Stephens, (1996), Bell and Jermy (2000), Kleyn and Bergh (2008)). Similar durability problems have also been identified in other countries originally including Australia (Cole and Sandy 1980) and the North-western parts of the USA (e.g. West et al. 1970, Higgs (1976)) and more recently in Greece (Rigopoulos et al. 2010), New Zealand (Moon and Jayawardane 2004), Turkey (Korkanc and Tugrul 2004) and Brazil (Gomes and Rodrigues 2007).

The current South Africa specifications that dictate the required durability of basic igneous rock aggregates (based on the Durability Mill Index (DMI) or 10% Fines Aggregate Crushing Tests (10%FACT)) seem to be insufficient to accurately identify all problem materials. The results presented by Leyland et al. (2013) show that materials within a single Karoo dolerite quarry can have significant variations in durability. It is therefore important that an accurate, reasonably quick and inexpensive method of determining the durability of materials is proposed and used during quarrying operations.

Numerous authors have promoted the use of the smectite clay content of materials either as a basic igneous rock durability specification or for use as an input into basic igneous rock durability prediction calculations. This paper discusses the clay content specifications proposed in previous research and the problems encountered when recent studies attempted to quantify the clay mineral contents of typical Karoo basic igneous rock aggregates.

## **2. Suggested smectite clay content specifications**

Higgs (1976) suggested that the total weathering products do not determine the durability of basic igneous rocks, but that the percentage of discrete montmorillonite is relevant. He showed that 11% of discrete montmorillonite is sufficient to cause basalts to degrade but suggested that additional testing (X-Ray Diffraction (XRD), wetting/drying and ethylene glycol tests) should be performed if a petrographic examination shows more than 5% discrete montmorillonite. These statements are unclear and do not suggest rejection or acceptance of a material based on the clay mineral content.

Van Atta and Ludowise (1976) noted that alteration products other than smectites only weaken the rock mechanically but that smectites and the textural distribution thereof determine the rate of degradation of basalt. This illustrates why mechanical strength tests are not sufficient to determine the durability of basic igneous rocks, since rocks that have sufficient strength can be of poor durability if the smectite distribution is unfavourable. They found that when unweathered rocks had a smectite content of less than 10% very little further smectite development occurred with weathering. Petrographic examinations of (benzidine) stained or unstained thin sections were prescribed to determine the quantity and textural distribution of smectites. Since the smectite mineral saponite is not stained by benzidine, supplemental XRD analyses are required if staining does not reveal smectites (van Atta and Ludowise 1976). XRD analyses can, however, only indicate the presence of smectites and not their textural distribution.

Cole and Sandy (1980) derived a secondary mineral index that requires accurate determination of the total amount of secondary mineral present using methods such as XRD, thermal methods, dye absorption and point counting. The calculation of the index, however, also requires a textural rating that can only be determined during petrographic thin section examination. The petrographic indices proposed by Frascá (1998) also required thin section analyses to determine the proportions of primary mineral, weathered primary minerals, interlinked smectite and smectite in micro fissures since X-ray diffraction cannot provide this data.

Weinert (1980) suggested that up to 10% smectite might be tolerable for a "pavement material". More recently van Rooy (1994) suggested a guideline value of less than 20% smectite as suitable for the use of basalts in concrete, roads and for rip rap. Paige-Green (2007) suggested that if an aggregate has a smectite content of less than 10% the durability can be considered adequate while aggregates with more than 10% smectite require additional testing before approval. Although Kleyn and Bergh (2008) reject actual poor durability claims, they

suggest that 3% smectite in rock can result in dolerite pavement construction materials transforming into a marginal or unacceptable material when physically broken down (such as during processing). Netterberg (personal communication) considers more than about 5% smectite as risky if the material is to be used as a surfacing stone or a base course aggregate. Table 1 is a summary of the smectite limits suggested by these authors.

Table 1. Summary of smectite content specifications suggested by authors.

Author	Suggested smectite content limit (%)	Suggested analyses
Higgs (1976)	5 (montmorillonite)	Petrographic
van Atta and Ludowise (1976)	10	Petrographic
Cole and Sandy (1980)	NA*	Petrographic or XRD
Weinert (1980)	10	None
Frasca (1998)	NA*	Petrographic
van Rooy (1994)	20	Petrographic or XRD
Paige-Green (2007)	10	Petrographic or XRD
Kleyn and Bergh (2008)	3	Petrographic or XRD
Netterberg (personal Communication 2012)	5	None

\*NA indicates value required for input into index calculation only

### 3. Quantitative XRD clay analysis

X-ray diffractogram peak intensities or peak areas are commonly assumed to be an indication of the quantities of minerals present in the sample (Carrol 1970). However, the intensities and areas of peaks are affected by not only the quantity of the material in the sample but also by the mass absorption of the different minerals, the grain orientations, the thickness of the mounts, weight of the sample, the evenness of the spread of the minerals, variations in crystal perfections, hydration state, polytypism and the chemical composition (Carrol 1970). Thus quantification of minerals from diffractogram analysis is not straightforward. Analytical difficulties in quantitative clay mineral analysis of rocks by X-ray diffraction are listed by Srodon et al (2001) to be those related to the chemical and structural characteristics of clay minerals which include the variable chemical composition and various defects that disturb three-dimensional continuity. These all result in large differences in the intensities of XRD reflections between different specimens of the same mineral and this can lead to large analytical errors in quantitative analysis.

Another major source of error in quantitative analysis of rocks containing clays is the platy habit of clay crystallites resulting in a tendency for preferred orientation of certain crystallographic planes to the X-ray beam (unlike anhedral, equidimensional mineral crystals). Clay minerals in a clay size-fraction are usually identified using oriented preparations (and tend to orientate to some degree in other preparations) and the degree of orientation affects diffraction peak intensities. Random preparations obtained with techniques described by, for example, Smith *et al.* (1979), Moore and Reynolds (1997), and Hillier (1999 and 2000) can, however, be used to overcome this problem (Srodon et al 2001). If such clay size fractions can be prepared and analysed to provide a representative quantification of the minerals in the clay fraction, the relative mineral proportions

within the analysed whole rock and clay samples can be used to quantify the clay mineralogy of the rock. This was done in a study by Lynch (1997) and also assumes that the clay fraction is a reasonable representation of the clay mineralogy of the total rock (in this case shale) (Hower et al. 1976 in Lynch 1994). Similar opinions regarding basic igneous rock clay fraction representativeness have not been found in literature. Reynolds (1989 in Lynch 1994) does however note that this quantitative clay mineralogy analysis technique yields results accurate to 10% relative for phases in abundance, and 20% relative for minor phases. Thus the technique is not accurate enough for durability investigations.

Another approach involving full-pattern fitting is the Rietveld method (Rietveld 1969), which was originally developed for crystal structure refinement and was adapted for quantitative XRD analysis (Bish 1994 in Harris and White 2007:24). This approach calculates the diffraction pattern based on the crystal structures of the minerals present in the samples and compares that pattern with the measured pattern. Then by variation of many parameters the difference between the two profiles is minimized and quantification of phases is completed. In order to perform a Rietveld refinement structure, data for all phases present in the sample is needed.

According to Srodon et al (2001), the Rietveld method is inaccurate when used for clay mineral analyses since clay structures are too complex to be modelled and refined for a routine quantitative analysis. However, Hillier (2000) performed quantitative XRD analysis of clay, and other minerals, on artificially prepared sandstones using Rietveld analyses and reported a  $\pm 3\text{wt}\%$  accuracy at the 95% level. He believed the success of his analysis to be the careful sample preparation and attention to the necessary reduction in particle size. He also notes that routine techniques generally do not provide sufficiently standardized samples and as such the accuracy of results from such samples are inferior. Dilution of clays may, for example, occur when sample grinding is performed (Harris and White 2007).

XRD identification of clay minerals also requires control of the saturating cations since these can affect the characteristic d-spacings. Commonly, saturation using glycerol [ $\text{C}_3\text{H}_5(\text{OH})_3$ ] or ethylene glycol [ $\text{C}_2\text{H}_6\text{O}_2$ ] is used to cause diagnostic changes in expansible phyllosilicates by solvation of the interlayer cations and further expansion of the minerals (Brindley 1966).

Glycerol exposure can cause low-charge smectites (e.g., montmorillonite, hectorite) to expand, even when exposed to only glycerol vapour, while higher-charge smectites (e.g., beidellite, saponite, nontronite) require exposure to liquid glycerol (Borchardt 1989 in Harris and White 2007:20). Heating to high temperatures ( $>300^\circ\text{C}$ ) also causes changes in d-spacings of some clay minerals. Another problem in interpreting diffraction patterns from smectite clays is that the d-spacings can also be variable when random interstratification of smectite with other phyllosilicates occurs. Since the two phases together establish the repeating periodic pattern of the unit cell the lowest angle peak for a regularly interstratified combination would be the sum of the individual angles (Harris and White 2007).

Due to the complications described above absolute quantitative results for clay minerals are very problematic and generally not reproducible.

#### **4. Methodology**

Newly exposed, unweathered dolerite samples from different quarries across South Africa and basalt samples from quarries in Lesotho were submitted to various laboratories for smectite content determination. The testing methods utilized were thin section analyses (with visual estimates and point counting) and XRD analyses. In the first phase of the study 25 samples were considered. All 25 were submitted for XRD analyses at the first laboratory, while 6 were submitted to two additional laboratories for XRD analyses. Thin sections were prepared from 22 of the samples and visual estimates of mineral composition were obtained during the analyses of the sections. Point counting was then performed on 9 of the thin sections (

Table 2). The different XRD facilities did not all use the same methods to perform the analyses, some performed semi quantitative estimates (using relative peak heights/areas proportions) while others performed Rietveld analyses.

Table 2. Summary of sample numbers and analyses performed on each sample in phase 1.

Sample number	Thin section		XRD		
	Estimation	Point counting	1 <sup>st</sup> analyses	2 <sup>nd</sup> analyses	3 <sup>rd</sup> analyses
1	✓	✓	✓		
2	✓	✓	✓		
3	✓	✓	✓		
4	✓	✓	✓		
5	✓	✓	✓		
6	✓	✓	✓		
7	✓	✓	✓		
8	✓		✓		
9	✓		✓		
10	✓	✓	✓		
16	✓		✓	✓	✓
17			✓	✓	✓
18	✓		✓	✓	✓
19	✓	✓	✓	✓	✓
20			✓	✓	✓
21			✓	✓	✓
23	✓		✓		
24	✓		✓		
25	✓		✓		
26	✓		✓		
27	✓		✓		
28	✓		✓		
29	✓		✓		
30	✓		✓		
31	✓		✓		

In the second phase 10 additional dolerite samples from different quarries were submitted for quantitative XRD analyses. First the materials were divided into three groups and submitted to different facilities and then all materials were submitted to a fourth facility for a second analysis. All facilities were requested to quantify the mineralogy (including clay mineralogy) of the materials using XRD techniques. Again the different facilities used different methods to analyse the materials including semi quantitative estimates (using relative peak heights/areas proportions) and Rietveld analyses (Table 3). All but one of the facilities performed clay fraction treatments.

Table 3. Summary of sample numbers and analyses performed on each sample in phase 2.

Sample number	First (A) analysis method	Second (B) analysis method
P1C1	Semi quantitative estimates of standard samples and both heat and glycol treated clay fractions using relative peak heights/areas proportions. Clay contents refined based on clay fraction results.	Average of results from Rietveld analysis and Rockjock pattern fitting (Eberl 2003) analysis after phase identification based on glycol and heat (550°C) treated observations.
P1D1		
P2B1		
P2B2		
P3A1	Semi quantitative estimates of standard samples using relative peak heights/areas proportions.	
P3B1		
P4A1	Rietveld analysis after phase identification based on glycol and heat (550°C) treated observations.	
P6B1		
P7C1		
P7D1		

## 5. Analytical procedures and results

### 5.1. Phase 1 smectite contents determined using different techniques

When the various smectite contents reported by different methods for each sample are compared (Figure 1) it is obvious that the methods give highly inconsistent results. Point counting generally gives the highest estimates when compared with the other results. Petrographic estimates and XRD results also differ significantly and there is no consistent trend in the differences between these. When comparing results for samples for which there are only XRD and petrographic estimates available (Figure 1B) extreme differences in smectite content estimation were obtained and again no consistent trend in differences between results is seen.

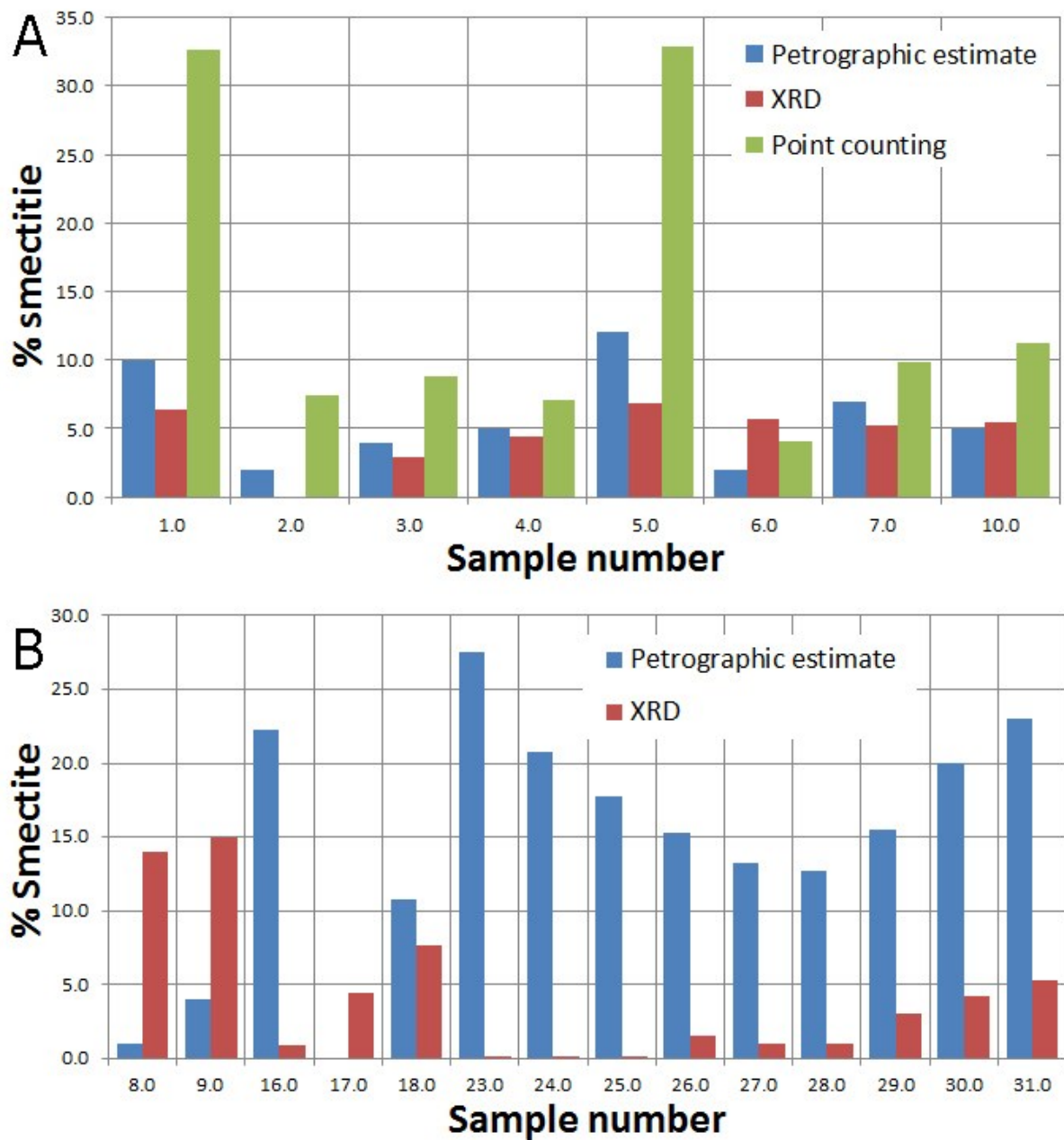


Figure 1. Smectite contents determined by different testing methods, A: Results for samples on which two or more analysis types were performed, B: Results for samples on which only XRD and petrographic estimates were performed.



## **5.2. Phase 1 smectite contents determined by three laboratories**

XRD analyses were performed on samples 16 through 21 (

Table 2) by three different laboratories using different analytical techniques. The results of these are referred to as XRD, XRD1 and XRD2 in this report. The analysis procedure used by the first laboratory (“XRD”) was a three step process similar to that discussed by Lynch (1997), which consisted of:

- Step 1: clay content determination on full rock sample using relative peak heights/areas proportions
- Step 2: smectite content determination on glycol treated clay fraction sample using relative peak heights/areas proportions
- Step 3: back calculation of absolute smectite content in rock

The weight percentages of clay minerals in the rock (Figure 2) may be incorrect if overlap of smectite and chlorite peaks had occurred and therefore additional analyses on the clay fraction separated out of the bulk sample (step 2) were performed.

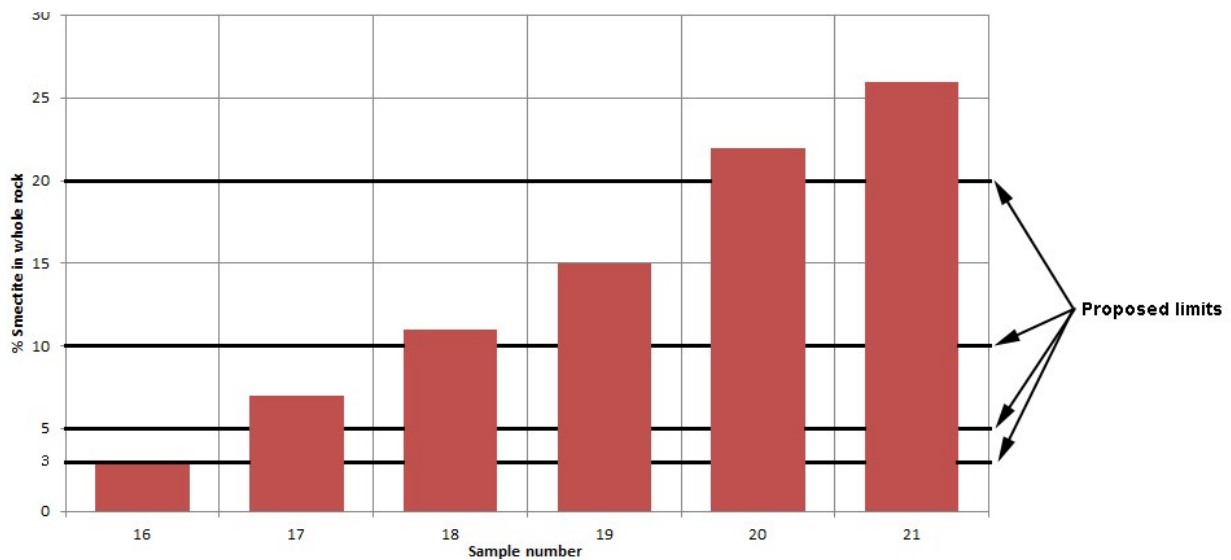


Figure 2. Clay percentages reported by whole rock XRD analyses with proposed limits from table 3 (Step 1).

The results (Figure 3) show a wide range indicating that significant interference of peaks was present in the first step. When the back calculations for the “XRD” results were performed the variation in smectite contents for the full rock samples (Figure 4) was reduced slightly but importantly the smectite contents of some samples had dropped to below some of the proposed limits (e.g. samples 16, 17 and 18).

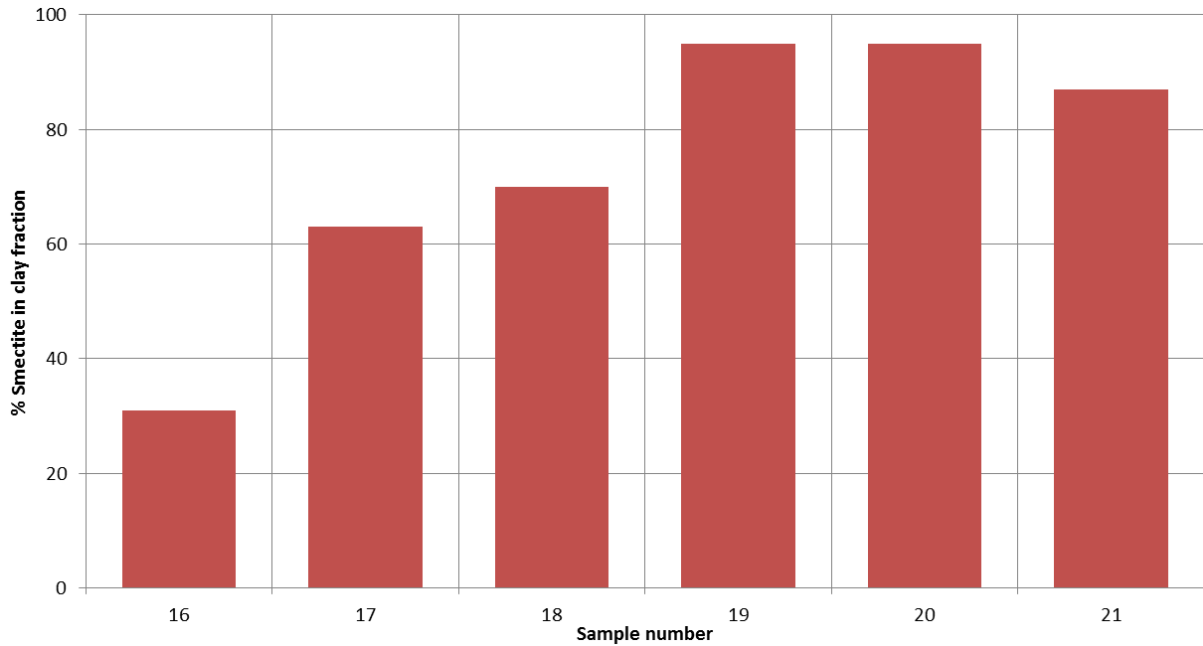


Figure 3. Smectite portion of clay fraction reported by XRD analyses (Step 2).

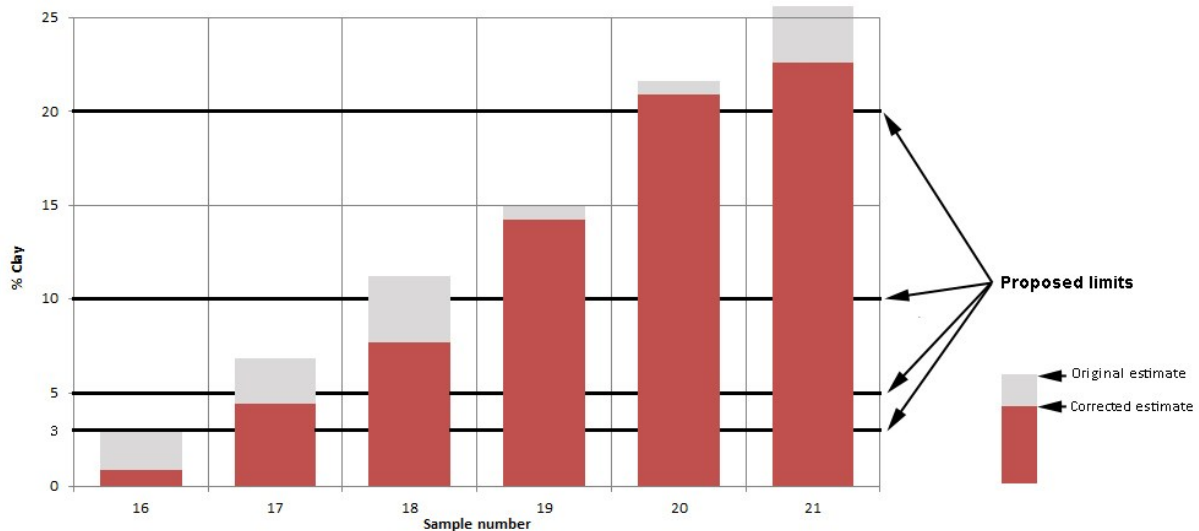


Figure 4. Absolute smectite clay contents determined by back calculations using XRD results (Step 3).

In the “XRD 2” and “XRD 3” analyses the weight percentages were estimated using the Rietveld method (Autoquan Program) and as such no corrections based on clay fraction analyses were required.

The results (before corrections were applied, Figure 5A) for samples that were submitted to three XRD facilities show how the results disagree and show no consistent differences. After the corrections were performed the differences in results decreased for some samples but the results are still by no means in agreement and all samples have a range of results that span at least one of the proposed smectite limits (Figure 5B). Since it has been reported previously that the method used by Lynch (1997) is not accurate for minor phases, this is to be expected. In practical terms any of these samples could have been accepted or rejected depending on the specification being followed and the analysis methods used to determine the clay content.

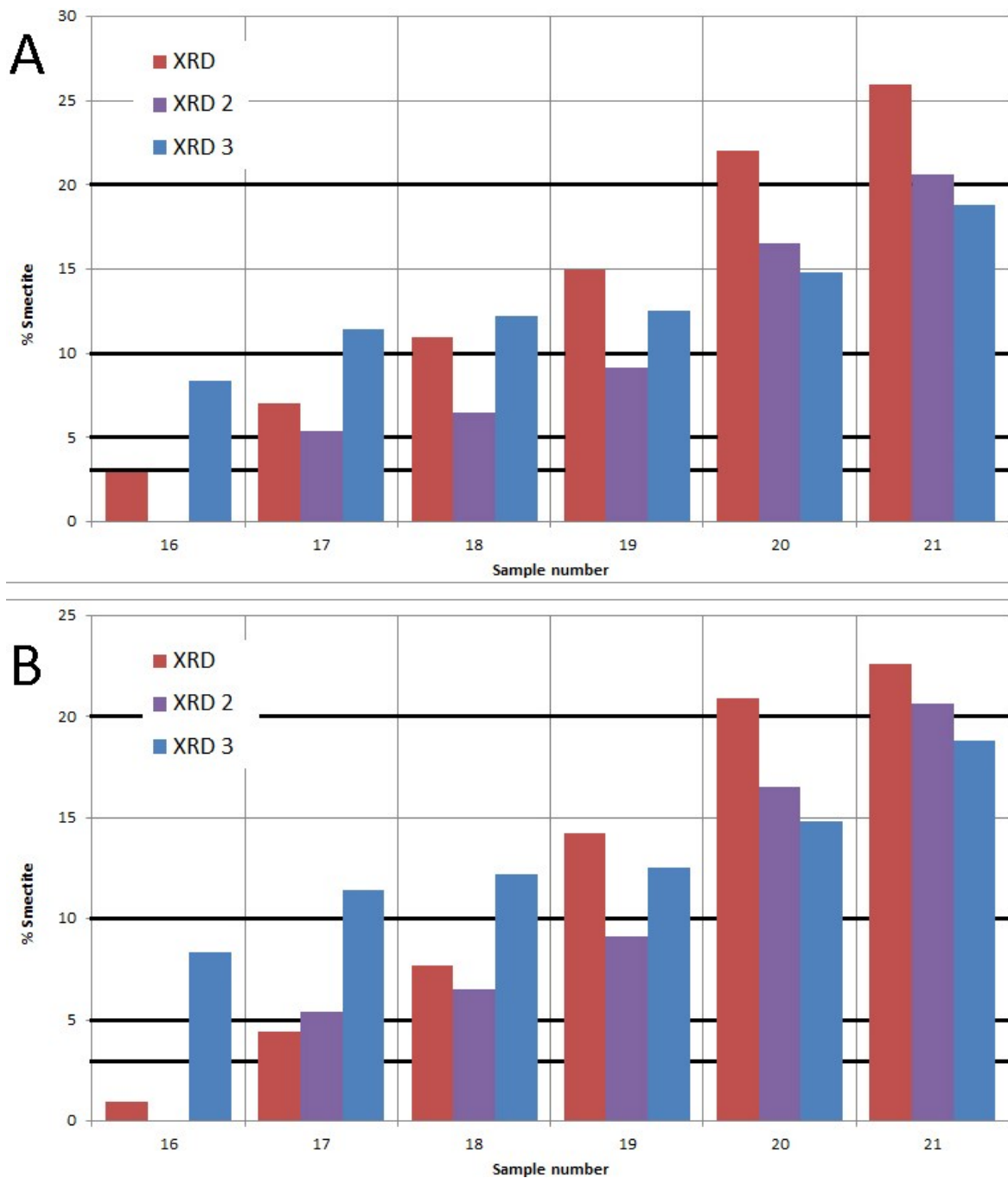


Figure 5. A: % smectite identified in whole rock and B % smectite after corrections for clay fraction analyses were performed (where applicable).

### 5.3. Phase 2 samples

The second facility (B analyses) performed analyses of the diffractograms obtained using two different software packages namely X'Pert Highscore Plus (V2.1.2 2005 by PANalytical B.V., Almelo, The Netherlands) and Rockjock (Eberl 2003). The former is a Rietveld analyses software. In both cases the crystal structure data were obtained from the AMCS Database (Downs 2003). The results from the analyses, summarized in Table 3, highlight some important problems that would have been encountered should the studied materials have been under consideration for use as aggregates.

The major mineral analyses produced consistently different results in which the Rietveld analysis provided a higher pyroxene content in almost all of the results while for plagioclase it was the Rockjock result that was always higher (Figure 6). Although such differences are unlikely to affect the rock as an aggregate they do reveal that the interpretation of XRD results should not be followed blindly.

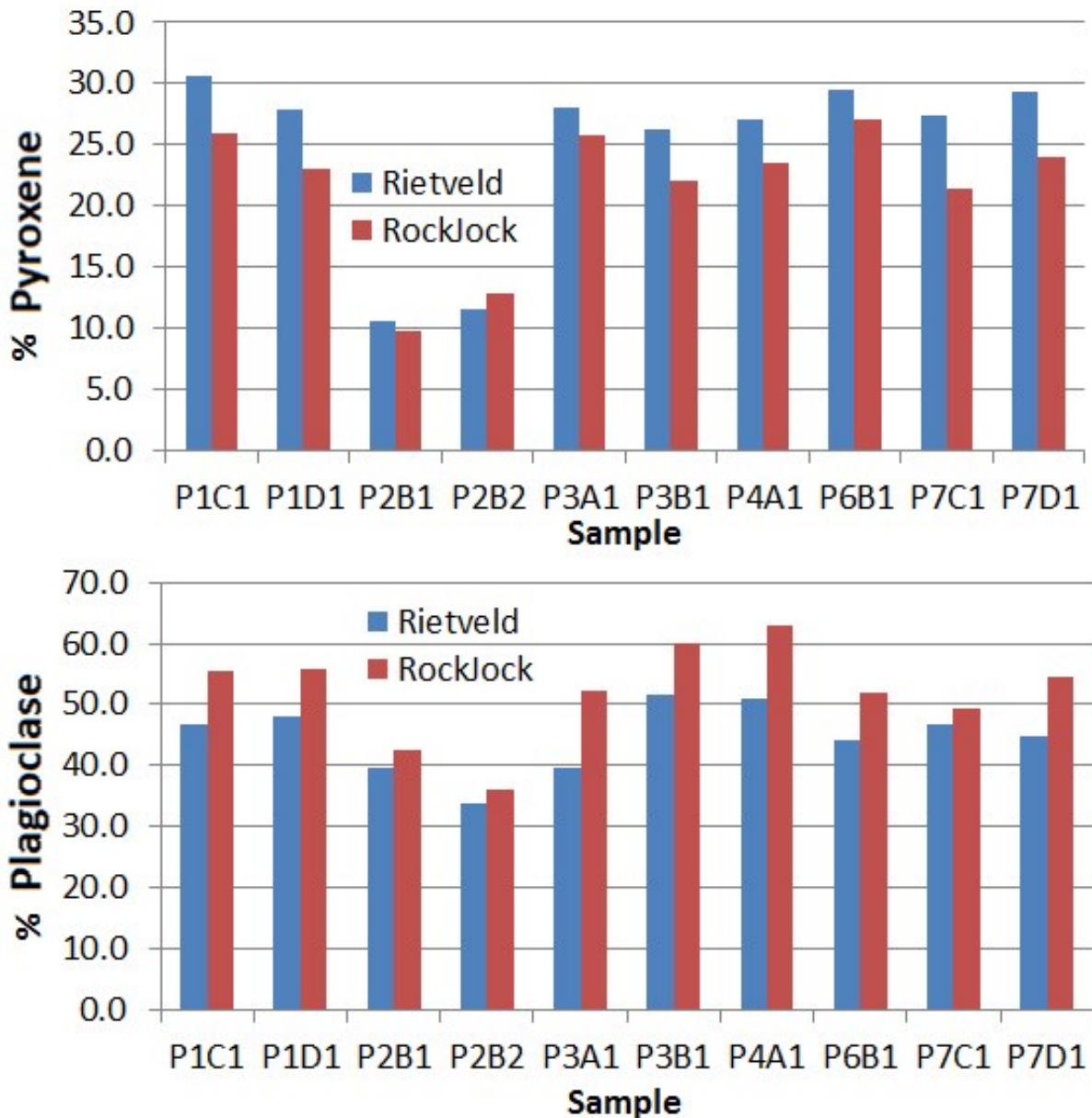


Figure 6. Comparison of major mineralogy composition as determined from Rietveld and Rockjock analyses on the same XRD data.

The secondary mineral analyses were, however, not in agreement at all. While the Rockjock results consistently provided results indicating the presence of vermiculite, the Rietveld analysis showed no vermiculite to be present. Both smectite and vermiculite potentially have diffractogram peaks at 14Å that shift after exposure to ethylene glycol. Differentiation of vermiculite requires no shift in the 14Å peak after treatment with glycerol (not ethylene glycol), additional base peaks, and the lack of additional peaks forming due to exposure to ethylene glycol or high temperatures. Closer inspection of the diffractograms produced in phase 2 reveal some cases in which vermiculite is likely to be present while smectite is unlikely but without glycerol treatment

final discernment between the two is not possible. The Rietveld analysis did show a significant amount of amorphous material to be present and the analyst assumed this to be vermiculite when reporting the final results. Even if this is the case the results do not agree and almost all materials had reported vermiculite and or smectite contents that lie on opposite sides of one of the proposed limits (Figure 7).

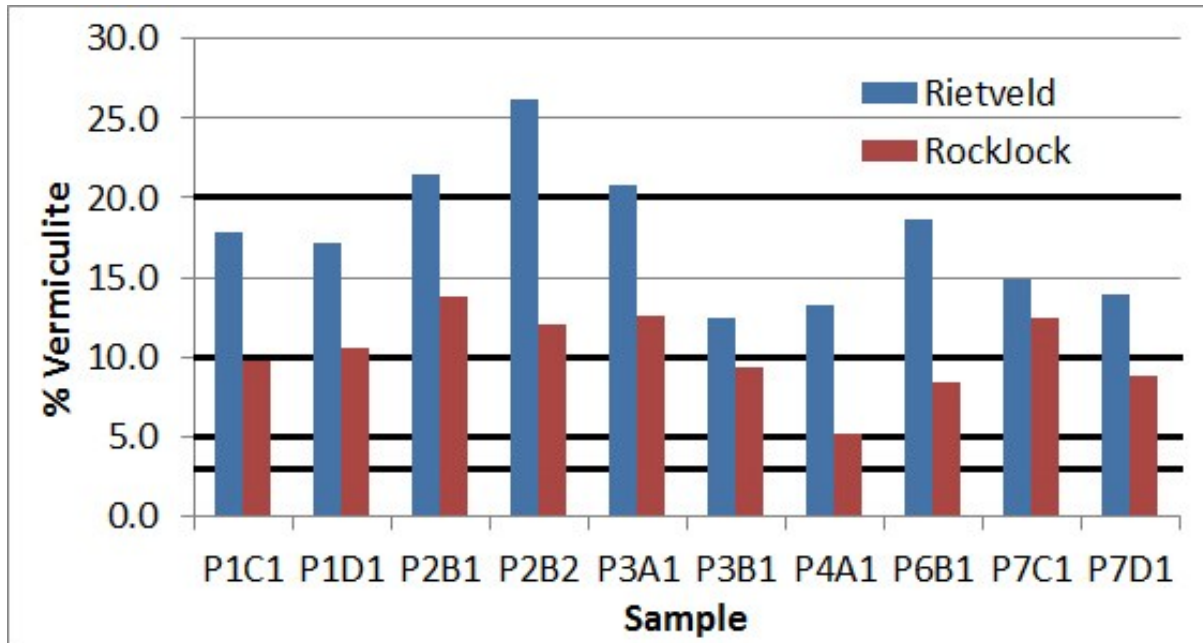


Figure 7. Vermiculite contents determined using different diffractogram analysis methods on the same XRD data).

The problem with the above secondary mineral interpretations is that no true smectite clays were incorporated into the Rietveld analysis done by the second facility. This makes comparison of these results with those from the first facilities difficult. It was decided to use the information shown in Figure 7 when comparing the data with the results from the first facilities. i.e. the vermiculite contents reported by phase 2 were compared with the smectite contents reported by phase 1. The comparison (Figure 8) shows how even more materials now fall on opposite sides of the proposed limits and in some cases now span more than one such limit. The “other” results refer to those performed by the first facilities. Samples P1C1 through P2B2 were all submitted to the same initial facility but the results (obtained using relative peak heights/areas proportions) do not show any consistent relationship with the Rietveld and Rockjock analyses. The P3 samples’ initial results were also obtained using relative peak heights/areas proportions but without doing glycol or heat treatments on clay fractions. Surprisingly the P3 results do show relative agreement with the Rietveld analysis. Finally the initial facility analysed the samples P4A1 through P7D1 using Rietveld analyses and therefore a large degree of correlation would be expected. This is, however, not the case. One reason for this may be that the “other” analysis did not incorporate vermiculite during data processing. In the extreme case of P4A1 material no smectite (or vermiculite) was identified in the initial analyses while the Rietveld analysis did identify significant amounts of amorphous material which were assumed to be vermiculite/smectite and the RockJock analyses also reported some vermiculite.

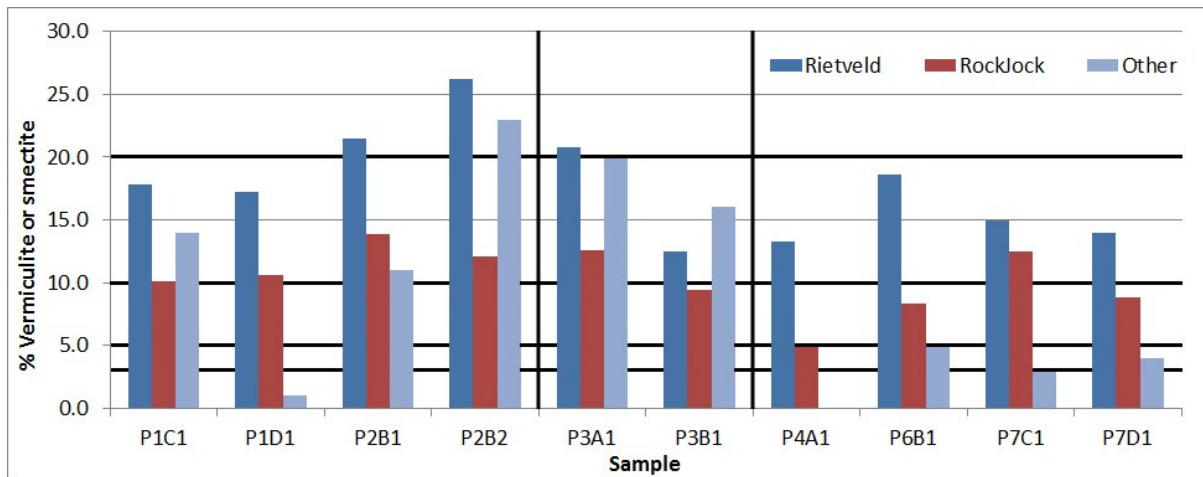


Figure 8. Vermiculite or smectite contents determined using different techniques and different analysis facilities.

## 6. Discussion

It is very likely that the smectite clay content of aggregates is, as proposed by different authors, directly related to their durability. The determination of the smectite clay content using different methods has, however, been shown to deliver conflicting results and the use of at least two methods and the comparison of results has proven to be a good way to identify potentially inaccurate results. Petrographic estimates are believed to be highly inaccurate and should, as all estimates, be used only to guide further testing requirements and not as an acceptance criterion. Point counting and XRD analyses potentially have equal accuracies and can be done in tandem and the results compared. If the results differ significantly or fall on opposite sides of the relevant specification being applied then it is suggested that one or both of the analyses be repeated. The results of this study do, however, show that repeating XRD analyses will not always simplify the interpretation of the mineralogy.

Thin section interpretations require accurate identification of smectite minerals, which are not as easy to identify as other groups of minerals. It is, for example, very possible that vermiculite and smectite minerals will have similar appearances even to the experienced analyst. The gradual replacement of primary minerals by smectite clay minerals can also result in minerals within thin sections that are not easily identifiable as either the primary mineral or the secondary product.

The accuracy of the XRD analyses is also dependent on the accurate identification of smectite clays as one of the phases to be modelled in the analyses. It has also proven beneficial to explain to the analyst prior to investigation the relevance and importance of the clay fraction analyses so that greater care is taken to accurately determine the smectite content. This eliminates the possibility that all weathered minerals will be considered as active smectite clays (in the case of thin section analyses) and that all clays will be considered to be smectite clays (in the case of XRD analyses). Great care should be taken when analysts identify potentially deleterious phases to be modelled in Rietveld (or similar) analyses. Here it would be wiser to incorporate all potential groups of clay minerals and other phyllosilicates (i.e. smectite, biotite, muscovite, vermiculite, chlorite and illite) to prevent potential ambiguity regarding the actual form of phyllosilicates present.

The effects of preferred orientation may also have contributed to the observed variations in results. Most of the facilities that did not use Rietveld analyses reported using orientated samples of clay fractions. This

would have resulted in accurate phase identification but possibly inaccurate quantification of phases in clay fraction. This error would then have been included in the back analyses of the clay fractions in the whole rock. Preferred orientation effects may also have been present in samples on which only Rietveld analyses were performed. However, Rietveld analysis also generally allows for modelling of preferred orientation and since these were whole rock samples and not only clay fractions the degree of preferred orientation would have been less.

It therefore seems that the lack of correlation between commonly utilized clay mineral quantification techniques makes the use of such information in studies to predict the durability of igneous rocks unlikely to be valuable. Why then have so many authors suggested smectite clay content limits? It is most probable that large databases observed by such authors may reveal some correlations between clay contents and observed (or interpreted) durability. If not the proposed specifications are also most likely erroneous. The issues presented, however, will still prevent the use of such data during routine material investigations and quality control testing.

## **7. Conclusions**

The use of quantitative clay analyses is most probably only suitable as indicative of the presence of smectite minerals and the probable range of their contents within a specific source and at best as a relative indication of one source's potential durability to that of another. If smectite clay content is to be introduced as an absolute specification for material acceptance a strict standard method of analysis will have to be prescribed. This will prevent errors due to, among others, dilution during sample preparations, variations in glycol exposure techniques and orientation of phyllosilicates. Such a method will also improve the reproducibility between different facilities.

Should clay minerals be accurately quantified in both whole rock and clay fraction samples the calculation of clay mineral quantities in the whole rock using relative results would still suffer from both poor accuracy (reported to be as low as 20% for minor phases) and a potentially incorrect assumption that the clay fraction sample is representative of the whole rock clay content.

Until the problems highlighted in this study are addressed it seems more feasible to employ point counting to determine the clay mineral content of an aggregate source. The results may be slightly less accurate but costs are generally lower and at least some information regarding the distribution and origin of secondary mineral phases can be obtained. XRD techniques may still be applied to obtain additional information and check the point counting results. Where large discrepancies exist it is advised that the point counting be redone.

It is suggested that the preliminary identification of smectite clays should be used primarily as an indication that other more direct durability tests involving ethylene glycol soaking are essential.



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