

QUANTITATIVE CLAY PETROLOGY: THE TREES BUT NOT THE FOREST?

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Abstract—Gravitational settling and centrifuge techniques have been criticized in the preparation of X-ray specimen mounts for quantitative clay petrology because of the marked mineral segregations that can occur. Although the same factors can operate to produce error in the separation of the traditional less-than-2- μm fraction, this potentially more important source of bias is seldom taken into consideration. A fair representation of the bulk sample deserves at least as much attention as a representative X-ray mount. The most accurate and precise X-ray analyses may be geologically misleading or meaningless otherwise and translate as exercises in precision for its own sake.

The principal reason for achieving greater precision in most quantitative X-ray diffraction studies of fine-grained sediments is to try to obtain meaningful information about the distribution of clay mineral species and for geologic interpretation of the observable trends. More than a few authors have directed their efforts at attempting to achieve a 'true' quantification in clay petrology. Several major sources of error have been described and emphasized and additional papers on the subject continue to appear in the literature. Most of these attempts to minimize error in quantitative X-ray clay petrology are undoubtedly valuable but in the zeal to reach the goal of true quantification it is possible that a forest of information may have been lost in the trees of experimentation. We have concentrated our efforts on techniques of X-ray diffraction analysis that will be representative, accurate, and reproducible. The preparation of sample mounts and the X-ray diffractometer procedures have been studied and the measurement of the X-ray data has been evaluated, but from the quantitative standpoint the treatment of the original geologic bulk sample has been all but ignored. The bias included in the selection of the traditional less-than-2- μm fraction (LTMF) has been given little attention indeed. The purpose of this paper then is to call some attention to what is really obvious: isolation of a gravity-settled size fraction must induce a significant bias to the fine-grain petrology of the bulk sample. The interpretation of comparative quantitative X-ray data may therefore be geologically misleading or meaningless regardless of the precision and reproducibility of the X-ray data. Thus the principal reason for precise quantification—the geological meaning of the samples—has been lost.

Why does this contradictory situation exist? Historically, the less-than-2- μm fraction was chosen because it was a preparation that was (1) free from most of the so-called non-clay minerals and (2) capable of producing a well-oriented X-ray sample mount. In the beginning both of these criteria were designed for *qualitative* analysis. An oriented sample mount enhances the critical 001 basal reflections of the structurally layered clay minerals which serve to identify the species present, while at the same time suppressing the usually nondiagnostic *hkl* reflections. The absence of quartz, feldspar, calcite, etc. makes the task of identification easier by minimizing overlapping diffraction maxima.

After having identified qualitatively the clay minerals the next obvious step is to ask for quantitative analysis of the phases present. At this point major assumptions are consciously or unconsciously invoked. By doing a quantitative analysis of the LTMF it is assumed that the quantitative distribution of clay minerals in fine-grained sediments is essentially independent of the size fractionation procedure. It is further assumed that quantitative sample-to-sample trends found in the LTMF's are geologically meaningful in terms of the clay mineralogy. In other words, the LTMF is usually equated with the original bulk sample both quantitatively and qualitatively.

Is there any justification for these assumptions? In *apparent* support of the assumptions is the clay mineral concept itself (see Grim, 1968) which states, in essence, that clay minerals are composed of extremely small particles of a limited number of mineral phases. To a large extent this must be true, intuitively if not also by definition, but to arrive at any conclusion on the basis of size analyses involving settling or centrifugation is

to assure the result before the experiment has been done. Stokes Law calculations will show that such procedures must bias the sample towards the definition of the concept.

Errors involved with Stokes Law settling procedures include, among others, those due to specific gravity, shape and temperature. Brindley (1961) has pointed out that the error due to temperature alone can be significant. Some examples can illustrate his point. A quartz grain of 2 μm equivalent spherical diameter (e.s.d.) will have settled in distilled water at 20°C a little less than 5 cm in 4 hr. The same grain will have settled at 25°C more than 5.5 cm in 4 hr. Under the same conditions a fully hydrated smectite particle (s. g. 1.75) of 2 μm e.s.d. will have settled only 2.25 cm at 20°C but 2.5 cm at 25°C. Such a range of temperature (20–25°C) is reasonable not only between different laboratories but also within the same laboratory.

The previous examples illustrate the potential influence of both specific gravity and temperature but the effect of specific gravity alone on biasing the sample at a constant temperature is even more pronounced. Examining the standard sedimentological Stokes Law settling procedures (which assume a quartz s. g. about 2.65) it is immediately obvious that any LTMF obtained as a supernate will be devoid of all minerals of 2 μm e.s.d. with higher specific gravities.

By way of example, consider that a hydrated illite particle (s. g. 2.35) of 2 μm e.s.d. will have settled after 4 hr 4.0 cm in distilled water at 20°C while a muscovite particle (s. g. 2.80) of the same size will be 5.35 cm down and thus eliminated in the supernate which would normally be drawn off at a depth of 5.0 cm. Geologically speaking, this could mean laboratory elimination of much of the 'detrital mica' often seen in thin-section. Hower *et al.* (1961) and Bailey *et al.* (1962) have shown this can be significant in geologically meaningful contexts. Any ilmenite, hematite, pyrite, magnetite, or zircon grains of 2 μm e.s.d. would all have settled over 10 cm in 4 hr and thus unquestionably eliminated. Is it any wonder then that the clay mineral concept viewed as a limited number of minerals of very fine grain size is in part self-fulfilling? The bias in favor of the concept is compounded even further by shape considerations—the flake-shaped particles settling less rapidly than the equant grains.

These potentially significant biases in sample preparation have been largely ignored or somehow rationalized by the majority of clay petrologists. It is ironic that the advocates of accuracy in clay mineral quantification have on the one hand so carefully (and justifiably so) demonstrated the dangers involved with settling in clay mineral mounting techniques and on the other hand so casually obtained their supernatant fractions

by the same procedures. Gibbs (1965, 1968) has clearly illustrated that a large error can be introduced in clay mineral X-ray mounts where settling or centrifugation is employed. Stokke and Carson (1973) have recently arrived at essentially the same conclusion. If gravitational settling or centrifugation produces such major errors in preparing the X-ray mounts, how is it that this same source of error has not been given equal consideration in the steps that precede the preparation of these mounts? Shouldn't the errors here be equally as significant?

A number of clay petrologic studies have been made on suites of samples separated into several size fractions in addition to the LTMF. Some of these have used the techniques of X-ray mount preparation recommended for accuracy and precision by Gibbs (1965); others have not. Those studies using the recommended techniques (see, e.g. Perry and Hower, 1970) have usually shown that both quantitative and qualitative differences can exist in the differing size fractions. Studies which have not used the recommended techniques sometimes claim little or no differences between the bulk or different size fractions (see, e.g. Towe and Grim, 1963 or Devine *et al.*, 1972). Unfortunately, these claims must be suspect because of the fact that even with bulk or coarser fractions there will be a tendency for the fines to concentrate at the top of the X-ray mounts during gravity preparations and thus make a coarser fraction appear similar to a finer fraction. Stokke and Carson (1973) have shown that sample X-ray transparency will not necessarily avoid this danger.

It has been suggested that standardization of technique is the answer and will allow geologically meaningful comparison from sample-to-sample and laboratory-to laboratory (Pierce and Siegel, 1969). There can be little doubt that a standardized procedure is better than half-a-dozen varied procedures but unless standardization also takes the bulk sample characteristics into account there can be no way to decide (except intuitively) whether sample-to-sample trends are geologically and sedimentologically meaningful or just vagaries and artifacts of the size fractionation procedures. If the depositional environment is capable of sorting the sediment sent to it by size, shape and specific gravity, then the clay petrologist must certainly be able to accomplish similar feats when obtaining a given size fraction by settling procedures.

A hypothetical example can illustrate the potential influence on results. Start with a two-component mixture of smectite and kaolinite in equal proportions and both with Gauss-normal size frequency distributions that overlap so that the smectite is on the average finer than the kaolinite. If this 50–50 starting material were introduced into a current of down-slope diminishing

competence we would expect (following Stokes Law and ignoring flocculation effects) to find the kaolinite because it is coarser and of higher specific gravity settling out faster than the smectite. Sampling the *bulk* deposits we would expect to find that bottom samples taken upstream would be enriched in kaolinite for this reason. But bringing these bulk samples back to the lab for accurate and precise quantitative clay petrology could change the order considerably if we use only the traditional LTMF. Thus a bulk sample of 60–40 kaolinite-to-smectite composition could come out of the graduated cylinder as a 40–60 mixture because in settling the smectite would tend to stay up in the supernate and be drawn off while much of the kaolinite would be settling faster and this time eliminated. The use of settling or centrifugation in preparing the X-ray mounts would emphasize this effect even more so that what started out to be a sample somewhat richer in kaolinite ends up being a sample much richer in smectite. Depending on the size-frequency distributions and the minerals involved such results could be dramatically different from the actual samples and geologically misleading regardless of how accurate and precise the X-ray techniques happened to be.

Is there a solution to this dilemma? There will probably never be any such thing as 'true quantification' free from sample bias of one sort or another, but some approaches seem worth considering depending on the geological problem and the time and energy of the researcher. Recognizing and facing the problem is, of course, at least half the battle. We can no longer continue to stick our heads in the sand (mud?) and hope the problem will go away while at the same time proudly announcing accuracy and precision in the handling of X-ray data. On the practical experimental side, it would seem worthwhile to try to study quantitatively the bulk sample in a random mount after having used a settled, oriented fraction as a qualitative guide to help identify which clay minerals to expect. This is, of course, easier said than done but the geological information obtained could be worth the effort involved. The continued use of more than one size fraction X-rayed under the appropriate conditions is certainly better than a simple LTMF alone. Finally, a suitable experimental protocol involving heavy liquids and density gradient centrifugation might produce interesting results. In any case, the continued use of the traditional less-than-2- μm fraction for quantitative (and perhaps even qualitative) clay petrology can only be viewed as an exercise in futility.

Is the general observation that illites are usually predominant over chlorites in geologically older shales a

true quantitative representation of the bulk sample mineralogy or a reflection of a coarser size frequency distribution ($> 2 \mu\text{m}$) for chlorites present in what may be larger quantities? Is the general lack of zeolites in many clay analyses of more recent sediments a result of a similar bias? Is the almost total absence of any heavy minerals in clays that have been slaked and settled more a reflection of the influence of specific gravity than of particle size? Are smectites, generally conceded to be of exceptionally fine particle size, really as abundant in bulk samples as they appear in many analyses of settled fractions? Many of these questions may be answered empirically but a blind adherence to a less-than-2- μm fraction will be of little help in seeing these forests perhaps lost among the trees.

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Résumé—Les techniques de sédimentation et centrifugation ont fait l'objet d'une étude critique en vue de la préparation d'échantillons destinés à l'analyse pétrographique quantitative de l'argile par diffraction X; cette étude est motivée par les ségrégations importantes qui peuvent exister entre les minéraux.

Quoique les mêmes facteurs peuvent intervenir pour produire une erreur dans la séparation de la fraction usuelle inférieure à deux microns, cette source d'écarts potentiellement plus importante est rarement prise en considération. Une représentativité correcte de la totalité de l'échantillon mérite au moins autant d'attention qu'un dispositif représentatif de mesure par rayons X. Les analyses par rayons X les plus précises et les plus fines peuvent être, au point de vue géologique, erronées ou même dépourvues de signification, ce qui les transforme en pur exercice de style dans la recherche de la précision.

Kurzreferat—Sedimentation unter dem Einfluß der Schwerkraft und Zentrifugentechniken sind als Methoden zur Herstellung von Röntgenpräparaten für quantitative petrologische Untersuchungen von Tonen wegen der ausgeprägten Mineralentmischungen, die vorkommen können, kritisiert worden. Obwohl dieselben Faktoren sich als Fehlerquelle bei der Abtrennung der traditionellen $< 2\mu\text{m}$ -Fraktion auswirken können, ist diese möglicherweise bedeutendere Ursache von Fehlbeurteilungen selten in Betracht gezogen worden. Eine richtige Wiedergabe der Probenmenge verdient mindestens ebensoviel Aufmerksamkeit wie ein repräsentatives Röntgenpräparat. Die genauesten und sorgfältigsten Röntgenanalysen können unternfalls irreführend oder bedeutungslos sein und sich als Übungen in Genauigkeit um ihrer selbst willen erweisen.

Резюме — Критикуются использование гравитационного осаждения и центрифугальной переработки при приготовлении образцов для рентгенографического изучения в количественной глинистой петрологии, вследствие могущей возникнуть заметной сегрегации минералов. Хотя, те же самые явления могут принимать участие во возникновении ошибок при разделении стандартной фракции менее чем в два микрона, этот потенциально более важный источник смещения редко принимается во внимание. Хороший показательный объемный образец заслуживает, по крайней мере, столько же внимания, как и показательный образец приготовленный для рентгенографического изучения. Самый точный и прецизионный рентгенографический анализ может геологически ввести в заблуждение или не иметь смысла и осуществляется только как упражнение ради прецизионности.