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METHODS FOR SEPARATION AND TOTAL STABLE ISOTOPE ANALYSIS OF ALUNITE

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ABSTRACT

Techniques are presented for the separation of alunite [$KAl_3(SO_4)_2(OH)_6$] from commonly associated minerals and subsequent stable isotope analyses for δD, $\delta^{18}O_{OH}$, $\delta^{18}O_{SO4}$, and $\delta^{34}S$. These analyses can be performed successfully on most natural samples containing at least 100 mg of alunite. Associated minerals (typically quartz, kaolinite, and pyrite) are first minimized by hand picking or microdrilling. Ultrasonic suspension followed by elutriation is usually sufficient to remove clays. Other silicates and quartz are removed by HF digestion. Pyrite is removed by heavy liquid separation or by $CrCl_2$-HCl digestion. For $\delta^{18}O_{SO4}$ and $\delta^{34}S$ analyses, alunite is selectively dissolved in a heated solution of 0.5N NaOH. The filtered solution is titrated with HCl; sulfate is precipitated as $BaSO_4$ which is subsequently analyzed for $\delta^{34}S$ and $\delta^{18}O_{SO4}$ by conventional procedures. δD analyses are performed on water derived from alunite by inductively coupled stepwise thermal decomposition that minimizes SO_2 and H_2SO_4 production and formation of K±Na oxides. $\delta^{18}O_{OH}$ analyses are performed using a total fluorination method modified from that of Pickthorn and O'Neil (1985). Bulk oxygen produced by fluorination of alunite ($\delta^{18}O_{BrF5}$), consists of 50±1% of the O_2 from the SO_4 site and 100% from the OH site. A large fractionation during fluorination of sulfates ($\Delta^{18}O_{SO4(GR\text{-}Fl)}$) is constant over the entire natural range of $\delta^{18}O_{SO4}$ values and is dependent on the ratio of K+Na to total oxygen. $\Delta^{18}O_{SO4(GR\text{-}Fl)alunite}$ (10.5‰ in this laboratory) was determined by comparison of $\delta^{18}O_{SO4}$ values obtained by conventional graphite-reduction (GR) with those by fluorination (Fl) of reagent mixtures. $\delta^{18}O_{OH}$ is calculated from a mass balance equation which includes terms for $\delta^{18}O_{BrF5}$, $\delta^{18}O_{SO4}$, (measured by graphite-reduction), $\Delta^{18}O_{SO4(GR\text{-}Fl)alunite}$, and the molar ratios of liberated OH and SO_4 oxygen. The calculated $\delta^{18}O_{OH}$ is insensitive to uncertainties in O_2 yield and generally reflects the total analytical uncertainty of the fluorination and sulfate graphite-reduction technique.

INTRODUCTION

Alunite is a characteristic mineral of acid sulfate mineral assemblages formed by several diverse processes (Rye, et al., 1992). It contains four stable isotope sites, more than any other common mineral except crystallographically similar jarosite. The isotopic composition each of the various sites provides different information about the formation of the mineral. Complete stable isotope analyses (δD, $\delta^{18}O_{SO4}$, $\delta^{18}O_{OH}$, and $\delta^{34}S$) of all sites, especially when accompanied by stable isotope analyses of coexisting minerals, can provide information on origins of components, processes (including rates), physical-chemical environments, and temperatures of formation (Bethke, 1984, Rye et al., 1989; 1991; 1992; Alpers et al., 1992). The occurrence of oxygen in both SO_4 and OH sites is of particular interest because of possibilities for a single mineral isotope geothermometer (Pickthorn and O'Neil, 1985).

The separation of alunite from a typical acid-sulfate alteration assemblage and subsequent complete stable isotope analyses is a complex, time-consuming task. It involves up to four mineralogical and chemical separation procedures, extraction of three elements in four different gas extraction lines, and measurement of isotopic ratios using three different mass spectrometer configurations. We have completed over 500 analyses on over 200 alunite bearing samples from examples of each of the major alunite forming environments. The results, interpretations, and geologic significance of these analyses have been presented elsewhere (Rye et al., 1992). In addition, the experimental hydrogen isotope alunite-water and oxygen isotope alunite SO_4-water and OH-water fractionation factors have been determined in this laboratory and presented elsewhere (Stoffregen et al., in press). The purpose of this report is to present a compilation of the laboratory methods and individual analytical techniques that we have used to separate and perform complete stable isotopic analyses of alunite and its commonly associated minerals.

This report is organized around a flow chart that traces the sampling scheme and the various analytical procedures (Fig. 1). Many of the techniques have long been standard in mineral separation or stable isotope analyses and these are indicated by appropriate references. Our principal contributions have been: 1) the development of a NaOH dissolution technique for $\delta^{18}O_{SO4}$ and $\delta^{34}S$ analyses of alunite and, 2) significant modifications of the BrF_5 technique of Pickthorn and O'Neil (1985) for $\delta^{18}O_{OH}$ analysis of alunite. Both of these analytical techniques are discussed in detail. In addition, some refinements of standard techniques are presented for δD analysis of alunite. The elutriation-centrifugation technique for the purification of kaolinite (or other clay minerals) or its removal from alunite is that of Jackson (1985) and is detailed here for the convenience of the reader.

INITIAL SAMPLING

Alunite formed in *magmatic-steam* and *supergene* (Rye, et al., 1992) environments is frequently found as veins and fracture fillings of almost pure alunite. Such samples need minimal preparation prior to isotopic analysis. However, the typical acid-sulfate alteration assemblage contains variable amounts of fine-grained alunite, quartz, kaolinite (dickite, halloysite or nacrite), and pyrite. Careful sampling using appropriate handpicking and microdrilling techniques often greatly reduces subsequent effort and time. Characterization of the sample, or sample splits, by optical microscopy, X-ray diffraction, or scanning electron microscopy (SEM), is critical in understanding the nature of each sample and how to treat it as well as to determine the amount starting material to be used in the various techniques.

MINERALOGICAL SEPARATIONS

Of the typical acid-sulfate assemblage, the most troublesome impurity is kaolinite, which must be physically removed (to where it constitutes <2% of the sample) for δD analysis of alunite and reduced to acceptable levels (5-10%) for the NaOH or HF dissolution techniques. Ultrasonic suspension followed by elutriation and centrifugation is usually sufficient to remove kaolinite and other clays from alunite. A detailed description of the procedure used in this study is presented in Appendix A. This technique, however, does not work well when both alunite and kaolinite are very fine grained as in some supergene samples. In such samples, kaolinite can be removed from alunite by dissolution in HF or NaOH, but large amounts of kaolinite relative to alunite can easily overwhelm the chemistry of these methods. For the other commonly associated minerals, quartz can be recovered during the NaOH dissolution of alunite and removed by HF dissolution, and pyrite can be removed gravimetrically, selectively extracted by $CrCl_2$-HCl digestion (Zhabina and Volkov, 1978), and recovered during NaOH dissolution.

CHEMICAL SEPARATION AND PURIFICATION OF ALUNITE

The analyses of $\delta^{18}O_{SO4}$ and $\delta^{34}S$ of alunite can be performed on relatively impure samples (10-15% contaminants) by selectively dissolving alunite in a heated solution of 0.5N NaOH. In contrast, δD and $\delta^{18}O_{OH}$ analyses of alunite require a mineral separate with less than 2% quartz and/or kaolinite. Although in some cases the mineralogical separation methods noted above will provide a sufficiently pure alunite separate, most natural alunite-bearing samples require additional chemical treatment to reach this level of purity. For these samples, controlled dissolution in HF will produce a silicate-free, isotopically unaltered alunite separate providing they contain a sufficient amount of alunite.

Alunite dissolution in NaOH

The procedure to prepare alunite for $\delta^{18}O_{SO4}$ and $\delta^{34}S$ analyses is normally performed on samples containing 40–100 mg of alunite; however, the procedure has been used successfully on samples containing as little as 15 mg of alunite when only a $\delta^{18}O_{SO4}$

analysis is required. The method consists of dissolving alunite in NaOH and precipitating the sulfate as $BaSO_4$. (A detailed step by step description of the procedure is included as Appendix B).

Alunite is selectively dissolved in a solution of 0.5N NaOH that is stirred and heated to 80°C for several hours. After the alunite has completely dissolved, the solution is filtered to remove insoluble minerals. The filtrate is warmed, acidified with HCl, and $BaSO_4$ is precipitated by addition of $BaCl_2$. The HCl acidification step is critical to prevent the co-precipitation of $Al(OH)_3$ or alunite with the $BaSO_4$. Figure 2 shows the solubility of Al^{3+} as a function of pH for dissolution of alunite under the conditions described above and the HCl tritation path for subsequent $BaSO_4$ precipitation. The procedure involves rapid titration with concentrated HCl, lowering the pH of the filtrate to below 2.8 within a few seconds, followed by back tritation with 0.5N NaOH to a pH of 2.8–3.0. In this way the $Al(OH)_3$ and alunite stability fields are crossed rapidly enough to prevent or minimize precipitation of these phases. Small amounts of $Al(OH)_3$ or alunite that may form during this step are redissolved when the pH has stabilized in the desired range. Once the pH has been adjusted in this manner, $BaSO_4$ is immediately precipitated by the addition of $BaCl_2$. The precipitate is aged for 3 hours at 80°C to increase grain size, acidified, and cooled to room temperature.

The NaOH dissolution technique works best with an alunite mixture mostly free of kaolinite. If the assemblage contains relatively large amounts of kaolinite and/or K-feldspar, the Al^{3+} concentration may become so high during NaOH dissolution that $Al(OH)_3$ formation cannot be prevented by rapid HCl tritation to pH <2.8. This problem can be solved by precipitating $Al(OH)_3$ intentionally by tritating with HCl to pH approximately 6 at 80°C. The hot solution is centrifuged to separate the $Al(OH)_3$ gel, and the liquid fraction is handled according to the standard $BaSO_4$ precipitation procedure.

$BaSO_4$ yields from 16 replicate dissolutions of high purity alunite from Alunite Ridge, Marysvale, Utah averaged 92±3% (1σ). The complete dissolution of alunite for grain sizes below 60 mesh normally requires 2 to 3 hours at 80°C. Dissolution is enhanced by stirring the solution to prevent the formation of hydrous Fe-oxides and possible armoring of the mineral grains. Complete dissolution is important because some alunites, particularly those from the *magmatic hydrothermal* alteration zones, may be isotopically zoned. For samples containing quartz and/or pyrite, the NaOH dissolution procedure provides a separate of those minerals for later purification and analysis.

Silicate removal by dissolution in HF

Quartz, feldspar and clay can be removed from alunite samples by room temperature dissolution in a 1:1 solution of concentrated HF-H_2O. Alunite is sparingly soluble in HF but the amount of dissolution can be controlled by varying the volume of HF solution. Typically, a sample containing 50 mg alunite is immersed in 20 ml cold HF solution at room temperature for 90 minutes. Timed dissolution experiments and X-ray analyses of prepared mixtures of alunite+quartz show that this method results in rapid removal of quartz and saturation of alunite in solution. The HF solution is subsequently centrifuged and decanted. After rinsing and recovery on filter paper, the insoluble fraction is ready for the fluorination procedure. For a sample ground and sized to 120-325 mesh, the procedure normally results in a loss of approximately 40% of the alunite, which includes a small amount lost during decantation. $\delta^{18}O_{OH}$ and δD analyses of the Marysvale working standard before and after the HF treatment gave identical results, indicating that the alunite does not undergo hydrogen or oxygen isotope exchange with the water in the HF.

ISOTOPIC ANALYSIS

Sulfur and oxygen in sulfate site ($\delta^{34}S$ and $\delta^{18}O_{SO4}$)

$\delta^{34}S$ and $\delta^{18}O_{SO4}$ analyses of alunite are carried out by conventional procedures on $BaSO_4$ precipitated by the NaOH technique. For $\delta^{18}O_{SO4}$ analysis, $BaSO_4$ is mixed with high purity graphite in a platinum foil boat, through which a 45 amp current is run under vacuum. CO_2 is produced directly and collected; any CO produced from incomplete reaction is converted to CO_2 by plating the excess carbon onto electroplates. The production of CO is avoided by slow incremental heating of $BaSO_4$. The overall procedure follows that of Rafter (1967) and Sakai and Krouse (1971). $\delta^{34}S$ analyses are carried out by direct thermal decomposition following the standard technique of Holt and Engelkemeir (1970).

The analytical uncertainty for all alunite standards analyzed in this laboratory during the development of the technique including those of low yields and those which were allowed to exchange with low pH solutions during HCl titration is ± 0.15‰ (1σ, $n = 7$) and ± 0.29‰ (1σ, $n = 16$) for $\delta^{34}S$ and $\delta^{18}O_{SO4}$, respectively. The principal potential sources of analytical uncertainty are: 1) incomplete dissolution of possibly isotopically zoned alunites and 2) possible oxygen isotope exchange between $SO_4^{=}$ and solution at low pH during the HCl titration. The possibility of low pH oxygen isotope exchange between $SO_4^{=}$ and water in the low pH solutions is suggested by the larger than normal standard deviation for the $\delta^{18}O_{SO4}$ measurements (± 0.29‰ as compared with ± 0.15‰ for samples of $BaSO_4$ directly analyzed by the graphite reduction technique). Our experiments to study this effect seem to suggest a shift to lower $\delta^{18}O_{SO4}$ values with increasing time at $pH \approx 1$, but are not conclusive within analytical uncertainty. As a precaution to minimize this possible effect, $BaCl_2$ is added immediately to precipitate $BaSO_4$ after HCl titration step. With this precaution the precision of $\delta^{18}O_{SO4}$ values for most alunites is typically close to the normal value of ±0.15‰.

Oxygen in OH site ($\delta^{18}O_{OH}$)

Oxygen isotope composition of the OH site in alunite is performed by first determining the total isotopic composition of the alunite (both OH and SO_4 sites) by fluorination with BrF_5 at 580° C following the standard analytical procedure for silicates of Clayton and Mayeda (1963). $\delta^{18}O_{OH}$ values of alunite are then obtained by material balance using the $\delta^{18}O_{SO4}$ value of oxygen in the SO_4 site determined independently by the dissolution in NaOH technique described above. The fluorination method was first used on alunite by Pickthorn and O'Neil (1985) to demonstrate the fractionation between OH and SO_4 sites and to indicate its potential use in geothermometry. Their procedure is based on the assumption that fluorination of alunite with BrF_5 will produce 100% of the O_2 in the OH site and 50% from the SO_4 site and that the fractionation is reproducible.

Our analysis of various anhydrous sulfates by graphite reduction ($\delta^{18}O_{SO4GR}$) and fluorination ($\delta^{18}O_{SO4Fl}$) methods shows that fluorination does indeed produce a 50±1% yield from the SO_4 site and that the fractionation of oxygen between sulfate and O_2 during fluorination is constant ($\Delta^{18}O_{SO4(GR\text{-}Fl)} = 9.0\pm0.2$‰) over the entire natural range of sulfate oxygen isotope compositions and is independent of cation composition (Fig. 3). Gas chemistry and X-ray analysis indicate that unreacted oxygen is in the form of small amounts of SO_2F_2 and an unknown inert solid phase that does not contribute oxygen to subsequent reactions in the BrF_5 extraction line.

Fluorination of alunite also produces a 50±1‰ yield of the O_2 from the SO_4 site as well as 100% from the OH site. Pure alunite, as well as mixtures of several different reagent sulfates and $Al(OH)_3$ that simulate the molar ratios of SO_4 and OH oxygen in alunite (0.57:0.43), all produced oxygen yields consistent with this assumption. The large ^{18}O fractionation measured during fluorination of various anhydrous sulfates was found to be dependent on the ratio of mono to divalent cations in the presence of aluminum, indicating that the $\Delta^{18}O_{SO4(GR\text{-}Fl)}$ determined for barite cannot be applied directly to alunite or mixtures of monovalent sulfates and $Al(OH)_3$ simulating alunite stoichiometry (Fig. 4). This also suggests that it may be important to obtain chemical analyses on some alunites such as those from the *magmatic hydrothermal* environment. which often contain significant amounts of Ca^{+2} and Sr^{+2} (c.f. Aoki, 1991).

$\Delta^{18}O_{SO4(GR\text{-}Fl)alunite}$ (10.5‰ in our laboratory) was determined by comparison of $\delta^{18}O_{SO4}$ values obtained by conventional graphite reduction with those by fluorination of reagent mixtures of K_2SO_4, $BaSO_4$ and $Al(OH)_3$ that bracket the cation ratios of stoichiometric alunite (Fig. 5). The empirically determined value for stoichiometric alunite takes into account all necessary corrections that must be applied for the fluorination technique. Thus, $\delta^{18}O_{OH}$ is calculated by solving for $\delta^{18}O_{OH}$ in the mass balance equation:

$$\delta^{18}O_{BrF5\ alunite} = 0.40\,[\delta^{18}O_{SO4} - \Delta^{18}O_{SO4(GR\text{-}Fl)alunite}] + 0.60\,\delta^{18}O_{OH}$$

where $[\delta^{18}O_{BrF5alunite}]$ represents the measured bulk oxygen composition by BrF_5 fluorination, $[\delta^{18}O_{SO4}]$ the sulfate oxygen composition measured independently by graphite reduction of $BaSO_4$ produced by the NaOH dissolution procedure, and $[\Delta^{18}O_{SO4(GR\text{-}Fl)alunite}]$ the experimentally determined fractionation for O_2 (10.5‰) produced by fluorination of alunite. The coefficients 0.40 and 0.60 represent the actual molar ratios of SO_4 and OH oxygen liberated by the fluorination of alunite which are calculated from the true molar ratio of 0.57:0.43 after taking into account the 50% oxygen yield from the sulfate site.

It is known that the value for the fractionation between anhydrous sulfates and O_2 liberated during fluorination by BrF_5 varies among laboratories. The modification in this fractionation due to the presence of cations along with aluminum appears to be a constant. Therefore it is useful to consider $[\Delta^{18}O_{SO4(GR\text{-}Fl)alunite}]$ as consisting of two parts: the large $BaSO_4$-O_2 fractionation which must be determined for each laboratory and a small constant due to presence of cations and aluminum during fluorination. This constant is 1.5‰ (.6/.4) as determined in Figure 5. It must be added to the individual $BaSO_4$-O_2 factor for each laboratory to determine the proper $[\Delta^{18}O_{SO4(GR\text{-}Fl)alunite}]$ for that laboratory. This procedure is important for interlaboratory comparison of data and for the proper application of experimental curves of Stoffregen et al. (in press) which were determined in this laboratory.

The uncertainty of the calculated $\delta^{18}O_{OH}$ values reflects the combined uncertainties of the $\delta^{18}O_{SO4}$ from graphite reduction and $\delta^{18}O_{BrF5}$ from fluorination procedures. The $\Delta^{18}O_{SO4(GR\text{-}Fl)alunite}$ and molar ratio coefficients are treated as constants in the equation and therefore do not enter into the calculation of the precision of $\delta^{18}O_{OH}$. The molar ratio coefficients are determined by the O_2 yield factor from the sulfate site which is based on over 80 BrF_5 analyses of various sulfate minerals. An uncertainty of 2% in this quantity (2σ for entire data set) results in an uncertainty on $\delta^{18}O_{OH}$ of only ± 0.05‰ (based on typical analyses of Marysvale alunite standard), which in relation to other analytical uncertainties can be ignored. Likewise, $\Delta^{18}O_{SO4(GR\text{-}Fl)alunite}$ is applied as a constant consistently to all calculated results and therefore affects only the accuracy of the overall population of $\delta^{18}O_{OH}$ data and not the precision of individual measurements. The normal precision (1σ) of the $\delta^{18}O_{SO4}$ analysis of alunite is about ± 0.15‰, as discussed in the previous section. Replicate (8) analyses of the Marysvale alunite standard (MAL) gave an analytical uncertainty (1σ) of ± 0.17‰ for $\delta^{18}O_{BrF5}$. The resulting uncertainty for calculated $\delta^{18}O_{OH}$ values is therefore about ± 0.3‰.

Hydrogen (δD)

The hydrogen isotopic composition of alunite is determined by a modification of the standard procedure originally developed by Godfrey (1962) for outgassing and induction heating of hydrous minerals. The main problem encountered during the analysis of δD in alunite is the poor precision that results from the formation of H_2SO_4 in the extraction line as SO_2 released during thermal break down reacts with H_2O. However, the formation of H_2SO_4 can be suppressed by careful step heating of the alunite only to a temperature high enough to just completely dehydrate the mineral. Alunite loses H_2O at about 500°C and starts to lose SO_2 at about 600°C. The step heating procedure results in a relatively clean separation that removes all of the H_2O before large amounts of SO_2 are evolved. The SO_2 that is formed during dehydration can be easily removed by fractional distillation before passing the water through the heated uranium trap. An added advantage of heating to only the temperature of complete dehydration is that the reaction vessels and manifold do not get contaminated by the highly volatile alkali oxides that form during the high temperature breakdown of alunite. With these modifications it is possible to measure δD values of alunite with a precision of better than ±3‰.

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APPENDIX A

ALUNITE-KAOLINITE SEPARATION PROCEDURE

The goals of this procedure are to obtain high purity concentrates of alunite and kaolinite from samples containing a mixture of the two. To do so several size fractions may have to be prepared. The size fractions that have been chosen arbitrarily are (in micrometers): >40, 40-10, 10-2, 2-0.2 and <0.2. The separation of the first fraction is necessary in order to achieve an effective separation of the finer particles. Generally, kaolinite will be concentrated in the finest size fraction (<0.2 µm) and the alunite in the intermediate fractions; however, if the sample contains very fine-grained illite, the 2-0.2 µm fraction may contain a larger proportion of kaolinite. Quartz, feldspar and pyrite (commonly associated minerals in acid-sulfate assemblages) are concentrated with alunite in the intermediate fractions and must be removed by other procedures. In many cases the laborious procedures required to make intermediate size fraction separations can be avoided; alunite concentrates are typically prepared from the coarse fractions by winnowing out the clays by repeated elutriation, and a high purity concentrate of kaolinite can often be obtained by filtration or evaporation of the supernatant liquid processed to contain a <2 or <0.2 size fraction.

Evaluation of the raw sample by XRD or SEM techniques is recommended; often it will provide useful guidance in choosing the separation procedures. It is particularly important to know if we are dealing with kaolinite, dickite or halloysite because the tubular halloysite crystals are generally very fine-grained and will concentrate in the finest fraction. Identification of halloysite is straight forward using XRD: the 001 and 002 reflections are broad and asymmetric toward the low-angle side, there is an almost total absence of well-defined non-basal reflections, and the diagnostic tubular morphology reflection at 4.42Å is more intense than the basal reflections (Wilson, 1987).

The procedure described below is a modification of Jackson's (1985) separation recipe. It gives excellent results for separation of clays and can also be used for the purification of quartz and alunite when they are coarser-grained. For illustration, X-ray diffractograms of two case examples from the Riaza alunite-kaolinite deposit, Spain, are shown: 1) Sample AAR6, composed of a mixture of quartz, alunite, kaolinite and illite (Fig. 6a) resulted in a <0.2 µm fraction consisting of kaolinite and minor illite (Fig.6b); 2) Sample AAR11(Fig. 7a), a mixture of alunite and halloysite produced two monomineralic separates in size fractions 10-4 µm (Fig. 7b) and <0.2 µm (Fig. 7c). This case was relatively exceptional because the two minerals formed two very distinctive size populations (Fig. 8).

Mineral separations is often an art. The procedure below describes a comprehensive, but complex and time consuming methodology long used successfully by clay mineralogists and soil scientists to produce various size fractions for a variety of analyses. In practice, because the grain size of alunite and kaolinite differs greatly in most samples, pure alunite and kaolinite can be obtained by selective use of just some of the appropriate steps listed below. It is often expedient to split the sample, processing one split to obtain a purified alunite split, the other to obtain a pure kaolinite split. Some samples, where both alunite and kaolinite are very fine grained (especially samples from supergene alteration zones) defy separation of pure alunite, although pure kaolinite can usually be obtained.

PROCEDURE

1. **Crushing.** Crush approximately 50 g of sample lightly with a ceramic or agate mortar and pestle. The goal is to separate the softer minerals, not to powder the sample.
2. **Separation of >0.5 mm fraction.** Sieve, label, and store the >0.5 mm fraction for future processing, if necessary to increase yield. Step 1 may be repeated with the > 0.5 mm fraction if desirable.

3. **Suspension**. Weigh 5-20 g of the <0.5 mm fraction into a 250 ml beaker. Add 150-200 ml distilled H_2O and shake. If a mechanical shaker is available, shake slowly overnight. Slow stirring overnight with a magnetic stirrer is an alternative method of initial dispersion.
4. **Adjusting pH.** Many samples of acid-sulfate alteration make a very acid suspension when added to water. This in turn often causes flocculation of clays. Check of suspension with litmus paper and, if necessary, add .2N NaOH to adjust pH to approximate neutrality. (note: repeated washing of the sample usually accomplishes the same result, but high speed or long term moderate speed centrifugation is required to avoid loss of the finest material).
5. **Addition of anti-flocculent**. Let stand for ~1 minute after shaking and check to see if the sample flocculates (you will see a sharp boundary in the suspension instead of a homogeneous mixture). If it does, add a few ml (always less than 5% by volume) of a 1% sodium-hexa-meta-phosphate solution . Increase the amount only if necessary.
6. **Ultrasonic suspension**. In most cases, the use of an ultrasonic probe will result in an excellent separation and dispersion of individual clay particles (a normal ultrasonic bath will not be powerful enough). Use 250 ml glass beakers for ~15 min. To avoid overheating the suspension and any possibility of oxygen or hydrogen isotope exchange, the beaker is immersed in an ice slurry while using the ultrasonic probe.
7. **Separation of the >40µm size fraction**. The removal of the >40 µm size fraction by wet sieving will leave a homogeneous suspension that will facilitate later centrifuge separations. Use a 500 ml beaker and a small glass funnel with a long stem to support the 325 mesh sieve. The sieve should be made of disposable nylon to reduce contamination. Allow the freshly stirred suspension to stand 40 sec. for each 10 cm of its depth before decanting it through the sieve. This action will speed the process by avoiding the obstruction of the sieve.
8. **Separation of 40 to 10 µm size fraction**. The suspension of particles <40 µm is transferred to graduated cylinder, shaken and then allowed to stand quietly for at least 150 seconds (but not over 200 seconds) for each 1 cm of depth (recommended, 10 cm) (Jackson, 1985). The supernatant liquid is then carefully decanted into a beaker. The sediment portion is brought into suspension again by the addition of distilled water and diluted to a depth of 5 cm. After allowing it to settle for 12 minutes, the supernatant liquid is decanted as before. The sediment is dispersed a third time in distilled water and allowed to settle for about 9 minutes, the exact time for the 10 µm limiting diameter at the existing temperature being obtained from the nomogram in Fig. 9.

8 **Separation of the 10-2 µm size fraction via centrifuge**. The separation of the <2 µm fraction can be achieved by column settling (syphoning after allowing to stand for more than eight hours for each 10 cm). However, a centrifuge separation procedure is preferred because it saves considerable time and is highly efficient. The apparatus used by Jackson (1985) is an International No. 2 centrifuge (International Equipment, Boston) with No 240 head, speed indicator and a rack of 100-ml centrifuge tubes. Any other centrifuge can be used as long as the exact parameters for the separation of different size fractions at given temperatures are known.

The suspension resulting from the 10 µm separation is transferred to the centrifuge tubes, to a suspension depth of 10 cm. The suspension is centrifuged for 4 min at 750 rpm and the supernatant suspension is decanted into a large flask. The sediment in the bottom of each tube is suspended into a small portion of distilled H_2O and the suspensions of one sample in the several tubes are combined by transfer to fewer centrifuge tubes (if possible to only one) as the successive centrifugation and decantations progress. Next, the tube is centrifuged at 750 rpm for 3.2 min (Table 2). Centrifuge speeds corresponding to various temperatures and size fractions can be found on Fig. 10. The processes of resuspension, centrifugation, and decantation are continued until the supernatant suspension is fairly clear. According to Jackson (1985), about 90% of the clay yield is obtained in the first 3 centrifugings. The fine silt (particles 10 to 2 µm), remaining in the bottom of the centrifuge tube, is washed into a ceramic evaporating dish lined with plastic wrap and allowed to evaporate in a vacuum oven at 50°C. Drying on the plastic film allows an easy and efficient collection of the sample. Before drying, an aliquot of the suspension can be pipetted and deposited on a glass slide for observation under the SEM and XRD analysis.

9 **Separation of the <0.2 µm fraction via centrifuge.** The apparatus and procedure are identical to the previous step and only the centrifugation time and speed are different. The first set of suspensions, brought to a depth of 10-cm in the tubes, is centrifuged in the International No. 2 centrifuge for 30 minutes at 2400 rpm. For the subsequent centrifuging periods use 2400 rpm and 25 minutes (see Table 2 and Fig. 10); usually 3 centrifugations suffice. Dry the coarse clay fraction (particles 2-0.2µm) in a ceramic evaporating dish lined with plastic wrap.

10 **Separation of the <0.2 µm fraction via ultrahigh speed centrifuge.** The procedure is again the same as before, this time requires a centrifuge capable of depositing the <0.2 µm particles, such as a Sorvall refrigerated centrifuge ideally with GSA and SS-34 heads. Start the centrifugation by using the six 250-ml beakers of the GSA head for 15 min at 10,000 rpm. Throw away the supernatant liquid, which should be totally clear. The sediment in the bottom of each tube is suspended into a small amount of dist. H_2O by shaking vigorously and the suspensions of one sample in several tubes are combined into one of the smaller tubes of the SS-34 head. Centrifuge for 10 min at 15,000 rpm, throw away the supernatant liquid, resuspend the bottom sediment in a small portion of distilled H_2O and wash into a ceramic evaporating dish lined with Saran Wrap. Prior to drying in the vacuum oven an aliquot can be pipetted for X-ray analysis and SEM observation.

Table 1. Time required at various centrifuge speeds and temperatures for sedimentation of particles using an International no. 2 centrifuge with No. 240 head and 100 ml tubes (Jackson, 1985).

Particle limiting diameter	Specific gravity of particle	Centrifuge speed	Centrifuging time require at a suspension temperature of:			
			20°C	25°C	30°C	35°C
mm	gr/cc	r.p.m	Min.			
5.0	2.65	300	3.3	2.9	2.6	2.4
2.0	2.65	750	3.3	2.9	2.6	2.4
0.2	2.50	2400	35.4	31.4	28.1	25.4

Note: 10 cm suspension depth, 1 cm of sediment, and 9 cm net depth of fall.
Centrifuging times for more extensive range of particles sizes, temperatures, and centrifuge speeds are given in Fig. 10.

APPENDIX B

DETAILED PROCEDURE FOR DISSOLUTION OF ALUNITE IN NaOH

The following wet chemical technique is used to prepare alunite samples for $\delta^{18}O_{SO4}$ and $\delta^{34}S$ analyses. Basically, alunite is dissolved in a sodium hydroxide solution and the sulfate precipitated as $BaSO_4$.

1 Weigh the alunite bearing sample and place in 400 ml beaker. 80–120 mg of pure alunite is a convenient amount that will provide enough sample for all analyses as well as duplicate runs if necessary. The sample should be sized to 120-325 mesh to assure complete dissolution with minimum loss of alunite.

2 Fill the beaker with freshly prepared 0.5N NaOH solution using approximately 2 ml/mg alunite. It is desirable to maintain a fixed ratio of solution to sample in order to restrict the Al^{3+} concentration to a narrow and predictable range. NaOH solution is prepared from "low carbonate" reagent grade NaOH pellets. The NaOH solution should be kept tightly covered between uses since it readily dissolves atmospheric CO_2. NaOH solutions which receive repeated exposure to the atmosphere over long periods of time may precipitate Na_2CO_3. Use of such solutions should be avoided since it complicates the alunite dissolution procedure.

3 Heat the sample on a hot plate at 80 ± 10°C for approximately 3 hours. Check visually for dissolution of alunite.

4 Cool samples until filtering can be performed.

5 Filter samples using large diameter 0.4 ml Nucleopore filter paper. Save the filtrate and return it to the beaker after rinsing the beaker with distilled water to remove any solid residue. Heat and stir at 80°C.

6 Measure the pH of the hot, filtered solution in the beaker and quickly acidify the solution by adding 10N HCl. The idea is to make the solution reach a pH of 2.8 to 2.95 rapidly, before $Al(OH)_3$ precipitates at the intermediate pH's. If the solution becomes too acidic (<2.7) back tritate with 0.5N NaOH to 2.8–2.95.

7 Immediately add one squirt of 0.5N $BaCl_2$ solution to precipitate $BaSO_4$. Continue stirring while heating. This will coarsen the precipitate and make final filtration much easier. Add another squirt of 0.5N $BaCl_2$ about 30 min after the initial application. Continue heating for 1–3 hours.

8 Acidify the solution to prevent formation of $Al(OH)_3$ upon cooling. A few drops of 2N HCl is sufficient.

9 Before filtering, add a few ml. of 10N HCl to each beaker. This will make filtration much faster. Filter, dry, weigh, and record yield.

FIGURE CAPTIONS

Fig. 1. Flow diagram showing an overview of the complete procedure for the separation and purification of alunite and associated minerals and subsequent stable isotope analysis. Branches of the diagram pertinent to the stable isotope analysis of alunite are highlighted. Those procedures that are new or represent substantial modifications of an existing method are discussed in detail in the text. The minimum amount of alunite required to perform a given analytical procedure is indicated, as are the typical amounts of products that result from the procedure. The milligram quantities that appear alone in small rounded rectangles represent the average minimum amount required for each of the standard stable isotope extraction techniques, as presently performed in our laboratory. Rounded rectangles indicate the product (mixture, separate, or other pure substance) of a procedure, ovals mark a process or procedure for separation or purification, rectangles show the standard stable isotope extraction procedures, circles indicate the gases, and diamonds mark the stable isotope analyses which are the object of the overall procedure.

Fig. 2. Diagram showing aluminum solubility as a function of pH for alunite dissolution in 0.5N NaOH at 80° C. The shaded region indicates the pathway followed during tritation with HCl from alunite dissolution to subsequent $BaSO_4$ precipitation in order to prevent coprecipitation of alunite or $Al(OH)_3$. The typical aluminum concentration range for alunite shown on the diagram is constrained by the requirement of maintaining a sufficiently high $SO_4^{=}$ concentration for efficient recovery of $BaSO_4$. The data for the diagram was calculated by G. Plumlee using the program SOLVEQ (Reed, 1982). Total molality of Al^{3+} was fixed assuming gibbsite saturation at high pH or alunite saturation at low pH, using Cl^- for charge balance.

Fig. 3. Comparison of $\delta^{18}O_{SO4}$ values of pure anhydrous sulfates obtained by graphite reduction and fluorination by BrF_5. All data points represent the average of a minimum of 5 measurements by fluorination and 1-2 measurements by graphite reduction. The 13 samples represented by square symbols correspond to natural and synthesized barites with values chosen to span the entire natural range of $\delta^{18}O_{SO4}$ values. Also shown on the diagram are results for two monovalent sulfates (K_2SO_4, Na_2SO_4) run by both methods. For analysis by graphite reduction, both of these samples were first converted to $BaSO_4$. The diagram demonstrates that the measured fractionation ($\Delta^{18}O_{SO4(GR\text{-}Fl)}$) of 9.0‰ is constant over the natural range of $\delta^{18}O$ values and is essentially independent of cation. This value is considered valid for pure anhydrous sulfates that do not contain aluminum. When the sulfate contains a monovalent cation in the presence of aluminum, $\delta^{18}O_{SO4}$ differs from the values obtained for pure $BaSO_4$, K_2SO_4 and Na_2SO_4 (see Fig. 4).

Fig. 4. Comparison of predicted versus measured $\delta^{18}O_{BrF5}$ for reagent mixtures of $Al(OH)_3$ plus mono or divalent sulfates which simulate the 0.57:0.43 molar ratios of SO_4 and OH oxygen in alunite. The size of the symbols is approximately equal to the analytical uncertainty.

Fig. 5. Comparison of $\delta^{18}O_{BrF5}$ Predicted-Measured versus molar ratio of K + Na to $[(OH)_3 + SO_4]$ for various mixtures of K_2SO_4, Na_2SO_4, $BaSO_4$ and $Al(OH)_3$.

Also shown is the value calculated for $\Delta^{18}O_{SO4(GR\text{-}Fl)alunite}$ (right side of vertical axis) which is used in the equation for calculation of $\delta^{18}O_{OH}$. Except Nos. 12 and 14, all data points represent mixtures of sulfates and $Al(OH)_3$ with molar ratios of oxygen in SO_4 and OH that are the same as stoichiometric alunite (0.57:0.43). This is essentially an experiment showing the result of varying K content while holding SO_4 + OH as well as the ratio of oxygen in SO_4 to OH constant. The data point No. 13 shows the effect of adding K only (as KCl) to the same mixture of $BaSO_4$ and $Al(OH)_3$ shown elsewhere on the diagram and sample No. 14 shows the effect of a mixture with a SO_4:OH ratio (0.2:0.8) different from that of alunite. Both points agree reasonably well with the regression line, supporting the conclusion that $\Delta^{18}O_{SO4(GR\text{-}Fl)alunite}$ is a function only of cation to total oxygen ratio in the sample.

Fig. 6. X-ray diffractograms from a rock sample formed by the typical acid-sulfate alteration assemblage: (**a**) whole rock, (**b**) <0.2 mm size fraction.

Fig. 7. X-ray diffractograms from a sample formed by supergene alunite and halloysite: (**a**) whole rock , (**b**) pure alunite separate in size fraction 10 - 4 mm, (**c**) halloysite separate in size fraction <0.2 mm.

Fig. 8. Secondary electron microphotographs of sample AAR11 (see Fig. 7a). Sample is composed of alunite rhombohedra and halloysite tubular crystals forming two distinct size populations.

Fig. 9. Settling time by gravity acceleration of particles of different grain size at various ambient temperatures (Jackson, 1985)

Fig. 10. Particle settling time at 20° C by centrifugal acceleration using a International No. 2 centrifuge and 100 ml tubes (Jackson, 1985).

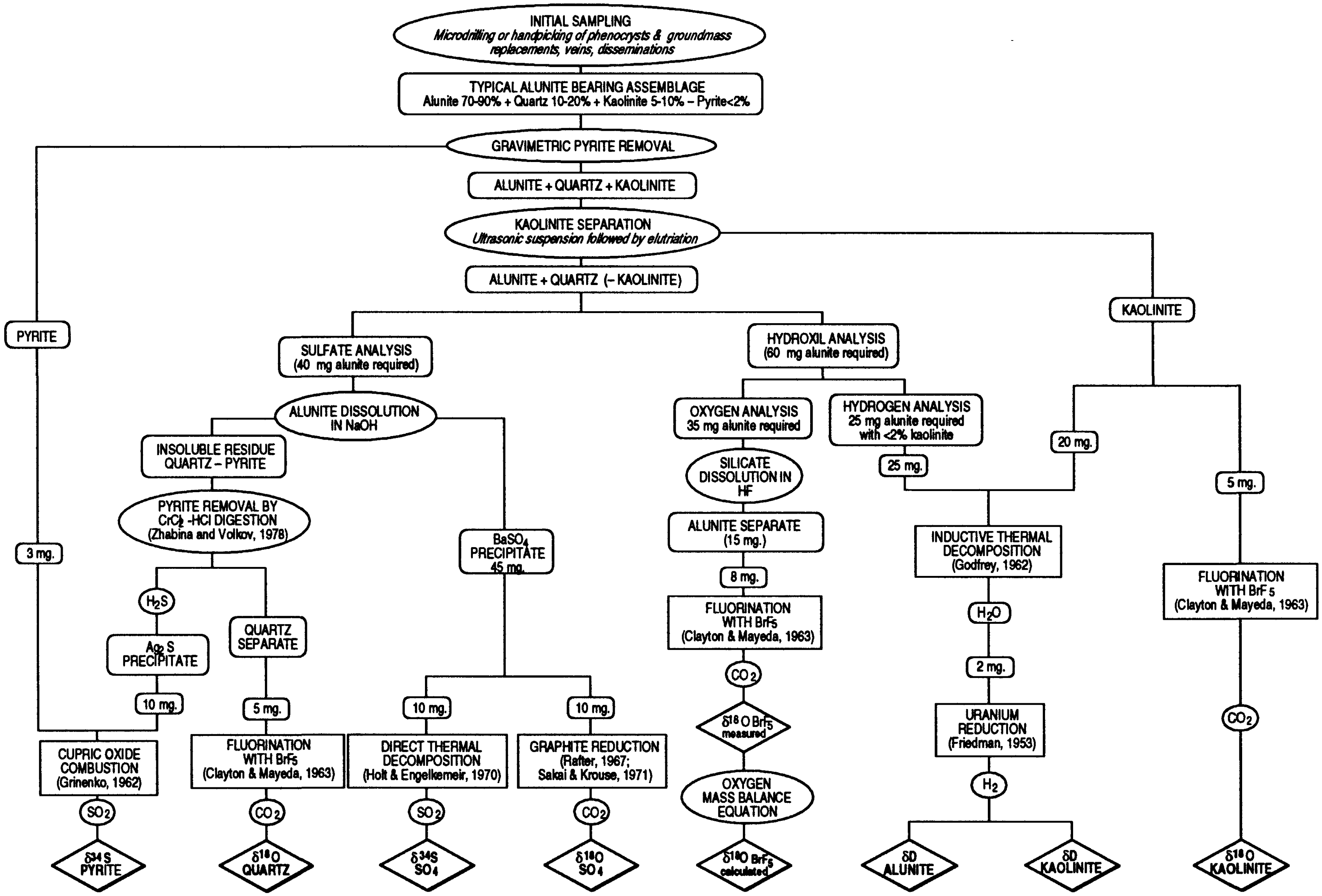
INITIAL SAMPLING
Microdrilling or handpicking of phenocrysts & groundmass replacements, veins, disseminations
TYPICAL ALUNITE BEARING ASSEMBLAGE
Alunite 70-90% + Quartz 10-20% + Kaolinite 5-10% – Pyrite<2%
GRAVIMETRIC PYRITE REMOVAL
ALUNITE + QUARTZ + KAOLINITE
KAOLINITE SEPARATION
Ultrasonic suspension followed by elutriation
ALUNITE + QUARTZ (– KAOLINITE)
PYRITE
3 mg.
SULFATE ANALYSIS (40 mg alunite required)
ALUNITE DISSOLUTION IN NaOH
INSOLUBLE RESIDUE QUARTZ – PYRITE
PYRITE REMOVAL BY $CrCl_2$ -HCl DIGESTION (Zhabina and Volkov, 1978)
H_2S
Ag_2S PRECIPITATE
10 mg.
CUPRIC OXIDE COMBUSTION (Grinenko, 1962)
SO_2
$\delta^{34}S$ PYRITE
QUARTZ SEPARATE
5 mg.
FLUORINATION WITH BrF_5 (Clayton & Mayeda, 1963)
CO_2
$\delta^{18}O$ QUARTZ
$BaSO_4$ PRECIPITATE 45 mg.
10 mg.
DIRECT THERMAL DECOMPOSITION (Holt & Engelkemeir, 1970)
SO_2
$\delta^{34}S$ SO_4
10 mg.
GRAPHITE REDUCTION (Rafter, 1967; Sakai & Krouse, 1971)
CO_2
$\delta^{18}O$ SO_4
HYDROXIL ANALYSIS (60 mg alunite required)
OXYGEN ANALYSIS 35 mg alunite required
SILICATE DISSOLUTION IN HF
ALUNITE SEPARATE (15 mg.)
8 mg.
FLUORINATION WITH BrF_5 (Clayton & Mayeda, 1963)
CO_2
$\delta^{18}O$ BrF_5 measured
OXYGEN MASS BALANCE EQUATION
$\delta^{18}O$ BrF_5 calculated
HYDROGEN ANALYSIS 25 mg alunite required with <2% kaolinite
25 mg.
KAOLINITE
20 mg.
INDUCTIVE THERMAL DECOMPOSITION (Godfrey, 1962)
H_2O
2 mg.
URANIUM REDUCTION (Friedman, 1953)
H_2
δD ALUNITE
δD KAOLINITE
5 mg.
FLUORINATION WITH BrF_5 (Clayton & Mayeda, 1963)
CO_2
$\delta^{18}O$ KAOLINITE

FIGURE 1

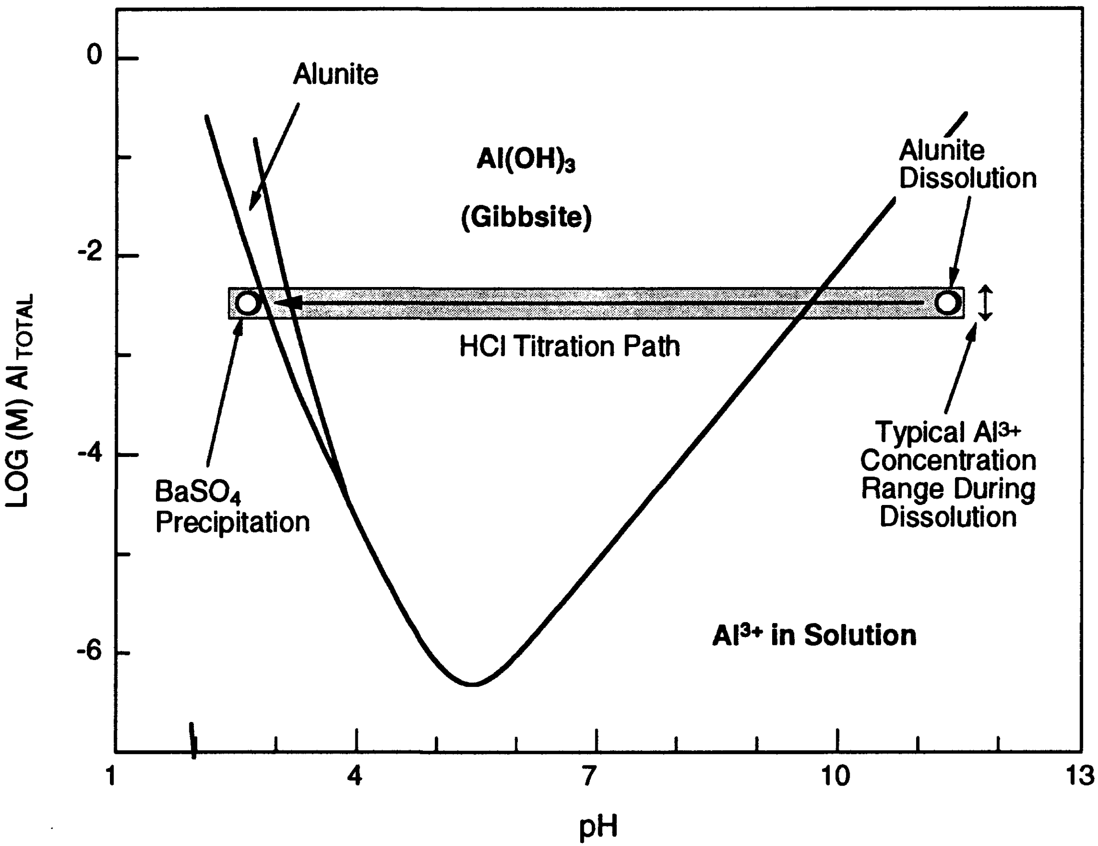

FIGURE 2

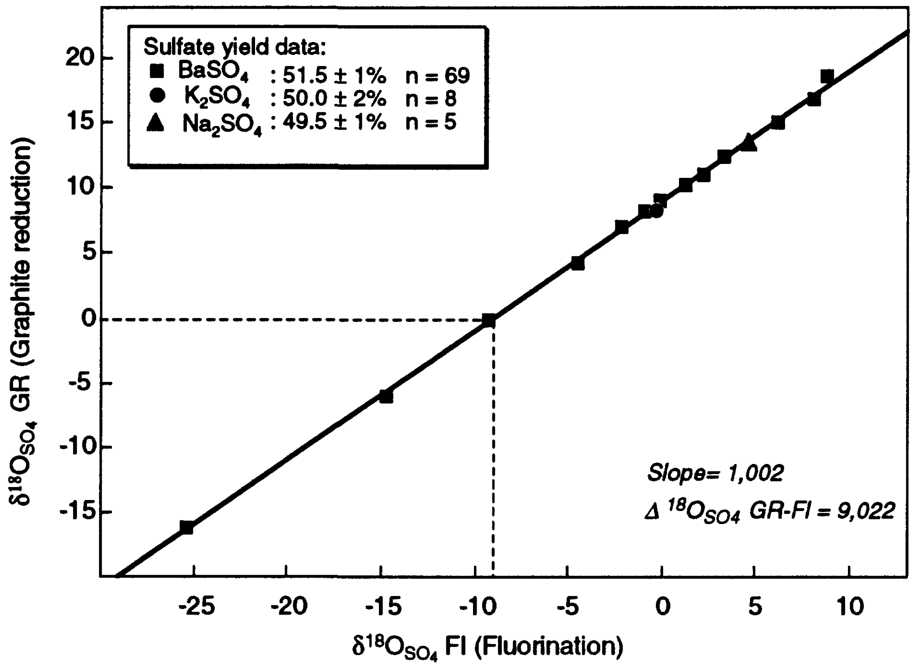

FIGURE 3

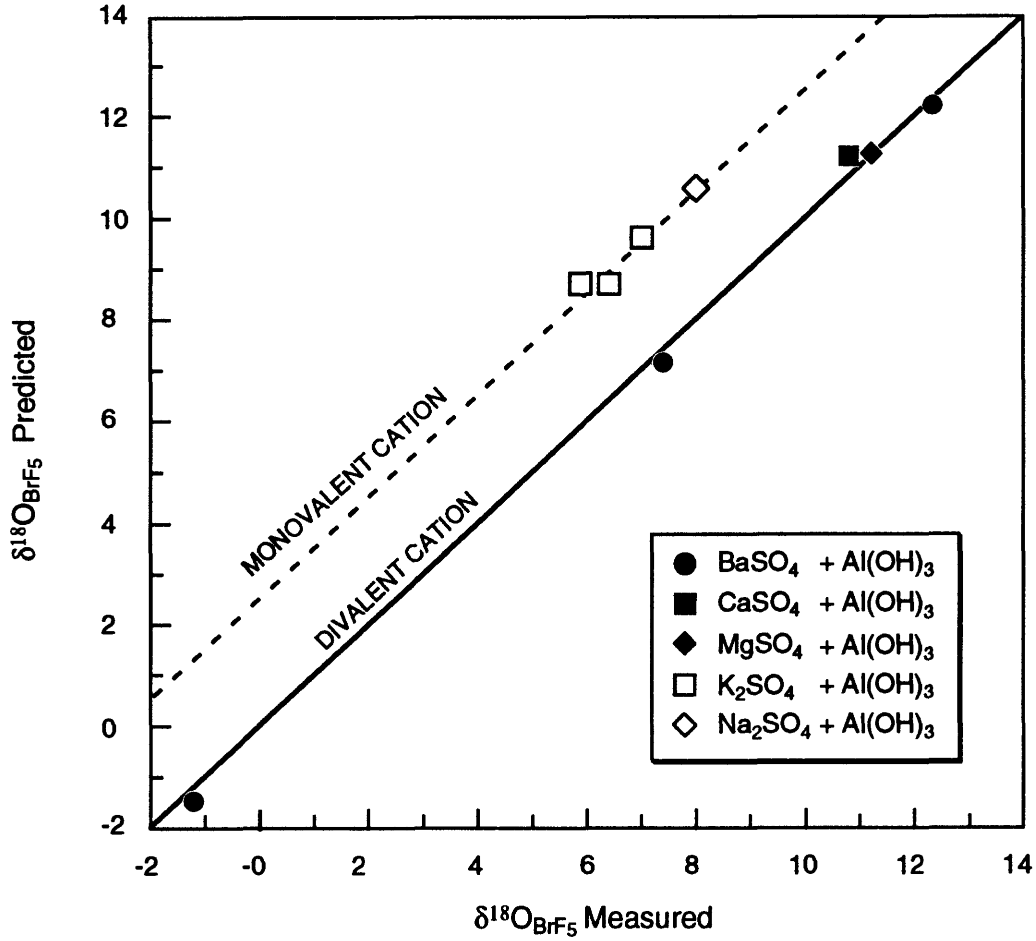

FIGURE 4

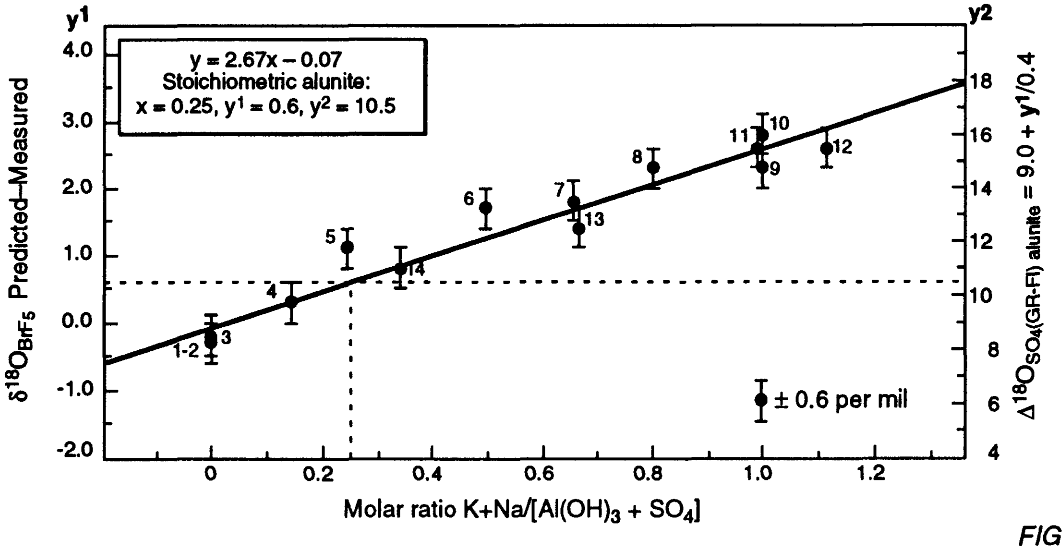

FIGURE 5

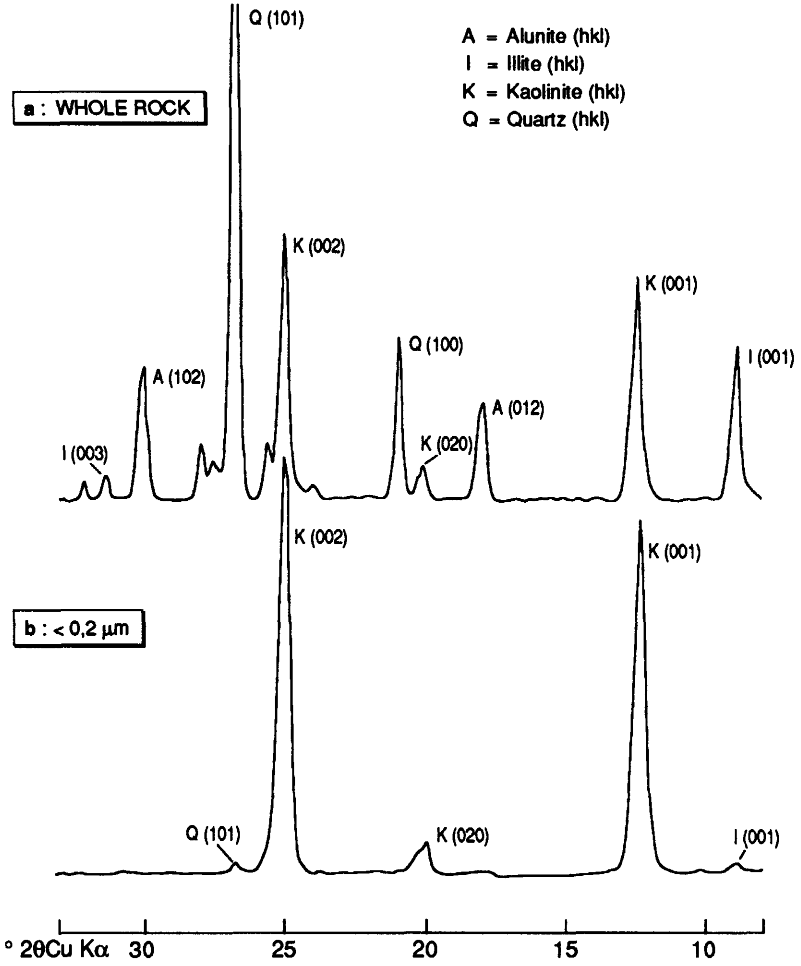

Fig. 6 X-ray diffractograms from a rock sample formed by the typical acid-sulfate assemblage: (**a**) whole rock, (**b**) <0.2 mm size fraction.

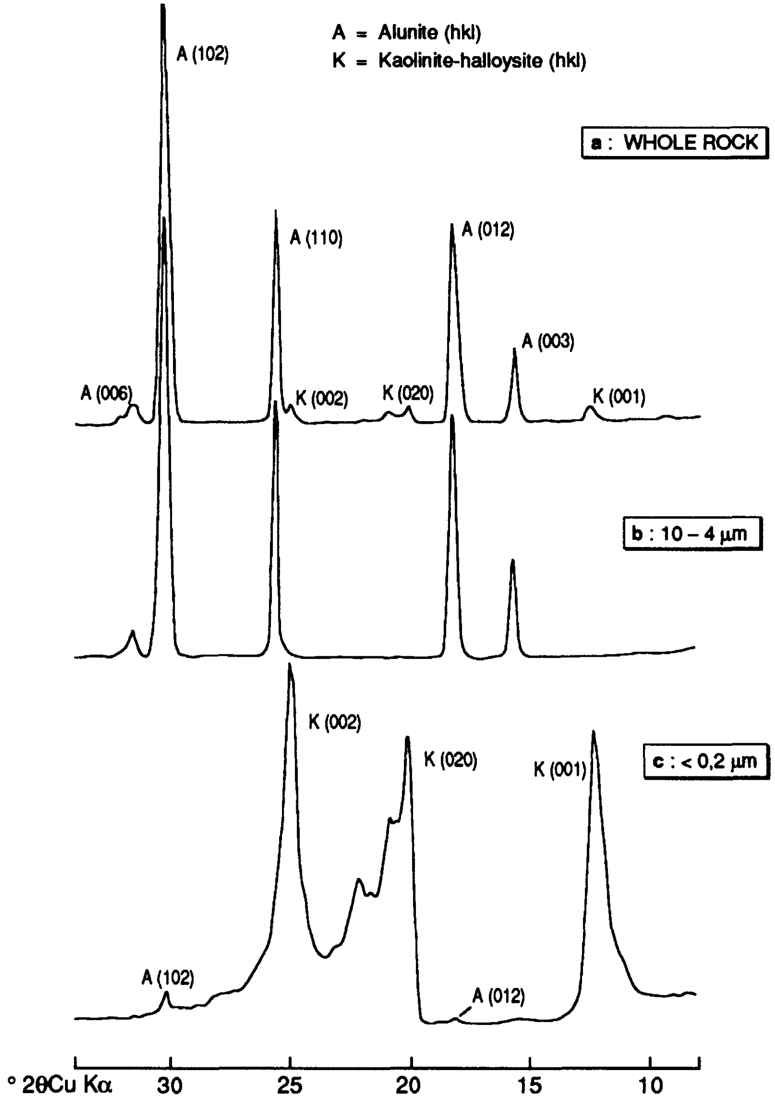

Fig. 7 X-ray diffractograms from a sample formed by supergene alunite and halloysite (see Fig. 9): (**a**) whole rock, (**b**) pure alunite separate in size fraction 10-4 µm, (**c**) halloysite separate in <0.2 µm size fraction.

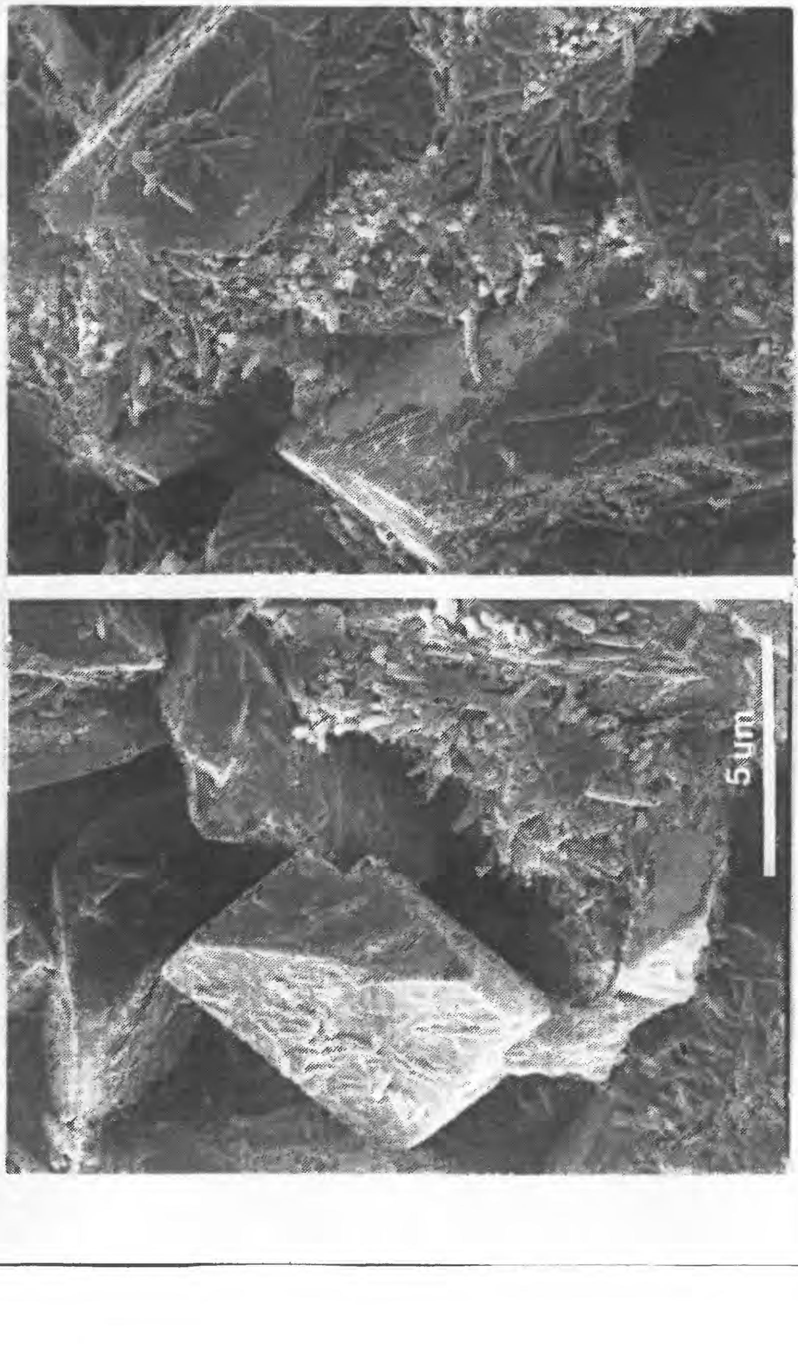

Figure 8

I. PARTICLE SETTLING TIME (GRAVITY ACCELERATION)

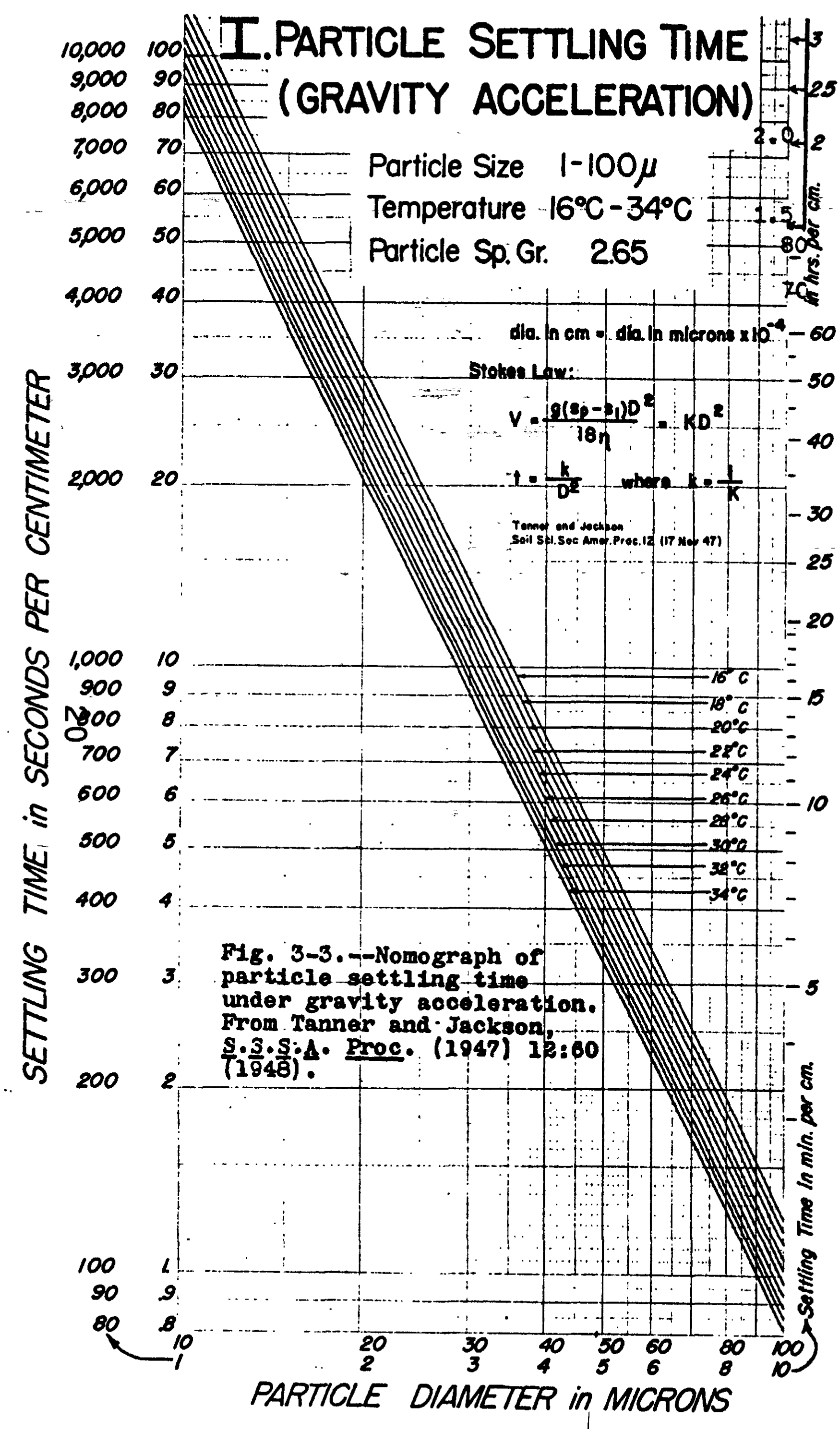

Fig. 3-3.--Nomograph of particle settling time under gravity acceleration. From Tanner and Jackson, S.S.S.A. Proc. (1947) 12:60 (1948).

Figure 9

II. PARTICLE SETTLING TIME - CENTRIFUGAL ACCELERATION

Particle Size: 0.2 - 5.0μ Temperature: 20°C

Particle Sp. Gr.: 2.5 (for particles greater than 1μ convert to 2.65 by Table I)

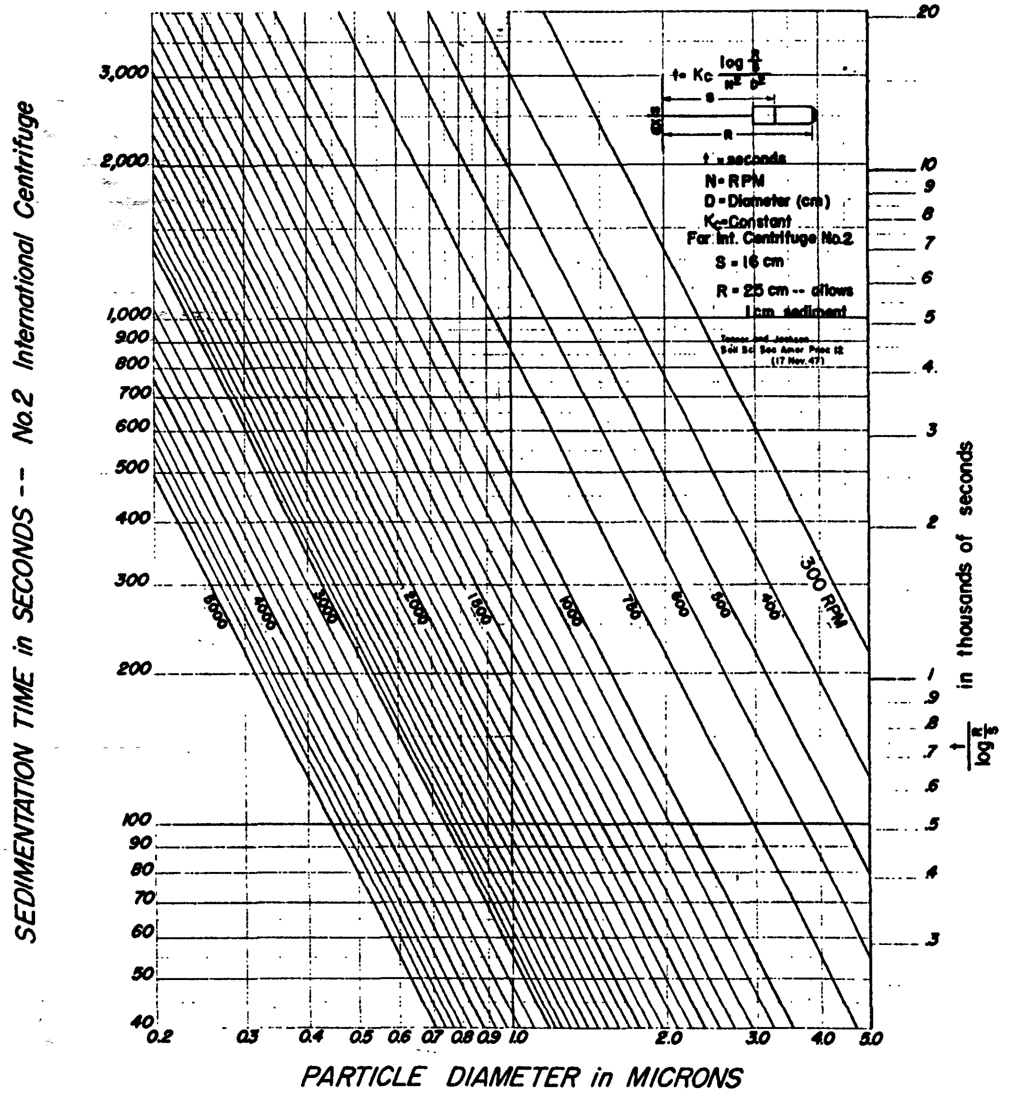

Figure 10