

APATITE IN A GLACIAL LAKE

by

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ABSTRACT

Apatite is a common accessory mineral in the source rocks for the glacial debris supplying recent sediments to many Canadian lakes. Chemical analyses of sediments in Kamloops Lake, British Columbia suggest that this apatite may comprise a significant portion of the total phosphorus load to the lake, thereby overestimating the trophic state that would be predicted by the relationship between total phosphorus load and the ratio of mean depth to flushing time. A method has been developed which uses scanning electron microscopy and energy dispersive X-ray spectrometry for direct identification of apatite. This method has been used to examine the apatite content of various size fractions in Kamloops Lake sediments. Apatite concentrations obtained by this direct examination correlate well with the apatite concentrations of the indirect chemical analyses and indicate that, in addition to comprising as much as 70% of the total phosphorus load, apatite may comprise as much as 20% of the "dissolved" ($<0.45 \mu\text{m}$) inorganic phosphorus load. Therefore, estimates of lake productivity could be erroneous even if dissolved rather than total phosphorus values are used for the estimation.

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INTRODUCTION

Phosphorus is often the limiting nutrient controlling organic growth in aquatic systems in temperate zones (Gakstatter et al., 1975). Vollenweider (1968) and Vollenweider and Dillon (1974) have developed an empirical relationship for lakes which relates annual total phosphorus load, mean depth and flushing time to the trophic state, or productivity of the lake. This relationship, seen in Figure 1, has been used in North America and in Europe as a guide to the degree of eutrophication of lakes and to permissible loading levels (Dillon and Kirchner, 1975; Yeasted and Morel, 1978).

Recent investigations of forms of phosphorus in lake sediments have shown that a large portion of the total phosphorus in some lakes is present as apatite (Williams and Mayer, 1972; St. John et al., 1976). The most abundant form of primary apatite in nature is fluorapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$ (Williams et al., 1976, Deer et al., 1966) and since the solubility of fluorapatite in lake water is extremely low, it is unlikely to be more than a minor source of phosphorus for biological growth. This conclusion is supported by Sagher and Harris (1972), Sagher et al. (1975), Syers et al. (1973), and Williams et al. (1976). Sagher and Harris (1972) and Sagher et al. (1975) investigated the availability of sediment phosphorus and concluded that the non-occluded Fe-bound phosphorus was the most available form of sediment phosphorus, whereas the apatite phosphorus was of limited availability. Syers et al. (1973, p.8) conclude that Ca-P (apatite) in lake water is "essentially immobile". Williams et al. (1976) comment that a high input of apatite-P to Lake Erie prior to 1850 did not render the lake eutrophic. However, Smith et al. (1978) have shown that naturally occurring apatites may provide a source of orthophosphate for growth of bacteria and algae. At present, the question

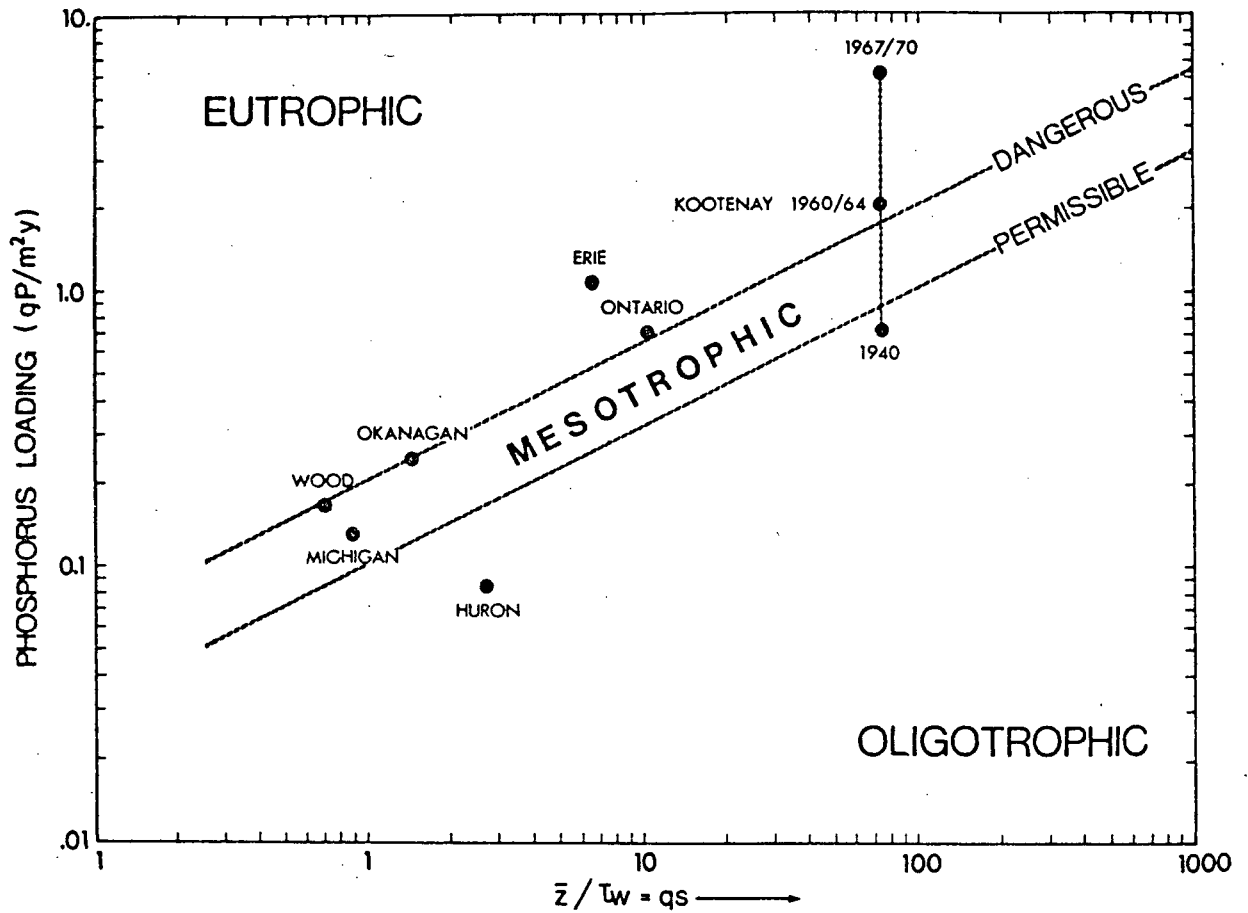


Figure 1. The relationship (Vollenweider, 1968) between trophic state, annual total phosphorus load, mean depth (\bar{z}) and flushing time (τ_w) shown for some Canadian lakes. Kamloops Lake is not plotted due to the difficulties discussed in the text. (from St. John *et al.* 1976)

of how much phosphorus detrital apatite contributes to the nutrient budget of a lake remains controversial.

If apatite phosphorus is largely unavailable for biological growth (or of very limited availability), it should not be included in the total phosphorus loading values used to estimate trophic state. This problem was recognized by Dillon and Kirchner (1975), Peters (1978), and Vollenweider himself (Vollenweider, 1968). Dillon and Kirchner (1975, p. 143) summarized as follows:

"However there will undoubtedly be certain cases where total phosphorus is not the most suitable fraction to work with; for example, some streams may carry a high total phosphorus content that is largely the result of erosion of apatite-bearing rock. In these cases, soluble phosphorus may be biologically a more important consideration. Such a condition exists in the Rhine as described by Vollenweider (1968)."

Fluorapatite is a common accessory mineral in the source rocks for the glacial debris supplying sediments to many Canadian lakes. Kamloops Lake, the subject of the present study, is a 25 km x 2.1 km fjord lake which occupies a glacial valley in the semi-arid, south-central region of British Columbia (Figure 2). Chemical analyses of water and sediment in the lake imply that 70% of the total phosphorus entering the lake is in the form of apatite and that apatite may occur in all size fractions of the lake sediment (St. John et al., 1976). This latter suggestion is significant, for if apatite is present in the lake as particles smaller than 0.45 μm , apatite particles could pass through the membrane filters used to separate "dissolved" from "particulate" materials and be included in the "dissolved" phosphorus

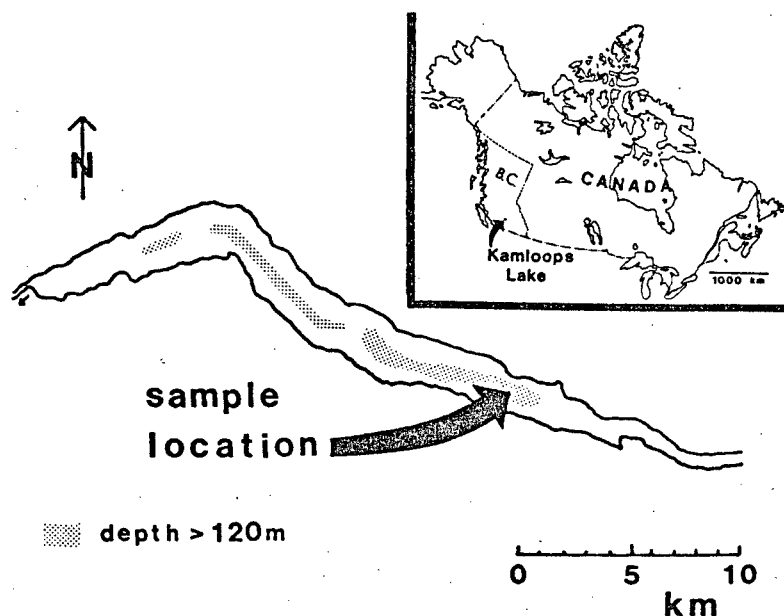


Figure 2. Sample location in Kamloops Lake, British Columbia, Canada.

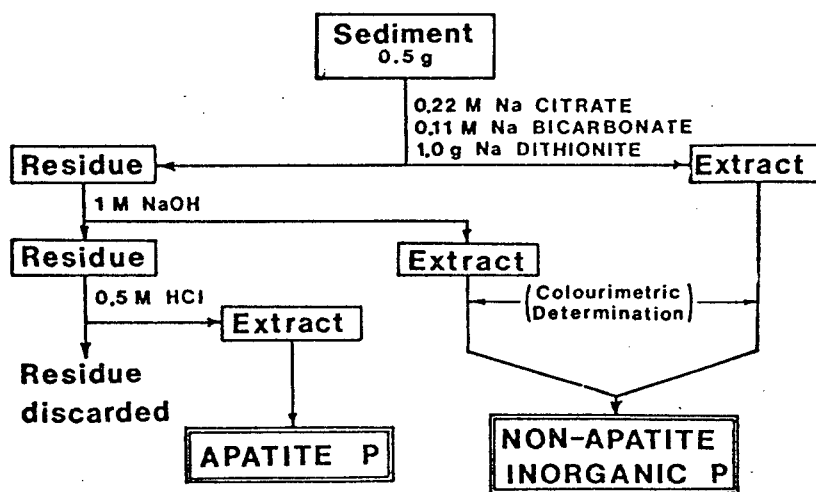


Figure 3. The selective chemical extraction scheme for identification of apatite phosphorus and Non-Apatite Inorganic Phosphorus developed by Williams *et al.* (1976). N.W.R.I. used 1M HCl, rather than 0.5M HCl, to extract apatite phosphorus from Kamloops Lake sediments, as discussed in text.

pool. Therefore, estimates of productivity could be erroneous even if dissolved rather than total phosphorus values are used for the estimation, as suggested by Dillon and Kirchner (1975). Both Williams et al. (1976) and Smith et al. (1978) state that the solubility of apatite increases with decreasing particle size, but no estimates have been made of the availability of phosphorus in apatite that is smaller than 0.45 μm .

The method used to identify apatite in the 1976 Kamloops Lake study was the selective chemical extraction technique of Williams et al. (1976) (Figure 3). In this procedure, sodium dithionite-sodium citrate-sodium bicarbonate (DCB) and NaOH release phosphorus associated with iron and aluminum complexes. The amount of orthophosphate released is determined colourimetrically in a reaction involving the formation of molybdophosphoric acid. The sum of the DCB and NaOH phosphorus is referred to by Williams et al. (1976) as Non-Apatite Inorganic Phosphorus (NAIP). Apatite phosphorus is then released as orthophosphate by dissolution of the apatite in 0.5 M HCl, and the orthophosphate is again measured colourimetrically. There are, however, problems associated with specificity of the colourimetric method for analysis of orthophosphate (Harwood and Hattingh, 1973). Complexes of silicate, arsenate and germanate can form heteropoly acids with molybdenum and interfere with the phosphorus determination. Labile organic phosphorus compounds may also interfere. In general, the chemical extraction technique for identifying forms of phosphorus in soils and sediments has developed as a result of extracting standard compounds in the laboratory and from statistical chemical correlations (Fisher and Thomas, 1935; Williams, 1937; Dean, 1938; Williams, 1950; Chang and Jackson, 1957; Williams et al., 1967; Williams et al., 1971a; Williams et al., 1971b).

Direct methods for identifying and quantifying phosphate minerals in soils and sediments have met with limited success because of the small quantities of these minerals and because of difficulties in petrographic determination (Lindsay and Vlek, 1977). Shipp and Matelski (1960) developed a technique whereby 2 to 3 drops of 10.7 N H_2SO_4 added to sediment on a glass slide caused needle-like calcium sulphate crystals to grow on the surface of apatite grains, thereby facilitating their recognition. In the presence of H_2SO_4 however, carbonate minerals also develop this needle-like growth and differentiation of the carbonates from the apatites is based on a difference in birefringence. Shipp and Matelski (1960) used this method to quantify apatite in a soil profile in Nebraska and correlated the results with the acid soluble phosphorus in a profile in an "adjacent quarter of the same section". The correlation would be more convincing if the measurements were made on samples from the same locality. Sawhney (1973) used the electron microprobe to examine the composition of phosphate grains, but his work is not quantitative. Kingston (1973, p.1) examined the "feasibility of detecting and quantitatively estimating phosphate minerals in lacustrine sediments by mineralogical methods". Kingston concentrated phosphate grains by heavy liquid and magnetic separations and suggested that the microprobe could be used effectively to obtain particle size distribution, relative abundance, and mineralogy of discrete phosphate grains. However, Kingston's method is not quantitative.

The purpose of the present study was to develop a method of physical separation, identification and quantification of apatite in lake sediments and to use this method to investigate the size distribution of apatite in Kamloops Lake. The apatite concentrations of various size fractions of Kamloops Lake sediment obtained by this method of direct observation would be

compared to the apatite concentrations obtained by the selective chemical extraction of the same size fractions. In addition, an attempt would be made to estimate the amount of apatite which may be contributing to the "dissolved" phosphorus load of the lake.

METHODS

Physical Separation, Identification and Quantification of Apatite

A sample of sediment was collected with a Shipek Grab Sampler from the basin floor of Kamloops Lake at a depth of 130 m in the pro-delta region of the Thompson River Delta at the east end of the lake (Figure 2). The particle size distribution of the total sediment was determined by hydrometer analysis. The sample was divided into eight size fractions from 125 μm to $<2 \mu\text{m}$. The 125 to 62 μm fraction was obtained by sieving, the five fractions between 62 and 10 μm by separation in a hydraulic cyclone elutriator (see Appendix 1) and the 10 to 2 and $<2 \mu\text{m}$ fractions by centrifugation. Sedigraph analyses of the 6 fractions from 62 to 2 μm were performed by the National Water Research Institute, (formerly the Canada Centre for Inland Waters) West Vancouver.

Each of the eight size fractions was further subdivided on the basis of density by separation with heavy liquids. As seen in Figure 4, 250 mg of sediment were centrifuged in 50 ml of diiodomethane to remove the particles with density $>3.3 \text{ g.cm}^{-3}$. The light particles from this separation were then centrifuged in 50 ml of an acetone diiodomethane mixture with a density of 3.05 g.cm^{-3} . Apatite was concentrated in the heavy fraction, which will be referred to as the apatite fraction and contains minerals with densities between 3.05 and 3.3 g.cm^{-3} . The theoretical density of fluorapatite is 3.199 g.cm^{-3} (McConnell, 1973); however, isomorphous substitutions in naturally occurring "fluorapatites" result in a range of densities from 3.1 to 3.2 g.cm^{-3} (Berry and Mason, 1959). Densities of some igneous apatites reported by McConnell (1973) range from 3.17 to 3.22 g.cm^{-3} .

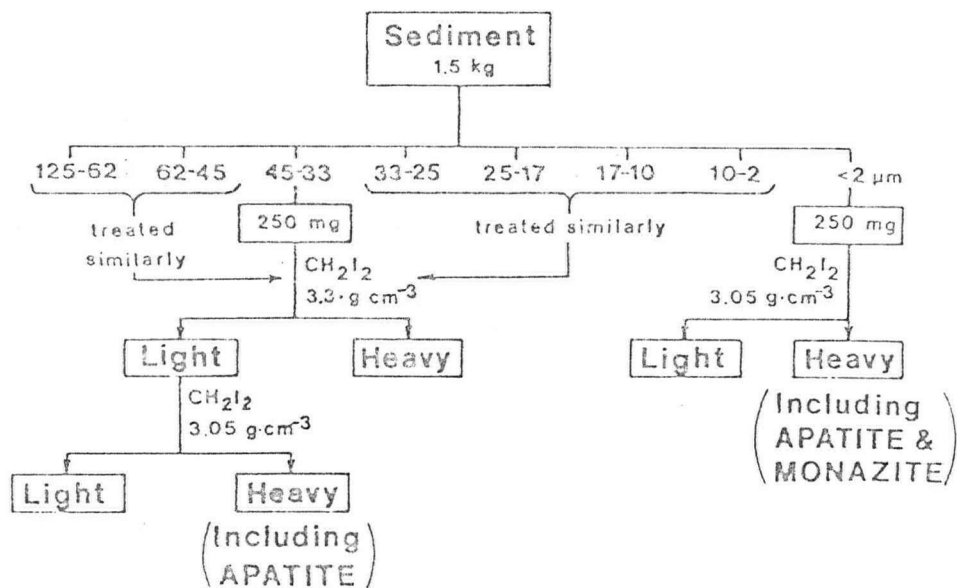


Figure 4. Scheme for heavy liquid separation of apatite.

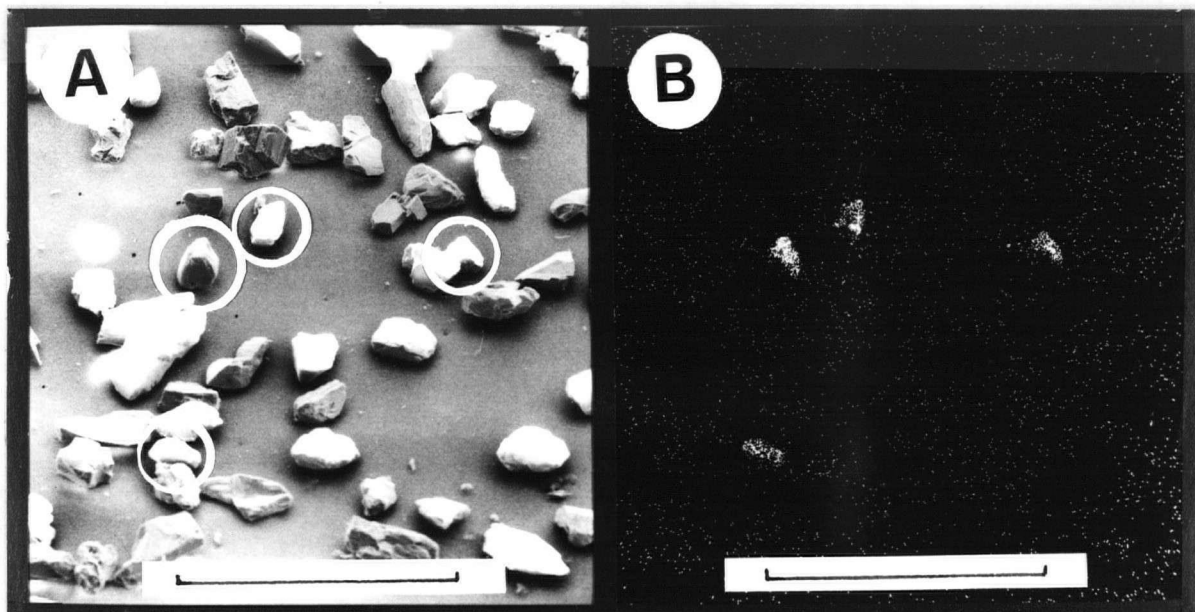


Figure 5. Identification of phosphate grains using a scanning electron microscope equipped with an energy dispersive X-ray spectrometer. Bar in (A) and (B) is 500 μm long.
(A) S.E.M. image. Apatite grains are circled.
(B) Phosphorus K_α image.

The separation procedure described above was followed for all size fractions of the Kamloops Lake sediment except the $<2\ \mu\text{m}$ fraction. Because of the very long centrifugation times required for separation of the $<2\ \mu\text{m}$ fraction, only the $3.05\ \text{g.cm}^{-3}$ separation was done. A detailed description of the separation procedure is presented in Appendix 2. Triplicate or quadruplicate heavy liquid separations of the 5 size fractions from 62 to $10\ \mu\text{m}$ were performed; single separations were done for the other 3 size fractions.

A subsample of each apatite fraction obtained by the heavy liquid separation was mounted on a graphite disc and examined at low magnification with an ETEC autoscan scanning electron microscope equipped with an ORTEC X-ray analytical system. The procedure for the S.E.M. sample preparation and examination is outlined in Appendix 3. Grains in the apatite fraction which contain phosphorus are easily identified in the X-ray image of the phosphorus K_{α} emission, as shown in Figure 5. Once identified, the phosphorus-containing grains may be examined individually at increased magnification and their elemental compositions determined from their X-ray emission spectra.

Since the grains in each sample are approximately equivalent in size and density, the number of grains containing phosphorus divided by the total number of grains in any one S.E.M. 'field', such as that of Figure 5, is a measure of weight per cent apatite in that particular apatite fraction. For each apatite fraction, five fields, each containing approximately 100 to 200 grains, were examined. The five apatite concentrations from the five fields were averaged to obtain a value representing the apatite concentration in the apatite fraction. This number was multiplied by the weight proportion of sample represented by the apatite fraction to obtain a measure of the concentration of apatite in the original size fraction.

Since the heavy liquid separation of fine-grained sediment may be incomplete, a weighed amount of fluorapatite of appropriate size was added to each of the five size fractions from 62 to 10 μm as an internal standard ("spike") to test the recovery of apatite in the apatite fraction. The apatite used for this internal standard was a single inclusion-free crystal of fluorapatite from Durango, Mexico (Sample S-4024, obtained from J. Nagel, U.B.C.). The apatite crystal was crushed and separated into the five size fractions by gravity settling and decantation. As in the unspiked samples for these 5 size fractions, triplicate or quadruplicate analyses (heavy liquid separation and S.E.M. examination) of the 5 spiked fractions were performed. As seen in equation 1, \bar{K}_{ob} , the mean concentration of apatite observed in the spiked sample should be equal to a recovery factor, p , times the amount of apatite added (I) plus p times the apatite in the original sediment (M). However, since p times the apatite in the original sediment is equal to \bar{M}_{ob} , the mean value observed for apatite in the unspiked sample (equation 2), the two equations can be combined to solve for p .

$$\bar{K}_{\text{ob}} = pI + pM \quad (1)$$

$$\text{But } pM = \bar{M}_{\text{ob}} \quad (2)$$

$$\text{so } p = \frac{\bar{K}_{\text{ob}} - \bar{M}_{\text{ob}}}{I} \quad (3)$$

Analysis of apatite from Durango, Mexico which were performed by the U.S.G.S. are reported by Young et al. (1969). The density of the apatite analyzed by Young et al. (1969) was 3.216 g.cm^{-3} .

Selective Chemical Extraction of Apatite

Selective chemical extractions of apatite for this study were performed by the National Water Research Institute, West Vancouver. N.W.R.I. modified the extraction scheme of Williams et al. (1976), Figure 3, in that 1 M HCl, rather than 0.5 M HCl, was used for the apatite extraction. Initial verification of the technique using apatite standards was followed by extraction of seven of the size fractions of Kamloops Lake sediments.

Verification of the selective chemical extraction technique involved extraction of an apatite standard, extraction of sediment with apatite added as an internal standard, and S.E.M. examination of the extracted sediment. The apatite used as the standard was the same crushed fluorapatite from the single crystal from Durango, Mexico which was used in the physical separation spiking procedure. Analyses of apatite from Durango by Young et al. (1969) suggest that impurities in the apatite are less than 1.5 weight per cent and that phosphorus comprises 17.8 weight per cent of the apatite.

ANALYTICAL RESULTS

Physical Separation

Particle size distributions for the total sample and for 6 size fractions are shown in Figures 6 and 7. The weights of each of the three density fractions obtained by heavy liquid separation of each size fraction are summarized in Appendix 4, and the results of point counting apatite grains in the apatite fraction with the scanning electron microscope are summarized in Appendix 5.

Four typical phosphorus-containing grains identified in Kamloops Lake sediment are shown in Figure 8. The phosphorus-containing grains observed in all size fractions, with one exception which will be discussed later, contained both Ca and P in proportions equivalent to those observed in an apatite standard. Some grains have X-ray emission spectra indicating the additional presence of minor amounts of Al, Si, and/or Fe, which are probably present as coatings on the apatite as the grains were not treated to remove sesquioxides. The numbers of grains with these coatings increased slightly in the $<10\text{ }\mu\text{m}$ sizes. A typical X-ray emission spectrum for the phosphorus-containing grains is shown in Figure 9. The X-ray energy from fluorine is not detected by the X-ray emission method used.

The observed apatite concentrations calculated for each sample are reported in Appendix 6. Observation with the scanning electron microscope showed that the "125 to 62 μm " fraction contains a large proportion of grains smaller than 62 μm . When point counting grains in the apatite fraction of this size fraction, only grains of approximate size 125 to 62 μm were counted.

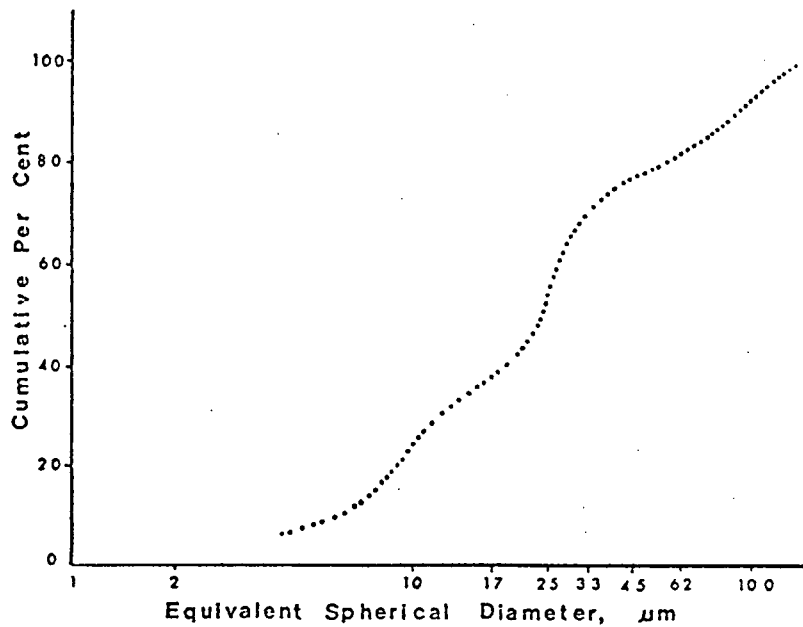


Figure 6. Hydrometer analysis showing particle size distribution of sediment from the pro-delta region of Kamloops Lake.

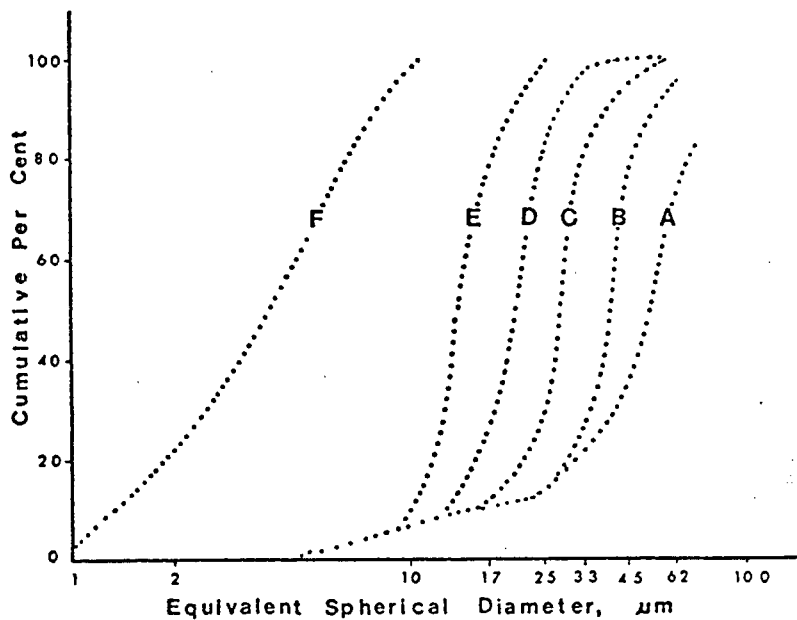


Figure 7. Sedigraph analyses showing particle size distribution of 6 size separated fractions of sediment from Kamloops Lake. Analyses performed at N.W.R.I.

- A = "62 to 45 μm " fraction
- B = "45 to 33 μm " fraction
- C = "33 to 25 μm " fraction
- D = "25 to 17 μm " fraction
- E = "17 to 10 μm " fraction
- F = "10 to 2 μm " fraction

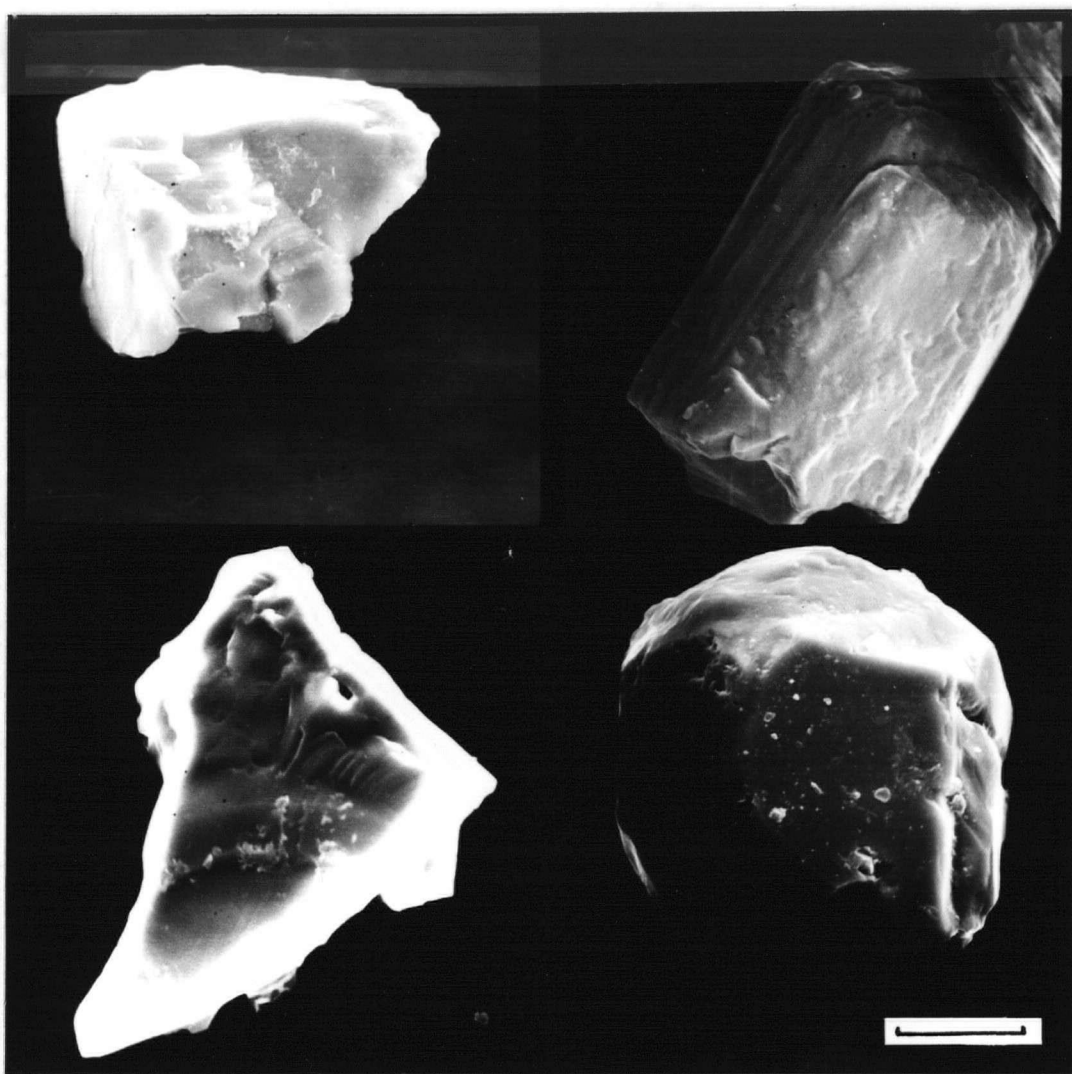


Figure 8. Four typical Kamloops Lake apatites. Bar is 25 μm long.

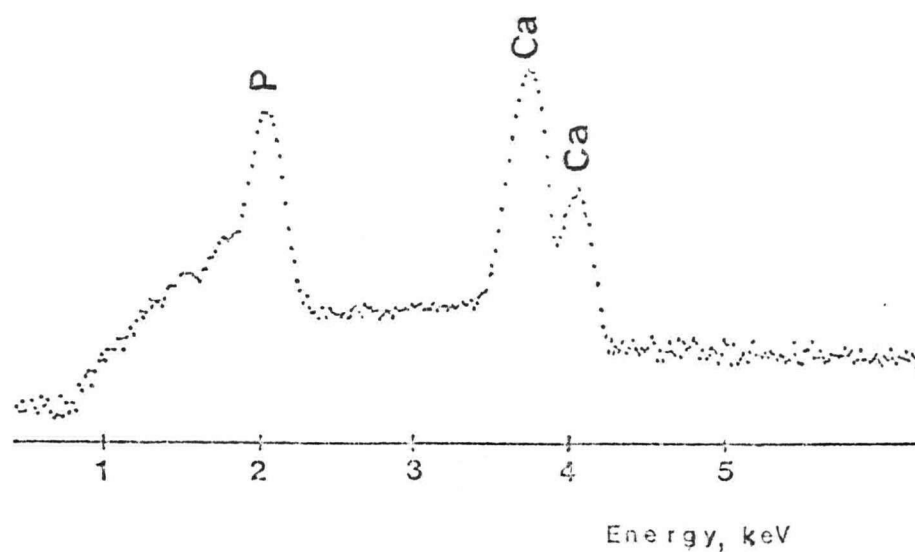


Figure 9. X-ray emission spectrum for Kamloops Lake apatite.

Heavy liquid separation and S.E.M. examination of the five size fractions of both unspiked and spiked samples from 62 to 10 μm were performed in triplicate or quadruplicate. The observed apatite concentrations calculated for these repeated analyses (Appendix 6) were averaged to obtain a mean observed apatite concentration for each of the five fractions. These mean concentrations (\bar{M}_{Ob} and \bar{K}_{Ob}) are summarized in Table 1. The relative standard error of each mean observed apatite concentration is generally about 5%. This error reflects differences between subsamples and variability in estimates of the weight per cent apatite in the apatite fraction.

The mean observed apatite concentration, \bar{M}_{Ob} , of the unspiked sample represents the amount of apatite in the size fraction if the heavy liquid separation of apatite is 100% complete. However, complete separation of fine-grained sediments is unlikely and the means of the spiked and unspiked samples for each size fraction were substituted in equation 3 to calculate the recovery factor, p . The observed apatite concentrations of the 5 unspiked samples were then corrected for incomplete separation in order to estimate the amount of apatite in the original size fraction (M , Table 1).

Recovery of apatite in the apatite fraction (p , Table 1) is seen to decrease with decreasing grain size. The relative standard errors of the recoveries, and consequently of the corrected apatite concentrations (M), are about 20%. However, the minimum apatite concentration for any size fraction is that observed in the unspiked fraction (\bar{M}_{Ob}).

No attempt was made to quantify the apatite in the $<2 \mu\text{m}$ fraction by point counting phosphorus-containing grains. Detection of phosphorus-containing grains smaller than 1 μm by X-ray spectrometry is extremely difficult since there is very little X-ray emission from these tiny grains.

TABLE 1. Apatite Concentrations from Physical Separation Method

Sample	\bar{M}_{ob} $\mu\text{g}\cdot\text{g}^{-1}$	\bar{K}_{ob} $\mu\text{g}\cdot\text{g}^{-1}$	I $\mu\text{g}\cdot\text{g}^{-1}$	p	M $\mu\text{g}\cdot\text{g}^{-1}$
125-62 μm	1180 (single observation)				
62-45 μm	7080 \pm 320	11430 \pm 590	4616	0.94 \pm .15	7500 \pm 1400
45-33 μm	4600 \pm 180	7280 \pm 530	2795	0.96 \pm .20	4800 \pm 1100
33-25 μm	3430 \pm 130	6220 \pm 210	3401	0.82 \pm .07	4200 \pm 500
25-17 μm	3260 \pm 240	5350 \pm 610	2699	0.77 \pm .24	4200 \pm 1500
17-10 μm	2220 \pm 200	3790 \pm 150	2264	0.69 \pm .11	3200 \pm 500
10-2 μm	1030 (single observation)				

Note: Numbers are not rounded to 2 significant figures until the final calculation (M).

\bar{M}_{ob} = Mean observed apatite concentration of unspiked sample (from Appendix 6),
 \pm the standard error of the mean.

\bar{K}_{ob} = Mean observed apatite concentration of spiked sample (from Appendix 6),
 \pm the standard error of the mean.

I = Amount of apatite added as an internal standard.

p = Recovery factor, calculated using equation 3 in text, \pm the calculated standard error.

M = Apatite concentration in the size fraction, corrected for incomplete recovery of apatite in the apatite fraction, \pm the standard error. $M = \bar{M}_{ob}/p$

Since only a 3.05 g.cm^{-3} density separation was attempted for this fraction, the apatite in the $<2 \text{ }\mu\text{m}$ fraction was less concentrated than in the apatite fractions for the other grain sizes. Two phosphorus-containing grains from the $<2 \text{ }\mu\text{m}$ fraction which have dimensions approaching $0.45 \text{ }\mu\text{m}$ are shown in Figure 10. Monazite is a cerium, lanthanum phosphate with small amounts of thorium and yttrium. Calcium substitutes in minor amounts for Ce and La. The X-ray emission spectrum of a monazite grain is shown in Figure 11. Monazite has a density of 4.6 to 5.5 g.cm^{-3} and so would not be included in the apatite fraction (3.05 to 3.3 g.cm^{-3}) of the other sizes. Monazite, like apatite, is an accessory mineral in igneous and metamorphic rocks and, again like apatite, has an extremely low solubility and is unlikely to be an important source of biologically available phosphate.

Chemical Extraction

The results of the chemical extraction of apatite standards are presented in Tables 2a and 2b. The phosphorus content of the apatite standard was assumed to be 17.8%, as measured in fluorapatite from the same locality by Young *et al.* (1969). Errors involved in weighing the apatite are less than 0.5%.

Recoveries of pure apatite ranged from 86 to 97%, with 2 to 5% of the apatite being extracted as Non-Apatite Inorganic Phosphorus (see Table 2a). Theoretical recoveries of apatite in the spiked sediment ranged from 75 to 102% (see Table 2b). However, the standard error of the mean sediment apatite extract values is about 3%, and the theoretical recoveries of the apatite added may be exaggerated by errors in the spiked and unspiked values. A spiked and an unspiked sample of 62 to $45 \text{ }\mu\text{m}$ sediment from

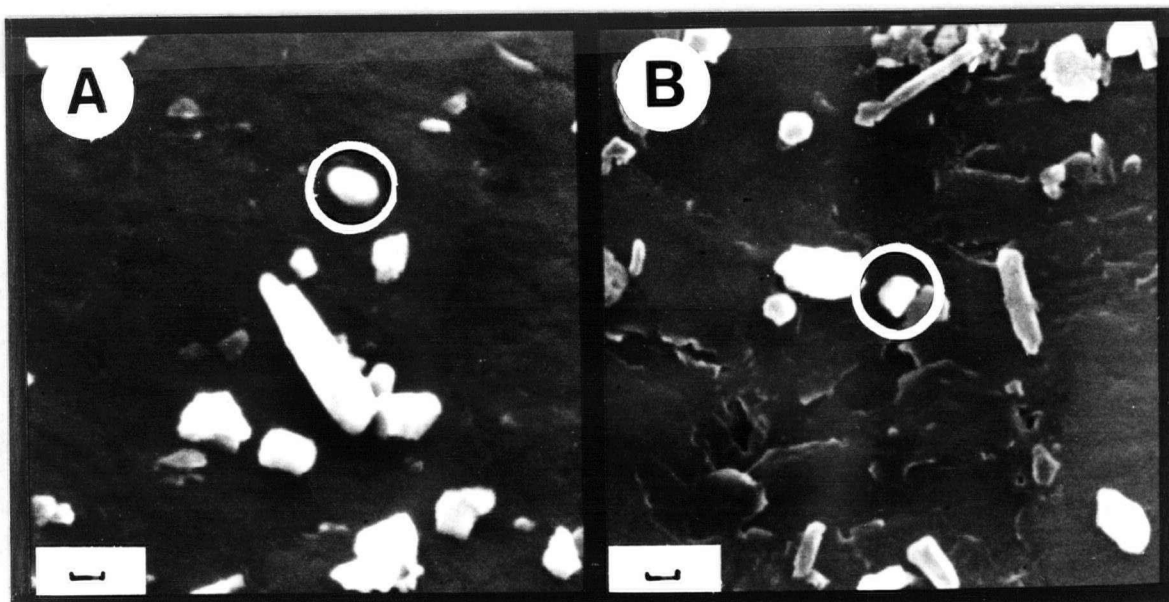


Figure 10. Apatite and monazite grains with dimensions approaching $0.45\ \mu\text{m}$ are circled. Bar in (A) and (B) is $0.45\ \mu\text{m}$ long.
 (A) Apatite
 (B) Monazite

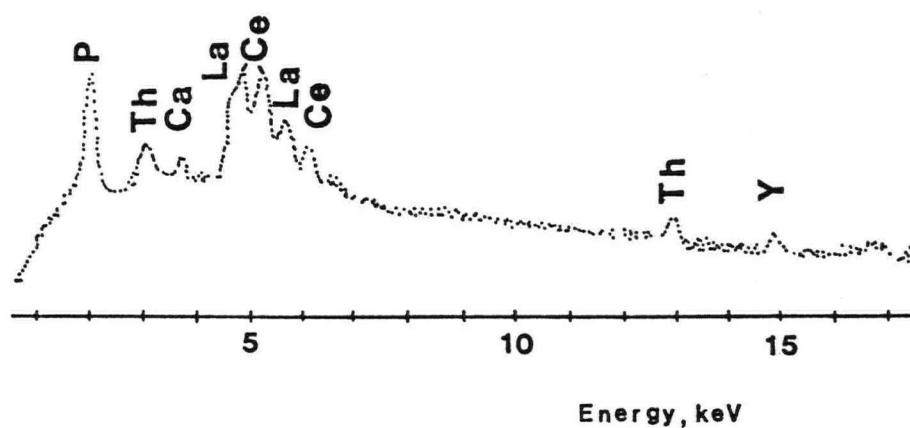


Figure 11. X-ray emission spectrum for Kamloops Lake monazite.

TABLE 2a Extraction of an Apatite Standard

Apatite Size	Initial Wt. µg P	NAIP-P µg P	$\frac{\text{NAIP-P}}{\text{Initial Wt.P}} \times 100$	Apatite-P µg	$\frac{\text{Apatite-P}}{\text{Initial Wt.P}} \times 100$
All sizes	2081	105	5%	1800	86%
10-2 µm	2183	85	4%	2100	96%
25-17 µm	2096	Not extracted		2000	95%
33-25 µm	2580	54	2%	2500	97%

TABLE 2b Extraction of Apatite from Spiked Sediment Samples

Sample	U Unspiked Sample (µg ap-P).(g sed.) ⁻¹	I Amt. Ap. Added (µg ap-P).(g sed.) ⁻¹	S Spiked Sample (µg ap-P).(g sed.) ⁻¹	Recovery of Apatite Spike (Assumes 3% error in S and U) $\frac{S-U}{I} \times 100$
KT Gen 1A (AP)	549	143	696	102%±18%
KT Gen 1A (AP+IP+OP)	549	148	660	75%±18%
KAM 62-45 µm (AP)	1293	821	2017	88%±9%

Kamloops Lake were separated with heavy liquids (as above) after being extracted for apatite and NAIP and were examined with the scanning electron microscope. No apatite grains were observed in the apatite fraction, indicating that all of the apatite was dissolved in the extraction. In general, the Williams et al. (1976) technique of selective chemical extraction of apatite seems to be >85% effective in recovering a fluorapatite standard. Wildung et al. (1977) found that the Williams method generally gave recoveries of >90% of inorganic phosphorus added to lake sediments.

The results of the apatite extractions of the seven size fractions of Kamloops Lake sediment are summarized in Table 3. The concentration of apatite is the concentration of apatite-phosphorus divided by 0.18, since the weight per cent of phosphorus in apatite is approximately 18%.

The apatite concentrations indicated by chemical extraction are plotted against those of the physical separation in Figure 12. The two methods give similar results (within 7%) for the five size fractions from 62 to 10 μm . The 10 to 2 μm point count value is considerably lower than the extraction value since this sample was not spiked to estimate recovery of apatite in the apatite fraction.

Since the point count value for the 10 to 2 μm sediment has not been corrected for incomplete separation and is too low, the chemical extraction numbers are plotted in Figure 13 to estimate the concentration of apatite in sediment smaller than 0.45 μm . Extrapolation of the extraction data suggests that this concentration may be as high as 1800 μg apatite per gram sediment. Therefore, apatite smaller than 0.45 μm probably contributes to the "dissolved" phosphorus load in Kamloops Lake. Data are not available to calculate how much this apatite is contributing to the "dissolved" load, but estimates (see Appendix 7) suggest that it is about 20%.

TABLE 3 Extraction of Apatite from Kamloops Lake Sediments

Sample	Mean Conc. Ap.-P. \pm Std.Error $\mu\text{g.g}^{-1}$	Mean Apatite Conc. \pm Std.Error $\mu\text{g.g}^{-1}$
62-45 μm	1293 \pm 13	7180 \pm 72
45-33 μm	912 \pm 57	5070 \pm 318
33-25 μm	738 \pm 19	4100 \pm 105
25-17 μm	756 \pm 19	4200 \pm 105
17-10 μm	607 \pm 11	3370 \pm 61
10-2 μm	571 \pm 23	3170 \pm 128
<2 μm	352 \pm 26	1960 \pm 144

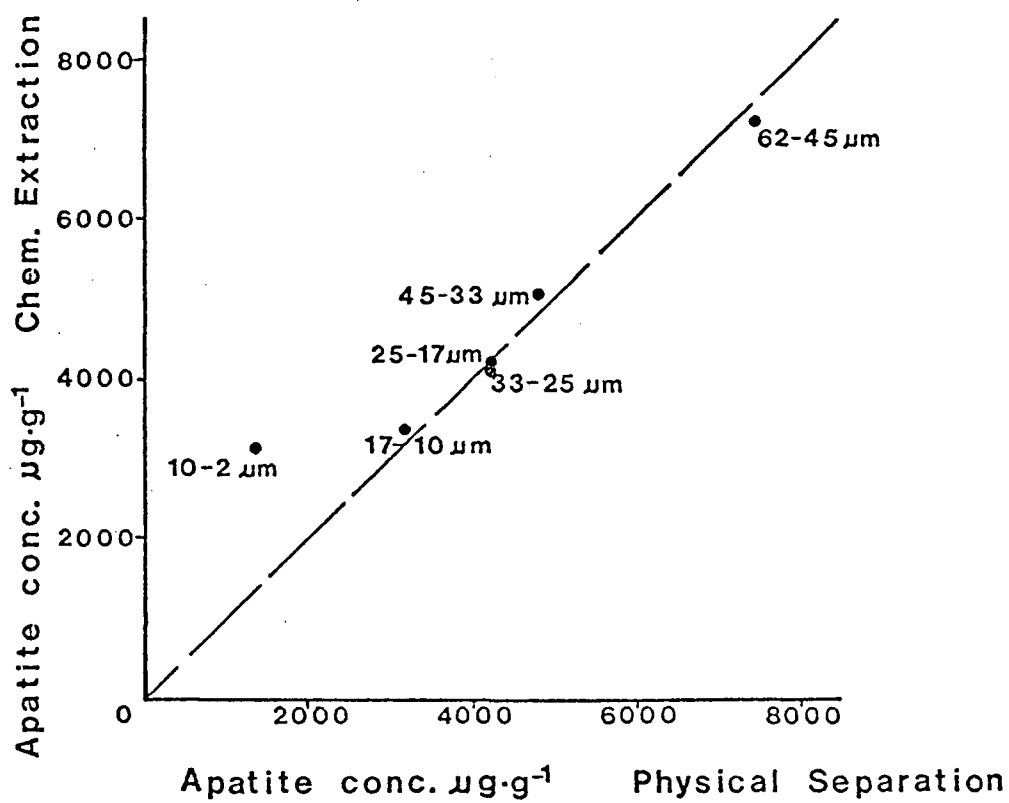


Figure 12. Correlation between apatite concentrations obtained by chemical extraction and by physical separation. Dashed line equals 100 per cent correlation.

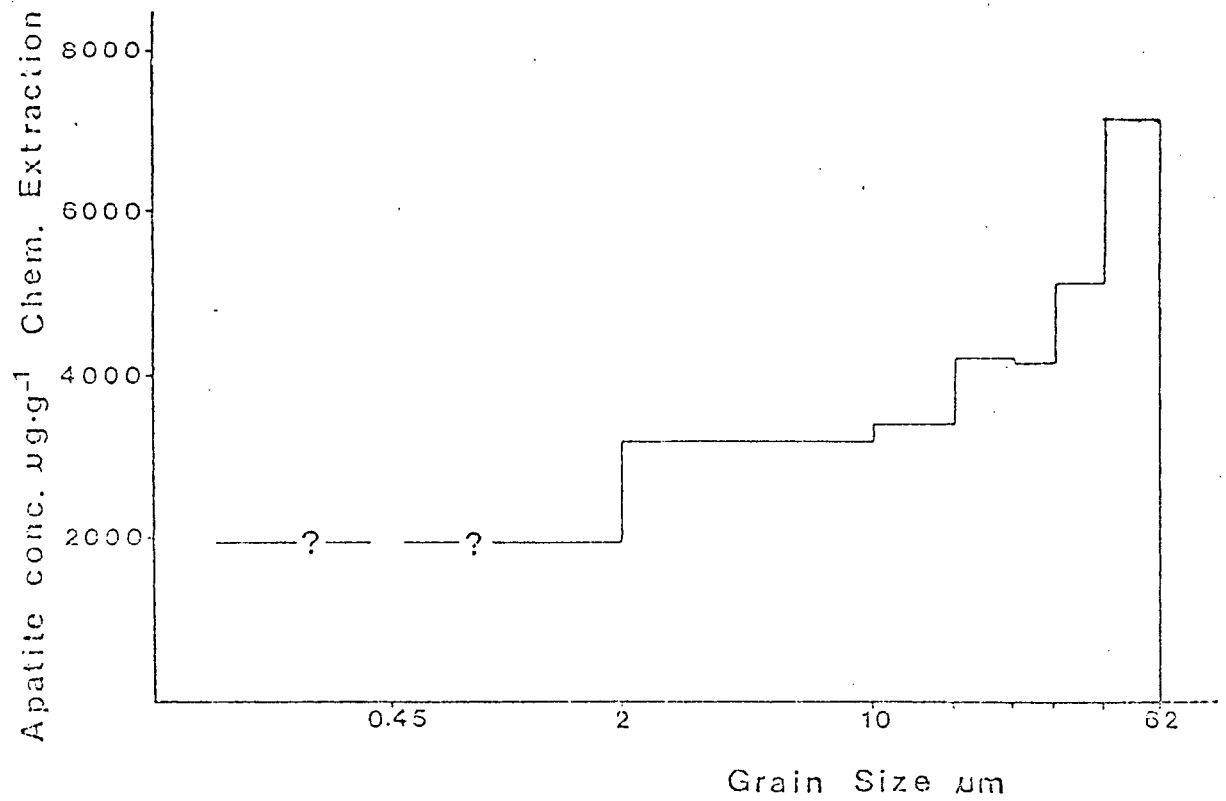


Figure 13. Apatite concentration (by chemical extraction) versus grain size.

CONCLUSIONS

A method has been developed which shows that the concentrations of apatite obtained by indirect chemical extraction of phosphorus in Kamloops Lake sediments are comparable to the values obtained by direct physical observation. The method developed is time consuming, tedious, and expensive, and is not recommended as a general procedure for evaluating concentrations of apatite in sediments. Rather it is a method which could be used to verify "apatite" concentrations from chemical extractions, and could, of course, be used for identification of other minerals as well. The scanning electron microscope with energy dispersive X-ray spectrometer has proven to be extremely useful and may be more versatile than the electron microprobe used in previous phosphate studies (eg., Kingston 1973) since it is capable of scanning at lower magnifications than most microprobes. The general technique of using an internal standard to test the recovery of a mineral in heavy liquid separation was also an important part of this study.

The apatite which has been observed in the sediments of Kamloops Lake accounts for a significant portion (approximately 70%, St. John et al., 1976) of the phosphorus in the total phosphorus load to the lake. In 1953, Kurtz summarized the use of total phosphorus measurements in soil science as follows:

"Except for research studies, determinations of total phosphorus in soils have been made rarely in recent years, since total phosphorus is generally recognized as of little value in assessing the phosphorus fertility of a soil." (Kurtz, 1953, p.61).

Total phosphorus measurements in lakes receiving sediment from glaciated igneous and metamorphic terrains are similarly likely to be of little value in assessing the "phosphorus fertility" of a lake.

The results of this study indicate that apatite smaller than $0.45\text{ }\mu\text{m}$ may be abundant in Kamloops Lake, comprising as much as 20% of the "dissolved" phosphorus load. The biological availability of phosphorus in apatite grains smaller than $0.45\text{ }\mu\text{m}$ requires investigation.

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APPENDIX 1. Size Separation of Silt Particles

The Cyclosizer is a hydraulic cyclone elutriator which separates sediment into five specific size fractions from 62 μm to 10 μm . The elutriation action takes place in a hydraulic cyclone where the fluid is spinning and centrifugal forces many times those due to gravity are acting on the particles (Cyclosizer, Operating Manual). In a comparatively short time (15 - 20 min.) the Cyclosizer is capable of yielding highly reproducible sub-sieve size divisions of sediment. Material rejected by the fifth cyclone (approximately 10 μm quartz) normally passes to waste (Kelsall et al., 1974). If this <10 μm material is needed for study, it may be decanted and collected before the cyclosizing procedure.

Approximately 430 grams of Kamloops Lake sediment from 62 to 10 μm were separated in the cyclosizer. Before cyclosizing, the >62 μm fraction was removed by sieving and the <10 μm fraction by settling and decantation. Thirty gram subsamples of the sediment were cyclosized for 15 minutes, with a water temperature of 11°C and a flow rate of 180 $\text{cm}^3.\text{sec}^{-1}$.

APPENDIX 2. Procedure for Heavy Liquid Separation of Apatite.

For grain sizes from 62 to 2 μm , the following procedure was followed:

1. Shake a dry sediment sample in a Spex Mixer for 20 minutes to homogenize.
2. Add 0.25 g sediment to a Pyrex 50 ml conical centrifuge tube.
3. Add 5 ml of acetone, which has been dried with anhydrous magnesium sulphate, to the sediment in the tube. Disperse the sediment in the acetone by hand swirling in an ultra sonic bath. Centrifuge and decant the acetone. Discard the used acetone. This step replaces water adsorbed onto grains with acetone, which is miscible with diiodomethane.
4. Add 50 ml of diiodomethane (density 3.32 g.cm^{-3}) to the tube. Centrifuge for the appropriate time (Table 2-1). Stir the light fraction from this separation with a thin glass rod to allow any heavy minerals to free themselves and settle. Centrifuge again.
5. Freeze the heavy fraction (density $>3.3 \text{ g.cm}^{-3}$) in the centrifuge tube by placing the lower half of the tube in liquid nitrogen. Decant the light fraction (density $<3.3 \text{ g.cm}^{-3}$) into a second 50 ml Pyrex conical centrifuge tube which contains 5 ml of dried acetone.
6. Thaw the $>3.3 \text{ g.cm}^{-3}$ fraction. Disperse this fraction in the diiodomethane remaining in the tube and recentrifuge. Refreeze the heavy fraction and add the light fraction from this separation to the light fraction of Step 5. Save the heavy fraction.
7. Fill the second centrifuge tube (Step 5) to 47 ml with diiodomethane. This tube now contains 5 ml acetone (density 0.7899 g.cm^{-3}), plus 42 ml diiodomethane (density 3.32 g.cm^{-3}) so that the solution has a density 3.05 g.cm^{-3} . Centrifuge for the appropriate time. Stir the light fraction and recentrifuge. The heavy minerals from this separation have

densities between 3.05 g.cm^{-3} and 3.3 g.cm^{-3} . This is the "apatite fraction". The lights have densities $<3.05 \text{ g.cm}^{-3}$.

8. Collect the 3 fractions (the $>3.3 \text{ g.cm}^{-3}$ fraction from step 6, and the apatite fraction and the $<3.05 \text{ g.cm}^{-3}$ fraction from step 7) on preweighed 5.5 cm filter paper by vacuum filtration using a 47 mm Millipore 300 ml Pyrex funnel with stainless screen filter support. Freeze the apatite fraction in the bottom of the tube with liquid nitrogen while the $<3.05 \text{ g.cm}^{-3}$ fraction is decanted. Use acetone to wash the diiodomethane from the sediment and filter paper. For grain sizes $> 10 \text{ }\mu\text{m}$, use Whatman No. 1 Filter paper; for grain sizes between 2 and $10 \text{ }\mu\text{m}$ use Whatman No. 42 filter paper. Preweigh the filter papers on a Mettler H20 balance.
9. Allow the filter papers and sediments to dry and then weigh on a Mettler H20 balance. The time elapsed between preweighing the paper and weighing the paper plus sediment should be kept to a minimum since humidity changes in the laboratory may significantly affect the weight of the filter paper.

For grain sizes $<2 \text{ }\mu\text{m}$, only the 3.05 g.cm^{-3} separation is performed. The procedure is as follows:

1. Steps 1, 2, 3 as above.
2. Add 5 ml of fresh dry acetone to the sediment from Step 3 and fill the tube to 47 ml with diiodomethane. Centrifuge, stir the light fraction and recentrifuge.
3. Collect the 2 fractions ($>3.05 \text{ g.cm}^{-3}$ and $<3.05 \text{ g.cm}^{-3}$). The $<3.05 \text{ g.cm}^{-3}$ fraction is collected on Whatman No. 42 filter paper and is washed with acetone. However, this filter paper has a pore size of 1 to $2 \text{ }\mu\text{m}$ and some sediment may pass through the paper. Therefore, the >3.05

g.cm^{-3} fraction (in this case, the "apatite fraction") is collected on a preweighed $0.01\ \mu\text{m}$ cellulose acetate membrane filter. Since this filter is soluble in acetone, the diiodomethane is first decanted from the apatite fraction and 20 ml of acetone are added to the centrifuge tube. The sediment is dispersed in the acetone and is then centrifuged. The acetone is decanted and water is added. The water-sediment mixture is filtered through the $0.01\ \mu\text{m}$ membrane filter paper to collect the apatite fraction. The weight of the apatite fraction may be determined but no quantitative S.E.M. point counting of apatite is possible for this size fraction.

TABLE 2-1 Centrifugation Times for Settling Apatite in Diiodomethane or Diiodomethane-acetone Mixture, as in Appendix 2.
IEC International Centrifuge, #240 Head

Minimum Particle Size	Centrifuge Speed RPM	Centrifugation Time	
		Calculated	Recommended
25 μ m	900	0.86 min	2 min
17 μ m	900	1.87 min	4 min
10 μ m	900	5.39 min	10 min
2 μ m	1500	48.00 min	1 hr 40 min
0.2 μ m	1500	75 hr.	

NOTE: Calculated centrifugation times, based on Stokes law, are given by Jackson (1956, p.127) as follows:

$$t_{min} = \frac{(63.0 \times 10^8) (\log_{10} R/S) (\eta)}{(N_m)^2 (D_u)^2 (\Delta s)}$$

where

t_{min} = time in minutes

η = viscosity in poises at the existing temperature
(.028 for diiodomethane at 20°C)

R = radius of rotation (in cm) of the top of the sediment in the tube
(23cm for 50 ml centrifuge tube)

S = radius of rotation (in cm) of the surface of the suspension in the tube
(13cm for 50 ml centrifuge tube)

N_m = centrifuge speed in rotations per minute.

D_u = particle diameter in microns

Δs = difference in specific gravity between the particle and the suspension liquid
(approximately 0.1 for both diiodomethane and diiodomethane-acetone mixture).

Recommended centrifugation times are generous to allow settling of apatites with specific gravities from 3.1 - 3.25.

APPENDIX 3. The Apatite Fraction: S.E.M. Sample Preparation and Examination.

The amount of apatite in the apatite fraction of the heavy liquid separation is determined by point counting apatite grains in this fraction with a scanning electron microscope equipped with an energy dispersive X-ray spectrometer. The sample preparation and method of examination is described below.

1. Cut a pie shaped wedge (approximately one eighth of the filter paper) from the paper on which the apatite fraction of the separated sediment has been collected.
2. Water wash the sediment from this wedge onto a 0.45 μm cellulose acetate membrane filter supported by the 13 mm diameter stainless steel screen of a Millipore Vacuum filtration apparatus. Disperse the sediment evenly on the filter paper.
3. Allow the 13 mm filter paper and sediment to dry and then use double sided paper tape to mount the paper on a circular carbon button (diameter 13 mm, thickness 5 mm).
4. Apply a carbon coat (approximately 25 nm) to the filter paper and sample.
5. Examine the sample with an ETEC autoscan scanning electron microscope with an ORTEC X-ray analytical system. Set the "region of interest" at 1.96 - 2.06 keV. Scan 5 fields, each containing 100 to 200 grains, in the north, south, east, west and middle of each button. The number of apatite grains in each field divided by the total number of grains in the field and multiplied by 100 gives an estimate of the weight per cent apatite in the apatite fraction. Average the weights per cent apatite for the five fields to obtain a single estimate of the weight percent apatite in the apatite fraction.

APPENDIX 4. Data from Heavy Liquid Separation.

The weights of each density fraction obtained by heavy liquid separation of each size fraction are summarized in Table 4-1. In general, 2 to 3% sediment loss occurred during the separation procedure. The weight per cent of each sample which is represented by the apatite fraction is calculated by dividing the weight of the apatite fraction by the sum of the weights of the three density fractions. This calculation assumes that the sediment loss from each density fraction during separation is proportional to the weight of the fraction. In sample 33-25 μm (subsamples 1,2 and 3), the $<3.05 \text{ g.cm}^{-3}$ separations spilt before being weighed, and the total sediment separated (E) was obtained by assuming a 2% loss during separation.

TABLE 4-1 Data From Heavy Liquid Separation

Sample	A Initial Wt.(g)	B Wt.<3.05g.cm ⁻³ Fraction(g)	C Wt.>3.3g.cm ⁻³ Fraction(g)	D Wt.apatite Fraction(g)	E Wt.Total Sed. Sep.(g) (B + C + D)	% Loss or Gain $\frac{E-A}{A} \times 100$	F Wt.% Apatite Fraction $\frac{D}{E} \times 100$
125-62 μm	0.25831	0.24542	0.00294	0.00643	0.25479	-1.4	2.52
62-45 μm							
1	0.25181	0.20006	0.02240	0.01955	0.24201	-3.9	8.08
2	0.25385	0.21569	0.01996	0.02052	0.25617	+0.9	8.01
3	0.25718	0.20070	0.02190	0.02157	0.24417	-5.1	8.83
62-45 μm (Spiked)							
1	0.24360	0.20188	0.02095	0.02169	0.24452	+0.4	8.87
2	0.21864	0.17861	0.01720	0.01800	0.21381	-2.2	8.42
3	0.23004	0.18932	0.01843	0.01932	0.22707	-1.3	8.51
45-33 μm							
1	0.25165	0.21149	0.01367	0.01506	0.24022	-4.5	6.27
2	0.24928	0.21761	0.01034	0.01819	0.24614	-1.3	7.39
3	0.26193	0.23069	0.01005	0.01562	0.25636	-2.1	6.09
4	0.24674	0.21643	0.01093	0.01502	0.24238	-1.8	6.20
45-33 μm (Spiked)							
1	0.18169	0.15554	0.00812	0.01239	0.17605	-3.1	7.04
2	0.25467	0.21766	0.01048	0.01722	0.24536	-3.7	7.02
3	0.24560	0.21169	0.01006	0.01591	0.23766	-3.2	6.69
33-25 μm							
1	0.24666	spilt	0.01049	0.01612	0.24173	-2 assumed	6.67
2	0.24901	spilt	0.00966	0.01547	0.24402	-2 assumed	6.34
3	0.24501	spilt	0.01005	0.01401	0.24010	-2 assumed	5.84
4	0.22805	0.19959	0.01030	0.01671	0.22660	-0.6	7.37
33-25 μm (Spiked)							
1	0.25940	0.22401	0.00910	0.01702	0.25013	-3.6	6.80
2	0.24479	0.21716	0.01014	0.01318	0.24048	-1.8	5.48
3	0.25472	0.22796	0.00657	0.01345	0.24798	-2.6	5.42
4	0.24575	0.21839	0.00869	0.01361	0.24069	-2.1	5.65
25-17 μm							
1	0.23664	0.20550	0.01067	0.01561	0.23178	-2.1	6.73
2	0.24425	0.21264	0.00949	0.01843	0.24056	-1.5	7.66
3	0.25687	0.22090	0.00927	0.01809	0.24826	-3.4	7.29
25-17 μm (Spiked)							
1	0.22912	0.19873	0.01079	0.01756	0.22708	-0.9	7.73
2	0.25073	0.22064	0.01241	0.01422	0.24727	-1.4	5.75
3	0.24885	0.21342	0.01017	0.01643	0.24002	-3.5	6.85
17-10 μm							
1	0.25598	0.23392	0.00959	0.01012	0.25363	-0.9	3.99
2	0.25542	0.23531	0.00967	0.00972	0.25470	-0.3	3.82
3	0.26694	0.23938	0.00818	0.00945	0.25701	-3.7	3.68
17-10 μm (Spiked)							
1	0.26723	0.24192	0.00899	0.01155	0.26246	-1.8	4.40
2	0.25574	0.23114	0.00944	0.01019	0.25077	-1.9	4.06
3	0.26782	0.25131	0.00915	0.00827	0.26873	+0.3	3.08
10-2 μm	0.25204	0.24294	0.00260	0.01028	0.25582	+1.5	4.02
<2 μm	0.25299	0.22744		0.00257	0.23001	-9.1	1.12

APPENDIX 5. Data from S.E.M. Examination

For each apatite fraction, five independent fields each containing 100-200 grains were examined with the scanning electron microscope, in the north, west, south, east and middle of each button (except for one sample in the 17-10 μm size fraction and 3 samples in the spiked 17-10 μm size fraction in which only 4 independent fields were examined). For each field, a measure of the weight per cent apatite in the apatite fraction is obtained by dividing the number of apatite grains observed by the total numbers of grains in the field. The 5 results are averaged to obtain a mean weight per cent apatite for each separation. The results are summarized in Table 5-1.

The weight per cent apatite numbers for each of the five fields are uncertain in the first decimal place and therefore the average of these five numbers is accurate only to the first decimal place. Data in Table 5-1 are reported to two decimal places but the final calculations obtained using these numbers are rounded to two significant figures (see Table 1).

TABLE 5-1 Data From S.E.M. Examination

Sample	Wt. % Apatite in Apatite Fraction					
	North	West	South	East	Middle	Mean
125-62 μm	4.03	5.56	4.92	5.61	3.23	4.67
62-45 μm						
1	7.75	6.96	10.38	7.47	9.25	8.36
2	12.23	10.86	6.82	6.55	5.79	8.45
3	8.49	6.59	9.35	8.41	10.79	8.73
62-45 μm (Spiked)						
1	11.77	13.73	11.77	7.14	13.94	11.67
2	12.00	15.65	14.27	11.61	15.00	13.71
3	14.75	12.77	11.77	15.91	17.60	14.56
45-33 μm						
1a	4.22	8.08	8.81	3.33	6.22	6.13
1b	10.19	6.11	8.33	10.97	13.79	9.88
2	4.07	4.00	10.07	7.79	4.96	6.18
3	5.62	10.42	5.70	11.36	5.11	7.64
4a	6.08	3.76	6.25	5.17	7.20	5.69
4b	5.67	9.48	7.87	8.73	6.64	7.68
45-33 μm (Spiked)						
1	12.14	11.06	8.33	9.52	12.78	10.77
2	10.35	11.96	12.37	10.97	11.43	11.42
3	7.69	8.76	10.19	10.44	9.63	9.34
33-25 μm						
1	3.37	5.88	6.79	5.45	2.78	4.85
2	5.18	6.31	4.45	5.23	5.76	5.39
3	4.73	5.21	4.87	6.79	6.75	5.67
4	5.71	6.28	3.14	5.28	5.21	5.12
33-25 μm (Spiked)						
1	9.73	7.64	12.50	9.47	8.26	9.52
2	13.42	9.09	9.38	12.11	7.53	10.31
3	9.20	11.65	15.04	13.74	11.11	12.15
4	12.27	11.98	10.71	7.27	12.12	10.87
25-17 μm						
1	2.45	7.46	7.14	6.59	3.57	5.44
2	4.58	4.73	2.96	4.08	5.26	4.32
3	2.91	6.79	1.65	4.79	3.20	3.87
25-17 μm (Spiked)						
1	5.53	9.96	9.90	5.21	11.33	8.39
2	7.01	5.56	10.43	9.55	5.81	7.67
3	6.38	9.85	7.98	2.75	10.69	7.53
17-10 μm						
1	4.49	4.94	12.50	5.48	4.88	6.46
2	4.52	6.10	4.88	7.64	-	5.78
3	5.89	5.09	3.72	3.97	6.81	5.10
17-10 μm (Spiked)						
1	8.92	9.15	7.61	8.00	-	8.42
2	9.66	9.60	7.74	8.38	-	8.85
3a	16.05	13.48	14.78	18.42	-	15.68
3b	10.53	9.80	11.39	13.04	9.52	10.86
10-2 μm	4.17	2.16	1.52	2.53	2.49	2.57

APPENDIX 6. Observed Apatite Concentrations

The numbers involved in the calculation of observed apatite concentrations are presented in Table 6-1. In three instances (45 to 33 μm , subsamples 1 and 4; and 17 to 10 μm , subsample 3) a second sample for S.E.M. examination was prepared from a single apatite fraction in order to check an anomalously high or low calculated apatite concentration. In these cases, the average concentration from the duplicate analyses from a single separation was the value used with the concentrations calculated for the other separations of the same size fraction to obtain an average observed apatite concentration for the fraction.

Explanation of Terms in Table 6-1

F =	Wt. of Apatite Fraction as in Appendix 4.
Wt.% Ap in Ap. Frac. =	Mean of 5 observations, as in Appendix 5.
Ob. Ap. Conc. =	Observed apatite concentration; Wt% Ap. in Ap. Fraction \times F.
Av. Duplicate =	Average observed apatite concentration of duplicate analyses of a single separation. This average is used with the apatite concentrations from the repeated separations to calculate the mean for the size fraction.
Std. Error of Mean =	Standard error (deviation) of the mean observed apatite concentration; $\sqrt{S_x^2 / n}$ where x is each observed apatite concentration and n is the number of x's.

TABLE 6-1 Observed Apatite Concentrations

Sample	F % (Appendix 4)	Wt. % Ap. in Ap. Fraction (Appendix 5)	Ob. Ap. Conc. $\mu\text{g}\cdot\text{g}^{-1}$	Av. Duplicate $\mu\text{g}\cdot\text{g}^{-1}$	Mean Ob. Ap. Conc. $\mu\text{g}\cdot\text{g}^{-1}$	Std. Error of Mean $\mu\text{g}\cdot\text{g}^{-1}$
125-62 μm	2.52	4.67	1180			
62-45 μm					7080	320
1	8.08	8.36	6750			
2	8.01	8.45	6770			
3	8.83	8.73	7710			
62-45 μm (Spiked)					11430	590
1	8.87	11.67	10350			
2	8.42	13.71	11540			
3	8.51	14.56	12390			
45-33 μm					4600	180
1a	6.27	6.13	3840			
1b	6.27	9.88	6190	5015		
2	7.39	6.18	4570			
3	6.09	7.64	4660			
4a	6.20	5.69	3530			
4b	6.20	7.68	4760	4145		
45-33 μm (Spiked)					7280	530
1	7.04	10.77	7580			
2	7.02	11.42	8020			
3	6.69	9.34	6250			
33-25 μm					3430	130
1	6.67	4.85	3230			
2	6.34	5.39	3420			
3	5.84	5.67	3310			
4	7.37	5.12	3770			
33-25 μm (Spiked)					6220	210
1	6.80	9.52	6480			
2	5.48	10.31	5650			
3	5.42	12.15	6590			
4	5.65	10.87	6140			
25-17 μm					3260	240
1	6.73	5.44	3660			
2	7.66	4.32	3310			
3	7.29	3.87	2820			
25-17 μm (Spiked)					5350	610
1	7.73	8.39	6490			
2	5.75	7.67	4410			
3	6.85	7.53	5160			
17-10 μm					2220	200
1	3.99	6.46	2580			
2	3.82	5.78	2210			
3	3.68	5.10	1880			
17-10 μm (Spiked)					3790	150
1	4.40	8.42	3700			
2	4.06	8.85	3590			
3a	3.08	15.68	4830			
3b	3.08	10.86	3340	4085		
10-2 μm	4.02	2.57	1030			

APPENDIX 7. Contribution of Apatite to the "Dissolved" Phosphorus Load.

Three stations in Kamloops Lake, each representative of approximately one third of the lake, have mean grain sizes of $10.2\ \mu\text{m}$ with no sediment smaller than $0.45\ \mu\text{m}$, $4.2\ \mu\text{m}$ with 4% of the sediment smaller than $0.45\ \mu\text{m}$, and $2\ \mu\text{m}$ with 16% of the sediment smaller than $0.45\ \mu\text{m}$ (Dr. C.H. Pharo, personal communication). The total phosphorus load to Kamloops Lake is $23\ \text{g.m}^{-2}.\text{y}^{-1}$ (St. John et al., 1976). 90% of this load, or $20.7\ \text{g.m}^{-2}.\text{y}^{-1}$ is "particulate" phosphorus i.e. $>0.45\ \mu\text{m}$ and 10% or $2.3\ \text{g.m}^{-2}.\text{y}^{-1}$ is "dissolved" phosphorus i.e. $<0.45\ \mu\text{m}$. If the size distribution of particulate phosphates is similar to that of the general sediment, 7% of the true particulate matter may be $<0.45\ \mu\text{m}$, and the loading of $20.7\ \text{g.m}^{-2}.\text{y}^{-1}$ would represent only 93% of the true particulate phosphorus. In this case, $1.5\ \text{g.m}^{-2}.\text{y}^{-1}$ of particulate phosphate $<0.45\ \mu\text{m}$ would be entering the lake. Approximately 80% of the particulate phosphate in the total sediment is apatite; however, the proportion of Non-Apatite Inorganic Phosphorus increases with decreasing sediment size. If 35% of the particulate phosphorus $<0.45\ \mu\text{m}$ is apatite (as indicated by extraction analyses of the $<2\ \mu\text{m}$ fraction by N.W.R.I.), this would represent a loading of $0.5\ \text{g.m}^{-2}.\text{y}^{-1}$. Therefore, about 20% of the so called "dissolved" phosphorus load of $2.3\ \text{g.m}^{-2}.\text{y}^{-1}$ may be particulate apatite.

Cautionary Note: This calculation is extremely approximate.