

SEDIMENTARY PHOSPHATES IN THE FERNIE BASIN: DEVELOPMENT OF NEW TECHNOLOGY FOR DIRECT APPLICATION TO SOILS (82G AND 82J)

By Virginia Marcille-Kerslake
University of Guelph

KEYWORDS: Economic geology, sedimentary phosphates, Fernie basin, zeolites, Princeton basin, agrogeology.

INTRODUCTION

The Canadian fertilizer and agriculture industries are entirely dependent on a reliable and economic source of phosphate rock. Canada currently imports all of its phosphate rock requirements from Florida and the western United States. Increased demand and expected depletion of the high-grade Florida deposits, however, suggest that Canada may have to seek a new source of supply, face considerably higher import costs, or develop its own resources in the future.

The most recent evaluation of phosphate potential in British Columbia has focused on the sedimentary phosphates of the Fernie basin in the southeastern part of the province. A province-wide inventory of phosphate resources conducted

by Butrenchuk (1987), reported that the best potential for development occurs at the base of the Jurassic Fernie Formation in the Fernie basin. At present, this phosphorite, which averages 18 to 20 per cent P_2O_5 , cannot compete with the Florida deposits.

The objective of this study is twofold: to evaluate the suitability of ground phosphate rock from the Fernie basin for direct application as a fertilizer, and to develop new technology for the utilization of British Columbia phosphate rock and zeolites in agriculture. This would provide an alternative to existing chemical fertilizers and increase the economic potential of the British Columbia deposits. This study is an extension of previous work on industrial zeolites in the Princeton basin (Marcille, 1989).

Using Butrenchuk's inventory as a guide, samples of the basal Fernie phosphorite were collected from seven exposed sections, VM89-1 to VM89-8 (Figure 5-2-1). These correspond to sample locations 3 (Highway 3), 31 (Alexander), 4 (Crow), 13 (Abby), 14 (Bingay), 42 (Bighorn), and 38 (Cabin) in the earlier study (Butrenchuk, 1987). This report summarizes the results of the laboratory characterization and initial dissolution experiments. Future work will include further laboratory and greenhouse studies.

GENERAL GEOLOGY

The Fernie basin is a broad, canoe-shaped synclinorium lying within the thrust and fold belt of the Rocky Mountains, and covering roughly 2000 square kilometres of southeastern British Columbia. In the basin, the phosphatic shales, pelletal phosphorite and lesser limestone, siltstone and sandstone of the Jurassic Fernie Formation unconformably overlie the fine clastic sediments and carbonates of the Triassic Sulphur Mountain and Whitehorse formations. The Fernie Formation shows a general thickening westward, reaching thicknesses of 70 to 365 metres (Butrenchuk, 1987) and is overlain by nonmarine, coal-bearing Cretaceous strata.

A pelletal phosphorite bed, 1 to 2 metres thick and averaging 20 per cent P_2O_5 occurs at the base of the Fernie Formation. Deposited as a single bed or as two beds inter-layered with phosphatic shale, the phosphorite reflects a period of rapid marine transgression and slow clastic accumulation during Sinemurian time. The phosphate occurs as dark brown pellets of apatite and organic matter in a finer grained matrix. Comprising 50 to 85 per cent by volume of the phosphorite, the pellets are well sorted, subrounded, essentially structureless and 0.1 to 0.3 millimetre in diameter. The basal phosphorite is overlain by phosphatic shales of variable thickness and a yellow, calcareous marker bed a few centimetres thick.

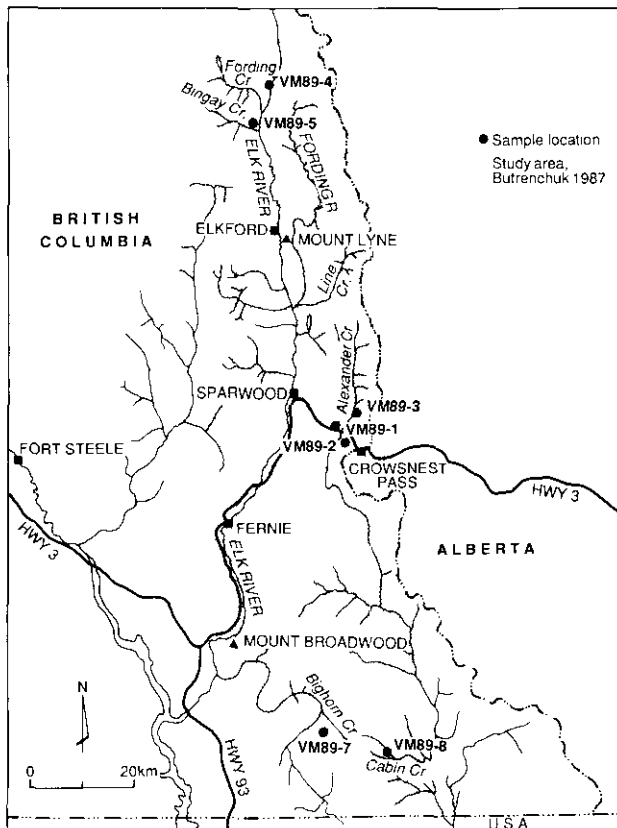


Figure 5-2-1. Simplified geological map of the Fernie basin showing sample locations. Modified from Butrenchuk (1987).

In addition to the synclinal fold of the Fernie basin, certain structural features are significant in the evaluation of the phosphate resources. Extensive structural deformation has resulted in repetition of beds and local thickening of the basal phosphorite. Areas of thickened phosphorite beds are of economic significance, as are overturned beds; the more competent Triassic strata form a more desirable back for underground mining (Butrenchuk, 1987).

MINERALOGY

The mineralogy of the phosphorite samples was determined using a Rigaku Geigerflex x-ray diffractometer under the following operating conditions: copper k-alpha radiation, step-scan mode, 4 second count time and 0.05° step width.

Apatite is present in all samples as are quartz and minor amounts of feldspar. Calcite is a constituent of VM89-1 to VM89-4, and dolomite occurs in trace amounts in VM89-1 and VM89-2.

Using a revision for microcomputers by Paul Benoit, University of Alberta, the least-squares powder diffraction program by Appleman and Evans (1975) was used to calculate the a-cell parameters for the apatites from their respective d-spacings. Values for VM89-2 to VM89-8 fit the range defined by McClennan and Gremillion (1980) for francolite (0.9322 to 0.9376 nanometres). The a-cell value of 0.9377 nanometres for VM89-1, however, suggests that the apatite in this phosphorite is fluorohydroxyapatite.

In addition to lowering the ore grade of the phosphate rock, the presence of certain accessory minerals has deleterious effects on commercial processing. Quartz and feldspar can interfere with grinding and beneficiation, increasing wear on plant equipment. Furthermore, the presence of acid-soluble silicates results in the release of impurities such as potassium, iron, aluminum and magnesium during acidulation. Carbonates, which generally cannot be removed by beneficiation, present problems in chemical processing. During acidulation, carbonates cause excessive foaming, consume acid and contribute impurities, particularly magnesium from dissolved dolomite. It is, however, possible to separate carbonate minerals from the phosphate rock by calcining, but this process, which converts carbonates to oxides, followed by slaking and separation, is costly (McClennan and Gremillion, 1980).

GEOCHEMISTRY

Three samples, VM89-3, VM89-4 and VM89-8, were selected for further study and were analysed using a Philips XRF spectrophotometer at the Department of Geology, McMaster University. The results are presented in Table 5-2-1.

The P₂O₅ contents range from approximately 30 to 34 per cent. While their relative order is consistent, the actual values are notably higher than those of 22 to 25 per cent cited by Butrenchuk (1987). Similarly, the silica contents are considerably lower than those determined in the earlier study. These differences may be due to variability within the phosphorite bed.

CaO/P₂O₅ and R₂O₃/P₂O₅ ratios were calculated and are presented in Table 5-2-1 (R₂O₃ = Al₂O₃ + Fe₂O₃ + MgO). The following ranges are those acceptable to commercial processing plants (Butrenchuk, 1987):

- P₂O₅ : 27 to 42 per cent
- CaO/P₂O₅ : 1.32 to 1.60
- R₂O₃/P₂O₅ : less than 0.1
- MgO : less than 1.0 per cent

All three samples fall within the acceptable ranges with the exception of the R₂O₃/P₂O₅ value of 0.12 for VM89-8. In the remaining categories, however, VM89-8 has the most desirable specifications.

TABLE 5-2-1
X-RAY FLUORESCENCE DATA FOR
VM89-3, VM89-4 AND VM89-8

	VM89-3	VM89-4	VM89-8
SiO ₂ (%)	5.34	7.56	10.97
Al ₂ O ₃ (%)	1.11	1.03	1.71
Fe ₂ O ₃ (%)	0.53	0.51	1.94
MgO (%)	0.40	0.40	0.35
CaO (%)	47.72	46.99	45.43
Na ₂ O (%)	0.34	0.30	0.26
K ₂ O (%)	0.15	0.15	0.31
TiO ₂ (%)	0.07	0.07	0.16
MnO (%)	0.01	0.01	0.02
P ₂ O ₅ (%)	29.81	31.15	33.96
S (%)	1.45	1.06	0.44
Total C (%)	3.75	2.97	2.04
Organic C (%)	1.94	1.69	1.89
Carbonate C (%)	1.81	1.28	0.15
LOI (%)	13.05	10.82	5.35
CaO/P ₂ O ₅	1.60	1.51	1.34
R ₂ O ₃ /P ₂ O ₅	0.07	0.06	0.12

DIRECT AVAILABLE PHOSPHORUS

When phosphate rock is to be used for direct application, the reactivity of the rock is a major concern. Although this is only one of several factors affecting its agronomic efficiency, the solubility of the rock, as determined by various extracting solutions, shows a strong correlation with both yield and plant uptake of phosphorus (IFDC, 1979). Leon *et al.* (1986) found that the relationship between reactivity and plant response was strongest when neutral ammonium citrate was the extractant: a modified version of their methodology was used in this study.

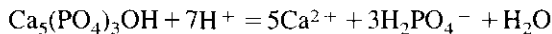
The values for direct-available P₂O₅ (expressed as per cent of rock) are 0.50, 0.63, 0.63, 1.10, 1.27, 1.19 and 1.17 respectively for VM89-1 to VM89-8. A comparison of these values with other phosphate rocks used for direct application indicates that these samples are moderately reactive (Leon *et al.*, 1986).

DIRECT APPLICATION OF PHOSPHATE ROCK

In 1979, the direct use of finely ground phosphate rock accounted for 4 per cent of world phosphate fertilizer consumption, with the U.S.S.R. accounting for over 70 per cent of the reported use (IFDC, 1979). This may, however, be an

underestimate of actual use due to unreported consumption and inclusion with chemical fertilizer use.

The effectiveness of direct application is limited in many soils by the relatively low solubility of phosphate rock. A simplified dissolution reaction for hydroxyapatite is as follows (Chesworth *et al.*, 1987):



By the law of mass action, an accumulation of calcium ions inhibits the breakdown of phosphate rock and the subsequent release of phosphorus to plants. A possible solution to this problem is the addition of zeolites, naturally-occurring aluminosilicate minerals which have a characteristically high cation exchange capacity and an affinity for certain cations. Acting as a sink for Ca^{2+} , zeolites can enhance the dissolution of phosphate rock (Lai and Eberl, 1986).

Natural zeolites suitable for this system are indigenous to British Columbia. Based on previous findings, a clinoptilolite from the Princeton basin was chosen for the current study. This zeolite, Tailings Ash (VM88-9), has an average cation exchange capacity of 147 milli-equivalents per 100 grams, and an average calculated zeolite content of 67 per cent (Marcille, 1989).

Given the negative effect of calcium ions on the dissolution of apatite, it is apparent that phosphate rocks with little or no calcite and dolomite are desirable for direct application. Of the sampled deposits, carbonates are absent in VM89-5, VM89-6 and VM89-8. A comparison of the $\text{CaO}/\text{P}_2\text{O}_5$ ratios in Table 5-2-1 suggests that VM89-8 is better suited for direct application than VM89-3 and VM89-4.

DISSOLUTION STUDIES

In an effort to better understand the mechanisms involved in the phosphate rock-zeolite system and to maximize its effectiveness, controlled dissolution experiments were conducted. In the first study, the effect of both untreated versus ammonium-exchanged zeolite of various grain sizes on the dissolution of VM89-8 phosphate rock was studied. In brief, the procedure involved shaking 200 milligrams of powdered phosphate rock with 1.00 gram of zeolite in 30 millilitres of distilled water for four days at 25°C. The solutions were then centrifuged and the supernatants were analysed colorimetrically for water-soluble phosphorus using a Technicon II Auto Analyser.

For the grain size fractions studied (powdered, 0.053 to 0.25 millimetre, 0.25 to 0.5 millimetre, and 0.5 to 1 millimetre), phosphorus released was proportional to grain size. Furthermore, the ammonium-exchanged zeolite was more effective than the untreated zeolite in increasing the solubility of the phosphate rock: The amount of phosphorus released from the exchanged samples was approximately twice that from the untreated samples. The increased effectiveness of ammonium-saturated zeolite is probably due to the fact that roughly 30 per cent of the exchange sites in the untreated zeolite are initially occupied by Ca^{2+} . Saturating the zeolite with ammonium ions removes this native Ca^{2+} , thereby increasing its capacity to adsorb calcium from the system.

In the second experiment, the relationship between the grain size of the zeolite and the rate of phosphate rock

dissolution was studied further in order to determine the most effective size. The procedure was similar to the previous experiment except that only ammonium-saturated zeolites were used, and two additional size fractions (1 to 2 millimetres, 2 to 4 millimetres) were included. As expected, the amount of phosphorus released increased with grain size, ranging from 2.82 ppm to 6.45 ppm. For grain sizes greater than 0.5 millimetre, however, this increase became negligible.

The third experiment compared the solubility of three phosphate rocks, VM89-3, VM89-4 and VM89-8, in the presence of zeolite over time. The procedure was similar to the previous study except that only one size fraction (0.5 to 1.0 millimetre) of zeolite was used and samples were shaken for time intervals ranging from 1 to 20 days. Control samples of VM89-8 without zeolite were shaken for each of the time periods.

The results of the third experiment are illustrated in Figure 5-2-2. After a slight decrease between Day 1 and Day 2, the amount of phosphorus released increased with time for each of the phosphate rocks, as expected. This rate of increase was most linear for VM89-8. After 20 days, the amount of phosphorus released was greatest for VM89-4 followed by VM89-3, VM89-8, and finally, VM89-8 without zeolite. A comparison of VM89-8 with and without ammonium-saturated zeolite reveals the positive effect the presence of zeolite has on phosphate rock solubility.

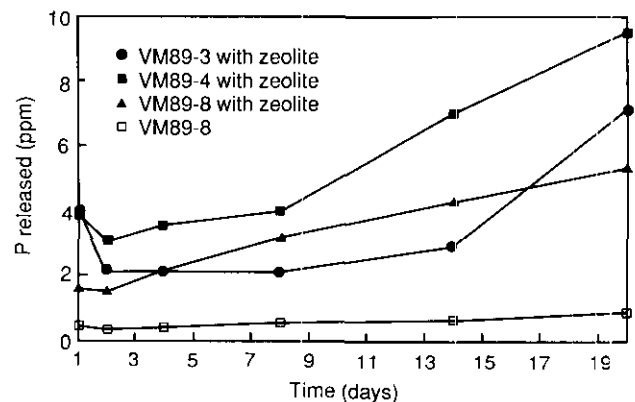


Figure 5-2-2. Plot of phosphorus released versus time for VM89-3, VM89-4 and VM89-8 with zeolite and VM89-8 without zeolite, as determined in experiment 3.

ECONOMIC CONSIDERATIONS

The basal phosphorite of the Fernie Formation is potentially significant to the Canadian fertilizer and agricultural industries. It has an estimated resource potential of 400 million tonnes of phosphate rock with an average P_2O_5 content of 20 per cent (Butrenchuk, 1987). Of this amount, the Cabin Creek deposit contains approximately 34 million tonnes and the Crow deposit has greater than 2 million tonnes.

Western Canada imports 2 million tonnes of phosphate rock annually from the United States at a cost of 70 to 85 Canadian dollars per tonne, including transportation costs

(MacDonald, 1988). Although phosphate rock is currently in oversupply, the availability of rock for export from the United States is expected to decrease by the end of the century. This prediction is based on a projected increase in demand and a depletion of the higher grade Florida deposits. In the near future, Canada will likely have to seek alternative sources for its phosphate rock. A Canadian source would not only lead toward national self-sufficiency, but may also result in lower fertilizer prices due to reduced transportation costs for raw materials.

The use of finely ground phosphate rock as a direct source of phosphorus for crops presents another potential market for the British Columbia deposits. As processing requirements are minimal, a wider range of P_2O_5 contents are acceptable. The viability of this market is increased in western Canada by its close proximity to suitable zeolite deposits, and the growing popularity of alternative agricultural practices (*i.e.* low-input and organic farming).

CONCLUSIONS

Direct application of ground phosphate rock to soils may provide an alternative to chemical fertilizers and a market for the basal Fernie phosphorite. While each of the deposits studied may be suitable for direct application, the Cabin Creek deposit (VM89-8) appears to have the greatest potential: calcite and dolomite are absent in the x-ray diffraction analysis, the ratio of CaO/P_2O_5 of 1.34 is relatively low, and its reactivity is relatively high (1.17 per cent direct available P_2O_5). Furthermore, Cabin Creek is a deposit of substantial size with an estimated 34 million tonnes of phosphate rock averaging 20 per cent P_2O_5 . Based on the results of the third dissolution experiment, the Crow deposit (VM89-3) may also be well suited for direct application.

The potential of the Fernie phosphorite for direct application is increased by the occurrence of zeolites in the nearby Princeton basin. Initial dissolution experiments indicate that the addition of a Princeton zeolite to a system containing phosphate rock from the Fernie basin increased the solubility of the phosphate rock. This effect was maximized by using a size fraction of 0.5 to 1.0 millimetre for the zeolite, and by presaturating the exchange sites with ammonium ion.

Future research will involve additional controlled laboratory studies to better understand the phosphate rock-zeolite system and to maximize its performance. Greenhouse experiments will be conducted to test its long and short-term effectiveness.

ACKNOWLEDGMENTS

This project is supported by British Columbia Geoscience Research Grant 1989-05. The assistance of Z. D. Hora and S. Butrenchuk is greatly appreciated, as are the contributions of Peter van Straaten, Peter Smith and Ward Chesworth of the University of Guelph.

REFERENCES

- Appleman, D. and Evans, H. (1975): Job 9214: Indexing and Least-squares Refinement for Powder Diffraction Data; *United States Geological Survey*, Washington, D.C.
- Butrenchuk, S.B. (1987): Phosphate in Southeastern British Columbia; *B.C. Ministry of Energy, Mines and Petroleum Resources*, Open File 1987-16, 103 pages.
- Chesworth, W., Van Straaten, P., Smith, P. and Sadura, S. (1987): Solubility of Apatite in Clay and Zeolite Bearing Systems: Application to Agriculture; *Applied Clay Science*, pages 291-297.
- International Fertilizer Development Center (IFDC) (1979): Fertilizer Manual; Reference Manual IFDC-R-1; *IFDC*, Muscle Shoals, Alabama, pages 149-154.
- Lai, T. and Eberl, D. (1986): Controlled and Renewable Release of Phosphorus in Soils from Mixtures of Phosphate Rock and NH_4 -exchanged Clinoptilolite; *Zeolites*, Volume 6, pages 129-132.
- Leon, L., Fenster, W. and Hammond, L. (1986): Agronomic Potential of Eleven Phosphate Rocks from Brazil, Columbia, Peru, and Venezuela; *Soil Science Society of America Journal*, Volume 50, pages 798-802.
- Marcille, V. (1989): Industrial Zeolites in the Princeton Basin; *B.C. Ministry of Energy, Mines and Petroleum Resources*, Geological Fieldwork 1988, Paper 1989-1, pages 511-514.
- McClellan, G. and Gremillion, L. (1980): Evaluation of Phosphatic Raw Materials, in *The Role of Phosphorus in Agriculture; Agronomy Society of America-Crop Science Society of America-Soil Science Society of America*, Madison, Wisconsin, pages 43-80.
- Macdonald, D. (1988): Sedimentary Phosphate Rock in Alberta and Southeastern British Columbia: Resource Potential, the Industry, Technology and Research Needs; *Canadian Institute of Mining and Metallurgy, Bulletin*, Volume 81, Number 913, pages 46-52.