THE EVALUATION AND IMPROVEMENT

OF SILICATE MINERAL FERTILISERS

by

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In Memoriam

John Douglas Harley ***MD, FRACP***

1929-1997

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Abstract

The use of silicate mineral fertilisers has been limited by low dissolution rates that release nutrient elements too slowly for adequate crop and pasture nutrition resulting in high application rates that are cost prohibitive. Research on silicate mineral fertilisers has generally focused on solution and plant nutrition chemistry rather than the surface mediated process controlling mineral dissolution and subsequent plant uptake. Consequently, no appropriate methodologies for evaluating silicate mineral fertilisers exist. This thesis is a contribution towards increasing our knowledge in these fields. Three common rock forming minerals, microcline, biotite and hornblende, were subjected to high-intensity attrition milling to produce materials with a wide range of structural, surface and chemical properties which were evaluated in dissolution and plant growth experiments.

Progressive attrition milling of minerals for up to 24 hours resulted in an overall reduction in median particle size and resultant increase in specific surface area in the order hornblende>biotite>microcline. X-ray diffraction analysis indicated that this reduction in particle size was accompanied by an increase in amorphous material as indicated by decreasing peak intensities and increasing background scatter with increasing milling time. Transmission electron microscopy showed the presence of both micron and sub-micron particles in minerals milled for 24 hours as well as the aggregation of sub-micron particles into larger masses. Aggregation was greater for hornblende and biotite than for microcline. The particles of milled minerals produced selected area electron diffraction patterns with both broad rings indicative of amorphous material and sharp, very spotty rings indicating the presence of large numbers of randomly oriented, single crystals. High-resolution field emission source TEM indicated that the presence of amorphous material was mostly limited to rims around particle edges and that rims were more pronounced for microcline than for biotite and hornblende. Energy dispersive spectra obtained during TEM of particles of unmilled and highly milled minerals showed no or minimal chemical changes associated with milling.

Dissolution of minerals in both deionised water and dilute acid increased with milling time by between 10 and 100 fold, with up to 10% of some milled minerals dissolving during a 16 day period. Dissolution was greater in acid solution than in deionised water. Initial

dissolution was incongruent with the base cations generally being in excess of Si except for octahedral Mg release from both biotite and hornblende and K release from biotite where it was exchanged from interlayer sites rather than being released by dissolution. Incongruent dissolution was generally greatest for the longest milling times, and dissolution tended towards congruency with dissolution time. Dissolution versus time curves for unmilled minerals were generally between parabolic and linear, tending towards linear with increasing milling time. Unit mass based dissolution rates increased with increased milling time and generally decreased with increased extent of dissolution. In several cases, elemental dissolution rates for highly milled minerals remained constant with increasing dissolution time. Si, K and Ca dissolution were linearly related to specific surface area, while Na and Mg dissolution were not systematically related to surface area.

Milled silicate minerals were less than 30% as effective as soluble fertilisers for ryegrass and clover grown on sand over a six-week period. Ryegrass growth was sustained for up to 268 days where milled microcline and biotite were supplying K and milled hornblende was supplying Ca. Applications of biotite and hornblende to supply Mg were generally too low to supply sufficient concentrations for maximum plant growth. Nutrient uptake increased with increased milling time, and for application rates up to between 10 and 20 (g mineral)(kg soil)$^{-1}$, beyond which increased application rate did not produce increased nutrient uptake. Exchangeable cations in the soil increased with increased milling time, and plant growth persisted where the exchangeable cation pool was not exhausted. The application of milled mineral increased soil pH with the lime equivalence of silicates being less than 10%. The uptake by ryegrass of nutrients was positively and linearly related to surface area values up to 100 m^2 kg^{-1} for K, 40 m^2 kg^{-1} for Ca and 300m^2 kg^{-1} for Si and at least 60 m^2 kg^{-1} for Mg. It is proposed that surface area may be used as a predictor of plant response to provide a measure for determining optimal milling treatments and application rates of milled silicate minerals.

A simple economic analysis indicates that milling microcline for one hour is optimal when milling costs, application rates, cost of material, transportation and spreading costs are considered. The much greater costs of milled silicate minerals fertiliser relative to soluble K fertilisers indicates that silicate minerals are unlikely to be economically viable replacement for soluble fertilisers for most agricultural settings. Further research is required to determine the benefits of milled silicates in highly leaching, acid soils and to determine non-nutritional benefits such as liming, improved soil charge characteristics and reduced leaching, and the influence of milled silicate rocks on microbial activity and organic matter dynamics in soils.

1 Introduction

1.1 General Introduction

Welch (1995) identifies 17 elements required by higher plants. Nine macronutrients are normally present in plant tissues at concentrations greater than 0.1% dry weight (C, H, O, N, K, Ca, Mg, P, S) and eight micronutrients at concentrations of less than 100 $\mu g\ g^{-1}$ dry weight (B, Cl, Cu, Fe, Mn, Mo, Ni, Zn). Some additional nutrients are required for some plants or under particular environmental conditions (Co, Na, Si). Nutrients essential to plant life occur at various concentrations in the aluminosilicate, ferromagnesian silicate and accessory minerals of rocks. The aluminosilicates and ferromagnesian silicates are major rock-forming minerals varying in structure and composition that may be a primary sources of many nutrients required for plant growth.

Ground rock has been proposed as a slow release fertiliser for highly weathered soils and leaching environments where soluble fertilisers may be easily removed (Chesworth et al., 1989; Coroneos et al., 1996; Gillman, 1980; Hinsinger et al., 1996; Leonardos et al., 1987; Sanz Scovino and Rowell, 1988; Weerasuriya et al., 1993). Nutrients from ground rock in leaching soils may be released at a rate that allows them to remain in the top soil to be utilised by plants (Coroneos et al., 1996). Ground rock may also be used in organic agriculture as an alternative source of nutrients to chemical fertilisers (Bockman et al., 1990), and in developing countries where the cost of importing fertilisers may be prohibitive (Chesworth et al., 1989; Sanz Scovino and Rowell, 1988). There is also interest in using the waste products of quarrying as fertilisers (Barak et al., 1983; Chesworth et al., 1989; Coroneos et al., 1996; Hinsinger et al., 1996).

The limited evidence in the literature indicates that there is potential for silicate rock powder to be fertilisers and/or soil conditioners. There is however concern about the effectiveness of this material with the low solubility of silicate rock powders potentially being the limiting factor. Pre-treatment and processing may increase the dissolution of silicate minerals and subsequently increase their effectiveness as fertilisers (Bakken et al., 1997; Weerasuriya et al., 1993). The process of attrition milling has been proposed in this thesis as a method that is potentially useful in increasing silicate mineral dissolution and fertiliser effectiveness.

1.2 Aim of Research and Organisation of Thesis

The central hypothesis of this research is that attrition milling increases silicate mineral dissolution and fertiliser effectiveness. To evaluate this hypothesis, the research was undertaken with the following principal objectives:

- To evaluate attrition milling of minerals as a means of altering crystal structure and physical characteristics;
- To characterise silicate minerals subjected to attrition milling by means of a number of analytical techniques including XRD, BET and TEM;
- To measure the release of nutrient elements into various solutions as a means of evaluating the effectiveness of attrition milling;
- To evaluate the fertiliser effectiveness of silicate minerals subjected to attrition milling by means of a glasshouse experiment;
- To determine those properties of milled minerals that influence dissolution in soils and plant uptake of nutrients; and
- To evaluate practical and economic considerations relating to the production of fertilisers by attrition milling of silicate rocks.

The thesis follows these objectives and is organised into 8 chapters. A literature review of previous research involving silicate mineral fertilisers, mineral dissolution and attrition milling is provided in Chapter 2. A description of minerals and milling techniques used in this research is in Chapter 3. The mineralogical and physical properties of milled minerals are in Chapter 4. Dissolution and plant growth experiments are in Chapters 5 and 6 respectively. Chapter 7 outlines economic considerations of using attrition milled silicate minerals as fertiliser. Summary, limitations and suggestions for future work are included in Chapter 8. Tables are placed within the text and figures are attached to the end of each chapter. References and Appendices follow Chapter 8. A CD room attached to this thesis includes the complete data set for this thesis as Excel spreadsheets, X-ray diffraction raw data, original negative TEM micrographs presented in Chapter 4, and digital images of the plant growth experiment.