A Study of Soil Humic Interactions with Calcium Phosphate and the Development of a Novel Method of Oxygen Isotope Analysis in Orthophosphate

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A thesis submitted to the University of Technology, Sydney in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Science.

CERTIFICATE OF AUTHORSHIP / ORIGINALITY

I certify that this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Rebeca Alvarez

Dedicated in loving memory of

Peter Benson

☼A true inspiration☼

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ABSTRACT

There is increasing interest in limiting quantities of applied phosphorus fertilizer both for economic reasons and for environmental protection purposes and in facilitating the release of normally unavailable phosphorus for plant growth. The work presented in this thesis seeks to identify and understand some of the chemical reactions that occur between phosphate, calcium and soil humic acids. In addition, a novel electrospray ionisation mass spectrometric (ESI-MS) analytical method, which measures both highly enriched and natural abundance levels of oxygen isotopes in orthophosphate-soil systems, was developed and validated. The significance of this novel method is in its capability to provide an accurate, simple and sensitive means of tracing the sources and sinks of phosphate in soils as well as enabling an effective way to follow chemical reactions and their mechanisms.

In soils, most of the phosphorus from fertilizers, if not washed away in runoff water, is converted to insoluble compounds, including calcium phosphates. Soil organic acids such as humic and fulvic acids may play an important role in influencing inorganic phosphate availability to plants by inhibiting the formation of thermodynamically stable calcium phosphates. Therefore, this work examines the formation of calcium phosphate phases in the presence of humic and fulvic acids extracted from soil sourced from the Sydney Basin in NSW, Australia. The combined techniques of pH-stat autotitration, Fourier transform infrared and laser Raman spectroscopy, as well as x-ray diffraction and elemental analyses facilitated this study.

At 25°C under conditions of high supersaturation and a pH of 7.4 humic materials were found to delay calcium phosphate phase transformation processes. Under these conditions there was a delayed transformation of unstable amorphous calcium phosphate (ACP) to thermodynamically more stable octacalcium phosphate (OCP) and thence to an apatitic phase resembling poorly crystalline hydroxyapatite (HAp). Investigations at the lower pH of 5.7, and in the presence of humic acids, revealed that ACP was also precipitated initially, however humic-free solutions at this pH produced the metastable phase, dicalcium phosphate dihydrate (DCPD). ACP produced in the presence of humic materials persisted longer than DCPD in their absence, before ultimately hydrolyzing to

OCP. Thus these results confirm that humic materials are geologically relevant inhibitors of calcium phosphate transformations and modify the availability of phosphate in soils by changing crystallisation behaviour from solution.

The work presented here also aimed to study phosphate reactions in soil environments with the use of stable oxygen isotope labelling (^{18}O) to monitor the change in orthophosphate oxygen isotopic distributions under acidic soil conditions. Current methods for determining oxygen isotope analysis in phosphate involve either lengthy procedures for conversion of the phosphate to carbon monoxide/dioxide, are insensitive, or are not amenable to rapid automated analyses. The ESI-MS analytical method developed in this thesis is rapid and can be readily applied to calcium phosphate materials, which are normally not amenable to this type of analysis.

Humic-induced oxygen exchange was not detectable in ^{18}O enriched calcium phosphate products that had been precipitated at pH 5.7 from solutions at 25 °C or 80 °C. Furnace temperatures of 600 °C caused the solid-state delabelling of calcium phosphate products in the absence of soil humic material, however, delabelling was accentuated in its presence. The furnace-induced delabelling was also evident when KH_2PO_4 (solid) was subjected to the same conditions. The implications of these results are discussed in terms of the importance of considering extreme heat conditions, for example in the case of forest or bush fires or volcanic conditions, when assessing oxygen exchange processes that occur in terrestrial environments.

PUBLICATIONS

The work presented in this thesis has resulted in the following publications:

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