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The reactivity of Tanzanian Minjingu phosphate rock can be assessed from the chemical and mineralogical composition

C. Szilas [a,1], C. Bender Koch [a], M.M. Msolla [b], O.K. Borggaard [a,*]

[a] *Department of Natural Sciences, University of Copenhagen, Thorvaldsensvej 40, DK-1871 Frederiksberg, Denmark*
[b] *Soil Science Department, Sokoine University of Agriculture, P.O. Box 3008, Morogoro, Tanzania*

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ABSTRACT

Minjingu phosphate rock (MPR) in northern Tanzania with an estimated reserve of 7 million tonnes consists of two types including hard MPR and soft MPR. Both types seem promising for direct application as phosphorus (P) fertilizers but improved knowledge about their reactivity is needed. Since mineral reactivity depends on the chemical and mineralogical composition and crystal size, these properties were investigated on different MPR samples by means of combined chemical, X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM)-microprobe analyses and compared with similar properties of five well-known sedimentary and igneous PR references. As a direct test on reactivity, the solubility of MPR and reference samples in neutral ammonium citrate (NAC) was determined. The chemical composition indicated that the apatites in both MPR types are fluorine deficient francolites. For hard MPR this is in agreement with the mineralogical investigation, while XRD suggests that soft MPR belongs to excess fluorine francolites with low carbonate substitution, which generally have low reactivity. However, the observed very small crystal size together with high substitution rates of carbonate for phosphate and of strontium for calcium can explain the high reactivity of soft MPR. In agreement with the rather high NAC solubility, i.e. 4.2% and 6.2% P_2O_5 for hard and soft MPR, respectively, these properties place hard MPR and soft MPR among the medium to highly reactive PR, respectively. Consequently, both hard and soft MPR may be considered suitable for direct application as P fertilizers. This is in good accordance with the results of previously performed field and pot trials showing that direct application of hard MPR or soft MPR resulted in maize yields comparable to the yields obtained using water-soluble phosphate (triplesuperphosphate) on acid soils low in available P and Ca in sub-humid to humid Tanzania.

1. Introduction

Constraints on crop production due to phosphorus (P) deficiency is a serious problem in Tanzania and other tropical countries due to limited or no-use of commercial fertilizers by resource-poor farmers (Semoka et al., 1992; Rajan et al., 1996; Sanchez, 2002; Vance et al., 2003). Instead of using expensive, imported superphosphate, direct application of reactive local phosphate rock (PR) seems an environmentally-friendly and foreign-currency saving way to alleviate P deficiency (Smalberger et al., 2006). In Tanzania, the most promising PR for direct application is the Minjingu phosphate rock (MPR) with an estimated reserve of 7 million tonnes (Mwambete, 1991; Semoka et al., 1992; Van Straten, 2002). The sedimentary apatite-containing MPR comprises two types: (i) Hard MPR, which occurs in layers of somewhat silica-cemented phosphates mixed with clays and other minerals; (ii) Soft MPR, which occurs as white, porous phosphate beds with sandy, clayey and marly interlayers (Van Kauwenbergh, 1991; Schlüter, 1997). Several field and pot trials with maize as test crop have demonstrated that both forms can be effective P fertilizers on acid soils low in available P and Ca (Msolla et al., 2005, 2007; Szilas et al., 2007a,b). These trials used beneficiated MPR with increased phosphate concentration obtained by removal of accessory minerals by hand picking, crushing, grinding and sizing.

Despite the positive field trial response, the observed delayed dissolution of MPR compared to water-soluble superphosphate calls for additional direct investigation of MPR reactivity (Szilas et al., 2007a,b). Since the reactivity of apatite depends on the chemical and mineralogical composition as well as crystal size or specific surface area (Chien and Hammond, 1978; Van Kauwenbergh and McClellan, 1990; Rajan et al., 1996; Guidry and Mackenzie, 2003), determination of these properties might be useful, especially if supported by chemical test of MPR solubility and comparison with PR from other well-known deposits (Van Straten, 2002; Zapata and Roy, 2004). Studies along these lines, currently lacking for MPR, will undoubtedly lead to improved knowledge about MPR. Together with results of plant growth experiments, such knowledge is needed to ensure optimal use and avoid misapplication of MPR, which undoubtedly becomes an

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[*] Corresponding author. Tel.: +45 35 332419; fax: +45 35332398.
E-mail address: okb@life.ku.dk (O.K. Borggaard).
[1] Present address: Alectia A/S, Algade 52, DK-4000 Roskilde, Denmark.

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even more important issue in the future, where P fertilizer prices are expected to rise (Vance et al., 2003).

Accordingly, this investigation aims at determining the chemical and mineralogical composition of guano-derived apatites in hard and soft MPR as well as of apatites in well-known PR samples from other deposits. The compositional data will be compared with results of a solubility test in order to get deeper insight in MPR reactivity.

2. Materials and methods

2.1. The Minjingu deposit

The phosphate deposit is located at 35°54.6′ E and 3°42.5′ S in Eastern Rift Valley near Lake Manyara around the footslopes of a small quartz-rich hill that served as resting and nesting place for a large piscivorous bird colony sometimes during Pleistocene, where Lake Manyara covered a much larger area than presently (Van Kauwenbergh, 1991; Schlüter, 1997). Due to transgressions and regressions during the two early major paleolake stages, the deposit is stratified with the guano-derived phosphate beds alternating with layers of clays and other sediments resulting in so-called hard MPR and soft MPR as indicated in Fig. 1. The two types have formed the same way but due to different landscape positions, hard MPR occurring at a higher position has been subject to weathering for longer time than the lower-laying soft MPR, which was submerged in saline lake water for longer periods.

A total of 9 samples from each of the two MPR forms were investigated. Five soft samples (S1–S5) representing a significant time span in the deposition, were taken from the profile wall in the south-eastern corner of the mining pit. Seven hard samples (H1–H5, H7, H8) were collected from the northern side, one soft sample (S6) from the current mining area and one sample entirely consisting of large non-guano fossil animal bones (S7). S8, S10, H10 and H11 are beneficiated soft and hard MPR, respectively. As references from other deposits were used sedimentary PR from North Carolina (R1) (International Fertilizer Development Center, IFDC stock no. R232,48) and Central Florida (R2) (IFDC stock no. R231,77) and igneous PR samples from Araxa, Brazil (R3), Kola, Russia (R4) and the Gardiner Complex, Greenland (R5). More information about composition and other aspects of R1–R4 can be found in Van Kauwenbergh (1997) and Zapata and Roy (2004), and the Gardiner Complex is described in Campbell et al. (1997).

All subsequently described analyses were carried out at Department of Natural Sciences, University of Copenhagen and GEUS.

2.2. Chemical and mineralogical analyses

Determination of F was done by means of fluoride selective electrode after dissolution in 2.5 M $HClO_4$ for 16 h (Evans et al., 1970). PR solubility in neutral ammonium citrate (NAC) was done by two consecutive extractions with hot (65 °C) 1 M neutral ammonium citrate for 1 h under continuous shaking using a PR:solution ratio of 1:100 followed by determination of extracted phosphate in both extracts by the molybdenum-blue method (Chien and Hammond, 1978; Zapata and Roy, 2004; Smalberger et al., 2006).

X-ray diffraction (XRD) of powdered samples was performed by a Siemens 5000 diffractometer using CoK_α radiation ($\lambda = 0.1791$ nm) from a tube operated at 40 kV and 40 mA and equipped with a monochromator to remove CoK_β radiation and interfering background scatter. Divergence, antiscatter and receiving slits were 1 mm, 0.6 mm and 0.1 mm wide, respectively. Medium resolution diffractograms (using a scanning rate of 0.6° 2θ min^{-1} at 0.05° 2θ increments in the range of 10–90° 2θ) were obtained from all samples for qualitative assessment of the phosphate minerals (apatites) and major accessory minerals. High resolution diffractograms (using a scanning rate of 0.05° 2θ min^{-1} at 0.05° 2θ increments in the range of 29–67° 2θ) were prepared from selected samples using silicon in 1–2% concentration as internal standard. Interplanar *d*-spacings were calculated using Bragg's equation and the lattice constants were calculated using a least squares method solving the general expression for hexagonal crystals using the Miller indices (e.g. Cullity, 1978) of 002, 300, 202, 310, 222, 312, 213, 321, 410, 402 and 004 by means of the freeware UnitCell (Holland and Redfern, 1995, 1997). The crystal size was estimated using the Scherrer formula (Cullity, 1978) on the broadening of the 002 apatite reflections; instrumental broadening was assessed from the 111 reflection of the internal silicon standard. Structurally bound CO_3^{2-} was estimated from the high resolution scans using the peak pair difference of both $\Delta 2\theta_{(004)-(410)}$ and $\Delta 2\theta_{(300)-(002)}$ according to Schuffert et al. (1990).

Fourier Transform Infrared (FT-IR) absorption spectra were obtained using the KBr pellet technique and a Perkin Elmer FTIR 2000 spectrometer. Absorption spectra were used for qualitative assessment of the accessory minerals present, and for the carbonate apatites

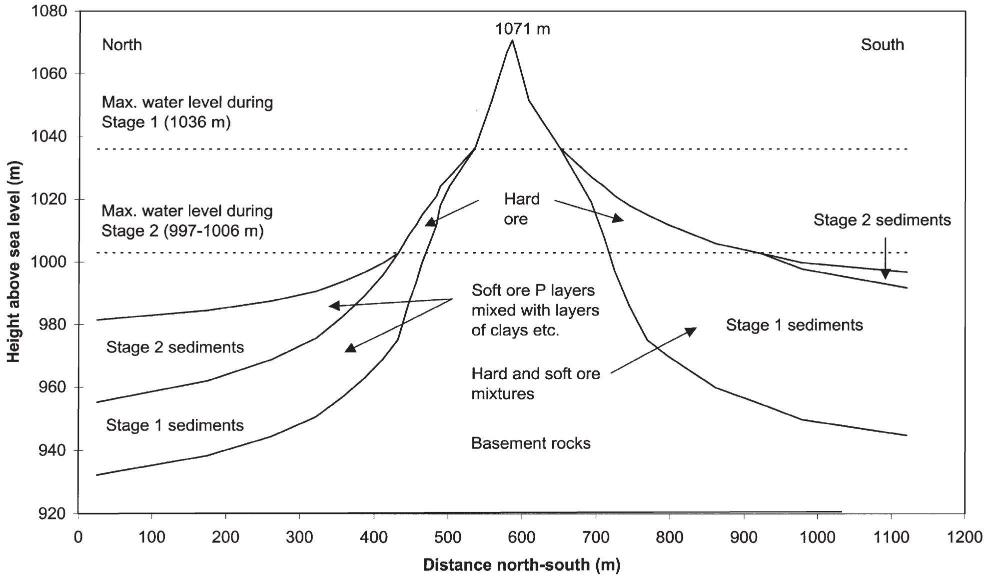

Fig. 1. A north–south transect through the Minjingu summit in northern Tanzania showing elevation and the relation between the hard and soft ore phosphates with the hard form at higher landscape positions than the soft form.