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Review and outlook for agromineral research in agriculture and climate mitigation

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Abstract. Agrominerals are finely ground rocks and minerals used as low-cost fertilisers, and they have received more attention in recent years as sustainable development and climate change mitigation have come to the forefront of societal concerns. Here, we summarise progress in agromineral research over the last 20 years, and discuss the challenges and opportunities of this discipline. The idea of agrominerals has been around since the early 19th century. However, widespread application is subject to economic practicality. In recent years, two big trends have dominated agromineral research. First, some global warming mitigation strategies, such as 'enhanced chemical weathering' and bio-energy carbon capture and storage call for the application of rock powders in arable land on a massive scale. This gives agromineral research an urgency and significance. Second, advances in knowledge of mineral weathering kinetics are poised to transform predictions of agronomic effectiveness from mere empirical studies to more quantitative evaluation. We now have a much better understanding of the factors that influence weathering and nutrient release rates. We forecast that rapid advances in some areas of biogeochemistry will enable advances in the study of agrominerals. In particular, we will be able to measure weathering and nutrient release rates at the field scale, and ultimately to predict kinetic processes of mineral dissolution or precipitation in soil—water—plant systems and the cycling of nutrients and toxic elements in agricultural land.

Additional keywords: agrogeology, agromineral, climate mitigation, enhanced weathering, kinetics.

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Introduction

With the continuing growth of the world's population, it is increasingly urgent to increase food security and practice sustainable agriculture (Manning 2015). Consequently, studies of agrominerals have attracted more attention in the past couple of decades (Harley and Gilkes 2000; Barral et al. 2005; Stamford et al. 2008; Abou-el-Seoud and Abdel-Megeed 2012; Ramezanian et al. 2013; Ramos et al. 2015; Manning et al. 2017). Agrominerals are naturally occurring geological materials that include both unprocessed and processed forms of rocks, and minerals that can be used in crop production systems to replenish the mineral contents of soils and both macro and trace nutrients or to amend the soil. Various names have been used for agrominerals such as 'stone bread' (Van Straaten 2002) or 'petrol fertilisers' (Leonardos et al. 2000). A range of rocks and minerals have been used as agrominerals. For example, limestone and dolomite have long been used in soil amendments. Farmers have also used perlite to enhance aeration in artificial growth media in greenhouses, volcanic scoria and pumice are used as rock mulch to reduce

evaporation, and vermiculite and zeolite are used to store moisture (Van Straaten 2002, 2006).

Compared with traditional chemical fertilisers, agrominerals have many unique advantages. Most synthetic fertilisers are soluble salts containing a single elemental nutrient or a combination of nitrogen (N), phosphorus (P) and potassium (K). In contrast, agrominerals can contain a broad spectrum of macro- and micro-nutrients, which the soil may lack naturally or have been exhausted from a long history of crop production (Van Straaten 2006; Manning 2015). Additionally, the cost of chemical fertilisers such as K can be an issue for developing countries, especially in Africa (Van Straaten 2006). Fertiliser imports have been hampered in many parts of the developing world by several challenges, such as the scarcity of foreign exchange, political problems, civil wars and transport problems (Van Straaten 2002). In addition, farmers there often get low prices for their agricultural products, leading to little incentive to use chemical fertiliser to increase crop production. However, local occurring agrominerals can be an alternative to access vital plant nutrient resources and, by amending soils in this way,

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farmers can replenish soil fertility at a low cost (Van Straaten 2002).

The releasing of nutrient elements is related to chemical, mechanical and biological weathering (Fig. 1). Enhancing the weathering of agrominerals is critical to their efficiency as soil fertilisers. In the last two decades, the dissolution kinetics of various minerals have been investigated experimentally by geochemists. Many different rate laws were established to describe the dissolution rate under different physical and chemical conditions (e.g. Brantley 2008 and references therein). Several databases were compiled to facilitate rate estimates (e.g. Palandri and Kharaka 2004; Marini 2006; Marty et al. 2015). However, weathering rates of silicate minerals measured in laboratory experiments can be 2-5 orders of magnitude higher than those inferred from field systems, which are mostly dominated by inorganic processes. The reasons for the discrepancy between laboratory experiments and field studies remain unclear. Furthermore, extrapolation of laboratorydetermined dissolution rates into agricultural field systems is an open question.

Although the idea of using agrominerals to replenish the mineral contents of soils has been around since the early 19th century (Van Straaten 2006), in recent years its application has been given a larger context. Since the early 1980s, it has been recognised that the application of agrominerals in agriculture may have a potential 'side benefit' in counteracting the global warming trend from anthropogenic greenhouse gas emissions (Manning *et al.* 2013). The base cations in agrominerals are released into soil by weathering, which can react with carbon dioxide (CO_2) in the atmosphere and form carbonate minerals (i.e. a CO_2 sink). For example, Köhler *et al.* (2010) theoretically investigated potential carbon (C) sequestration from artificially enhanced weathering of olivine, described by the following equation:

$$\begin{split} Mg_2SiO_4(olivine) + 2CO_2 + 2H_2O &\rightarrow 2MgCO_3(magnesite) \\ &\quad + H_4SiO_4(aq) \end{split} \tag{1}$$

Their calculations indicated that if olivine is distributed as a fine powder over land areas in the humid tropics, up to 1 Pg of C per year could be sequestrated directly.

However, dissolution kinetics of agrominerals is still poorly understood. Here, in order to promote the research of agrominerals, we first review the most recent studies on mineral weathering kinetics and discuss their implications. Then we review the progress in agrominerals research on phosphate and silicate rock fertilisers. Finally, we discuss the role of agrominerals as it pertains to the greenhouse effect (the increase in temperature and CO₂ concentration, and related C mitigation strategies).

Implications of recent developments in geochemistry for agromineral research

Chemical weathering plays a significant role in the effectiveness of agrominerals as fertilisers in agricultural practices (Harley and Gilkes 2000; Van Straaten 2006). Below, we present current understanding of the dissolution mechanisms and the implications for future research on agromineral dissolution kinetics.

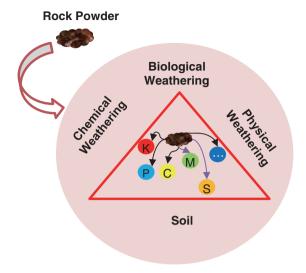


Fig. 1. Schematic diagram for the nutrient release from agrominerals in the soil, which is a complex function of biological, chemical and physical weathering.

Advances in mineral dissolution mechanisms

Some silicate mineral dissolution rate data determined in laboratories at 25°C and near-neutral pH are given in Table 1 and dissolution rates increase by orders of magnitude from top to bottom of the table. Accordingly, the relatively unstable silicate minerals may be more effective as soil fertilisers than stable ones. For example, rocks containing nepheline are considered more effective in improving soil productivity than those containing K-feldspar (Manning 2010).

It is important to note that, although the order of weathering rates in Table 1 is established, the values of experimentally derived dissolution rates listed are not directly applicable to the soil environment. Weathering rates of silicate minerals measured in laboratory experiments can be 2-5 orders of magnitude higher than those inferred from field studies (Schnoor 1990; Stumm 1992; van Grinsven and van Riemsdijk 1992; Anbeek 1993; Casey et al. 1993; Velbel 1993; Blum and Stillings 1995; White and Brantley 2003; Zhu et al. 2004a, 2004b, 2010, Zhu 2005; Ganor et al. 2007). Such discrepancy may arise from the differences between conditions in the laboratory and those in the field. Factors such as soil solution composition, formation of leached layers, surface coatings, differences in hydrologic settings and heterogeneous distribution of saturation states in the soil pore space may lead to the apparent fieldlaboratory discrepancy (Zhu 2005). More importantly, secondary clay precipitation can be the rate-limiting step that controls the overall dissolution rate of silicate minerals (Zhu et al. 2004a, 2010).

In addition, the dissolution rates of many silicate minerals are a function of pH (showing a 'U' or linear shape) (Fig. 2). For example, dissolution rates of feldspar decrease with increasing pH under acidic conditions, become independent of pH under circum-neutral pH and increase with increasing pH under basic conditions. Sudden changes in soil pH due to local chemical or biological processes such as those that occur in the rhizosphere are important in determining dissolution rate. Using a pot

Table 1.	Far-from-equilibrium dissolution rates of silicate minerals at 25°C and pH near neutral (Palandri and
Kharaka	2004) and K contents of K-bearing silicate minerals widely used in previous studies (adapted from
	Manning 2010)

Mineral	Formula	Log dissolution rate (mol/m²/s)	K ₂ O content (wt %)	
Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH,F) ₂	-13.55	11.8	
Kaolinite	$Al_2Si_2O_5(OH)_4$	-13.18	_	
Albite	NaAlSi ₃ O ₈	-12.56	_	
Biotite	$K(Mg,Fe^{2+})_3$ (AlSi ₃ O ₁₀) (OH,F) ₂	-12.55	10.9	
Potassium feldspar	KAlSi ₃ O ₈	-12.41	16.9	
Phlogopite	$KMg_3(Si_3Al)O_{10}(F,OH)_2$	-12.40	11.2	
Oligoclase	(Na,Ca) (Si,Al) ₄ O ₈	-11.84	_	
Andesine	(Na,Ca) (Si,Al) ₄ O ₈	-11.47	_	
Diopside	MgCaSi ₂ O ₆	-11.11	_	
Forsterite	Mg_2SiO_4	-10.64	_	
Hornblende	(Ca,Na) ₂₋₃ (Mg,Fe,Al) ₅ (Al,Si) ₈ O ₂₂ (OH,F) ₂	-10.3	_	
Bytownite	(Ca,Na) (Si,Al) ₄ O ₈	-9.82	_	
Leucite	$KAlSi_2O_6$	-9.2	21.6	
Anorthite	$CaAl_2Si_2O_8$	-9.12	_	
Wollastonite	CaSiO ₃	-8.88	_	
Nepheline	(Na,K)AlSiO ₄	-8.56	8.0	

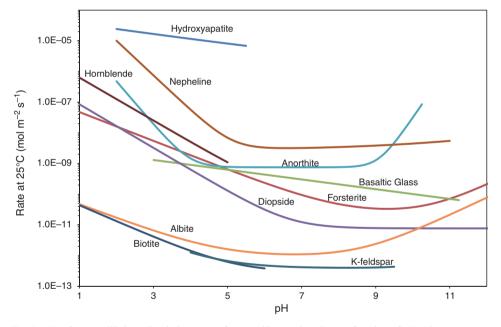


Fig. 2. Far-from-equilibrium dissolution rates of many silicate minerals as a function of pH. The rates were calculated using the kinetic data of Palandri and Kharaka (2004).

experiment, Hinsinger and Jaillard (1993) showed that mineral weathering can be accelerated in the rhizosphere because root exudates contain H⁺ ions, organic acids and chelating molecules (Dakora and Phillips 2002). Additionally, naturally occurring organic matter may also be an important factor in influencing silicate mineral weathering. For example, the enhancement ratio (the ratio between dissolution rate with organic matter and dissolution rate under the same temperature and pH but without organic matter) of oxalate on the dissolution rates of albite is in the range of 0.73–24 (Ganor *et al.* 2009).

These mechanisms have been extensively studied over many decades because they are essential in quantifying many basic geological and environmental processes such as rock weathering and diagenesis, toxic waste, radioactive waste, acid rain, acid drainage, global elemental cycling and global climate over geologic time (Lasaga *et al.* 1994; Berner and Berner 1997). Many mechanisms of silicate mineral dissolution have been debated over the last several decades, but some consistent views have emerged.

The dissolution of silicate minerals arises from a rapid exchange reaction between alkali or alkaline-earth ions and H⁺-ions, H₃O⁺-ions or water molecules (Chou and Wollast 1985; Casey and Bunker 1990; Bunker 1994). Upon dissolution, structural elements are released by the destruction

of metal-oxygen or metal-hydroxide bonds (Holdren and Speyer 1985; Casey and Ludwig 1995; Sverdrup and Warfvinge 1995). Depending on the materials and leaching conditions, various secondary phases may precipitate from dissolved elements (Alekseyev et al. 1997). In some cases, an amorphous, porous, enriched-in-Si and/or -Al, hydrated laver. commonly referred to as a 'gel', will form on the surface of the mineral (Chou and Wollast 1985; Casey et al. 1993; Nugent et al. 1998; Zhu et al. 2006). The layer may constitute a barrier for diffusion of species between the pristine material and the solution and become rate-limiting (Casey et al. 1988; Hellmann et al. 1990; Casey and Ludwig 1995). Some believe this is a leached layer in which the alkali ions are leached out (Nesbitt and Skinner 2001). The rate of this last step is controlled by the decomposition of the active surface complex whose configuration depends on the solution properties, such as pH, the concentration of dissolved Al and alkali ion concentration (Chou and Wollast 1985). Others believe that this layer is re-precipitated silica gel on the dissolving mineral surfaces (Hellmann et al. 2003). The ubiquitous presence and role of this amorphous layer are still debated.

Research gaps and future research directions in agromineral dissolution kinetics

There are still large uncertainties in the determination of kinetic parameters. For example, Guidry and Mackenzie (2003) used a fluidised bed and stirred tank reactor to measure the dissolution rate of igneous fluorapatite over a range of temperature and pH. The dissolution rate at 25°C and 1 atm decreased from $\sim\!10^{-6.9}$ to $\sim\!10^{-10.4}$ mol/m²/s when pH increased from 2 to 6; whereas, at 6 < pH < 8.5, the dissolution rate was pH-independent. These rates are about 2–3 orders of magnitude lower than the rate suggested by Palandri and Kharaka (2004), who compiled laboratory experimental rate data. Hence, it is necessary to improve the accuracy of kinetic parameters for agrominerals to enhance nutrient supply prediction ability.

Recently, there has been great development in isotope analysis techniques. The compositions of many isotopes in a mineral such as silicon (Si), lithium (Li), iron (Fe) and magnesium (Mg) can be precisely measured. These 'non-traditional stable isotopes' emerge to be useful tools in studying the dissolution kinetics of minerals. For example, the use of stable Si isotopes in laboratory experiments has increased in sensitivity by several orders of magnitude for the slow-reacting silicate minerals (Gruber *et al.* 2013; Zhu *et al.* 2016). Using these isotope tools may provide new insight into agromineral weathering kinetics.

In addition, how global temperature change affects the dissolution of agrominerals should be investigated. Rising temperatures can increase dissolution rates of agrominerals by affecting the kinetic rate constant (Guidry and Mackenzie 2000, 2003). IPCC (2007, 2014) projected that global mean surface temperature in 2100 could increase by about 1.8–4.0°C (relative to 1980–1999), and the atmospheric $\rm CO_2$ concentration in 2100 could rise to 550–970 ppm, much higher than the value in 2008 (~390 ppm). How global warming and increased atmospheric $\rm CO_2$ will affect the nutrient release rates from agrominerals is unknown.

We must note that many other factors may affect the release of nutrients from agrominerals such as plant physiology, microbial activities, water availability and soil physics. To better apply agrominerals, how these factors affect the release of nutrients of agrominerals also need to be investigated in future studies.

Dissolution kinetics of silicate minerals in agricultural soils

Although we can draw from studies on the kinetics of weathering rates in inorganic geochemistry to provide insights, the weathering of agrominerals in the field occur in different environments, which must be addressed. An extended database for a robust assessment of the dissolution kinetics of agrominerals in the soil—water—plant system is needed.

- (1) There are abundant organic acids in this environment, and they probably accelerate weathering.
- (2) If due to grinding processes, agrominerals with fresh and possibly activated surfaces are applied, different dissolution kinetics could result compared with naturally occurring minerals (Kleiv and Thornhill 2007; Baláž et al. 2008; Haug et al. 2010).
- (3) It is known that the biological pump removes dissolved matter from the soil solution (Lucas 2001) and changes consecutive saturation state conditions due to the release of CO₂ and ions via the root system, while certain matter like Si, Mg or calcium (Ca) are accumulated in plants (Hinsinger *et al.* 2001; Akter and Akagi 2005, 2010). However, it is not known how the removal of elements like Si or Mg from the soil solution affects the soil solution saturation state with respect to minerals. There is a lack of well constrained experiments addressing this issue. For example, the increased silica uptake by Si-accumulating plants changes the silica concentrations in the compartments of soil, decreasing concentrations during peak plant growth and, therefore, affecting the saturation state of the soil solution.
- (4) Another process affecting the dissolution of fresh rocks is the dry-wet cycle in the upper soil compartment, specifically during peak plant growth, when plants cause a significant reduction in soil moisture. During this period, top soils can dry out and soil solution saturation with respect to minerals will increase, thus decreasing the dissolution rate of added rock powders and causing precipitation of minerals or amorphous phases. During the wetting processes, this would be reversed (c.f. Goddéris et al. 2013). It is necessary to further quantify the effect of this dry-wet cycle process.
- (5) Bioturbation, for example by earthworms, affects the surface properties of minerals and weathering processes (Carpenter *et al.* 2007; Nahmani *et al.* 2007; Sizmur and Hodson 2009; Blouin *et al.* 2013; Hodson *et al.* 2014). Therefore, it is necessary to quantify this process to identify its relevance to the observed weathering kinetics of minerals.

All these indicate that agrominerals will likely weather much faster than in inorganic systems.

Application of agrominerals in practice

Phosphate rocks as P fertiliser

Most of the world's phosphate fertilisers are produced from phosphate rocks (Oelkers and Valsami-Jones 2008; Van Kauwenbergh *et al.* 2013; Manning 2015). Phosphate rock occurs in all geologic settings – sedimentary, metamorphic and igneous deposits exist across the world with abundant reserves. Phosphate rock is a general term that describes naturally occurring minerals that contain a relatively high concentration of P, such as apatite. The P content or grade of phosphate rocks is commonly assessed by the content of phosphorus pentoxide (P_2O_5). For example, the content of P_2O_5 in pure fluor-apatite ($Ca_5(PO_4)_3F$) is 42%, and in francolite ($(Ca,Mg,Sr,Na)_{10}(PO_4,SO_4,CO_3)_6F_{2-3}$) may be 34%.

In the last few decades, there has been considerable research on the use of phosphate rock resources for direct application and their strategies under different local conditions (Léon *et al.* 1986; Chien 1993; Ghani *et al.* 1994; Chien and Menon 1995*a*; von Wilpert and Lukes 2003). From years of investigation, researchers have found that decisions to use phosphate rocks directly without chemical modification should be based on several factors, such as the properties of phosphate rocks, soil properties, plant species and management practices (Chien and Menon 1995*b*), which are described below.

The properties of phosphate rocks largely depend on their source and impurities. Sedimentary-origin phosphate rocks have been found to be more effective than igneous phosphate when applied directly to soils, because of differences in the degree of carbonate substitution and specific surface area (Van Straaten 2002). The form and concentration of impurities in phosphate rocks are also crucial for evaluating agronomic effectiveness. For instance, minerals like dolomite (CaMg (CO₃)₂) and calcite (CaCO₃) can restrain the release of P because the Ca from these impurities can inhibit the dissolution of phosphate rocks through the common ion effect (Chien and Menon 1995b). Phosphate rocks with Carich carbonates are less effective than those with accompanying silicates (Van Straaten 2002).

The soil is another factor to consider in choosing a phosphate rock for direct application. Acidic soil with high cation exchange capacity (CEC) and P-sorption capacity and low exchangeable Ca is most appropriate for the direct application of phosphate rocks (Chien and Menon 1995b). The more acidic the soil, the faster phosphate rocks weather or dissolve. The effectiveness of P release from phosphate rocks decreases as soil pH increases (Kanabo and Gilkes 1987; Rajan *et al.* 1991). High P-sorption capacity or CEC can sink the P or Ca in the soil solution and decrease their concentration. Therefore, this property also can enhance the dissolution of phosphate rocks (Chien and Menon 1995b).

The efficient use of P from phosphate rocks also depends on plants. Phosphate rocks were found to dissolve more efficiently in the presence of plants than in their absence (Hinsinger and Gilkes 1997). Hinsinger and Gilkes (1997) also suggested that Ca uptake by plants in the rhizosphere depletes the dissolved Ca and may promote the dissolution of phosphate rocks. Additionally, it is well known that the agronomic effectiveness of phosphate rocks varies among different plant

species due to different properties of root exudate and rhizosphere microflora (Hinsinger and Gilkes 1997; Hinsinger 2001). For example, non-mycorrhizal plants, including those in the Cruciferae family or plants such as white lupin (*Lupinus albus* L.) that form root clusters, have been found to effectively utilise P from phosphate rocks, particularly when soils are deficient in P or in response to aluminium (Al) toxicity (Hinsinger and Gilkes 1995; Arcand and Schneider 2006).

However, direct application of phosphate rocks does not give satisfactory results when the reactivity of phosphate rocks is low, soil pH is high or periods of plant growth are short. The phosphate rocks must be modified before application in order to optimise the P utilisation under local conditions. Several modification processes have been developed to enhance P nutrient release from phosphate rocks, such as mechano-milling and microorganism-mixing. Lim et al. (2003) explored the feasibility of mechano-milling to enhance the solubility of phosphate rocks. Rock phosphates were ball-milled in their experiment, and the fertiliser relative effectiveness of milled phosphate rocks increased by a factor of up to three based on P content of wheat plants. In addition, some microorganisms are capable of solubilising phosphate rocks. For example, some filamentous fungi such as Penicillium and Aspergillus species show great phosphate-solubilising ability in both liquid and solid media (e.g. Barea et al. 2002). Mycorrhizal fungi can also increase P uptake (e.g. Trolove et al. 2003). Mixing the microorganism with phosphate rocks when replenishing soils may increase the fertiliser effectiveness. Other processes like fusion and calcination, acidulation or partial acidulation, blending with sulfur, heap leaching, blending and granulation, ion exchange, phosphorcomposting, green manuring, bio-solubilisation, mycorrhizal inoculation and phytoextraction were introduced in Van Straaten (2006).

Although phosphate rocks can provide P for soil, they can also be sources of heavy metals and radioactive elements, such as arsenic (As), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni), vanadium (V), cadmium (Cd), uranium (U) and thorium (Th) (Mortvedt 1995; Ogunleye et al. 2002; Manning 2008; Sabiha-Javied et al. 2009). The range of various heavy metal concentrations in phosphate rocks is given in Table 2. The U concentration in phosphate rocks of different origin is in the range of 23-220 mg/kg worldwide (Kratz and Schnug 2006). Heavy metals can become toxic if accumulated in excessive amounts. Accumulation of heavy metals in soil has potential to restrict the soil function, cause toxicity to crops, contaminate the food chain and be detrimental to human health (Mclaughlin 1996). Additionally, if crushed phosphate rocks are applied directly to soils, radionuclides of the decay series are distributed in agricultural soils, risking overexposure by farmers and plants. Therefore, how to get rid of these heavy elements in phosphate agrominerals before spreading them in soil is an urgent need for future studies.

Silicate minerals and rocks as K fertilisers

While N fertiliser is produced from fossil fuels, P and K fertilisers are produced from phosphate and potash ores. With a rapidly growing world population, the potash ore reserve may

Region	Heavy metal concentration (mg/kg)						Reference		
_	Cr	Pb	Cd	Zn	Mn	Со	Cu	Ni	
Algeria	208	_	_	134	_	0.41	_	_	Pantelica et al. (1997)
Egypt	_	_	_	13.2	_	385	-	_	Abdel-Rahman (2001)
Israel	56	_	_	372	_	0.37	-	_	Pantelica et al. (1997)
Middle East	129	4	9	315	_	_	43	29	Kongshaug et al. (1992)
Morocco	291	7	30	345	_	0.48	22	26	Pantelica et al. (1997)
Nigeria	28	_	_	59	5716	19.8	_	_	Ogunleye et al. (2002)
North Africa	105	6	60	420	_	_	45	33	Kongshaug et al. (1992)
Russia	23.3	3	0.1	19	_	2.05	30	2	Pantelica et al. (1997)
Saudi Arabia	176	_	_	88	_	_	-	_	Aksoy et al. (2002)
South Africa	1	35	2	6	_	_	130	35	Kongshaug et al. (1992)
Syria	136	_	_	269	_	0.41	-	_	Pantelica et al. (1997)
Togo	75	_	_	143	149	1.2	_	_	Ogunleye et al. (2002)
Tunisia	161	_	_	515	_	0.67	-	_	Pantelica et al. (1997)
USA	142	12	11	403	2235	0.44	23	37	da Conceição and Bonotto (2006)
Pakistan	17	89	7.2	67.2	178	9.4	5.5	28	Sabiha-Javied et al. (2009)

Table 2. The global range of heavy metal concentrations in sedimentary phosphate rocks

be exhausted in the near future, and the shortage of worldwide potash ores is further exacerbated by its non-optimal geographic distributions, with Africa mostly lacking (Manning 2010, 2017). Mineral sources of K from agrominerals may become a necessity to feed the world. Silicate minerals, such as K-feldspar, leucite, nepheline, kalsilite, muscovite, biotite and phlogopite, can readily provide K to plants. Several studies have used silicate minerals as a source of K for plants; the most widely used K-bearing silicate minerals are listed in Table 1. Detailed information of these studies was reviewed by Manning (2010). Investigations into the possible use of silicate minerals as soil fertiliser have yielded varying results.

For example, sanidine was proposed as a slow-release fertiliser in low-input agricultural systems, particularly on leached soils of low effective CEC (e.g. Mohammed *et al.* 2014; Ramos *et al.* 2015). Barral *et al.* (2005) suggested that granite powders could be used as soil amendments and fertilisers in acid soil because they are alkaline and release cations (Ca, Mg, Na and K) when exposed. Hinsinger *et al.* (1995) found an increase in exchangeable K and soil pH due to granite application at the rate of 20 t/ha, and also showed that wheat biomass wheat responded to granite application. Hinsinger *et al.* (1995) concluded that the positive response of wheat growth to granite application was due to K supplied by granite dissolution. Gillman (1980) and Gillman *et al.* (2001, 2002) demonstrated improved chemical properties of highly weathered soils (increases in pH, Ca, Mg and K) due to the application of silicate, such as basalt.

Benefits of using agrominerals for mitigating climate change

Traditionally, the study of agrominerals has focused on its potential for re-mineralising soils and improving soil productivity. However, in recent years, the benefits of applying agrominerals for mitigating climate change have also come into focus. Although the release of nutrient elements such as P and K from mineral dissolution could increase the fertility of soils and biological productivity, the simultaneous release of cations such as Mg or Ca can form carbonate minerals and sequestrate atmospheric CO₂. Hartmann *et al.* (2013) described a global

deployment of an enhanced weathering strategy. They envisioned spreading one to tens of gigatonnes of crushed rock powder per year to cover ~14 700 000 km² of potential application areas (Fig. 3). It is also proposed that selective applications of these rock powders to arable land will achieve the goal of a simultaneous increase in soil productivity. However, as we mentioned above, poorly constrained kinetic parameters of mineral dissolution or precipitation in the field soil—water—plant system hampers accurate prediction of the effectiveness of applying agrominerals for mitigating climate change. More experimental and theoretical work is required in the future.

A step further towards the marriage of agricultural use and climate mitigation use of agrominerals is BECCS, bio-energy C capture and storage (Fuss et al. 2014). This strategy calls for growing biomass feedstocks on an additional 0.5 billion hectares of land worldwide. The growth of fast and hardy crops extracts atmospheric CO2. The CO2 from combustion of biomass in energy production is captured and subsequently sequestered into geologic formations. Thus, a 'net negative emission' is achieved. The general strategy is to grow highgrowth plants on less fertile land using intensive agricultural practices, such as applying large quantities of fertilisers. This process demands more geogenic nutrients than the growth of food crops, and thus risks their rapid depletion. This is partly because of supply limitation and permanent removal of geogenic nutrients from the soil-rock-system due to harvesting. Additionally, the demand for large quantities of fertilisers makes the use of synthesised chemical fertilisers either not economically viable or environmentally sustainable. Runoff of N and P fertiliser will contaminate surface water bodies and groundwater. Therefore agrominerals are desirable.

These arguments (BECCS and 'enhanced weathering') point out that a globally increased application of rock powder or agrominerals on top of or mixed into soils may be driven by the quest to mitigate global warming. This will lead to an increased alteration of element fluxes through the critical zone or weathering zone and will alter the biological pump, which redistributes portions of the released elements. On the technical side, it remains to be determined how an optimal rock powder should be designed. This requires research on comminution, which

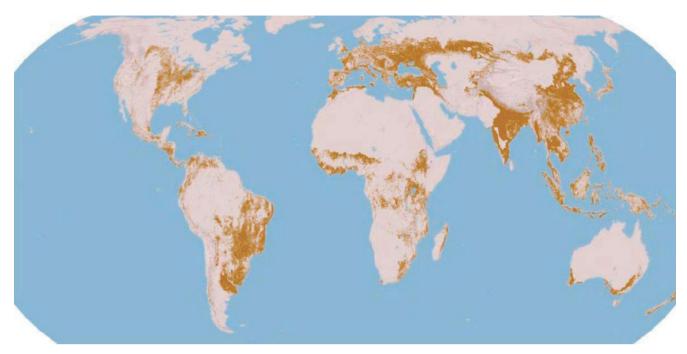


Fig. 3. Potential application areas (indicated by brown) of the ultramafic rock flour for CO₂ sequestration, which includes many arable areas for added benefits of increased agriculture production. Reprinted from Moosdorf *et al.* (2014) and with permission of the American Chemical Society.

requires large amounts of energy (Renforth 2012; Moosdorf *et al.* 2014; Ciceri *et al.* 2017), the selection of source rocks in order to tweak element release rates, and the mixing of soil organic matter with agrominerals and *in situ* material of different grain sizes to optimise hydrologic properties and CEC.

Conclusions

We reviewed advances and needs in agrominerals research over the last 20 years, in particular on the understanding of dissolution kinetics as well as the effectiveness of using agrominerals as low-cost fertilisers. The application of phosphate rocks has been researched most intensively, including studies of direct application, modification processes and the factors influencing agronomic effectiveness. Although multi-nutrient silicate rock fertilisers have displayed effectiveness in agricultural practice, the contradictory experimental data result in confusion concerning their nutrient release rates.

In addition, the applying of agrominerals in agriculture can bring benefit to climate mitigation. Dissolution of spread rocks releases cations (e.g. Mg or Ca), which convert dissolved CO₂ in natural waters to carbonate minerals, thus realising the goal of sequestration of atmospheric CO₂. Besides, deployment of atmospheric CO₂ removal strategies (e.g. BECCS and 'enhanced weathering') for mitigating global warming will lead to highintensity agriculture and potentially increase the significance of agrominerals. We predict that, with this societal need and advances in geochemical research of the kinetics process of mineral dissolution and precipitation, there will be increased interest in agromineral research.

Conflicts of interest

The authors declare no conflicts of interest.

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References

Abdel-Rahman AFM (2001) Peraluminous plutonism: nature and origin of the Moly May leucogranite and its Coast Plutonic Complex granitic host-rocks, northwestern British Columbia. *Canadian Mineralogist* **39**, 1181–1196. doi:10.2113/gscanmin.39.4.1181

Abou-el-Seoud II, Abdel-Megeed A (2012) Impact of rock materials and biofertilizations on P and K availability for maize (Zea Maize) under calcareous soil conditions. *Saudi Journal of Biological Sciences* **19**(1), 55–63. doi:10.1016/j.sjbs.2011.09.001

Aksoy A, Ahmed M, Matter WSA (2002) Gamma-ray spectroscopic and PIXE analysis of selected samples from the phosphorite deposits of Northwestern Saudi Arabia. *Journal of Radioanalytical and Nuclear Chemistry* 253(3), 517–521. doi:10.1023/A:1020450310197

Akter M, Akagi T (2005) Effect of fine root contact on plant-induced weathering of basalt. *Soil Science and Plant Nutrition* **51**(6), 861–871. doi:10.1111/j.1747-0765.2005.tb00121.x

Akter M, Akagi T (2010) Dependence of plant-induced weathering of basalt and andesite on nutrient conditions. *Geochemical Journal* 44(2), 137–150. doi:10.2343/geochemj.1.0052

Alekseyev VA, Medvedeva LS, Prisyagina NI, Meshalkin SS, Balabin AI (1997) Change in the dissolution rates of alkali feldspars as a result of secondary mineral precipitation and approach to equilibrium. Geochimica et Cosmochimica Acta 61, 1125–1142. doi:10.1016/S00 16-7037(96)00405-X

Anbeek C (1993) The effect of natural weathering on dissolution rates. Geochimica et Cosmochimica Acta 57(21–22), 4963–4975. doi:10.1016/S0016-7037(05)80002-X

Arcand MM, Schneider KD (2006) Plant-and microbial-based mechanisms to improve the agronomic effectiveness of phosphate rock: a review. Anais da Academia Brasileira de Ciencias 78(4), 791–807. doi:10.1590/S0001-37652006000400013

- Baláž P, Turianicová E, Fabián M, Kleiv RA, Briančin J, Obut A (2008) Structural changes in olivine (Mg, Fe)2SiO4 mechanically activated in high-energy mills. International Journal of Mineral Processing 88(1-2), 1-6. doi:10.1016/j.minpro.2008.04.001
- Barea J, Toro M, Orozco M, Campos E, Azcón R (2002) The application of isotopic (32 P and 15 N) dilution techniques to evaluate the interactive effect of phosphate-solubilizing rhizobacteria, mycorrhizal fungi and Rhizobium to improve the agronomic efficiency of rock phosphate for legume crops. Nutrient Cycling in Agroecosystems 63(1), 35-42. doi:10.1023/A:1020589732436
- Berner RA, Berner EK (1997) Silicate weathering and climate. In 'Tectonic uplift and climate change'. (Ed. WF Ruddiman) pp. 353-364. (Springer US: New York)
- Blouin M, Hodson ME, Delgado EA, Baker G, Brussaard L, Butt KR, Dai J, Dendooven L, Peres G, Tondoh JE (2013) A review of earthworm impact on soil function and ecosystem services. European Journal of Soil Science 64(2), 161-182. doi:10.1111/ejss.12025
- Blum AE, Stillings LL (1995) Feldspar dissolution kinetics. In 'Chemical weathering rates of silicate minerals'. (Eds AF White, SL Brantley) pp. 291-346. (Mineralogical Society of America: Washington, D.C.)
- Brantley SL (2008) Kinetics of Mineral Dissolution. In 'Kinetics of water-rock interaction'. (Eds SL Brantley, JD Kubicki, AF White) pp. 151-210. (Springer New York: New York, NY)
- Bunker B (1994) Molecular mechanisms for corrosion of silica and silicate glasses. Journal of Non-Crystalline Solids 179, 300-308. doi:10.1016/ 0022-3093(94)90708-0
- Carpenter D, Hodson ME, Eggleton P, Kirk C (2007) Earthworm induced mineral weathering: Preliminary results. European Journal of Soil Biology 43, S176-S183. doi:10.1016/j.ejsobi.2007.08.053
- Casey WH, Bunker BC (1990) The leaching of mineral and glass surfaces during dissolution. In 'Mineral-water interface geochemistry'. (Eds M Hochella, A White) pp. 397-426. (Mineralogical Society of America: Washington, D.C.)
- Casey WH, Ludwig C (1995) Silicate mineral dissolution as a ligandexchange reaction. Reviews in Mineralogy and Geochemistry 31(1), 87 - 117.
- Casey WH, Westrich HR, Arnold GW (1988) Surface chemistry of labradorite feldspar reacted with aqueous solutions at pH=2, 3, and 12. Geochimica et Cosmochimica Acta 52(12), 2795-2807. doi:10.1016/ 0016-7037(88)90147-0
- Casey WH, Banfield JF, Westrich HR, McLaughlin L (1993) What do dissolution experiments tell us about natural weathering? Chemical Geology 105(1-3), 1-15. doi:10.1016/0009-2541(93)90115-Y
- Chien S (1993) Solubility assessment for fertilizer containing phosphate rock. Fertilizer Research 35(1-2), 93-99. doi:10.1007/BF00750223
- Chien S, Menon R (1995a) Agronomic evaluation of modified phosphate rock products. Fertilizer Research 41(3), 197-209. doi:10.1007/BF00
- Chien S, Menon R (1995b) Factors affecting the agronomic effectiveness of phosphate rock for direct application. Fertilizer Research 41(3), 227-234. doi:10.1007/BF00748312
- Chou L, Wollast R (1985) Steady-state kinetics and dissolution mechanisms of albite. American Journal of Science 285, 963-993. doi:10.2475/ajs.
- Ciceri D, de Oliveira M, Stokes RM, Skorina T, Allanore A (2017) Characterization of potassium agrominerals: Correlations between petrographic features, comminution and leaching of ultrapotassic syenites. Minerals Engineering 102, 42-57. doi:10.1016/j.mineng. 2016.11.016
- da Conceição FT, Bonotto DM (2006) Radionuclides, heavy metals and fluorine incidence at Tapira phosphate rocks, Brazil, and their industrial (by) products. Environmental Pollution 139(2), 232-243. doi:10.1016/ j.envpol.2005.05.014

- Dakora FD, Phillips DA (2002) Root exudates as mediators of mineral acquisition in low-nutrient environments. Plant and Soil 245(1), 35-47. doi:10.1023/A:1020809400075
- Fuss S, Canadell JG, Peters GP, Tavoni M, Andrew RM, Ciais P, Jackson RB, Jones CD, Kraxner F, Nakicenovic N (2014) Betting on negative emissions. Nature Climate Change 4(10), 850-853. doi:10.1038/ nclimate2392
- Ganor J, Lu P, Zheng Z, Zhu C (2007) Bridging the gap between laboratory measurements and field estimations of weathering using simple calculations. Environmental Geology 53(3), 599-610. doi:10.1007/ s00254-007-0675-0
- Ganor J, Reznik IJ, Rosenberg YO (2009) Organics in water-rock interactions. Reviews in Mineralogy and Geochemistry 70(1), 259-369. doi:10.2138/rmg.2009.70.7
- Ghani A, Rajan S, Lee A (1994) Enhancement of phosphate rock solubility through biological processes. Soil Biology & Biochemistry 26(1), 127-136. doi:10.1016/0038-0717(94)90204-6
- Gillman G (1980) The effect of crushed basalt scoria on the cation exchange properties of a highly weathered soil. Soil Science Society of America Journal 44(3), 465-468. doi:10.2136/sssaj1980.03615995 004400030005x
- Gillman G, Burkett D, Coventry R (2001) A laboratory study of application of basalt dust to highly weathered soils: Effect on soil cation chemistry. Soil Research 39(4), 799-811. doi:10.1071/SR00073
- Gillman G, Burkett D, Coventry R (2002) Amending highly weathered soils with finely ground basalt rock. Applied Geochemistry 17(8), 987-1001. doi:10.1016/S0883-2927(02)00078-1
- Goddéris Y, Brantley SL, François LM, Schott J (2013) Rates of consumption of atmospheric CO2 through the weathering of loess during the next 100 yr of climate change. Biogeosciences 10(1), 135-148. doi:10.5194/bg-10-135-2013
- Gruber C, Harpaz L, Zhu C, Bullen TD, Ganor J (2013) A new approach for measuring dissolution rates of silicate minerals by using silicon isotopes. Geochimica et Cosmochimica Acta 104(3), 261-280. doi:10.1016/ j.gca.2012.11.022
- Guidry MW, Mackenzie FT (2000) Apatite weathering and the Phanerozoic phosphorus cycle. Geology 28(7), 631-634. doi:10.1130/0091-7613 (2000)28<631:AWATPP>2.0.CO;2
- Guidry MW, Mackenzie FT (2003) Experimental study of igneous and sedimentary apatite dissolution: Control of pH, distance from equilibrium, and temperature on dissolution rates. Geochimica et Cosmochimica Acta 67(16), 2949-2963. doi:10.1016/S0016-7037(03)00265-5
- Harley A, Gilkes R (2000) Factors influencing the release of plant nutrient elements from silicate rock powders: a geochemical overview. Nutrient Cycling in Agroecosystems 56(1), 11-36. doi:10.1023/A:1009859309453
- Hartmann J, West AJ, Renforth P, Köhler P, De La Rocha CL, Wolf-Gladrow DA, Dürr HH, Scheffran J (2013) Enhanced chemical weathering as a geoengineering strategy to reduce atmospheric carbon dioxide, supply nutrients, and mitigate ocean acidification. Reviews of Geophysics 51(2), 113-149. doi:10.1002/rog.20004
- Haug TA, Kleiv RA, Munz IA (2010) Investigating dissolution of mechanically activated olivine for carbonation purposes. Applied Geochemistry 25(10), 1547–1563. doi:10.1016/j.apgeochem.2010.
- Hellmann R, Eggleston CM, Hochella MF Jr, Crerar DA (1990) The formation of leached layers on albite surfaces during dissolution under hydrothermal conditions. Geochimica et Cosmochimica Acta **54**(5), 1267–1281, doi:10.1016/0016-7037(90)90152-B
- Hellmann R, Penisson JM, Hervig RL, Thomassin JH, Abrioux MF (2003) An EFTEM/HRTEM high-resolution study of the near surface of labradorite feldspar altered at acid pH: evidence for interfacial dissolution-reprecipitation. Physics and Chemistry of Minerals 30(4), 192-197. doi:10.1007/s00269-003-0308-4

- Hinsinger P (2001) Bioavailability of inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant and Soil* **237**(2), 173–195. doi:10.1023/A:1013351617532
- Hinsinger P, Gilkes R (1995) Root-induced dissolution of phosphate rock in the rhizosphere of lupins grown in alkaline soil. Australian Journal of Soil Research 33(3), 477–489. doi:10.1071/SR9950477
- Hinsinger P, Gilkes RJ (1997) Dissolution of phosphate rock in the rhizosphere of five plant species grown in an acid, P-fixing mineral substrate. *Geoderma* 75(3–4), 231–249. doi:10.1016/S0016-7061(96) 00094-8
- Hinsinger P, Jaillard B (1993) Root-induced release of interlayer potassium and vermiculitization of phlogopite as related to potassium depletion in the rhizosphere of ryegrass. *European Journal of Soil Science* 44(3), 525–534. doi:10.1111/j.1365-2389.1993.tb00474.x
- Hinsinger P, Bolland M, Gilkes R (1995) Silicate rock powder: effect on selected chemical properties of a range of soils from Western Australia and on plant growth as assessed in a glasshouse experiment. *Fertilizer Research* **45**(1), 69–79. doi:10.1007/BF00749883
- Hinsinger P, Barros ONF, Benedetti MF, Noack Y, Callot G (2001) Plant-induced weathering of a basaltic rock: experimental evidence. Geochimica et Cosmochimica Acta 65(1), 137–152. doi:10.1016/ S0016-7037(00)00524-X
- Hodson ME, Black S, Brinza L, Carpenter D, Lambkin DC, Mosselmans JFW, Palumbo-Roe B, Schofield PF, Sizmur T, Versteegh EAA (2014) Biology as an agent of chemical and mineralogical change in soil. *Procedia Earth and Planetary Science* 10, 114–117. doi:10.1016/j.proeps.2014.08.039
- Holdren GR, Speyer PM (1985) pH dependence changes in the rats and stoichiometry of dissolution of an alkali feldspar at room temperature. *American Journal of Science* 285, 994–1026. doi:10.2475/ajs.285. 10.994
- IPCC (2007) 'Climate change 2007: the physical science basis.' (Cambridge University Press: Cambridge, UK and New York, NY, USA)
- IPCC (2014) Carbon dioxide: projected emissions and concentrations. Available at http://www.ipcc-data.org/observ/ddc co2.html
- Kanabo IAK, Gilkes RJ (1987) The role of soil pH in the dissolution of phosphate rock fertilizers. Nutrient Cycling in Agroecosystems 12(2), 165–173.
- Kleiv RA, Thornhill M (2007) Production of mechanically activated rock flour fertilizer by high intensive ultrafine grinding. *Minerals Engineering* 20(4), 334–341. doi:10.1016/j.mineng.2006.08.017
- Köhler P, Hartmann J, Wolfgladrow DA (2010) Geoengineering potential of artificially enhanced silicate weathering of olivine. *Proceedings of* the National Academy of Sciences of the United States of America 107(47), 20228–20233. doi:10.1073/pnas.1000545107
- Kongshaug G, Bockman OC, Kaarstad O, Morka H (1992) Inputs of trace elements to soils and plants. In 'Chemical climatology and geomedical problems'. (Eds J Låg) pp. 185–216. (Norsk Hydro: Oslo, Norway)
- Kratz S, Schnug E (2006) Rock phosphates and P fertilizers as sources of U contamination in agricultural soils. In 'Uranium in the environment'. (Eds BJ Merkel, A Hasche-Berger) pp. 57–67. (Springer: Netherlands)
- Lasaga AC, Soler JM, Ganor J, Burch TE, Nagy KL (1994) Chemical weathering rate laws and global geochemical cycles. *Geochimica et Cosmochimica Acta* 58(10), 2361–2386. doi:10.1016/0016-7037(94) 90016-7
- Léon L, Fenster W, Hammond L (1986) Agronomic potential of eleven phosphate rocks from Brazil, Colombia, Peru, and Venezuela. Soil Science Society of America Journal 50(3), 798–802. doi:10.2136/sssaj 1986.03615995005000030046x
- Leonardos OH, Theodoro SH, Assad ML (2000) Remineralization for sustainable agriculture: a tropical perspective from a Brazilian viewpoint. *Nutrient Cycling in Agroecosystems* 56(1), 3–9. doi:10.1023/A:1009855 409700

- Lim H, Gilkes R, McCormick P (2003) Beneficiation of rock phosphate fertilisers by mechano-milling. *Nutrient Cycling in Agroecosystems* **67**(2), 177–186. doi:10.1023/A:1025505315247
- Lucas Y (2001) The role of plants in controlling rates and products of weathering: importance of biological pumping. *Annual Review of Earth and Planetary Sciences* **12**(29), 313–316.
- Manning DAC (2008) Phosphate minerals, environmental pollution and sustainable agriculture. *Elements* 4(2), 105–108. doi:10.2113/GSELE MENTS 4 2 105
- Manning DA (2010) Mineral sources of potassium for plant nutrition. A review. *Agronomy for Sustainable Development* **30**(2), 281–294. doi:10.1051/agro/2009023
- Manning DAC (2015) How will minerals feed the world in 2050? *Proceedings of the Geologists' Association* **126**(1), 14–17.
- Manning DA (2017) Innovation in resourcing geological materials as crop nutrients. Natural Resources Research. doi:10.1007/s11053-017-9347-2
- Manning DAC, Renforth P, Lopez-Capel E, Robertson S, Ghazireh N (2013) Carbonate precipitation in artificial soils produced from basaltic quarry fines and composts: An opportunity for passive carbon sequestration. *International Journal of Greenhouse Gas Control* 17, 309–317. doi:10.1016/j.ijggc.2013.05.012
- Manning DAC, Baptista J, Sanchez Limon M, Brandt K (2017) Testing the ability of plants to access potassium from framework silicate minerals. The Science of the Total Environment 574, 476–481. doi:10.1016/j.scitotenv.2016.09.086
- Marini L (2006) 'Geological sequestration of carbon dioxide: thermodynamics, kinetics, and reaction path modeling.' (Elsevier: The Netherlands)
- Marty NCM, Claret F, Lassin A, Tremosa J, Blanc P, Madé B, Giffaut E, Cochepin B, Tournassat C (2015) A database of dissolution and precipitation rates for clay-rocks minerals. *Applied Geochemistry* 55, 108–118. doi:10.1016/j.apgeochem.2014.10.012
- Mclaughlin MJ (1996) Review: the behaviour and environmental impact of contaminants in fertilizers. *Australian Journal of Soil Research* **34**(8), 3091–3102.
- Mohammed S, Brandt K, Gray N, White M, Manning D (2014) Comparison of silicate minerals as sources of potassium for plant nutrition in sandy soil. *European Journal of Soil Science* **65**(5), 653–662. doi:10.1111/ejss.12172
- Moosdorf N, Renforth P, Hartmann J (2014) Carbon dioxide efficiency of terrestrial enhanced weathering. Environmental Science & Technology 48(9), 4809–4816. doi:10.1021/es4052022
- Mortvedt JJ (1995) Heavy metal contaminants in inorganic and organic fertilizers. *Nutrient Cycling in Agroecosystems* **43**(1), 55–61.
- Nahmani J, Hodson ME, Black S (2007) A review of studies performed to assess metal uptake by earthworms. *Environmental Pollution* **145**(2), 402–424. doi:10.1016/j.envpol.2006.04.009
- Nesbitt HW, Skinner WM (2001) Early development of Al, Ca, and Na compositional gradients in labradorite leached in pH 2 HCl solutions. *Geochimica et Cosmochimica Acta* **65**(5), 715–727. doi:10.1016/S0016-7037(00)00530-5
- Nugent MA, Brantley SL, Pantano CG, Maurice PA (1998) The influence of natural mineral coatings on feldspar weathering. *Nature* 395(6702), 588–591. doi:10.1038/26951
- Oelkers EH, Valsami-Jones E (2008) Phosphate mineral reactivity and global sustainability. *Elements* 4(2), 83–87. doi:10.2113/GSELE MENTS.4.2.83
- Ogunleye PO, Mayaki MC, Amapu IY (2002) Radioactivity and heavy metal composition of Nigerian phosphate rocks: possible environmental implications. *Journal of Environmental Radioactivity* **62**(1), 39–48. doi:10.1016/S0265-931X(01)00149-7
- Palandri JL, Kharaka YK (2004) 'A compilation of rate parameters of watermineral interaction kinetics for application to geochemical modeling.' (Geological Survey: Menlo Park, CA)

Pantelica AI, Salagean MN, Georgescu II, Pincovschi ET (1997) INAA of some phosphates used in fertilizer industries. *Journal of Radioanalytical* and Nuclear Chemistry 216(2), 261–264. doi:10.1007/BF02033788

- Rajan SSS, Fox RL, Saunders WMH, Upsdell M (1991) Influence of pH, time and rate of application on phosphate rock dissolution and availability to pastures. *Nutrient Cycling in Agroecosystems* 28(1), 85–93.
- Ramezanian A, Dahlin AS, Campbell CD, Hillier S, Mannerstedt-Fogelfors B, Öborn I (2013) Addition of a volcanic rockdust to soils has no observable effects on plant yield and nutrient status or on soil microbial activity. *Plant and Soil* 367(1–2), 419–436. doi:10.1007/s11104-012-1474-2
- Ramos CG, Querol X, Oliveira MLS, Pires K, Kautzmann RM, Oliveira LFS (2015) A preliminary evaluation of volcanic rock powder for application in agriculture as soil a remineralizer. *The Science of the Total Environment* 512–513, 371–380. doi:10.1016/j.scitotenv.2014. 12.070
- Renforth P (2012) The potential of enhanced weathering in the UK. International Journal of Greenhouse Gas Control 10(10), 229–243. doi:10.1016/j.ijggc.2012.06.011
- Sabiha-Javied , Mehmood T, Chaudhry MM, Tufail M, Irfan N (2009) Heavy metal pollution from phosphate rock used for the production of fertilizer in Pakistan. *Microchemical Journal* 91(1), 94–99. doi:10.1016/j.microc.2008.08.009
- Schnoor JL (1990) Kinetics of chemical weathering: a comparison of laboratory and field weathering rates. In 'Aquatic chemical kinetics'. (Ed. W Stumm) pp. 475–504. (John Wiley & Sons Inc.: New York)
- Barral MT, Hermo BS, García-Rodeja E, Freire NV (2005) Reutilization of granite powder as an amendment and fertilizer for acid soils. *Chemosphere* **61**(7), 993–1002. doi:10.1016/j.chemosphere.2005.03.010
- Sizmur T, Hodson ME (2009) Do earthworms impact metal mobility and availability in soil?—a review. Environmental Pollution 157(7), 1981–1989. doi:10.1016/j.envpol.2009.02.029
- Stamford NP, Lima RA, Lira MA, Santos CRS (2008) Effectiveness of phosphate and potash rocks with Acidithiobacillus on sugarcane yield and their effects on soil chemical attributes. World Journal of Microbiology & Biotechnology 24(10), 2061–2066. doi:10.1007/ s11274-008-9710-x
- Stumm W (1992) 'Chemistry of the solid-water interface: processes at the mineral-water and particle-water interface in natural systems.' (Wiley: Chichester)
- Sverdrup H, Warfvinge P (1995) Estimating field weathering rates using laboratory kinetics. Reviews in Mineralogy and Geochemistry 31(1), 485–541.
- Trolove S, Hedley M, Kirk G, Bolan N, Loganathan P (2003) Progress in selected areas of rhizosphere research on P acquisition. *Soil Research* 41(3), 471–499. doi:10.1071/SR02130

- van Grinsven J, van Riemsdijk W (1992) Evaluation of batch and column techniques to measure weathering rates in soils. *Geoderma* 52(1–2), 41–57. doi:10.1016/0016-7061(92)90074-H
- Van Kauwenbergh SJ, Stewart M, Mikkelsen R (2013) World reserves of phosphate rock: a dynamic and unfolding story. Better Crops with Plant Food 97(3), 18–20.
- Van Straaten P (2002) 'Rocks for crops: agrominerals of sub-Saharan Africa.' (Icraf Nairobi: Kenya)
- Van Straaten P (2006) Farming with rocks and minerals: challenges and opportunities. Anais da Academia Brasileira de Ciencias 78(4), 731–747. doi:10.1590/S0001-37652006000400009
- Velbel MA (1993) Constancy of silicate-mineral weathering-rate ratios between natural and experimental weathering: implications for hydrologic control of differences in absolute rates. *Chemical Geology* **105**(1–3), 89–99. doi:10.1016/0009-2541(93)90120-8
- von Wilpert K, Lukes M (2003) Ecochemical effects of phonolite rock powder, dolomite and potassium sulfate in a spruce stand on an acidified glacial loam. *Nutrient Cycling in Agroecosystems* 65(2), 115–127. doi:10.1023/A:1022103325310
- White AF, Brantley SL (2003) The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? *Chemical Geology* **202**(3–4), 479–506. doi:10.1016/j.chemgeo. 2003.03.001
- Zhu C (2005) In situ feldspar dissolution rates in an aquifer. Geochimica et Cosmochimica Acta 69(6), 1435–1453. doi:10.1016/j.gca.2004. 09.005
- Zhu C, Blum AE, Veblen DR (2004a) Feldspar dissolution rates and clay precipitation in the Navajo aquifer at Black Mesa, Arizona, USA. In 'Water-rock interaction'. (Eds RB Wanty, RRI Seal) pp. 895–899. (A.A. Balkema: Saratoga Springs, New York)
- Zhu C, Blum AE, Veblen DRD (2004b) A new hypothesis for the slow feldspar dissolution in groundwater aquifers. Geochimica et Cosmochimica Acta 68, A148.
- Zhu C, Veblen DR, Blum AE, Chipera SJ (2006) Naturally weathered feldspar surfaces in the Navajo Sandstone aquifer, Black Mesa, Arizona: Electron microscopic characterization. *Geochimica et Cosmochimica Acta* 70(18), 4600–4616. doi:10.1016/j.gca.2006.07.013
- Zhu C, Lu P, Zheng Z, Ganor J (2010) Coupled alkali feldspar dissolution and secondary mineral precipitation in batch systems: 4. Numerical modeling of kinetic reaction paths. *Geochimica et Cosmochimica Acta* 74(14), 3963–3983. doi:10.1016/j.gca.2010.04.012
- Zhu C, Liu Z, Zhang Y, Wang C, Scheafer A, Lu P, Zhang G, Georg RB, Yuan HL, Rimstidt JD (2016) Measuring silicate mineral dissolution rates using Si isotope doping. *Chemical Geology* 445, 146–163. doi:10.1016/j.chemgeo.2016.02.027