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Identifying the origin of rock phosphates and phosphorus fertilizers through high-precision measurement of the strontium isotopes ^{87}Sr and ^{86}Sr

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Abstract

This work presents a precise and accurate determination of $R(^{87}\text{Sr}/^{86}\text{Sr})$ by Thermal Ionization Mass Spectrometry (TIMS) to identify the origin of rock phosphates used for manufacturing of phosphorus (P) fertilizers. The Sr isotope ratios allowed to classify rock phosphate samples into four different groups: the first group includes igneous rock phosphates from Russia (Kola), the second group sedimentary rock phosphate samples from Algeria, Israel, Morocco, Tunisia and Syria, the third group sedimentary rock phosphates from the USA, while rock phosphate samples from Senegal and Togo are located in the last group. The $R(^{87}\text{Sr}/^{86}\text{Sr})$ isotope ratios in P fertilizers reflect the Sr isotopic composition of rock phosphates from which they were produced. Therefore Sr isotope ratios are suggested as a suitable indicator to track the origin of rock phosphates and P fertilizers.

Keywords: fingerprint method, geographical origin, isotope ratios, phosphorus, fertilizers, radiogenic isotopes, rock phosphates, strontium

Zusammenfassung

Identifizierung der Herkunft von Rohphosphaten und Phosphor-Düngern durch hochgenaue Bestimmung des Verhältnisses der Strontium Isotope ^{87}Sr und ^{86}Sr

Der Beitrag beschreibt die hochgenaue Bestimmung der Strontium Sr-Isotope ^{87}Sr und ^{86}Sr mit Hilfe der Thermischen Ionisations-Massen-Spektrometrie (TIMS) zur Kennzeichnung und Identifizierung der Herkünfte von Rohphosphaten für die Herstellung von P-Düngern anhand des Verhältnisses $R(^{87}\text{Sr}/^{86}\text{Sr})$. Mit Hilfe des Verhältnisses der Sr-Isotope konnten vier Gruppen identifiziert werden: 1. magmatische Rohphosphate aus Russland (Kola), 2. sedimentäre Rohphosphate aus Algerien, Israel, Marokko, Syrien und Tunesien, 3. sedimentäre Rohphosphate aus den USA und 4. Rohphosphate aus Senegal und Togo. Das $R(^{87}\text{Sr}/^{86}\text{Sr})$-Verhältnis in P-Düngern spiegelte das Isotopenverhältnis ihrer Ausgangsstoffe wider und erscheint daher gut zur Identifizierung von Rohstoffherkünften geeignet.

Schlüsselworte: Düngemittel, geographische Herkunft, Isotopenverhältnis, Phosphor, Rohphosphate, radiogene Isotope, Strontium

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1 Introduction

Fertilization with phosphorus (P) is essential in agricultural production. The main sources for phosphate fertilizers are rock phosphates (Van Kauwenbergh, 1997). All rock phosphates contain hazardous elements including heavy metals, e.g. Cd, Cr, Hg, Pb etc., and radioactive elements, e.g. U, Th and Ra that are considered to be toxic to human and animal health (Mortvedt and Sikora, 1992; Kpomblekou and Tabatabai, 1994). Rock phosphates vary considerably in their content of heavy metals and radionuclides depending on the geographical area from which they were mined (Mortvedt *et al.*, 1995; Schnug *et al.*, 1996; Mortvedt, 1996).

Since the amount of heavy metals and radionuclides in P fertilizers is primarily due to impurities in the rock phosphate used for fertilizer manufacturing (Kratz and Schnug, 2005; McLaughlin *et al.*, 1996; Raven *et al.*, 1997), it is preferable to select rock phosphates which are low in heavy metal contents in order to decrease the transfer of these metals into the human food chain. The possibility of fingerprinting rock phosphate samples using their chemical composition might be helpful to identify the origins of rock phosphate samples. However, in order to successfully obtain a fingerprint by elemental pattern, several requests should be considered, e.g. determination of as many elements as possible, investigation of a large number of samples as background, standardized sampling procedures and accurate analytical methods (Djingova *et al.*, 2004). While fingerprinting has been used on environmental materials (rocks, soil, sediments and plants) (Djingova *et al.*, 2004), it is not useful to indicate the origin of P fertilizers because the amounts of heavy metals and radionuclides that are fractionated to P fertilizers vary significantly depending on the manufacturing processes (IAEA, 2003; Rutherford *et al.*, 1993; El-Mrabet *et al.*, 2003). Therefore, elemental composition of a rock phosphate and P fertilizers made of that particular rock may differ considerably.

A possible solution to identify the origin of rock phosphates and P fertilizers is the use of isotope ratios. Since P is a monoisotope (with only 1 stable isotope), it cannot be used as indicator to the P sources (Kendall, 2004). Strontium (Sr) isotopes were selected in this study because Sr isotope ratios in rocks and minerals are known to vary depending on geological age and geographical location (Marisa *et al.*, 2004; Barbaste *et al.*, 2002). Since rock phosphates are mined from different geographical origins, it should be possible to identify their sources by their Sr isotopic composition. Strontium has 32 isotopes, of which only ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr are stable isotopes; they have naturally proportions of 0.56: 9.87: 7.00: 82.58 (Moore *et al.*, 1982; Korea Atomic Energy Research Institute, 2000). Three of them (^{84}Sr, ^{86}Sr and ^{88}Sr) are non-radiogenic and their amounts remain constant over the time. The fourth (^{87}Sr) is radiogenic: ^{87}Rb (rubidium) decays to ^{87}Sr with a half life of $4.7 * 10^{10}$ years, therefore, the amount of ^{87}Sr in a mineral or rock containing Rb increases continuously with time t. Thus, the ^{87}Sr/^{86}Sr ratio depends on the initial *Rb/Sr* ratio, the age of the rock and the Sr isotope ratio at the time of rock formation $(^{87}\mathrm{Sr}/86\mathrm{S})_0$ (Griss, 1999; Koch, 1995; Dicken, 1995; Barbaste, 2002). Recently, isotope ratio measurements have been applied in different studies, for example to identify the geographical origin of agricultural products (heroin, cocaine, alcohol, wine, meat, bio-eggs), to determine the origin of cement and ivory (Boner, 2004, Barbaste, 2002; Guillou, no year; Graham *et al.*, 2000; Koch *et al.*, 1995; James *et al.*, 2000, Boner, 2003; Augenstein, 2004), to study animal origins and movements, e.g. African elephants, bats, birds, migratory fish etc. (Hobson, 1999), and to study human remains, human residential change or human migration through history (Price *et al.*, 2002; Bentley *et al.*, 2003 ; Knudson *et al.*, 2004; Schutkowski *et al.*, 2001). In marine carbonate rocks, the natural variation in the Sr isotope ratio reflects the isotopic composition of seawater from which they were precipitated (Ehrlich *et al.*, 2001) and the chemical environment of their formation (Norbert, 1992). The variation of Sr isotope ratios in seawater over time, especially the rapid and steady increase in ^{87}Sr during the Late Sedimentary (3.5 Byr) (Hess, 1986; Veizer, 1989), provides information about the geological history of sedimentary rock phosphates. Therefore, it is expected that Sr isotope ratios will also yield information about the origin of rock phosphates. However until now, this method has never been applied to provenance studies on rock phosphates and P fertilizers.

In this study, elemental patterns of rock phosphates and P fertilizers were determined by means of key elements such as Sr, U and Cd, and high precision measurement of $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ in different samples was carried out in order to identify the origin of rock phosphates. In addition, it was investigated if the Sr isotopic composition in P fertilizers reflects the origin of the rock phosphates from which they are produced.

2 Materials and methods

2.1 Description of samples

A collection of 46 samples of eleven different origins (Table 1), including three igneous rock phosphate samples from Russia (deposit Kola), one biogenic rock phosphate sample from Curacao, thirty one sedimentary rock phosphate samples of different origins, two phosphogypsum samples and nine P fertilizers was analyzed for their content of P, U, Cd, Sr and their Sr isotope ratio.

Table 1:

Description of rock phosphates (RP) and P fertilizers used in this study

Origin	Type	Number of samples (*n*)
Russia	Igneous RP	3
Morocco	Sedimentary RP	7
Senegal	Sedimentary RP	3
Tunisia	Sedimentary RP	2
Algeria	Sedimentary RP	1
Israel	Sedimentary RP	2
USA/Africa	Sedimentary RP	1
USA	Sedimentary RP	9
Togo	Sedimentary RP	5
Curacao	Biogenic RP	1
Syria	Sedimentary RP	1
Algeria	P fertilizer	1
Israel	P fertilizer	1
USA	P fertilizer	1
Morocco	P fertilizer	2
Kola	P fertilizer	3
Syria	P fertilizer	1
Morocco	Phosphogypsum	1
USA	Phosphogypsum	1
Total n		46

2.2 Analytical methods

2.2.1 Determination of the Sr and P contents

Samples were digested using aqua regia according to DIN EN 13346 (DIN, 2000). All samples were analyzed for their contents of U, Cd and Sr by ICP-QMS (VG Elemental PlasmaQuad 3), P contents in the samples were determined using ICP-OES (Spectro Flame, Spectro Analytical Instruments GmbH, Germany).

2.2.2 High precision measurements of Sr isotope ratios by TIMS

Sr isotope ratios were measured using Thermal Ionization Mass Spectrometry (TIMS). This analytical tool was selected because of its high precision and high sensitivity isotope ratio measurements (Barshick *et al.*, 2000). For TIMS it is necessary to isolate the element of interest, because the sample matrix has a strong influence on evaporation and ionization. Rb must be separated from Sr to avoid ^{87}Rb and ^{87}Sr isobaric interference. In this study, the separation of Sr was performed on a cation exchange column (Dowex W50 - x8 resin) with HCl as eluent (Figure 1).

2.2.2.1 Chemical separation of strontium

25 ml of the extraction solutions (aqua regia digests) were evaporated to dryness in crucibles on a sand bath adjusted to 170 ºC. After that, 4 ml distilled water were added to each sample and evaporated. This step was repeated two or three times until all samples had a medium pH of 7 (neutral). The samples were dissolved in 25 ml distilled water by means of stirring with a Teflon rod and then filtered.

For the separation of Sr, the samples were loaded onto a cation exchange column (Dowex W50 - X8 resin) and subsequently washed into the resin bed with 100 ml water in 5 steps (20 ml each time). For the elution, 214 ml of 2 M HCl and 116 ml of 5M HCl were used and fractions of 4 mL were collected (Figure 1). Each of the obtained fractions was analyzed by ICP-OES (Spectro Sciros CCD, Spectro Analytical Instruments GmbH, Germany) to determine the fraction containing the main part of the Sr. The elements were eluted from the cation exchange column in the following order: Fe, Na, Mg, K, Rb, Ca, Sr, Ba and rare earth elements (Crock *et al.*, 1984). With this method, it is possible to collect about 68 % of Sr while removing about 99.72 % of the Ca matrix (Figure 2).

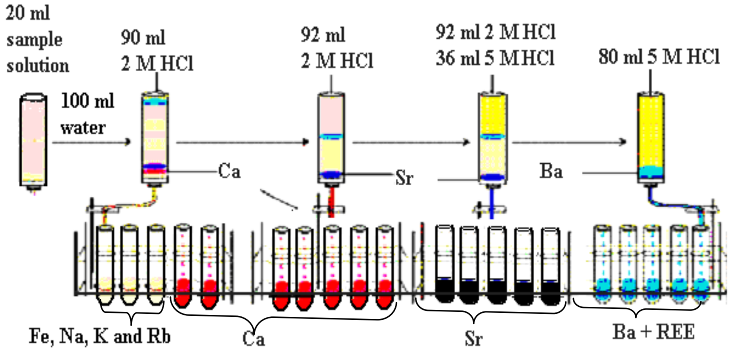

Figure 1:

Chemical separation of Sr and Ca with a cation exchange column (Dowex W50-x8 resin)

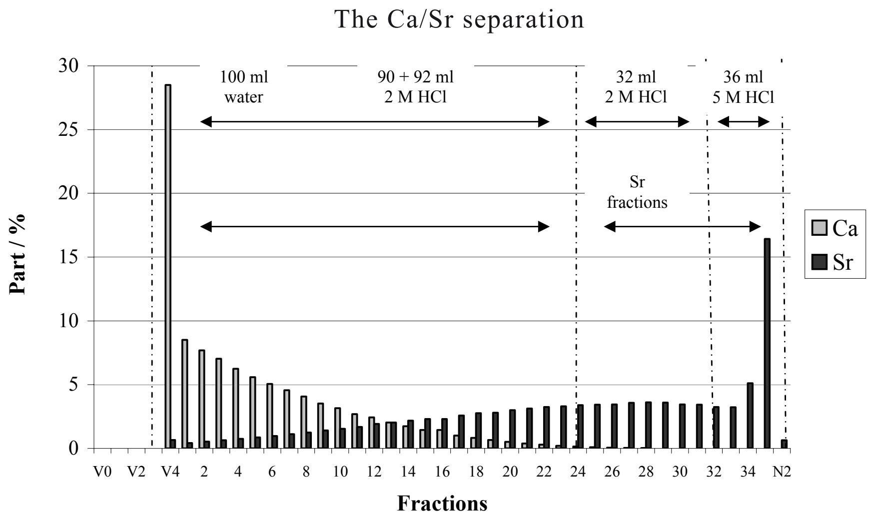

Figure 2:

Ca and Sr content in different fractions collected from cation exchange resin Dowex W50 x 8

2.2.2.2 Measurements of Sr isotope ratios

After Sr was isolated from its matrix, the determination of Sr isotope ratios was performed by double filament technique on a multicollector Thermal Ionization Mass Spectrometer (Finnigan TRITON, Thermo Electron GmbH, Germany). The isolated Sr fraction was evaporated to dryness at 70 ºC. Then the residues were dissolved in 200 µL or 1 mL (depending on the Sr amount) of 2.5 % HNO_3. The sample solution was placed drop wise on the rhenium evaporation filament and evaporated applying a current of 0.6 A. When about 1 µg of Sr was deposited, the current was increased to 1.5 A for 60 s to dry the sample completely and to fix it on the filament. Measurements were performed using a current of 2900 - 3100 mA (about 1480 °C) for the ionization filament and a current of about 700 mA for the evaporation filament. Parameters for data acquisition were set following the application note for high precision strontium and neodymium isotope analyses supplied by Thermo Electron (Tuttas, no year). Rubidium interferences were determined simultaneously by monitoring ^{85}Rb, but a correction was only necessary in a few cases. Since the ratio $R(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})$ is assumed to be constant for all terrestrial samples, it was possible to perform an internal fraction correction using $R(^{86}\mathrm{Sr}/^{88}\mathrm{Sr}) = 0.1194$ and exponential law. For each sample at least two independent measurements were performed and it was tested whether these measurements agreed within their measurements uncertainties (calculated according to the ‘guide to the expression of uncertainty in measurement’, GUM (ISO, 1995)). In cases of discrepancy further replicates were measured and an additional uncertainty component was added to cover unknown contributions introduced by different ionization characteristics of the individual filaments. This way, standard measurement uncertainties of about $u = 10^{-5}$ (corresponding to a relative uncertainty of $1.4 * 10^{-5}$) were obtained. Only a few samples showed larger measurement uncertainties, up to $u = 6 * 10^{-5}$. Applying a coverage factor $k = 2$ results in combined uncertainties $U = k * u$ of about $2 * 10^{-5}$. It is thus in most cases possible to distinguish samples with isotope ratios $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ that differ by more than $4 * 10^{-5}$. However, to make the results comparable to results obtained in other laboratories, it is common practice to calibrate measurements via the reference material NIST SRM 987. Such a calibration step introduces additional uncertainty components covering the measurement uncertainty for SRM 987 and the uncertainty of the certified reference value (NIST, 2000). The values given in this work are calibrated using SRM 987, with the resulting total combined uncertainties U of $2.7 * 10^{-4}$ ($k = 2$) being mainly determined by the uncertainty of the certified reference value.

2.3 Statistical analysis

Differences in Sr content and Sr isotopic composition of different rock phosphates were determined by analysis of variance (ANOVA). The rock phosphate samples were grouped and classified using cluster analysis based on Sr isotopic composition. Hierarchical cluster analysis, using Average Linkage (Between Groups) was used (Everitt, 1993). The cluster analyses objective is to sort samples into groups, or clusters, so that the degree of association is strong between members of the same cluster and weak between members of different clusters (Everitt, 1993). All statistical analyses were performed by SPSS version 12.0 for Windows.

3 Results and discussion

3.1 Strontium contents in rock phosphates of different origins

Sr contents in rock phosphates of Kola (igneous rock phosphates) ranged from 18.6 to 23 g kg^{-1} and were significantly higher than those in sedimentary rock phosphates, which ranged from 0.35 to 3.74 g kg^{-1} (Table 2).

Table 2:

Ranges of Sr contents measured in this study in comparison to literature values

	Range of Sr content (g kg^{-1})	
	present study	literature values
Algeria	1.88	1.8 - 2.8 ^{b}
Tunisia	1.7 - 1.76	1.7 d - 4.1 ^{b}
Morocco	0.29 - 3	0.7 - 1.4 ^{a}
Syria	1.42	1.9 ^{b}
Togo	0.35 - 1.15	no data
Israel	2.5 - 3.7	0.12 - 2.7 ^{b}
Senegal	0.75 - 1.2	0.59 ^{a}
USA	0.67 - 2.6	0.57 - 1.18 ^{a}
Kola	18.6 - 23	30 ^{b}

^{a}Heiland (1986) and ^{b}Kharikov (2000)

Table 3:

P and Sr contents in rock phosphates of different origins

	n	P content	Sr content	
		(%)	(g (kg RP)$^{-1}$)	(g (kg P)$^{-1}$)
Algeria	1	12.9	1.88 *	14.55 *
Morocco	7	14.8	1.33 ± 0.94 ^{a}	8.93 ± 6.24 ^{a,b}
Senegal	3	16.3	0.99 ± 0.24 ^{a}	6.09 ± 1.42 ^{a,b}
Togo	5	16.2	0.54 ± 0.34 ^{a}	3.44 ± 2.38 ^{a}
Syria	1	10.9	1.42	13.02
Tunisia	2	12.4	1.73 ± 0.04 ^{a,b}	14 ± 0.43 ^{b,c}
Israel	2	14.7	3.12 ± 0.87 ^{b}	21.13 ± 5.28 ^{c}
USA	10	14.7	1.10 ± 0.55 ^{a}	7.57 ± 3.92 ^{a,b}
Curacao	1	14.0	0.83 *	5.95 *
Kola	3	17.2	20.94 ± 2.22 ^{c}	121.4 ± 11.12 ^{d}

^{a,b,c,d} Mean values followed by different letters are significantly different by Duncan's test at 0.05 level

* No statistical analysis is performed because number of samples n < 3

Within the group of sedimentary rock phosphates, only the samples from Israel differed significantly from other samples (mean content 3.12 g kg^{-1}). Between the samples from other sedimentary origins, statistically no difference was found (Table 3). The same statistical pattern can be found when Sr related to the P content of the samples is considered. While the mean Sr content for Kola phosphates was 121 g per kg P, it ranged from 3.44 to 21.1 g Sr for the sedimentary rock phosphates (Table 3). In Table 2, Sr contents of samples studied here are compared to data obtained from Kharikov *et al.* (2000) and Heiland (1986). The results show that the Sr content in rock phosphate samples of one origin may vary considerably, e.g. in rock phosphates from Israel in the present workit ranged from 2.5 to 3.7 g kg^{-1}, while it ranged from 0.12 to 2.7 g kg^{-1} in the study performed by Kharikov *et al.* (2000). In this work the Sr content in rock phosphates of Senegal was found to be between 0.75 and 1.2 g kg^{-1}, while Heiland (1986) found a Sr content of about 0.59 g kg^{-1}. Thus it can be concluded that the Sr content in rock phosphates allows to distinguish between igneous rock phosphates and sedimentary rock phosphates, however, this parameter by itself is not sufficient to further distinguish between sedimentary rock phosphates of different origins.

3.2 Transfer of Sr, Cd and U from rock phosphates to P fertilizers

Most P fertilizers are produced of rock phosphates by the wet acid process. In this method, rock phosphates are treated with H_2SO_4 to produce phosphoric acid and by-product (phosphogypsum):

Table 4:

Sr, Cd and U in rock phosphates and P fertilizers of the same origin

	Sr content [g kg^{-1}]		Cd content (mg kg^{-1})		U content (mg kg^{-1})	
	rock phosphate	P fertilizer	rock phosphate	P fertilizer	rock phosphate	P fertilizer
Algeria	1.88	2.30	25.50	11.1	61.8	59.9
Israel	2.50	1.63	18.90	22.0	129	99.8
USA	1.15	0.65	8.37	6.17	121	66.4
Morocco	0.95	0.54	18.34	6.65	133	64.0
	1.00	0.72	22.90	15.7	129	94.7

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \longrightarrow 6H_3PO_4 + 10CaSO_4\cdot 2H_2O + 2HF$$

In this production process, significant amounts of heavy metals can be transferred from rock phosphates to P fertilizers; the remainders of the heavy metals are mainly present in the phosphogypsum. Most of the U and Cd ends up in fertilizers produced from the crude phosphates. Table 4 shows Sr, Cd and U contents for five sedimentary rock phosphates of different origins and for the P fertilizers made of these rock phosphates. As it can be clearly seen from Table 4, variable amounts of Sr, Cd and U transfer from rock phosphates to P fertilizers. These differences are due to the type of manufacturing process applied for fertilizer production (Mortvedt 1996; Mortvedt *et al.*, 1995). Due to these variations in transfer factor, it is very difficult if not impossible to trace back the origin of P fertilizer solely by its elemental pattern.

3.3 Sr isotope ratios in rock phosphate samples

Sr isotope ratios $R(^{87}Sr/^{86}Sr)$ in rock phosphates, P fertilizers and phosphogypsum are reported in Table 5. The hierarchical cluster analysis revealed that the rock phosphate samples divided into two main groups: igneous rock phosphates of Kola in the first group and sedimentary rock phosphates in the second group (Figure 3). The second group can be divided into two sub groups, with the first sub group including all samples of USA and the second sub group including all samples of Morocco, Israel, Tunisia, Algeria and Syria. Sedimentary rock phosphates of Togo and Senegal were located separately (Figure 3). Thus, based on the Sr isotope ratios four different groups can be distinguished (Figure 4). The first group includes rock phosphates of Kola, the second group rock phosphates of USA, the third rock phosphates of Morocco, Israel, Tunisia, Algeria and Syria, the last group includes rock phosphates of Togo and Senegal. The differences in isotope ratio between these groups were significant by ANOVA test (P < 0.0001). Furthermore, the differences in isotope ratio between these groups (Table 6) are significantly larger than the minimum detectable difference of 4 * 10^{-5} which is limited by the measurement uncertainty (see Material and methods).

Table 5:
$R(^{87}Sr/^{86}Sr)$ in rock phosphates (RP), P fertilizers and phosphogypsum

Origin	$R(^{87}Sr/^{86}Sr)$ in RP	Mean of $R(^{87}Sr/^{86}Sr)$ in RP	$R(^{87}Sr/^{86}Sr)$ in P fertilizers	$R(^{87}Sr/^{86}Sr)$ in phosphogypsum
Algeria	0.707 97	0.707 98	0.708 01	
	0.708 01		0.708 03	
	0.708 03			
Morocco	0.708 01	0.707 95 ^{c}	0.708 48	0.708 10
	0.707 81			
	0.708 92			
Florida	0.708 96	0.708 90 ^{b}	0.709 09	0.705 34
	0.708 83			
	0.708 89			
Togo	0.707 42	0.707 42		
Israel	0.707 92	0.707 92	0.707 90	
Tunisia	0.708 01	0.708 01		
Senegal	0.706 86	0.706 86		
Syria	0.707 90	0.707 90	0.707 91	
	0.703 45		0.703 54	
Kola	0.703 39	0.703 42 ^{a}	0.703 38	
	0.703 43		0.703 48	

^{a,b,c} Mean values followed by different letters are significantly different by Duncan's test at 0.05 level.
The combined measurement uncertainty U (using a coverage factor $k = 2$) is 0.00027 for all samples.

Table 6:
Ranges of Sr isotope ratios in rock phosphates (RP), P fertilizers and phosphogypsum

Origin of samples		USA	Algeria, Tunisia, Israel, Syria and Morocco	Togo, Senegal	Kola
$R(^{87}Sr/^{86}Sr)$ in RP	Maximum	0.708 96	0.708 03	0.707 42	0.703 45
	Minimum	0.708 83	0.707 81	0.706 86	0.703 39
$R(^{87}Sr/^{86}Sr)$ in P fertilizers	Maximum	0.709 09	0.708 48		0.703 43
	Minimum		0.707 90		
$R(^{87}Sr/^{86}Sr)$ in phosphogypsum		0.705 34	0.708 01		

The combined measurement uncertainty U (using a coverage factor $k = 2$) is 0.00027 for all samples.

The variation in $R(^{87}Sr/^{86}Sr)$ isotope ratio of rock phosphates of different origins is a result of *Rb/Sr* decay system and therefore depends on the age of ores or samples, the *Rb/Sr* ratio and the $R(^{87}Sr/^{86}Sr)$ ratio at time of formation (Fortunato *et al.*, 2003; Barbaste, 2002; Koch, 1995). Since igneous rock phosphates from Kola contain a high amount of Sr (about 21 g kg^{-1}), the *Rb/Sr* ratio is very low and as a result the $R(^{87}Sr/^{86}Sr)$ isotope ratio is expected to be low, too. The ratio $R(^{87}Sr/^{86}Sr)$ of 0.7034 in the rock phosphate samples from Kola in our study agreed well with a study by Bizzarro *et al.* (2003), who found that igneous minerals (apatites and carbonates) had $R(^{87}Sr/^{86}Sr)$ isotope ratios ranging from 0.7025 to 0.7031. The second reason for this variation is the initial $R(^{87}Sr/^{86}Sr)$ isotope

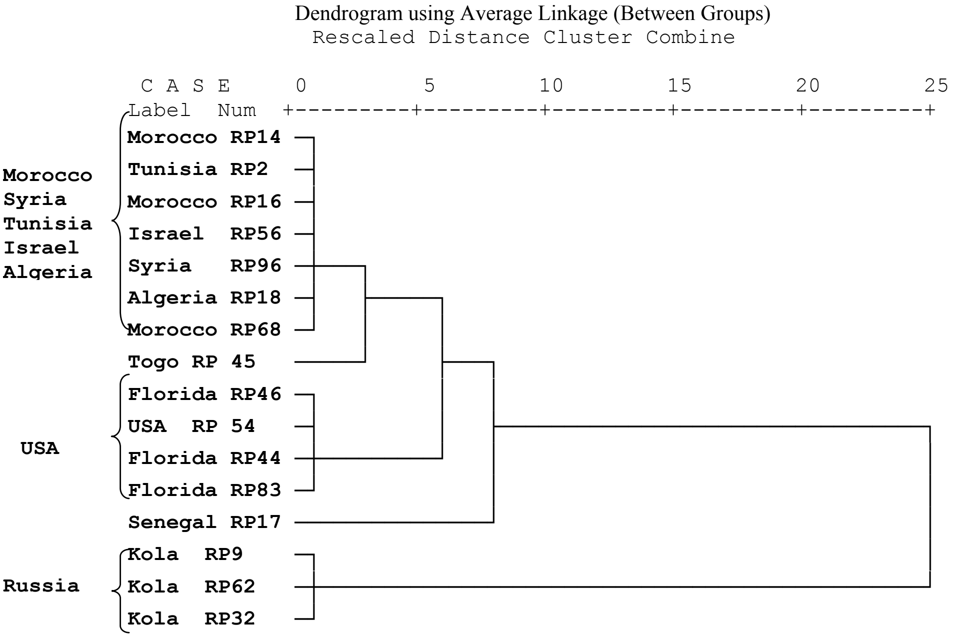

Figure 3:
Hierarchical cluster analysis of rock phosphate samples based on Sr isotope ratio

ratio. The initial $R(^{87}Sr/^{86}Sr)$ isotope ratio in sedimentary rock phosphates at the time of formation is equal to the Sr isotope ratio in seawater from which they were precipitated during this period. As Sr isotopic composition in seawater changed during the geological ages (Veizer, 1989), rock phosphates of different geological age will have different Sr isotope ratios. E.g. in the present work, rock phosphate samples of the USA, which were formed in Moicen-Recent age (25 - 0 myr) (Shields, *et al.*, 2000), have a significantly higher Sr isotope ratio than older samples such as those of Morocco, Tunisia, Syria, Algeria or Israel, which were formed in the Late Cretaceous-Eocene (75 - 35 myr) (Shields *et al.*, 2000). The third reason for $R(^{87}Sr/^{86}Sr)$ isotope ratio variation can be related to mass fractionation which is caused by the different masses of Sr isotopes. Such a variation, however, is very small for heavy isotopes because the relative mass differences between these isotopes (dm/m) is small, while it is largest for the light stable isotopes which have a low atomic weight, such as H, C, N or O (Horn, 2005).

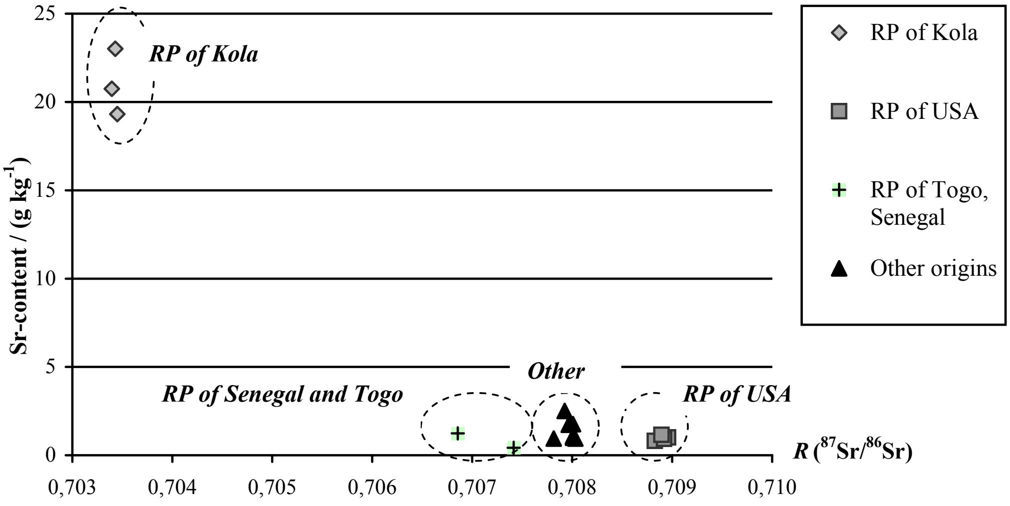

Figure 4:
Grouping of rock phosphates (RP) based on $R(^{87}Sr/^{86}Sr)$ isotope ratio and total Sr content

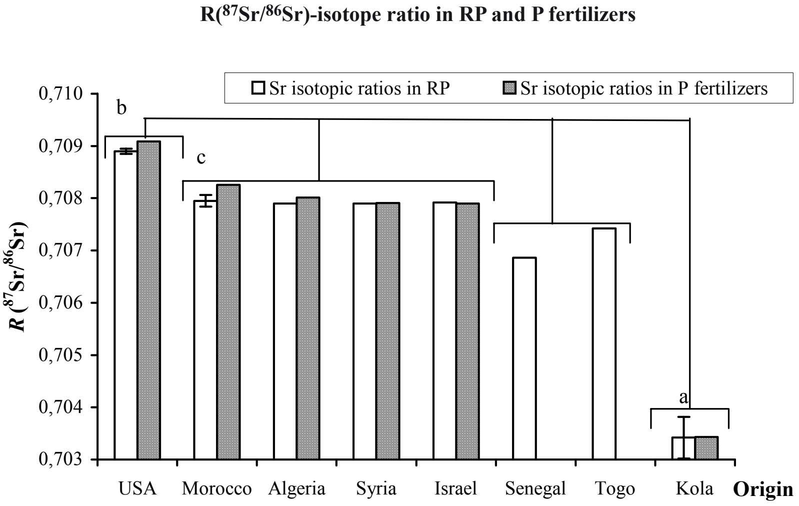

Figure 5:

Sr isotopic ratio in rock phosphates (RP) and P fertilizers sorted by origin. Different letters denote significant differences between Sr isotopic ratio in RP of different origins by Duncan's test at $P < 0.0001$. No test performed for Senegal and Togo because $n < 3$

3.4 Sr isotope ratios in P fertilizers

The natural abundance of ^{87}Sr in P fertilizers varies depending on the rock phosphates from which they were produced. It was observed that R(^{87}Sr/^{86}Sr) is similar in P fertilizers and rock phosphates in the case of Israel and Syria (Figure 5). However, in P fertilizers from other origins, this ratio was slightly higher (up to 0.00048) than in their corresponding rock phosphates (Table 5). Generally, the relationship of Sr isotopic ratio in rock phosphates and in P fertilizers can be described by a linear regression function with a high positive correlation (Figure 6), and significantly different values were present in rock phosphate and P fertilizers of different provenance regions. Sr isotope ratio in P fertilizers thus reflects the origin of the rock phosphate from which they were produced. The linear regression function shows a small increase of ^{87}Sr in P fertilizers that may be due to isotope effects during production processes of P fertilizers: Kinetic isotope effects generally occur due to the fact that lighter isotopes (with low atomic mass) form weaker chemical bonds than the heavier isotopes. Therefore, the lighter isotopes react faster and can, in case of a non-quantitative reaction, be enriched in the product (Dawson *et al.*, 2002; Kendall and Caldwell, 1998; Criss, 1999). If during the manufacturing processes of P fertilizers (Figure 7) ^{86}Sr (light isotope) reacts faster with

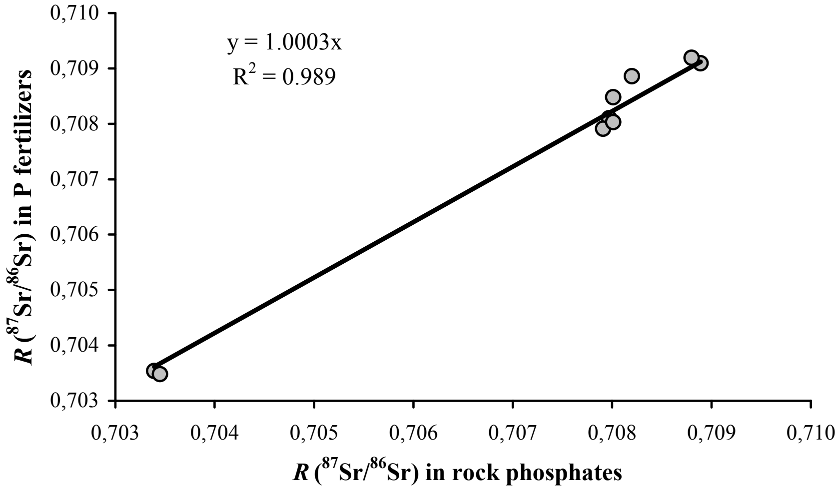

Figure 6:

Relationship between Sr isotope ratio in rock phosphates and P fertilizers of the same origin

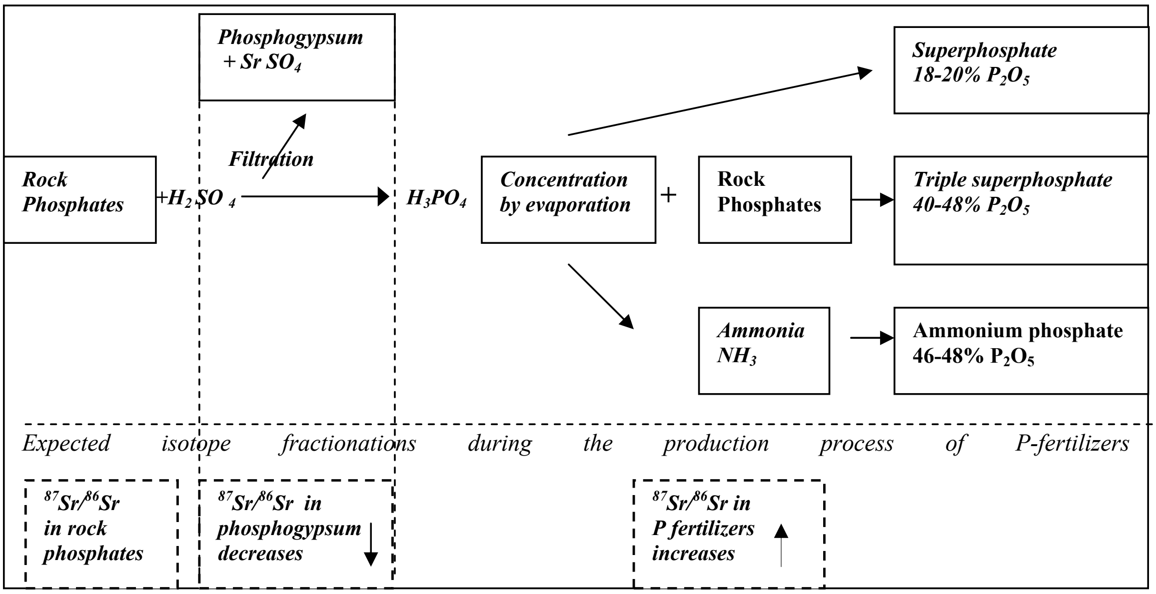

Figure 7:

Flow chart for phosphate fertilizer production by sulphuric acid attack (modified after Kratz and Schnug, 2005) and the expected change of Sr isotope ratios during production processes

sulfuric acid than ^{87}Sr (heavy isotope), as a result, $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ would be slightly increased in P fertilizers, while the ratio of the Sr remaining in the phosphogypsum would be decreased. Sr isotope ratio in P fertilizers supports this theory, the data in Table 5 shows that $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ isotope ratio is higher or equal to their corresponding rock phosphate samples. In addition, the $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ isotope ratio in phosphogypsum from USA is lower than the one in the corresponding rock phosphate. However, this is not true for the Moroccan samples analyzed in this study. Unexpectedly, in this case the $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ in the Moroccan P fertilizer and phosphogypsum was higher than in the rock phosphate samples from that country. Possibly the Moroccan P fertilizers and phosphogypsum were produced from rock phosphates which came from another deposit than the rock phosphates analyzed in this study. Another explanation may be that the chemical substances (such as sulphuric acid) used to produce these samples were contaminated with Sr with high $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ isotope ratio.

4 Conclusions

In this work, elemental pattern (based on the key elements Sr, U and Cd) as well as strontium isotope ratios $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ were investigated as a means to characterize the origin of rock phosphates and P fertilizers of different origins.

The total Sr content was significantly higher in igneous rock phosphates of Kola than in sedimentary rock phosphates; therefore, it can be used to distinguish between each other. However, Sr contents cannot be used to further differentiate within the group of sedimentary rock phosphates. Moreover, the amounts of Sr and other heavy metals (e.g. Cd and U) that transfer from rock phosphate to P fertilizers vary considerably depending on the production process, so heavy metal patterns are not suitable to identify the origin of P fertilizers.

Significant differences of Sr isotope ratios as analyzed by TIMS seem to be suitable to classify rock phosphates from different sources into four different groups: 1: Igneous RP of Russia (Kola), 2: RP of Morocco, Israel, Tunisia, Algeria and Syria, 3: RP of USA, 4: RP of Senegal and Togo.

The determination of Sr isotope ratios in different rock phosphates and P fertilizer samples in this study provides information about the geographic origin of rock phosphates and P containing fertilizers. The present data shows that the most important difference between Sr isotope ratios and total Sr content is the fact that the latter are changed by application of chemical processes, whereas changes of Sr isotope ratios during P fertilizers production processes are usually negligible. As a result, the Sr isotope ratio fingerprint method allows to obtain information about the origin of samples even after application of various separation or purification procedures. Therefore, the measurement of Sr isotope ratios represents a valuable tool to identify the origin of rock phosphates and P fertilizers. However, high precision measurement of Sr isotope ratio requires not only a high quality chemical separation of Sr, and thus a long time for sample preparation (time consuming), but also, expensive mass spectrometers (TIMS or MC-ICP-MS), which are not available in most agricultural institutes.

Since samples within one group, e.g. Morocco, Tunisia, Algeria show a very similar Sr isotopic pattern, they cannot be distinguished by the method described here. Future research should therefore investigate whether the isotopic pattern of other elements (especially the ratio of radiogenic to non-radiogenic isotope such as ^{234}U/^{238}U, ^{143}Nd/^{144}Nd, ^{208}Pb/^{204}Pb etc.) could help to further classify these samples.

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