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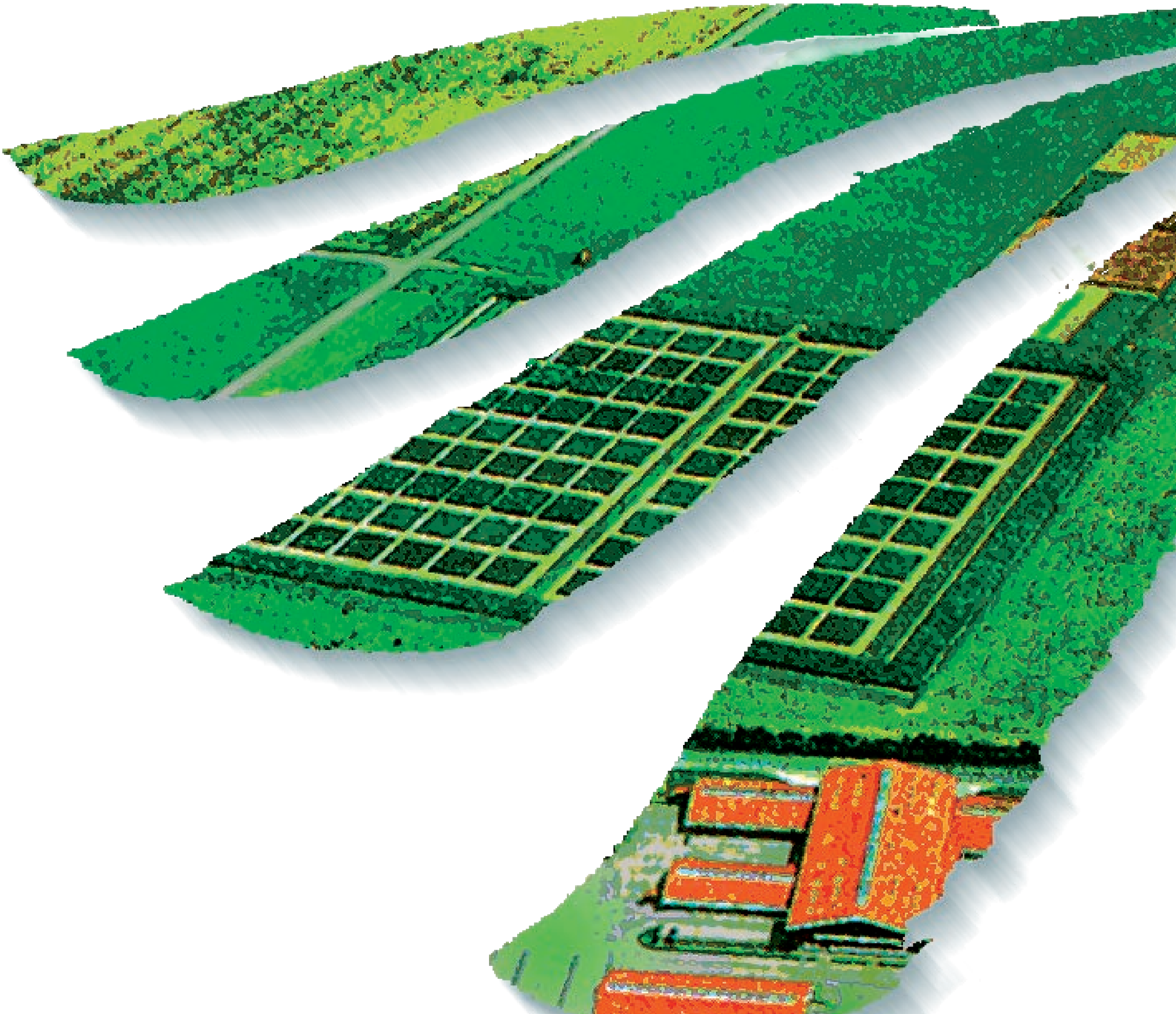
Identifying the Origin of Rock Phosphates and Phosphorous Fertilisers Using Isotope Ratio Techniques and Heavy Metal Patterns

Mamdoh Sattouf



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LIST OF SYMBOLS, ACRONYMS AND ABBREVIATIONS

Ac	actinium
As	arsenic
ANOVA	analysis of variance
ATSDR	agency for toxic substances and disease registry
α	alpha particle
B	boron
Ba	barium
β	beta particle
Be	beryllium
Bi	bismuth
Bq	becquerel (A unit of radioactivity)
C	carbon
Ca	calcium
Ci	Curie (A unit of radioactivity)
Cd	cadmium
Co	cobalt
Cr	chromium
Cu	copper
D	deuterium (^{2}H)
DA	discriminant analysis
dm/m	the relative mass difference between two isotopes = (mass of heavy isotope-light isotope)/light isotope
DU	depleted uranium
Fe	iron
HCA	hierarchical cluster analysis
IAEA	the international atomic energy agency
ICP-MS:	inductively coupled plasma mass spectrometry
ICP-OES:	inductively coupled plasma optical emission spectrometry
K	potassium
MC-ICP-MS:	multicollector thermal ionisation mass spectrometer
M	mass number
Mn	manganese
Mo	molybdenum
N	nitrogen
Ni	nickel
NIST	national institute of standard and technology, USA
NIST SRM 987:	Certified Sr standard obtained from the national institute of standards and technology (NIST)
NOR	naturally occurring radionuclides
Np	neptunium
O	oxygen
P	phosphorous

Pa	Protactinium
Pb	lead
PCA	principal components analysis
Po	polonium
Pu	plutonium
Ra	radium
R	isotope ratio
Rb	rubidium
Rn	radon
RP	rock phosphates
Sb	antimony
Se	selenium
Sr	strontium
$T_{1/2}$	half-life of radioactive nuclide
Th	thorium
Ti	titanium
TIMS	Thermal Ionisation Mass Spectrometry
Tl	thallium
U	uranium
γ	gamma ray
λ	decay constant
Z	atomic number
Zn	zinc

1 Introduction

Fertilisation with Phosphorus (P) is essential in agricultural production. The main sources for phosphates fertilisers (P-fertilisers) are rock phosphates (Van Kauwenbergh, 1997). All rock phosphates contain hazardous elements including heavy metals, e.g., Cd, Cr, Pb etc., and radioactive elements, e.g., U, Th and their daughters, which are considered to be toxic to human and animal health (Mortvedt and Sikora, 1992; Kpomblekou and Tabatabai, 1994). Rock phosphates vary considerably in content of heavy metals and radionuclides depending on the geographical area from which they were mined (Mortvedt and Beaton, 1995; Schnug *et al.*, 1996; Mortvedt 1996; Schnug *et al.*, 1987; Makweba and Holm, 1993). In general, sedimentary rock phosphates contain much higher concentrations of potentially hazardous elements (Cd, Cr, Se, and U) than igneous rock phosphates (Kratz and Schnug, 2006; Kratz and Schnug, 2005; Tufail et al. 2006; Van Kauwenberg, 1997). Compared to shale, the averages of U and Cd concentrations in sedimentary rock phosphate are enriched by a factor of 32 for U and 60 for Cd over an average of shale (Van Kauwenbergh, 1997). Varying amounts of these toxic and radioactive elements are transferred to P-fertilisers during the production process; therefore, P-fertilisers and phosphogypsum also contain different amounts of these toxic elements (Kratz and Schnug, 2005; Mortvedt and Beaton, 1995).

These heavy metals and radionuclides will be loaded onto a soil with applied fertilisers and many of these contaminants can accumulate in soil, so long-continued application of rock phosphate-based fertilisers can increase these contaminants in soil over time (Brigden *et al*., 2002). Researchers in Australia and the UK reported that long-term applications of P-fertilisers increased concentration of Cd in surface soil (Huang *et al*. 2004). The addition of radionuclides to soil by an average P-fertilisation of 100 kg ha^{-1} raises U activity by 34%, Th activity by 6% and ^{40}K activity by 1.5% in 100 years (Schnug *et al*., 1996). Some of these heavy metals and radionuclides may be leached out of the fertilised zone and into ground water that drains from these fields (Hamamo *et al*. 1995) or transferred via the food chain to humans (Abdel-Haleem et al., 2001). At high levels, heavy metals are toxic to animals and humans.

To minimize the risks associated with the transfer of heavy metals from P-fertilisers into the environment, it is preferable that rock phosphates of such origins are used which is low in heavy metal contents. Rock phosphates from different origin contain a distinctive heavy metal assemblage which is characteristic of the formation processes or indicative of subsequent modification by diagenesis or weathering (Weissberg, 1982). Thus, it should be possible to identify the origin of a particular rock phosphate by its heavy metal pattern.

The possibility of fingerprinting rock phosphate samples using their chemical composition might be helpful to identify the origin of rock phosphate samples. However, in order to successfully obtain a fingerprint by elemental pattern, several conditions should be fulfilled, e.g., determination of as many elements as possible, investigation of a large number of samples as background, standardized sampling procedures, accurate analytical methods (Djingova *et al.,* 2004). This method has been used on environmental materials such as rocks, soil, sediments and plants (Djingova *et al.,* 2004; Market, 1992). However, it is not useful to indicate the origin of P-fertilisers because the amounts of heavy metals and radionuclides that are fractionated to P-fertilisers vary significantly depending on the manufacturing processes (IAEA, 2003; Rutherford *et al.*, 1994; El-Mrabet *et al.,* 2003). Therefore, elemental composition of a rock phosphate and P-fertilisers made of that particular rock may differ considerably. Furthermore, it is difficult, if not impossible, to use heavy metal patterns to trace back the origin of rock phosphates used in the production of compound fertilisers. The reason for this is the fact that the heavy metals in compound fertilisers may have many sources such as rock phosphates, P-mineral fertilisers, potassium salts, nitrogen compound, sulphur, organic manure, limestone, etc. So it is complex, if not impossible, to determine the amount of heavy metals from each source (component).

A possible solution to identify the origin of rock phosphates and P-fertilisers is the use of isotope ratio techniques. Since P is a monoisotope (has only 1 stable isotope), it cannot be used as indicator for the P sources. 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 isotope ratio. Sr has 4 stable isotopes, ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr, they have naturally proportions of 0.56: 9.87: 7.00: 82.58, respectively (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 time. The fourth (^{87}Sr) is radiogenic: ^{87}Rb decays to ^{87}Sr with a half-life $4.7*10^{10}$ years, therefore, the amount of ^{87}Sr in a mineral or rock containing Rb increases continuously with time t. The use of $R(^{87}\text{Sr}/^{86}\text{Sr})$ led to the identification of the origins and sources of an enormous number of materials (Table 1.1).

The natural variation of isotope ratio has been used to control the authenticity of many products such as wine, etc. to identify the geographical origin of agricultural products such as meat, bio-eggs, wine and other alcohols, heroin and cocaine based on the relation between stable isotope ratios and location; to determine the origin of cement, ivory (Boner and Forstel, 2004; Barbaste et al., 2002; Graham *et al*., 2000; Koch *et al*., 1995; Augenstein, 2004; Ehleringer et al., 2000; Kelly et al., 2005); to study animal origins and movement, 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).

Table 1.1: Characterisation of the geographical origin of different materials using $R(^{87}\text{Sr}/^{86}\text{Sr})$ and other elements

Material	**Parameter measured**	**Instrumental**	**References**
Butter	^{13}C/^{12}C, ^{15}N/^{14}N, ^{18}O/^{16}O, ^{34}S/^{32}S, ^{87}Sr/^{86}Sr	IRMS, TIMS	Rossmann et al., 2000
Meat of Beef	^{2}H/^{1}H, ^{13}C/^{12}C, ^{15}N/^{14}N, ^{18}O/^{16}O, ^{34}S/^{32}S, ^{87}Sr/^{86}Sr	-	Kelly et al., 2004; Schmidt et al., 2005
Cheese	^{2}H/^{1}H, ^{13}C/^{12}C, ^{15}N/^{14}N, ^{18}O/^{16}O, ^{34}S/^{32}S, ^{87}Sr/^{86}Sr, multi elements	IRMS, TIMS Q-ICP-MS,	Pillonel et al., 2003
Cheese	^{87}Sr/^{86}Sr	MC-ICP-MS, TIMS	Fortunato et al., 2003; Pillonel et al., 2003
Rice	^{11}B/^{10}B, ^{87}Sr/^{86}Sr, Cd concentration	Q-ICP-MS, MC-ICP-MS	Oda et al., 2001
	^{87}Sr/^{86}Sr	MC-ICP-MS	Kawasaki et al., 2002
Wine	^{87}Sr/^{86}Sr, ^{18}O/^{16}O ^{87}Sr/^{86}Sr ^{87}Sr/^{86}Sr	TIMS, IRMS, MC-ICP-MS Q-ICP-MS	Horn et al., 1998 Barbaste et al., 2002 Marisa et al., 2004
Cement	^{87}Sr/^{86}Sr	TIMS	Graham et al., 2000
Elephant ivory	^{87}Sr/^{86}Sr, ^{13}C/^{12}C		Koch et al., 1995
Ancient class	^{87}Sr/^{86}Sr	TIMS	Freestone et al., 2003
Birth place and mobility of human and animals	^{87}Sr/^{86}Sr		Knudson et al., 2004
Geographical origin and migration of wildlife	^{2}H/^{1}H^{13}, C/^{12}C, ^{15}N/^{14}N, ^{34}S/^{32}S, ^{87}Sr/^{86}Sr		Hobson, 1999

In marine carbonate rocks, the natural variation in the $^{87}Sr/^{86}Sr$-isotope ratio reflects the isotopic composition of seawater from which they were precipitated (Ehrlich *et al.*, 2001) and the chemical environment of their formation. The variation of Sr isotope ratios in seawaters over time, especially the rapid and steady increase in ^{87}Sr in the Late Sedimentary (3.5 Byr) (Hess et al., 1986; Veizer, 1989), provides information about the geological history of sedimentary rock phosphate. Therefore, it is expected that Sr isotope ratio 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-fertilisers.

On the other hand, it is known that phosphate ores contain, for geological reasons, considerable amounts of natural radioactivity, mainly U isotopes and daughter isotopes of their decay chain. Several publications have reported that sedimentary rock phosphates are characterised by a high U concentration compared with igneous rock phosphates (Kratz and Schnug, 2006; Garcia-Leon *et al*, 1995). Most of the U present in the rock phosphates passes to the phosphate fertilisers and the remaining amount to the waste product phosphogypsum (Schnug *et al.*, 1996; Hamamo *et al.*, 1995). As a result, the amount of U and other toxic heavy metals in P-fertilisers is primarily due to impurities in the rock phosphates used for fertiliser manufacturing (McLaughlin *et al.*, 1996; Tufail *et al.*, 2006). The annual global production of rock phosphates has been around 140 million tons, which is equivalent to about 40 million tons of P_2O_5 per year for the last decade (Jasinski, 2007; Van Kauwenbergh, 1997). Taking into account an average U-content in sedimentary rock phosphates of 120 mg U kg^{-1} (Van Kauwenbergh, 1997, WISE, 2006), this represents for each year about 16800 t of U, while worldwide U resources associated with rock phosphates deposits are estimated at approximately 9 million t U (IAEA, 2001). At least 70% of U stays in final products (P-mineral fertilisers). Therefore, the main cause of U discharge to agricultural soils is fertilisation with mineral P-fertiliser. Since all U isotopes are radioactive, U loads to cultivated soil with P-fertiliser should be controlled due to both their chemical and radiological hazards. High levels of U have negative effects for human health and ecological systems. Natural U consists of three radioisotopes: ^{234}U, ^{235}U and ^{238}U, with a relative abundance of 0.0055, 0.720, and 99.27 percent, respectively (WHO, 2001). In many instances, the natural abundance has been altered either due to geological processes or due to anthropogenic U enrichment (WHO, 2001; Richter *et al.*, 1999), therefore U isotopic composition data can be used as a fingerprint of natural or anthropogenic sources of U (Goldstein *et al.*, 1997). There are two different natural radioactive decay chains: ^{238}U-

series, ^{235}U-series. The ^{238}U-series has been used in many studies in earth and environmental science, geology, oceanography, hydrology, and science-based archaeology (Calsteren and Thomas, 2006). The ^{238}U-series decay chain contains 14 daughters. The ratio between the radiogenic isotopes ^{234}U to their parent ^{238}U is the most interesting in this study because the relative mass difference between these isotopes (dm/m) is small. Therefore, the isotope effect during chemical processes (such as fertiliser production) is very small (Horn, 2005). As result it is expected that no or only very small changes of isotope ratios of $R(^{234}\mathrm{U}/^{238}\mathrm{U})$ can occur during P-fertilisers production. That means that with the isotopic fingerprint method, information about the origin of samples can be obtained even in P mineral fertilisers.

Previous studies focused on the possibilities of using ^{234}U/^{238}U-isotope ratio for dating purposes. It was reported that $R(^{234}\mathrm{U}/^{238}\mathrm{U})$ varies between recent and old rock phosphates (Calsteren and Thomas, 2006). Since $R(^{234}\mathrm{U}/^{238}\mathrm{U})$ provides information about the geological history of sedimentary rock phosphates, it is expected that U isotope ratio will yield information about the origin of rock phosphates. However, no attempt to identify the source of P-fertiliser and their raw materials based on U isotopic composition has been made until now.

$R(^{238}\mathrm{U}/^{235}\mathrm{U})$, the other isotope ratio of U, can provide information for identifying anthropogenic sources of U (Goldstein et al., 1997). The natural $R(^{238}\mathrm{U}/^{235}\mathrm{U})$ has not been found to deviate from $R(^{238}\mathrm{U}/^{235}\mathrm{U}) = 137.5 \pm 0.5$ (equal $R(^{235}\mathrm{U}/^{238}\mathrm{U}) = 0.72\% \pm 2.6\mathrm{E}{-06}$) in most environmental samples (Fujikawa *et al.*, 2000), therefore, other than $R(^{234}\mathrm{U}/^{238}\mathrm{U})$, this ratio is expected to be constant and independent of the origin of the sample. Any statistically significant difference from this natural ratio must be attributed to anthropogenically altered U. $R(^{235}\mathrm{U}/^{238}\mathrm{U})$ can be used as indicator for both enrichment of ^{235}U in relation to ^{238}U in the process of making fuel for reactors and nuclear weapons and depletion of ^{235}U (depleted U) in the remaining U after removal of the enriched fraction. Therefore, $R(^{235}\mathrm{U}/^{238}\mathrm{U})$ can be used to distinguish natural from anthropogenic U while it is useless as an indicator of origin of different materials such as rock phosphate and P-containing fertilisers.

Isotope ratios, especially for the heavy elements such as U and Sr may be a possible solution to trace back the origin of rock phosphates used in mineral P-fertiliser production. The reason for this is that Sr and U isotope ratios should transfer from rock phosphate to P-fertilisers or other mineral fertilisers without change or only with minute fractionation during the production process of fertilisers due to their high atomic weight (greater than 50), and the relative by small mass differences (dm/m) of the isotopes (Horn et al., 1998).

Chapter 2 contains a literature review on phosphates and their application in agriculture as well as on heavy metal input into the environment. Furthermore, a short introduction into isotopic chemistry and the application of isotope techniques for the identification of materials is given. Based on current knowledge, key questions to be answered by this research work are devised.

In chapter 3, the sample material and the analytical methods for the determination of heavy metals are described. The sample preparation for mass spectrometry involves the chemical separation of Sr from high Ca-samples matrices, chemical separation of U from its matrix using UTEVA® resin. Furthermore, high precision measurements of Sr and U isotope ratios by thermal ionisation mass spectrometer are discussed.

Chapter 4 includes the results of the present work. In this chapter, the ability to discriminate the origin of rock phosphate samples and P-fertilisers through their elemental patterns based on principal component analysis and cluster analysis is investigated. U and Sr isotope ratios are studied as a means to identify the origin of different rock phosphates and P-containing fertilisers. Following the identification of rock phosphates by their isotope ratios, U and Sr isotope ratios in farmyard manure, organo- mineral fertilisers, and compound fertiliser (NP, PK, NPK) are reported.

$R(^{235}\mathrm{U}/^{238}\mathrm{U})$ as indicators to anthropogenic U and the possibility to trace back the origin of P-fertilisers and rock phosphates using $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$-, $^{234}\mathrm{U}/^{238}\mathrm{U}$-isotope ratios, and heavy metal patterns are discussed in chapter 5.

2 Literature review and objectives of this study

2.1 Heavy metals in rock phosphates and P-fertilisers

2.1.1 Types and world production of rock phosphates

Rock Phosphate is a general term that describes naturally occurring mineral assemblages containing a high concentration of phosphate minerals (Zapata and Roy, 2004). Rock phosphates are generally apatite, containing varying percentages of P_2O_5 in a calcium matrix.

There are different types of phosphate resources being mined worldwide:

1 Marine sedimentary phosphate deposits (phosphorite): Sedimentary rock phosphate deposits make up 75% of world’s phosphate resources. Large sedimentary deposits are found in Morocco, USA and China (Van Kauwenbergh, 1997; Zapata and Roy, 2004). Sometimes sedimentary rock phosphate is called phosphorite.

2 Igneous phosphate deposits: Igneous deposits have provided about 10-20% of world production in the last ten years. Most production is in the Russian Federation, Canada, South Africa, Brazil, Finland and Zimbabwe (Van Kauwenbergh, 1997; Zapata and Roy, 2004).

*3 Biogenic deposits***:** These deposits mainly consist of bird and bat guano accumulations called biogenic deposits. They make up 1-2% of world’s phosphate resources (Van Straaten, 2002).

The most common members of the mineral phosphates are those belonging to the apatite family (Table 2.1). The group of apatites has this general formula: [$A_5 (XO_4)_3 (OH, F, Cl)$] with A=Ca and X=P. The apatite structure is shared by a large group of relatively common minerals, A may be Ca, Sr, Pb, Ba, Na, Cd, Mg, Mn, Fe and others. X may be P, PO_4, Si, SO_4, As, CO_3, V, and others (Mathew and Takagi, 2001; Sudarsanan *et al*., 1972).

Table 2.1: Main varieties of apatite and their formulae (Van Kauwenbergh, 1997)

Variety	Formula
Francolite	$Ca_{10-x-y}\ Na_x\ Mg_y\ (PO_4)_{6-Z}\ (CO_3)zF_2F_{0.4z}$ $Ca_{10-a-b}\ Na_b\ Mg_b\ (PO_4)_{6-c}\ (CO_3)cF_2F_{0.185c}$
Hydroxyl-fluor-carbonate apatites	$Ca_{10}\ (PO_4, CO_3)_6\ (OH, F)_2$
Fluorapatite	$Ca_{10}\ (PO_4)_6F_2$
Hydroxyl apatite	$Ca_{10}\ (PO_4)_6, (OH)_2$
Chlorapatite,	$Ca_{10}\ (PO_4)_6Cl_2$

Igneous apatite rocks are found as three primary species, chlorapatite, hydroxylapatite, and fluorapatite. Sedimentary apatites are found as two species, carbonate-fluorapatite (Francolite) and hydroxyl-fluor-carbonate apatites (McClellan *et al.*, 1990; Van Kauwenbergh, 1997). Biogenic rock phosphates are found as hydroxyl apatites and carbonate hydroxyl apatites (Van Straaten, 2002).

These rock phosphates of varying quality are mined throughout the world. The main producing countries (about 69% of total world rock phosphates) are United States, China, Morocco, Western Sahara, and Russia. South Africa, Jordan, Syria, Tunisia, Brazil, Senegal and Togo produce about 23% of total world rock phosphates. About 7.8% of world rock phosphates are produced by other countries (Fig. 2.1, Jasinski, 2007).

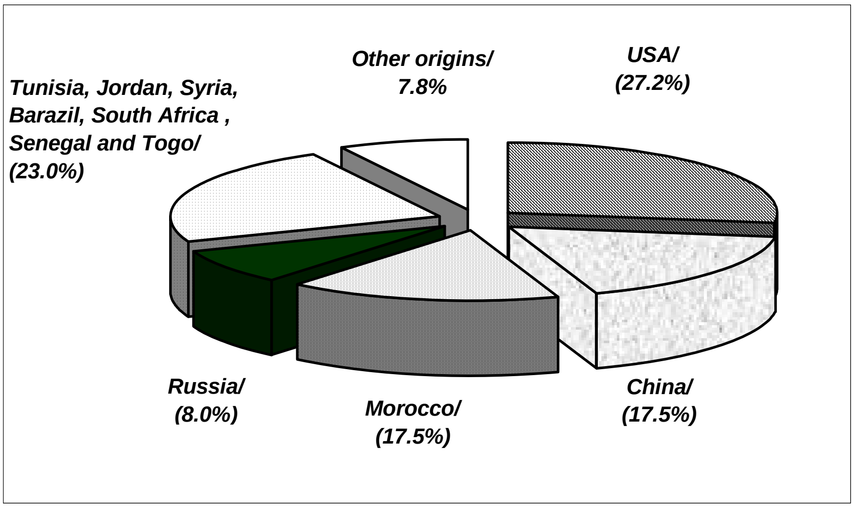

Fig. 2.1: World rock phosphates productions from different origin, ratios calculated based on a six- years average (from 1999 to 2004)

2.1.2 Heavy metals in rock phosphates from different origin

Heavy metals are placed in a group of chemical elements with a density of more than 5 g cm^{-3}, e.g., Cd, Cu, Fe, U, etc. (Kharikov and Smetana, 2000). The semi-metals’ density is less than 5 g cm^{-3} such as As, Sb, etc. (Kratz and Schnug, 2005). Some heavy metals are essential to plant and animal life, called microelements because under low concentrations they are useful and necessary to living organisms. Some of the most common microelements are Cu, Zn, Mo, Mn and Fe. However, at high concentrations they can also be toxic. Other heavy metals are not essential to life and may be detrimental to health when consumed in high quantities. The hazardous elements which are of great concern in agriculture and as far as human health is concerned include As, Cd, Cr, Pb, U, etc. Heavy metals do not break down over time, so increased attention must be placed on ways to minimize or reduce the level of heavy metals applied to agricultural soils, and reduce the toxic heavy metals present in animal and human foodstuffs (Kharikov and Smetana, 2000, Ribera et al., 1996). The term “heavy metal” will be used in this research to refer to the hazardous elements e.g., As, Cd, Pb, U, etc.

All rock phosphates contain hazardous elements including heavy metals, e.g., Cd, Cr, and Pb, and radioactive elements, e.g., U, Th and their daughter isotopes, such as radium, that are considered to be toxic to human and animal health (Kpomblekou and Tabatabai, 1994; Viisimaa et al., 1991). Rock phosphates vary considerably in content of heavy metals and radionuclides depending on the geographical area from which they were mined (Mortvedt and Beaton, 1995). In general, sedimentary rock phosphates contain much higher concentrations of potentially hazardous elements (As, Cd, Cr, Pb, Se and U) than igneous rock phosphates (Table 2.2). Sometimes, As and Pb concentrations may be lower in sedimentary than igneous rock phosphates (Kharikov and Smetana, 2000; Van Kauwenberg, 1997).

Table 2.2: Average phosphorus and heavy metal concentrations in rock phosphate from different origin (Kratz, 2005; Kharikov and Smetana, 2000; Van Kauwenberg, 1997)

Country	**Deposit**	**Type**	**P_2O_5**	**As**	**Cd**	**Cr**	**Pb**	**Hg**	**Ni**	**U**	**Sr**
			[%]	**[mg kg^{-1}]**							**[%]**
Algeria	Djebel Onk	S	28.3	4.50	22.5	174	3.00	190	28.0	25.0	0.18-0.28
Togo	Unknown	S	36.7	10.0	58.4	101	8.33	365	nd	93.5	Nd
Tunisia	Unknown	S	29.3	4.50	39.5	144	4.00	nd	15.0	44.0	0.41
Morocco	Khouribga	S	32.6	13.4	15.1	200	10.3	855	nd	87.7	Nd
	Youssoufia	S	31.2	9.20	29.2	255	14.0	120	nd	97.0	Nd
Syria	Khneifiss	S	31.9	4.00	3.00	140	6.00	28.0	53.5-60.0	75.0	0.19
Senegal	Taiba	S	35.9	17.4	86.7	140	6.00	270	nd	67.0	Nd
Israel	Arad	S	32.4	5.50	14.3	130	2.00	129	61.0-80.0	150	0.19
	Oron	S	33.6	8.00	5.00	107	1.00	128	nd	99.0	Nd
USA	Florida	S	31.9	11.3	9.13	60.0	16.8	199	nd	141	Nd
	North Florida	S	31.2	7.00	6.14	64.7	11.7	nd	nd	80.7	Nd
	Idaho	S	31.7	23.7	92.3	637	12.3	290	nd	107	Nd
	North Florida	S	29.9	11.2	38.2	158	8.33	233	nd	65.3	Nd
Finland	Siilinjarvi	I	39.5	3.00	<2.00	14.0	4.00	42.0	nd	37.0	Nd
Russia	Russian Kola Peninsula	I	35.6	10.0	1.25	nd	33.0	nd	nd	27.0	Nd

S: Sedimentary rock phosphate; I: Igneous phosphate; nd: no data.

The rock phosphates are either applied directly to the soil, especially in organic farming, or manufactured to produce water-soluble phosphorus fertilisers. It is reported that sedimentary rock phosphates are suitable for direct application as fertilisers only under certain conditions (Chien, 1993; Chien and Friesen, 2000; Van Kauwenbergh, 1992; Chien and Menon, 1995; Rajan *et al.*, 1996; Zapata and Roy, 2004). The contamination of rock phosphates with heavy metals does limit the suitability of rock phosphates as a source for agriculture P in organic farming (Schnug et al., 2003). Therefore, the safe management of this farming requires monitoring and measurement of radionuclide and toxic heavy metals in applied rock phosphates.

2.1.3 Transfer of radionuclides and heavy metals from rock phosphates to P-fertilisers during the production process

Rock phosphates are the raw material used in the manufacture of most commercial P-fertilisers. Most of the rock phosphates mined in the world (about 80%) is used for the production of P-fertilisers. The remaining amount is used for making detergents (12%), animal feed supplements (5%) and specialty applications and other users (3%) (Bigu *et al.*, 2000; IFA, 2002). The solubility and availability of P differ widely in rock phosphates depending on their structure. For example, pure fluorapatite is much less soluble than hydroxylapatite or even than carbonate substituted fluorapatites. This very low solubility precludes its direct application as a fertiliser. Therefore, it is classified as unreactive (Rajan *et al.*, 1996; Bolan *et al.*, 1990). Since fluorapatite, the main component of rock phosphate, is very insoluble in its original chemical state, chemical treatment with strong acids (sulphuric, phosphoric or nitric acids) is necessary to produce soluble phosphate products. Most acidulation (95%) is done with sulphuric acid, which leads to the formation of superphosphate, if more sulphuric acid is added to the fertiliser, a mixture of phosphoric acid and phosphogypsum ($CaSO_4$ x H_2O) are formed. Generally, 4–5 tons of phosphogypsum are produced per ton of phosphoric acid (P_2O_5) (IAEA, 2003). Triple super phosphate is obtained by adding phosphoric acid to rock phosphates. If ammonia is added to phosphoric acid, ammonium phosphate fertilisers are formed (Guzman *et al.*, 1995). Varying amounts of heavy metals and radionuclide contaminants in rock phosphates will be transferred into P-fertilisers depending on the manufacturing processes (Schnug, 2005; IAEA, 2003; El-Mrabet *et al.*, 2003). The by-product (phosphogypsum) will also contain a fraction of the heavy metals and radionuclides from the rock phosphates (Mortvedt, 1996; Rutherford *et al.*, 1995) as shown in Fig. 2.2. A close relationship between concentrations of P and Cd in superphosphates and their respective rock phosphates was reported (Mortvedt and Beaton, 1995). In general, about 80% of the ^{226}Ra, 30% of the ^{232}Th and 14% of the ^{238}U is left in the phosphogypsum. U and Th become enriched in the fertiliser to about 150% of their original value.

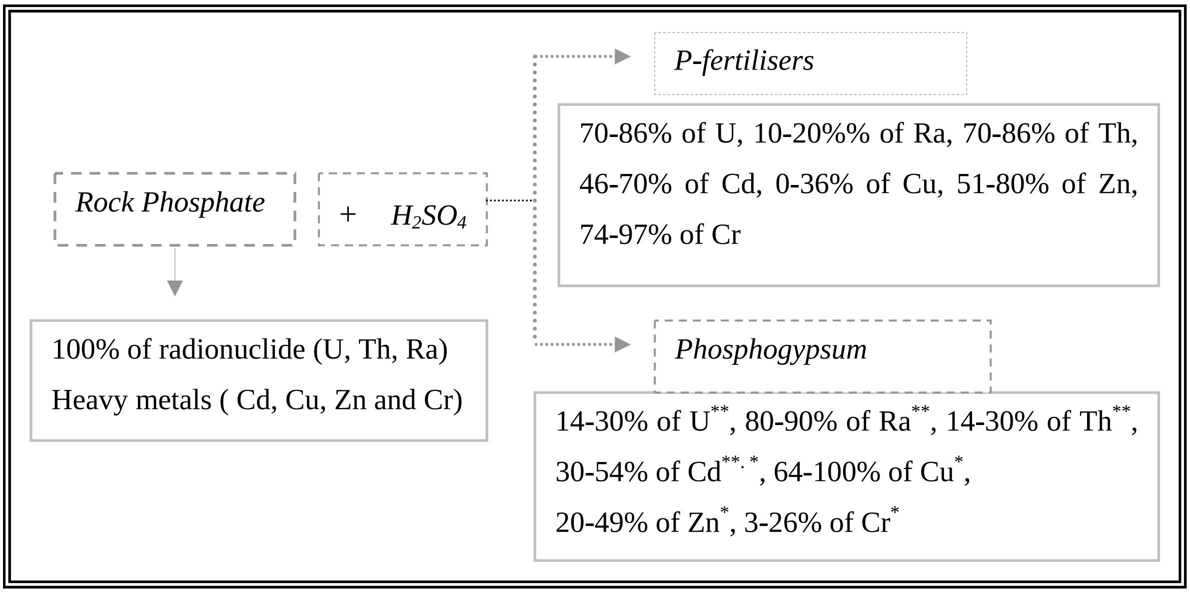

Fig. 2.2: Transfer of most important radionuclides and heavy metals from rock phosphate to P-fertilisers and phosphogypsum during the production process (*Rutherford *et al*., 1994; **IAEA 2003; ***Garcia-Leon *et al*., 1995; El-Mrabet *et al*., 2003)

The amount of heavy metals and radionuclides in P-fertilisers is primarily due to impurities in the rock phosphate used for fertiliser manufacturing (McLaughlin *et al*., 1996; Tufail *et al*. 2006). The concentrations of heavy metal in P-fertilisers is highly variable and depends not only on the heavy metal content of the raw material from different origin (rock phosphate ores), but also on the type of manufacturing process applied for fertiliser production (Mortvedt, 1996). Therefore, the concentrations of heavy metal and radionuclide contaminants in P-fertilisers vary considerably even within same type of mineral P-fertilisers (Table 2.3) depending on the rock phosphate source (Raven and Loeppert, 1997).

Some metals of possible significance are: As, Cr, Pb, Hg, Ni, and V. The concern about the entry of these toxic elements into the human food chain has increased recently. However, these metals are of less concern than Cd, probably because it represents the most harmful heavy metal to human health. For example, most of the retained Cd is found in kidneys, liver and other organ tissues rather than in muscle tissue. Cadmium at toxic levels in the liver and kidneys impairs the function of these organs (Geldmacher et al., 2004).

The main radionuclide contaminants in rock phosphate are U and Th and their daughters (Mortvedt and Beaton, 1995; Ahmed and El-Arabi, 2005). Regarding different types of fertilisers, in general, the trace and heavy metal concentrations decrease in the following order: rock phosphate > P-fertilisers > organic amendments > K-fertilisers > N-fertilisers (Raven and Loeppert, 1997).

Table 2.3: Variability of heavy metal concentrations in P-fertilisers depending on the origin of their rock phosphate source (Raven and Loeppert, 1997)

	As	**Cd**	**Pb**	**Ni**	**Sr**	**U**
	----------------------------------[mg kg^{-1}]------------------------------------					
Monoammonium phosphate	10.9±0.8	<0.3	<0.2	7.4±0.1	314±93	<5.82
	13.7±0.2	4.0±0.0	2.90±0.1	22.2±0.2	nd	nd
Diammoniumphosphate	9.9±0.3	4.6±0.1	3.70±0.4	15.5±0.1	nd	nd
	16.2±0.7	35.5±0.2	2.10±0.2	48.3±0.2	<296	198
Triple super phosphate	16.2±1.0	5.00	11.1±0.6	25.2±0.8	736±29	232
	15.3±0.3	6.20	13.2±1.3	15.6±0.1	nd	nd

nd: not determined.

2.1.4 Effects of heavy metals applied with P-fertilisers on soil-plant-human system

I Accumulation of heavy metals and radioactive elements in soil

The continuous application of large amounts of fertilisers and other soil amendments to agricultural lands has raised concern regarding the possible accumulation of toxic levels of their trace element constituents and potential harm to the environment. The potential environmental hazard of fertilisers or other soil amendments depends on the amounts used, the elemental composition of the material, the fraction of constituent elements that are released, the mobility and toxicity of the released elements in the environment, and the ease of incorporation of toxic elements into the biota. The total elemental composition of a material can give a preliminary view of its potential for environmental contamination, and when composition and quantity applied are both taken into account, an estimate of the maximum possible pollution caused through the use of the material can be determined (Raven and Loeppert, 1997). There are also radioactive elements with enormous half decay periods of 5 - 10 billion years. First of all, there are ^{238}U and ^{232}Th. The soil accumulation of different toxic metals such as Cd, U, Sr, Th and Ra can be related to the application of phosphate fertilisers (Kharikov and Smetana, 2000 and El-Bahi, *et al.*, 2004*)*. It is known that the ^{238}U concentration in surface soils has doubled after 80 years of application of phosphoric fertilisers in some USA states (Kharikov and Smetana, 2000).

II Accumulation of heavy metals and radioactive elements in plants

Depending on the soil characteristics, metals may be readily available to plants, especially in acid soils (Charter *et al.,* 1995). The most important factors influencing the bioavailability of metal in soil are: pH, CEC, clay content and organic matter content, P and Ca content (Prasad and Hagemeyer, 1999;). In addition, the uptake of one metal could be affected by other metals by competition at the uptake sites, e.g., Zn content in bush beans is decreased with increasing uptake of Cd, Pb and Cu (Hardiman *et al.*, 1984; Alloway, 1995). The uptake of metals increases with increasing metal concentration in the external medium. However, the uptake is not linear in correlation to the concentration increase. This is due to the fact that the metals are bound in the tissue, causing saturation that is governed by the rate at which the metal is conducted away. The uptake efficiency is highest at low external concentrations. However, the uptake and translocation may vary considerably depending on plant species and metals (Greger, 1999).

III Runoff of heavy metals and radioactive elements from soil via the water pathway

The enormous utilization of rock phosphates and P-fertilisers has the potential of being an important factor in the contamination of aquifers with alpha emitting radionuclides and heavy metals (Hamamo e*t al.,* 1995). Human activities caused the severe pollution of rivers with heavy metals, and other types of pollution. Recently, increasing attention has been given to the fate of heavy metals and radionuclides contained in municipal wastes, phosphogypsum and in commercial fertilisers applied to agriculture soils.

VI Transfer of heavy metals into the human food chain

The ongoing addition of fertilisers containing heavy metals to the soil can result in their accumulation in the soil over time (Brigden *et al.,* 2002). These heavy metals are transferred via the food chain to humans either directly through crops or animals (meat), or after erosion and leaching – through drinking water. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time compared to the chemical's concentration in the environment. Compounds accumulate in living things at any time. The heavy metals applied with fertilisers tend to accumulate in cultivated soil because heavy metals are non-degradable (Voet, et al. 2000; Abdel Haleem *et al*., 2001). The use of rock phosphates with a relatively high heavy metal-content as fertilisers could possibly endanger animal and human health by accumulation of heavy metals through the food chain. It may be possible to select varieties for low heavy metal accumulation in order to decrease the transfer of these metals into the human food chain.

V Toxic effects of heavy metals and radioactive elements on human health

Heavy metals in fertilisers and other soil inputs are a threat to the sustainability of farming practices. Heavy metals, such as Hg, Pb, Cd, As, Cu, Co, Ni, etc, are dangerous because of their ability to be accumulated in food products (Lenntech, 2004; Kharikov and Smetana, 2000). The most toxic are Hg, Cd, Pb and As (Kharikov and Smetana, 2000). Heavy metals can cause chronic and acute health problems. Sometimes the absorption or contact with a large amount of these toxic heavy metals within short time (e.g. 24 h) is able to generate toxic effects in short time (acute exposure). However, the real problem of heavy metals in our food is chronic exposure, which is related to long-term absorption (months, years) of small doses of heavy metals with food (Islam et al., 2007). It was reported that high levels of toxic heavy metal may cause various toxicity mechanisms (Table 2.4).

Table 2.4: The toxicity of heavy metals for humans (Merian, 1984; Geldmacher et al., 2004)

Heavy metals	The negative effect on human body
As, Bi, Cr, Cu Fe, Mn and Sb	Impair the function of liver
Au, Cd, Hg, Pb and U	Impair the function of kidney
As, Pb	Impair the function of hematopoiesis system
As, Bi, Pb	Cause illnesses of heart - circulation system or illnesses of the respiratory system with inhalation absorption
As, Hg, Mn, Pb, Tl	Cause damage of the central and peripheral nervous system
As, Cr, Hg	Cause mutagenicity
Pb, Hg	Cause teratogenicity
As, Be, Cd, Cr, Ni, U	Cause human carcinogens

For Sr, the stable isotopes of Sr at the levels typically found in the environment are generally not known to be a great danger to human health. The only Sr compound that is considered a danger to human health, even in small quantities, is strontium chromate. Strontium chromate is known to cause lung cancer. For children, Sr at high level may be a health risk, because it can cause problems with bone growth. So much strontium was taken into bone instead of calcium that growing bones were weakened (Alfred et al., 2004). Sr can also exist as radioactive isotope ^{90}Sr with a half-life of about 29 years, which is produced by nuclear fission of ^{235}U in nuclear reactors or during the explosion of nuclear weapons. ^{90}Sr decays to ^{90}Y (yttrium), and ^{90}Y decays by emitting beta particle with a half-life of 64 hours to zirconium (^{90}Zr) which is a stable isotope. The harmful effects of radioactive ^{90}Sr, like other radioactive elements, are caused by their effects of radiation. Some of these isotopes been used in medical applications such as ^{85}Sr. ^{89}Sr has also been used as a cancer therapeutic to alleviate bone pain (Alfred et al., 2004).

U presents both chemical and radiological hazards. The damage causes by exposure to low-dose exposure is invisible and not immediate. U accumulates in kidneys, brain and other organs. Many negative effects can be induced after the alpha particle taken inside the body even for non-toxic dosages. The ionisation radiation causes cellular toxicity, DNA damage; genetic damage such as blindness, deafness and chronic diseases as well as it induced the cancer. Depends on kind of radiation, absorbed radiation dose (dosimetry), type of tissue, the cell can be harmed or destroyed by ionisation radiation. Cells can be killed but at low level of radiation, cells are slightly damaged and left alive. If the cell left alive and damaged, it can produce a cancer in addition the damage of the ovum or/and the sperm is trouble because any changes made in their structures can lead to deformed babies (Bertell, 1986; Bertell, 1986; Sheppard et al., 2005). Furthermore, U has several radiotoxic decay products such as ^{226}Ra. ^{226}Ra is considered as one of the most toxic radionuclides that Ra can be taken into bone because the metabolic behaviour of radium in the body is similar to that of calcium. The enrichment of ^{226}Ra in bones causes a long-lasting and therefore dangerous exposure of tissue to radiation. ^{226}Ra decays slowly producing radon (^{222}Rn) with a half-life of 3.8 days, an alpha emitter, which inhaled can cause lung cancer (Lloyd et al., 1997).

The application of P-fertilisers, which contain a high amount of toxic heavy metals, can increase the level of these toxic metals in vegetable food. In order to avoid toxicity of heavy metals and to offer healthy food to humans, many countries have legislation to recommend maximum limits of each toxic element in our food. Legal regulations exist in most other European countries. The most attention has been directed towards regulation of maximum Cd concentrations permitted in fertilisers (especially P-fertilisers). EFMA (European Fertiliser Manufacturers Association) recommended to the European Commission to limit Cd level for phosphoric fertilisers produced in EC to 60 mg kg^{-1} P_2O_5 (Kharikov and Smetana, 2000). On the other hand, maximum levels for U or Sr have not been installed yet.

2.2 Isotopic fingerprint method (isotopic signature)

2.2.1 Definition and types of isotopes

Isotopes are atoms whose nuclei contain the same number of protons (same atomic number) but a different number of neutrons and therefore have different atomic weights. The term isotope is derived from the Greek (meaning equal places) and indicates that isotopes occupy the same position in the periodic table. It is convenient to denote isotopes in the form ${}^{M}{}_{Z}E$ where the superscript (M) denotes the mass number (sum of the number of protons (Z) and neutrons in the nucleus) and the subscript (Z) denotes atomic number of an element. For example ${}^{88}{}_{38}Sr$, ${}^{87}{}_{38}Sr$, ${}^{86}{}_{38}Sr$ are the isotopes of Sr, all these isotopes have 38 protons but they have different number of neutrons: 50, 49 and 48 neutrons (N) respectively (Hoefs, 1997).

Isotopes are found in the earth, the atmosphere, and biosphere in two natural forms: stable, which do not change into another type of atom by themselves, and unstable (radioactive) isotopes, which can spontaneously change into other types of atoms (Criss, 1999).

I Radioactive (unstable) nuclides

The nuclei of atoms consist primarily of a combination of protons and neutrons collectively called nucleons. The combinations of protons and neutrons in nuclei are only stable in a certain ratio. A graph of neutron versus proton for nuclei has a narrow area called the belt of stability, where all stable isotopes are located (Fig 2.3). If the protons to neutrons relations are upset by any means, adding or losing a neutron, an unstable nuclide will result. The resulting structure would be above the belt of stability, and would be expected to return to the belt of stability by radioactive decay. Radioactivity is a way of adjusting this ratio in a nucleus to achieve a stable configuration. Nuclides decay into different forms, called daughter atoms, by emitting radiation such as α-particles (${}^{4}{}_{2}He$), β-particles, or γ-rays. This process can take place in one step or in decay through a series of radionuclides to stable isotopes. Rates of radionuclide decay are usually expressed in terms of half-life. Half-life is the time required for a given amount of radionuclides to lose 50% of its activity, for example ${}^{87}Rb$ is radioactive and decays to the stable ${}^{87}Sr$ by emission of β-particles and antineutrino ῦ, it has a half –life of $4.7*10^{10}$ years. The half-life is equal to Ln2/γ =0.693/γ (Dickin, 1995; L`Annunziata, 1998). Where: γ is decay constant. The half-life varies widely ranging from nanoseconds to thousands of years. Sr has for example, 32 isotopes (${}^{73}Sr$- ${}^{104}Sr$), of which only four isotopes (${}^{84}Sr$, ${}^{86}Sr$, ${}^{87}Sr$ and ${}^{88}Sr$) are stable. The others are radioactive isotopes with different half-lives as illustrated in Table 2.5.

Table 2.5: Isotopic masses and half-lives of Sr radioisotopes (Korea Atomic Energy Research Institute, 2000)

Isotope	Mass	Half life	Isotope	Mass	Half life
^{73}Sr	72.9659	Unknown	**^{91}Sr**	90.910	9.63 h
^{74}Sr	73.9563	>1.2 x 10^{-5} s	**^{92}Sr**	91.911	2.71 h
^{75}Sr	74.9499	71 x 10^{-2} s	**^{93}Sr**	92.914	7.423 min
^{76}Sr	75.9416	8.9 s	**^{94}Sr**	93.915	75.3 s
^{77}Sr	76.9377	9.0 s	**^{95}Sr**	94.919	23.90 s
^{78}Sr	77.9321	2.5 min	**^{96}Sr**	95.922	1.07 s
^{79}Sr	78.9297	2.25 min	**^{97}Sr**	96.926	429 x 10^{-2} s
^{80}Sr	79.9245	106.3 min	**^{98}Sr**	97.928	0.653 s
^{81}Sr	80.9232	22.3 min	**^{99}Sr**	98.933	0.269 s
^{82}Sr	81.9184	25.55 d	**^{100}Sr**	99.935	202 x10^{-2} s
^{83}Sr	82.9175	32.41 h	**^{101}Sr**	100.945	118 x 10^{-2} s
^{85}Sr	84.9123	64.84 d	**^{102}Sr**	101.943	69 x 10^{-2} s
^{89}Sr	88.9077	50.53 d	**^{103}Sr**	102.949	150 ns
^{90}Sr	89.9077	28.79 years	**^{104}Sr**	103.952	150 ns

Another radioisotope is U, which is found in P-fertilisers. U is the heaviest metal in the nature, and all U isotopes are radioactive with different half-life (Table 2.6). There are three natural U isotopes: ^{234}U, ^{235}U, and ^{238}U. The U series are the longest known series, ^{238}U decays into ^{234}Th, then protactinium (^{234}Pa), ^{234}U, ^{230}Th and so on, until ^{206}Pb, which is stable, is reached. Similarly, ^{235}U decays through a series of radionuclides until reaching the stable, non-radioactive isotope ^{207}Pb. ^{232}Th decays in several steps, producing different radioactive isotopes **(**daughters), until ^{208}Pb is formed as illustrated in Table 2.7. ^{234}U is a third generation decay of the very long half-life radionuclide (^{238}U). ^{234}U is present only in trace amounts in natural U due to its short half-life ($t_{½} = 2.5×10^5$ y) compared to the half-lives of ^{238}U and ^{235}U ($t_{½} = 4.47x10^9$yr and $7.04x10^8$yr respectively).

Table 2.6: The most important isotopes of U and their half-lives (Kromphorn, 1996)

Radio-isotopes	Half-life	Discoverered by	Radioisotopes	Half-life	Discoverered by
$^{226}\mathbf{U}$	≈ 0.2 s	Viola, Minor, Roche 1973	$^{234}\mathbf{U}$	2.455 x 10^5 y	Gieger, Nuttall 1912
$^{227}\mathbf{U}$	1.1 min.	Meinke, Ghiorso, Seborg 1952	$^{235}\mathbf{U}$	7.038 x 10^8 y	Dempster, 1935
$^{228}\mathbf{U}$	9.1 min	Meinke, Ghiorso, Seborg 1949	$^{236}\mathbf{U}$	2.342 x 10^7 y	Williams, Yuster 1945
$^{229}\mathbf{U}$	58 min	Meinke, Ghiorso, Seaborg 1949	$^{237}\mathbf{U}$	6.75 d	Nishina, Yasaki, Ezoe, Kimura, Ikawa 1940; MC Millan 1940
$^{230}\mathbf{U}$	20.8 d	Studier, Hyde 1946			
$^{231}\mathbf{U}$	4.2 d	Osborne, Thompson, Van Winkle 1942	$^{238}\mathbf{U}$	4.468 x 10^9	Klaproth 1789
$^{232}\mathbf{U}$	68.9 yr.	Gofmann, Seaborg 1942	$^{239}\mathbf{U}$	23.45 min	Meitner, Hahn, Strassmann 1937
$^{233}\mathbf{U}$	1.592 x 10^5 y	Seaborg, Gofmann, Stoughton 1942	$^{240}\mathbf{U}$	14.1 h	Hyde, Studier 1948

Table 2.7: ^{238}U, ^{235}U and ^{232}Th decay chain (http://www.soes.soton.ac.uk, 05.07.2005)

$^{238}\mathbf{U}$ **series**	**Half-life**	$^{232}\mathbf{Th}$ **series**	**Half-life**	$^{235}\mathbf{U}$ **series**	**Half-life**
$^{238}\mathbf{U}$	4.47×10^9yr	$^{232}\mathbf{Th}$	1.40×10^{10}yr	$^{235}\mathbf{U}$	7.04×10^8yr
$^{234}\mathbf{Th}$	24.1 day	$^{228}\mathbf{Ra}$	5.75 yr	$^{231}\mathbf{Th}$	25.5 day
$^{234}\mathbf{Pa}$	1.18 min	$^{228}\mathbf{Ac}$	6.13 hr	$^{231}\mathbf{Pa}$	3.25×10^4yr
$^{234}\mathbf{U}$	2.48×10^5yr	$^{228}\mathbf{Th}$	1.91 yr	$^{227}\mathbf{Ac}$	21.8 yr
$^{230}\mathbf{Th}$	7.52×10^4yr	$^{224}\mathbf{Ra}$	3.66 day	$^{227}\mathbf{Th}$	18.7 day
$^{226}\mathbf{Ra}$	1.62×10^3yr	$^{220}\mathbf{Rn}$	55.6 sec	$^{223}\mathbf{Ra}$	11.4 day
$^{222}\mathbf{Rn}$	3.82 day	$^{216}\mathbf{Po}$	0.15 sec	$^{219}\mathbf{Rn}$	3.96 sec
$^{218}\mathbf{Po}$	3.05 min	$^{212}\mathbf{Pb}$	10.6 hr	$^{215}\mathbf{Po}$	1.78×10^{-3}sec
$^{214}\mathbf{Pb}$	26.8 min	$^{212}\mathbf{Bi}$	60.6 min	$^{211}\mathbf{Pb}$	36.1 min
$^{214}\mathbf{Bi}$	19.7 min	$^{212}\mathbf{Po}$	3.0×10^{-7}sec	$^{211}\mathbf{Bi}$	2.15 min
$^{214}\mathbf{Po}$	1.64×10^{-4}sec	$^{208}\mathbf{Pb}$	Stable	$^{207}\mathbf{Tl}$	4.77 min
$^{210}\mathbf{Pb}$	22.3 yr			$^{207}\mathbf{Pb}$	Stable
$^{210}\mathbf{Bi}$	5.01 day				
$^{210}\mathbf{Po}$	138 day				
$^{206}\mathbf{Pb}$	Stable				

II Stable nuclides

Stable nuclides do not decay. The stability of nuclides is characterised by several rules. The most important is the symmetry rule, which states that in stable nuclides with a low atomic mass, the greatest stability is achieved when the number of neutrons (N) and protons (Z) are approximately equal (N=Z). When atomic mass increases, the neutron/proton (N/Z) ratio will increases until N/Z = 1.5 (Hoefs, 1997). If the ratio N/Z is outside the belt of stability, then the isotopes spontaneously emit particles and/or electromagnetic radiation (radioactive) (Hoefs, 1997).

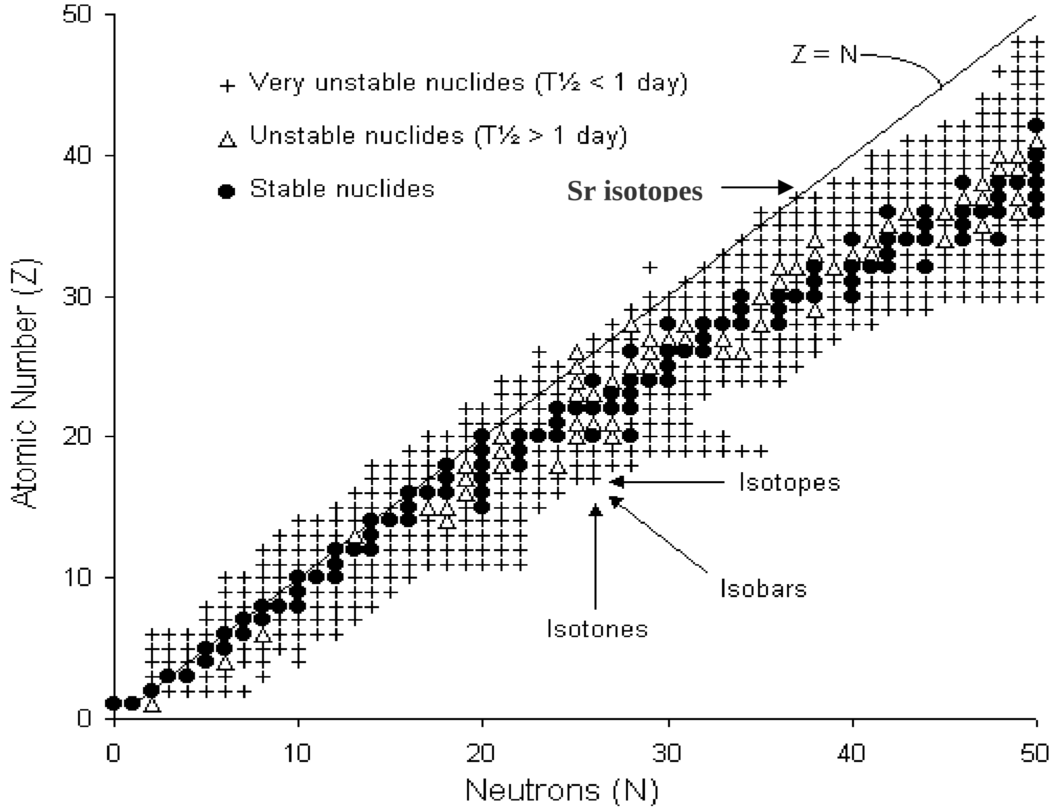

Fig. 2.3: Plot of atomic number (Z) versus neutrons (N) showing the belt of stability. The Z: N ratio is 1 for the light nuclides and increases towards 1.5 for the heavier nuclides (Clark and Fritz, 1997)

There are two forms of stable nuclides: Radiogenic stable nuclides and nonradiogenic stable nuclides.

I Nonradiogenic stable nuclides: The nonradiogenic stable nuclides have been present since the formation of the earth so their overall abundance is independent of time. Important examples are ^{84}Sr, ^{86}Sr, ^{88}Sr, ^{13}C, ^{12}C and ^{18}O (Criss, 1999).

II Radiogenic stable nuclides: The radiogenic stable nuclides are daughter isotopes continuously formed by the decay of radioactive parent nuclides. Examples of these are ^{87}Sr, ^{40}Ar and ^{207}Pb.

Because the radioactive atoms do not disappear, but instead are transformed into another atomic form, in a closed system the number of radiogenic daughter atoms D* is equal to the number of parent atoms consumed, which can be written as:

$$D^* = N_0 - N \quad \text{(A)}$$

where: N is the number of radioactive atoms present at any time (t).

N_0 is the number of radioactive atoms present at some initial time.

The law of radioactive decay is: $N = N_0\, e^{-\gamma t}$ .... *(B)*

Therefore equation B can be written: $N_0 = N\, e^{\gamma t}$ ....*(C)*

Substituting No in equation (A) gives the number of daughter atoms:

$$D^* = N\,(e^{\gamma t}-1) \quad \text{(D)}$$

If the number of daughter atoms at time t = 0 is D_0, then the total number of daughter atoms after time t is given as: $D = D_0 + N\,(e^{\gamma t}-1)$ ....*(E)*

Rb-Sr- Decay systems

The Rb-Sr- Decay system is one example of radioactive nuclides decay over time. As radioactive nuclides decay over time radiogenic isotopes are formed, and variations in isotopic abundance are produced in the elements involved (Koch et al., 1995). Rubidium has two naturally occurring isotopes: ^{85}Rb (72.17%) and ^{87}Rb (27.83%). ^{87}Rb is radioactive, and decays to the stable isotope ^{87}Sr by emission of β^- particles and antineutrons:

$$^{87}\mathbf{Rb} \rightarrow {}^{87}\mathbf{Sr} + \beta^- + \acute{\upsilon} + \mathbf{Q}$$

where: β^- is beta particles, ύ is an antineutron, Q represents the decay energy (0.275 Me V).

The number of radiogenic daughters (Sr*) increases with time (Fig. 2.4) and is given as:

$$^{87}\mathbf{Sr}^* = {}^{87}\mathbf{Rb}\,(e^{\lambda t}-1)$$

The decay constant of ^{87}Rb is (λ=1.42 x 10^{-11} y^{-1}), half – life $T_{1/2}$ = 48.8 x 10^9 years.

The total ^{87}Sr is equal to Sr content in the rock at the time of its formation ($^{87}Sr_0$) plus the number of radiogenic daughter (Sr), so:

$$^{87}\mathbf{Sr}_{\text{total}} = {}^{87}\mathbf{Sr}_0 + {}^{87}\mathbf{Rb}\,(e^{\lambda t}-1)$$

This equation for Sr isotopic composition can be written as:

$$R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\text{total}} = R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_0 + {}^{87}\mathrm{Rb}/^{86}\mathrm{Sr}\,(e^{\lambda t}-1)$$

As it is clear from this equation, the variations in *R*(^{87}Sr/^{86}Sr) are primarily caused by the amount of parent nuclides (^{87}Rb), the amount of time (t) and the Sr isotope ratio at the time of rock formation $R(^{87}Sr/^{86}S)_0$ (Criss, 1999; Dickin, 1995). Most igneous, metamorphic and sedimentary rocks contain Rb and Sr. Over time the decay of ^{87}Rb to ^{87}Sr (Fig. 2.4) increases the $R(^{87}Sr/^{86}Sr)$ in rocks and minerals because the amount of ^{86}Sr remains constant.

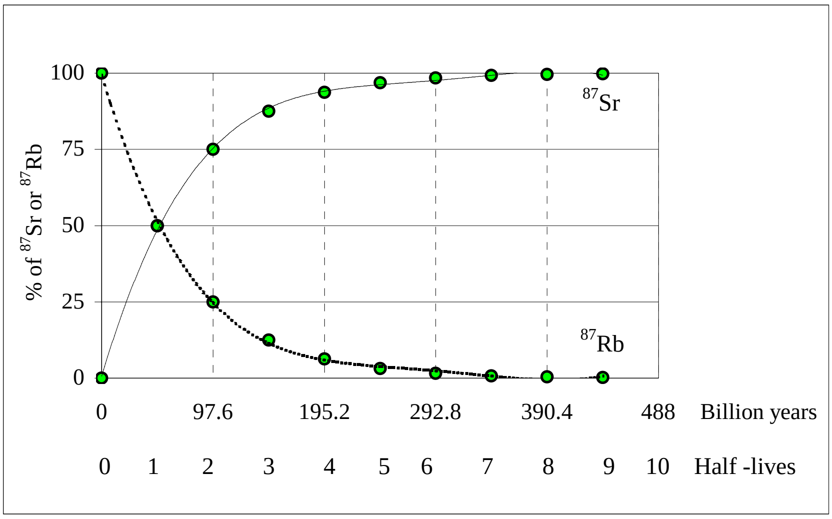

Fig. 2.4: Decay curve of ^{87}Rb to the radiogenic daughter ^{87}Sr

The ratio $R(^{87}Sr/^{86}Sr)$ depends on Rb/Sr ratio of the rock and the age of these rocks and the Sr isotope ratio at the time of rock formation $R(^{87}Sr/^{86}S)_0$ (Criss, 1999; Koch et al., 1995; Dickin, 1995; Barbaste et al., 2002). Rocks which are rich in Rb and have a high Rb/Sr ratio, generally tend to have high $R(^{87}Sr/^{86}Sr)$ such as mica and K-feldspar. In contrast, this ratio is low in rocks that have low Rb/Sr ratios, e.g., $R(^{87}Sr/^{86}Sr)$ in basalt is about 0.703. Furthermore, $R(^{87}Sr/^{86}Sr)$ ratios in rocks vary from one origin to another depending on the local geology (Graustein, 1989; Price et al., 2002) because the local $R(^{87}Sr/^{86}Sr)$ depends on geological features (type and age of samples, initial Rb/Sr and $^{87}Sr/^{86}Sr$ ratio at the time of formation). This propriety can be used in many different research fields such as ecology, archaeology, forensic, criminal, dating rock and mineral and identifying and fingerprinting the origin of various materials. E.g. $^{207}Pb/^{204}Pb$ can be used to determine the sources of pollutant lead in the environment (Gulson *et al.*, 1997). Because, ^{208}Pb, ^{207}Pb, ^{206}Pb are produced by radioactive decay of ^{232}Th, ^{235}U, ^{238}U respectively. The amounts (abundances) of these isotopes have increased over time, while ^{204}Pb is nonradiogenic and its amount remains constant. The isotope ratio for several elements can be used in research fields mentioned above. Only the most important radioactive elements, their daughter isotopes (radiogenic), the reference isotopes and the range of isotope ratio values are summarised in Table 2.

Table 2.8: Some of the important long-life radioactive elements and their daughter isotopes (radiogenic) which can be used to date rocks and minerals (Banner 2004, Horen et al., 1998)

Radioactive elements	**Half life billion years**	**Daughter (Radiogenic nuclide)**	**Reference isotopes**	**Ratio**	**Value**
^{40}K (0.01167)	1.397	^{40}Ca (96.9821)	^{42}Ca (0.6421)	^{40}Ca/^{42}Ca	151-152
	11.93	^{40}Ar (99.6)	^{36}Ar (0.337)	^{40}Ar/^{36}Ar	295.5- 10^4
^{82}Se (9.19)		^{82}Kr (11.56)	^{84}Kr (57)	^{82}Kr/^{84}Kr	0.202-1.1
^{87}Rb (27.8346)	48.8	^{87}Sr (7.04)	^{86}Sr (9.87)	^{87}Sr/^{86}Sr	0.702->1
^{130}Te (34.48)		^{130}Xe (4.1)	^{132}Xe (26.9)	^{130}Xe/^{132}Xe	0.152->0.4
^{147}Sm (14.996)	106	^{143}Nd (12.2)	^{144}Nd (23.8)	^{143}Nd/^{144}Nd	0.51-0.514
^{187}Re (62.6)	42.3	^{187}Os (1.51)	^{186}Os (1.6)	^{187}Os/^{186}Os	0.9->10
^{232}Th (100)	14.0	^{208}Pb (52.4)	^{204}Pb (1.4)	^{208}Pb/^{204}Pb	33-52
^{235}U (0.7202)	0.704	^{207}Pb (22.1)	^{204}Pb (1.4)	^{207}Pb/^{204}Pb	14-28
^{238}U (99.2743)	4.47	^{206}Pb (24.1)	^{204}Pb (1.4)	^{206}Pb/^{204}Pb	13-120
U, Th		^{4}He (>99.99)	^{3}He (1.38-10^{-4})	^{4}He/^{3}He	2.10^4-10^9
^{238}U (99.2743)		^{234}U (0.005)	^{238}U (99.27)	^{234}U/^{238}U	4.10^{-5}-10^{-3}

* The numbers between brackets are the natural atomic percent abundances of the isotope.

2.2.2 Abundance of the isotopes on earth

Most of the 2500 known nuclides are artificial radioisotopes with half-lives of several seconds or less. Only 287 nuclides are either stable or very long-lived radioactive types, and only 21 elements are pure elements, i.e., they have only one stable isotope (so-called mono-isotope). Examples of these mono-isotopes are arsenic, sodium, manganese, and cobalt (Taylor, 2001). All other elements are mixtures of at least two isotopes, these two or more isotopes are found in the earth, the atmosphere, and all living things. Average literature values for the abundance of Sr and U isotopes are given in Table 2.9 and Table 2.10. In fact, isotope ratio for several elements varies from sample to sample. A good example of this variation is the range of $R(^{234}\text{U}/^{238}\text{U})$ found in different types environmental samples and even in different types of water (Table 2.11). ^{234}U/^{238}U-activity ratio in water is from 0.5 to 40 (Fujikawa et al., 2000), it is in natural water 1 to 2, but in groundwater it ranges from 0.52 to 9.02, it is in majority of rivers from 1 to 2.14, while in seawater about 1.14 (Skwarzec et al., 2001). ^{234}U/^{238}U-activity ratio in soil rang of 0.5-1.2 (Steven et al., 1997), in sediment about 1 (Skwarzec et al., 2001). The reason behind the enrichment of ^{234}U in seawater is probably due to radiation damage of crystal lattices, caused both by α-emission and by caused by alpha recoil of ^{234}U. In addition, radioactive decay may leave ^{234}U in more soluble +6 charge state than its parent. These processes together enable preferential leaching of the ^{234}U into water (Dickin, 1995).

Table 2.9: Isotopic masses and natural abundance of Sr isotopes on earth (Moore et al., 1982; Korea Atomic Energy Research Institute, 2000)

Isotope	Mass	Atomic Percent Abundance%
^{84}Sr	83.913	0.56
^{86}Sr	85.909	9.86
^{87}Sr	86.909	7.00
^{88}Sr	87.906	82.58

Table 2.10: Isotopic masses, natural abundance and isotope ratios for natural U isotopes (Rosman et al., 1999; WHO, 2001, Kromphorn, 1996)

Isotope	Mass	Atomic Percent Abundance%	Activity in g natural U	Activity%
^{238}U	238.050783	99.2745	1.235 x 10^4 Bq	48.9
^{235}U	235.043923	0.7200	5.685 x 10^2 Bq	2.2
^{234}U	234.040946	0.0055	1.243 x 10^4 Bq	48.9
^{235}U/ ^{238}U		0.00725		
*^{234}U/ ^{238}U		0.0000554		1

* Range from 0.000 05 to 0.0004 in atmospheric dusts (US EPA, 1994) and 0.000 03 to 0.0014 in natural waters (WHO, 2001).

Table 2.11: Typical range in $R(^{234}U/^{238}U)$ activity ratios for various natural materials (Bailey et al. 2002; Goldstein *et al.*, 1997)

Material	^{234}U/^{238}U- activity ratio	Material	^{234}U/^{238}U- activity ratio
Open-ocean water	1.10-1.18	**Peat deposits**	0.90-2.00
Terrestrial surface waters	0.80-2.50	**Igneous rocks**	0.60-2.10
Underground waters	0.60-12.00	**Volcanic tuffs**	0.50-1.60
Waters of U mineralisation	1.20-8.80	**Sandstones**	0.80-2.00
Various surficial carbonates	0.90-3.00	**Minerals and extracts of minerals**	0.80-8.00
Fossil shells and bones	1.00-2.50	**Soils**	0.5-1.20

2.2.3 Isotopic fractionation

Isotopic fractionation means the partitioning of substances or two phases (A and B) of the same substance with different isotope ratio (Hofes, 1996; Criss, 1999). A natural way to represent such effects is the isotopic fractionation factor, referred to by the symbol α.

$$[\alpha_{A\text{-}B} = R_A/R_B]$$

where: R refers to the atomic ratio e.g. N*/N of a heavy N* to light N isotope (Criss, 1999).

Isotopic effects, which cause isotope fractionation, are caused by the different masses of the isotopes. In general, molecules bearing the light isotope will react slightly more rapidly than those with the heavy isotope during a chemical reaction in the case of non-quantative reaction (Criss, 1999), because the bonds formed by the light isotope are weaker than bonds involving the heavy isotope. Consequently, there will be differences in the abundance of the stable isotopes between substrate and product (Hoefs, 1997; Criss, 1999). The lighter molecule will diffuse or evaporate faster than the molecule bearing the heavy isotope. Since the isotopic effects relate to differences in masses, these fractionations are largest for elements that have low atomic weights. They are particularly large for H and are significant for C, N, and S because the atomic weights of these elements are low. The differences of one or more neutrons translate to significant relative differences in the masses of these isotopes. Since the relative mass difference (dm/m) between the isotopes of low mass element such as H, C, N or S is higher than that of heavy elements (Sr, U), light elements are more likely to exhibit isotopic fractionation than heavy isotopes. Isotopic fractionation for heavy elements with atomic weight of more than 50, such as Sr, Nd, Hf, Os, U, or Pb, and where the relative mass differences (dm/m) of the isotopes are small, is minute and can be ignored. Mono-isotopes such as P, Al, and F will not be fractionated (Johnson, 2004; Horn, 2005).

For radiogenic elements such as ^{234}U and ^{87}Sr the main reason for the variation in an elements' isotope ratio can be related to the radioactive decay system. There are some radioactive elements, which decay straight to stable isotopes (radiogenic nuclides), e.g., ^{87}Rb decays to ^{87}Sr. The variations in $R(^{87}\text{Sr}/^{86}\text{Sr})$ (where ^{87}Sr is radiogenic while ^{86}Sr is non radiogenic) in nature are a function of the Rb/Sr decay system as discussed in Chapter 2.2.1. The local ratio of ^{87}Sr to ^{86}Sr depends on geological features (type and age of samples, original Rb/Sr (at the time of formation), initial $R(^{87}\text{Sr}/^{86}\text{Sr})_0$). The higher the Rb/Sr ratio and the older the rock (older than 1000 million years), the higher $R(^{87}\text{Sr}/^{86}\text{Sr})$ will be, it may show $R(^{87}\text{Sr}/^{86}\text{Sr})$ of 0.750 or more (Graustein, 1989) such as in K-feldspar minerals (Jones and Jenkyns, 2001; Banner, 2004). In contrast, rocks that are geologically young and have low

Rb/Sr, generally have *R*(^{87}Sr/^{86}Sr) lower than 0.706, e.g. about 0.703 in basalts (Price *et al*., 2002; Graustein, 1989). These natural abundances of stable isotopes are different from sample to sample, according to their origin. As a result, stable isotope ratios have been used as indicators of the geographical origin of a wide variety of materials (Graham *et al*., 2000). Some radioactive elements decay through a series of radionuclides until turning to a stable isotope. E.g. the ^{238}U series decay chain contains 14 daughters including ^{234}U (Calsteren and Thomas, 2006).

2.2.4 Isotope ratios as a fingerprint to identify the origin of different materials

Recently, the interest in determining the natural abundances and isotope ratios of different elements in various materials was increased, because the natural isotope ratios can vary according to the geographical origin of the matrix. These natural isotope ratios have been used in ecology, archaeology, forensic, and criminal studies as fingerprinting technique to identify the origin of different materials such as rocks, soil, human remains, food products such as cheese, lamb meat, honey, wine, rice. They can also be used to determine the geographic region of an animal or human because natural materials of different regions tend to have distinct isotopic compositions.

Since the relative mass difference between Sr isotopes (dm/m) as well as for the other heavy isotopes (high mass element) is lower than that of light isotopes, any mass-dependent isotope fractionation would be so small during geological or biological processing that it can be ignored (Beard and Johnson, 1999). Based on the assumption that no isotopic fractionation for isotopes occurs during the uptake of an element from soil by plant, stable isotope ratio analysis is increasingly spreading as a tool to identify the geographical origin of agricultural products (meat, bio-eggs and different «Emmental» type cheese samples, heroin, cocaine) based on the relation between stable isotope ratios and location (Boner and Forstel, 2004, Barbaste et al., 2002; Graham *et al*., 2000; Koch *et al*., 1995; Augenstein, 2004; Fortunato *et al*., 2003). Another widely practised application is the verification of the authenticity of wine, because the isotope ratio of wine reflects that of the soil on which the wine is grown and is characteristic of the geographical origin of the wine. The analysis of wines of different origin showed a clear difference between wines produced on basaltic, mixed and granitic soils (Barbaste et al., 2002).

These characteristic isotope ratio „signatures“ of food species are passed on to consumers (higher trophic levels) because the mass difference between ^{87}Sr and ^{86}Sr is small and the ratio is not affected by biological fractionation. So, the isotopic differences in diet are reflected in herbivore tissues and $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ values are constant through the food chain (Blum *et al*., 2000; Price *et al*., 2002). Thus the isotopic composition of an animal reflects its food source (Peterson and Fry, 1987). Therefore, Sr isotope ratio can be used to study animals' origins and movements of living or dead animals, e.g., African elephants, bats, birds, migratory fish, etc. (Hobson, 1999). It can also be used to study human remains, human residential change or human migration through history (Price *et al*., 2002; Bentley, *et al*., 2003; Knudson *et al*., 2004; Katzenberg and Krouse, 1989), to reconstruct past diets of dead animals (Sillen *et al*., 1998; Ehleringer and Thure, 2001; Koch et al., 1995) as well as to indicate to the origin of different materials such as ivory (Koch et al., 1995).

Isotope ratios are not only useful to identify the origin of various materials, but can also be used in many other fields such as: (1) to control food products. Many studies have been focused on the application of stable isotopes for the detection of fraud in food products (Schmidt et al., 2005). Isotope ratios can be used to recognize the non-allowed substance (water, sugar, vitamin C) in wine, honey, or juice. E.g., plants prefer to take up carbon dioxide containing the lighter carbon isotope (^{12}C-CO_2) in photosynthesis. African trees and most shrubs, herbs, and cool-climate grasses and beet are C3 plants, those using the Calvin-Benson photosynthetic pathway, with low α^{13}C values (about -27 per mil), whereas warm-climate grasses are C4 plants that use the Hatch –Slack Pathway, with less negative values (-13 per mil) such as cane (Kelly, 2003; Ertl, 1997). The different ^{13}C/^{12}C ratios that result can be used to distinguish C3 from C4 plants, e.g., it is possible to determine the source of sugar (beet or cane) by measuring its ^{13}C content by IRMS. Also ^{13}C/^{12}C or D/H can be used to detect addition of sugar in winemaking (Guillou *et al.*, 2001).

(2) Another interesting application of isotope ratios is to discriminate conventional from organic products (Karyne, 2004). Nitrogen in composted manure is enriched in ^{15}N > (10 ‰) compared to synthetic N-fertiliser < (2 ‰), due to ammonia volatilisation. Crops and soil fertilised with manure or compost may show higher δ^{15}N than those treated with inorganic fertiliser. Therefore, the N isotope composition (^{15}N) of crops and soil may be different depending on the kind of N inputs (Bateman *et al.*, 2004; Bateman *et al.*, 2005). Alison *et al.* (2005) found that the nitrogen in crops grown using synthetic nitrogen fertiliser was isotopically lighter than those grown using chicken manure. Furthermore, the analyses of multi-element stable isotopes of beef meat provide information about the sources and kind of meat (organic or inorganic) (Renou et al., 2004; Piasentier, 2003). Boner and Forstel (2004)

found that it is possible to use nitrogen, sulphur, oxygen and hydrogen isotope ratio to distinguish between inorganic and organic beef coming from Germany and other beef from Argentina. This technique can be applied in the case of beef crises to overcome the problem of identifying the original sources of beef (Kelly *et al*., 2004). So, the analysis of stable isotopes seems to be a promising method for identification in that it provides a fraud-resistant, unique signature to the area from which certain materials originate.

(3) Furthermore, isotope ratios can be used to fingerprint the source of contamination in order to study the fate and pathway of contaminants in the environment (Dresel *et al* 2002; Jesse, 2001). For example, $^{234}U/^{238}U$-isotope ratio can be used to indicate the source of the U as natural (from weathering of igneous rocks and ore bodies) or man-made (from industrial use, manufacturing or handling of depleted U) (Dresel *et al* 2002). Also it is possible in some cases to study the pathway of U applied with P-fertilisers from an agricultural field downstream based on the differences between the $^{234}U/^{238}U$-isotope ratio of fertilisers and this ratio in nature (Zielinski *et al.*, 2000). Numerous studies have been carried out using the ^{15}N and ^{18}O data of dissolved nitrate in order to discriminate between organic (e.g., human or animal manure) and inorganic (e.g., synthetic fertilisers) nitrogen contaminants in waters (Vitoria and Otero, 2004). Also S isotopes of dissolved sulphate have been used to estimate the contribution of fertilisers to water pollution and soils (Vitoria and Otero, 2004). Böhlke and Horan, (2000) found that agriculture can alter significantly the isotope geochemistry of Sr in streams and that effects could vary depending on the types, sources, amount of added fertilisers, the long term fertilisation and groundwater residence times. In addition, the isotopic composition of Sr in groundwater depends on the $^{87}Sr/^{86}Sr$-isotope ratios of the rocks with which it interacted. The isotopic composition of one material may indicate its source, and it is a useful tool for monitoring environmental radioactivity in order to study the migration mechanisms and the fate of the elements in the biosphere (Zielinski et al., 2006).

Isotope ratios can be used to study the pathway of heavy metals in the human food chain. The $^{87}Sr/^{86}Sr$-isotope ratio of the soil and water will be reflected in the plants, which will be passed on to an herbivore. The Sr isotope ratio of each point along the composition chain will be the same (Beard and Johnson, 1999).

2.3 *Objectives of this study*

The problem

Toxic heavy metal and radionuclide contents in rock phosphates and P-fertilisers, which often contain more heavy metals than non P-fertilisers, vary considerably depending on the geographical origin of samples. The long-continued application of fertilisers with high concentrations of these toxic substances to soil may increase their accumulation in the surface soil layer over time and the metals may be transferred via the food chain to humans. At high level they are toxic to humans and to ecological system.

In order to reduce the transfer of heavy metals into the food chain, toxic heavy metals should be avoided whenever possible. Therefore, rock phosphates from origins which are characterised by their low content of toxic heavy metals should be used to produce all P-containing fertilisers to decrease the loaded toxic heavy metals to cultivated soil with P-fertilisers.

In this context a reliable method is needed which allows to identify and characterise the origin of rock phosphates. In this study, two possible fingerprinting methods were test: heavy metal patterns and isotope ratios of Sr and U.

The aim of U and Sr isotope ratios analysis was two fold:

I- Fingerprinting the geographical origin of rock phosphates using $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ and $R(^{234}\mathrm{U}/^{238}\mathrm{U})$, to cheek if these ratios can be used to distinguish the geographical origin of rock phosphates as well as P-fertilisers from which they produced.

II- Monitoring the pollution with anthropogenic U using $R(^{235}\mathrm{U}/^{238}\mathrm{U})$.

The following key questions were specified:

1- Is it possible to identify the origin of rock phosphates or P-fertilisers depending on their content of heavy metals? Or, Is the elemental pattern of rock phosphates or P-fertilisers a reliable fingerprint for the provenance?

2- Do rock phosphates of different origin show different (distinctive) Sr and U isotope ratios? If so, can certain isotope ratios (e.g., Sr, U) be used to determine the source of P-fertilisers? Or, do Sr and U isotope ratios in P-fertilisers reflect the origin of their parent materials?

3- Is it possible to use the isotope ratio to trace back the origin of rock phosphates or P-fertilisers in compound mineral fertiliser or organo mineral fertilisers using U and Sr isotope ratio as fingerprint?

4- Is it possible to use $R(^{235}U/^{238}U)$ to investigate if the sample is polluted with anthropogenic U?

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3 Material and methods

3.1 Selection of samples

In this study three samples sets were analysed.

Set (1) consisted of rock phosphates and P-fertilisers from ten different origin (Fig. 3.1) including sedimentary rock phosphates from Algeria, Israel, Morocco, Senegal, Syria, the USA, Togo, Tunisia, igneous rock phosphates from Russian Kola Peninsula, and biogenic rock phosphates from Curacao (Table 3.1 and Table A. 1.1). Set (1) was used to evaluate U and Sr isotope ratios and heavy metal patterns as fingerprinting methods to identify the origin of rock phosphates and P-fertilisers.

Set (2) consisted of farmyard manures of different types of animals, K-fertilisers, organo-mineral fertilisers, and an additional set of rock phosphates and P-fertilisers from different origin (Table 3.1 and Table A. 1.2). Set (2) was used to characterise the different types of fertilisers by their content and isotopic composition of Sr and U, to check if it is possible to identify the origin of the P-component in compound mineral fertiliser and organo-mineral fertilisers.

Set (3) consisted of P-fertilisers and compound fertilisers (NP, PK, NPK) from different manufacturers including BASF (Ludwigshafen), Ruhr-Stickstoff AG (Bochum), Guano-Werke AG, and Hoechst (Table 3.1 and Table A. 1.5). Set (3) was used to check if it is possible to trace back the origin of rock phosphates used for P-fertiliser production by different manufacturers.

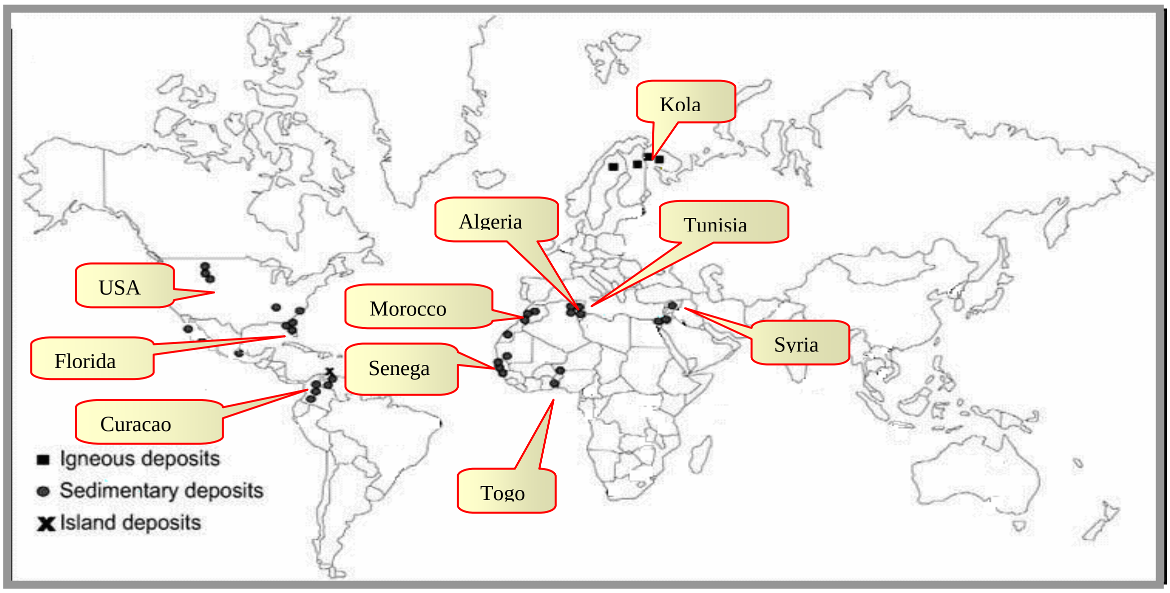

Fig. 3.1: Origins of the phosphate samples analysed in this study (adapted from Dahanayake et al., 1995 and Zapata and Roy, 2004)

Table 3.1: Rock phosphates and different type of P-containing fertilisers analysed for heavy metal contents and isotope ratios of Sr and U

Type of samples	**Origin/descriptive**	**Deposit**	**Number of samples analysed for:**			
			heavy metals	**U and Sr content**	**Sr isotope ratio**	**U isotope ratios**
Sedimentary rock phosphates	Morocco	3 deposits	6	9	4	4
	Senegal	Taiba	3	3	1	1
	Tunisia	Gafsa	2	6	1	1
	Algeria	Unknown	1	5	1	1
	Israel	2 deposits	3	8	1	1
	USA	4 deposits	10	14	4	4
	Syria	Unknown	1	1	1	1
	Togo	Unknown	5	5	1	2
	Curacao	Unknown	1	1		
Igneous rock phosphates	Russia	Kola	3	5	3	3
	Finland	Unknown		1	1	1
Mineral fertilisers	P-fertilisers	Different origin	6	10	10	10
	PK-fertilisers	Different manufacturers		10	2	3
	NP-fertilisers	Different manufacturers		5	5	5
	NPK-fertilisers	Different manufacturers		21	20	18
	K-fertilisers			2	2	
Phosphogypsum	Phosphogypsum	Different origin		3	2	
Farmyard manures	Chicken			3	3	3
	Dairy cows and calves			4	3	3
	Pigs			3	3	3
Organo-mineral fertilisers	NPK with Mg			4	4	4
Total			**34**	**123**	**72**	**68**

3.2 Analytical methods of heavy metal determination

For this study, analysis by ICP-MS (VG Elemental PlasmaQuad 3, Thermo Gmbh Bremen, Germany) was used to determine the concentration of As, Be, Cd, Co, Cr, Ni, Pb, Sb, Se, Sr, Ti and U in rock phosphate, P-fertiliser and phosphogypsum samples. P was analysed by ICP-OES Spectro Flame (Spectro Flame M 120S, Spectro Analytical Instruments GmbH, Germany). Sr and U isotope ratios were analysed by Thermal Ionisation Mass Spectrometer (Finnigan TRITON, Thermo Element GmbH, Bremen, Germany).

I Analysis of heavy metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

The samples were ground in a sintered aluminium oxide (sintered corundum) mortar, and depending on the samples type, 5 or 2.5 g of each sample were transferred to a 250 ml reaction vessel. After that 25 ml of aqua regia (mixture of three volumes of concentrated hydrochloric acid and one of nitric acid) were added. The samples were left for 12 h at room temperature and then boiled under reflux conditions for 2 h, afterwards, they were allowed to cool. The digest was filled to 100 ml with distilled water and then filtered (DIN 13346, 2000). The content of heavy metals was determined in each sample by ICP-MS.

3.3 Measurements of Sr and U isotopes using Thermal Ionisation Mass Spectrometry (TIMS)[*]

Mass spectrometry is a technique for separating the ions by their mass-to-charge ratio (m/z). Each element has at least one isotope that appears at a specific mass/ charge (m/z) value in the mass spectrum. Since a mass spectrometer separates and detects ions of slightly different masses, it easily distinguishes different isotopes of a given element (Christopher, 2000; Taylor, 2001).

In TIMS, the sample is placed on a filament that gets very hot to ionise the elements inside a high-vacuum chamber (Platzner, 1997). For TIMS it is necessary to isolate the element of interest, because the sample matrix has a huge influence on evaporation and ionisation. In this study, the separation of Sr was performed on a cation exchange column (Dowex W50-x8 resin) with HCl as eluent, whereas the separation of U was performed by UTEVA® resin.

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[*] These measurements were performed at the Physikalisch-Technische Bundesanstalt (PTB), Department 3.1 Metrology in Chemistry, Inorganic Analysis in Brauschweig.

3.3.1 *Measurements of R(^{87}Sr/^{86}Sr) in rock phosphates and P-fertilisers by Thermal Ionisation Mass Spectrometry*

This analytical tool was selected because of its high precision and high sensitivity isotope ratio measurements. In order to measure Sr isotope ratios in rock phosphates or P-fertilisers using TIMS, it is important to reduce impurities to a level low enough so they can not cause a significant error in the measurements of Sr (Moore *et al.,* 1982). Rb must be eliminated from Sr because ^{87}Rb is a direct isobaric interference onto ^{87}Sr. Small levels of Rb is not a problem because the Rb burns off before Sr data collection begins. However, the presence of significant amounts of Ca in the Sr cut prevents Rb burn-off, causing major interference problems (Dickin, 1995). Therefore, to obtain high-precision measurements of Sr isotope ratio (^{87}Sr/^{86}Sr), high purification of the Sr solution is required. Therefore, the normal starting point of precise isotopic measurements by mass spectrometry is chemical separation of the element to be analysed (Dickin, 1995). The separation of Sr was performed on a cation exchange column eluted with HCl then Sr isotope ratio was measured using TIMS (Fig. 3.2).

I Chemical separation of Sr

A The first experiment:

To avoid the matrix effect and to obtain high precision measurements of Sr isotope ratio, the separation of Sr from samples was tested in this experiment. To find out which fractions contain the most amounts of Sr and minimum amount of other elements, 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 deionised water in 5 steps (20 ml each time). For the elution, 214 ml of 2 M HCl in three steps (90, 80 and 40 ml) then 116 ml 5 M HCl were used as illustrated in Table A. 3.1. Five fractions (V0, V1, V2, V3 and V4) of 82, 20, 20, 45, 45 ml, as well as other 34 fractions (1 to 34) of 4 ml, and 2 fractions (N1, N2) of 20, 64 ml were collected and each of the obtained fractions was analysed by ICP-OES (Spectro Sciros CCD, Spectro Analytical Instruments GmbH, Kleve, Germany), to determine the fraction containing the main part of the Sr (Fig 3.3). This separation was performed at the Physikalisch-Technische Bundesanstalt (PTB), Department 3.1 Metrology in Chemistry, Inorganic Analysis in Braunschweig.

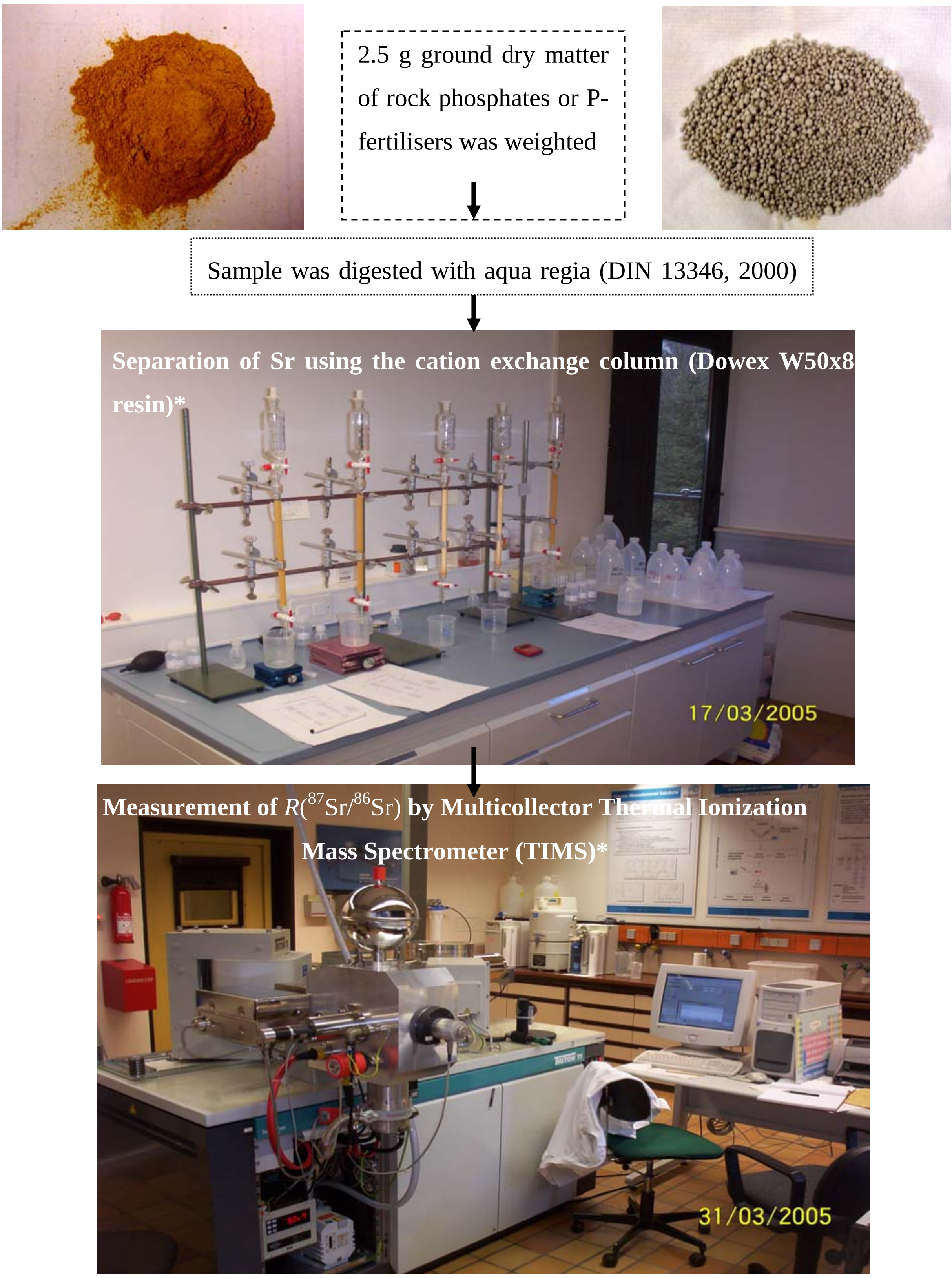

Fig. 3.2: Scheme for the separation and measurements of Sr isotopes in rock phosphates and P-fertilisers[*]

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[*] These measurements were performed at the Physikalisch-Technische Bundesanstalt (PTB), Department 3.1 Metrology in Chemistry, Inorganic Analysis in Brauschweig.

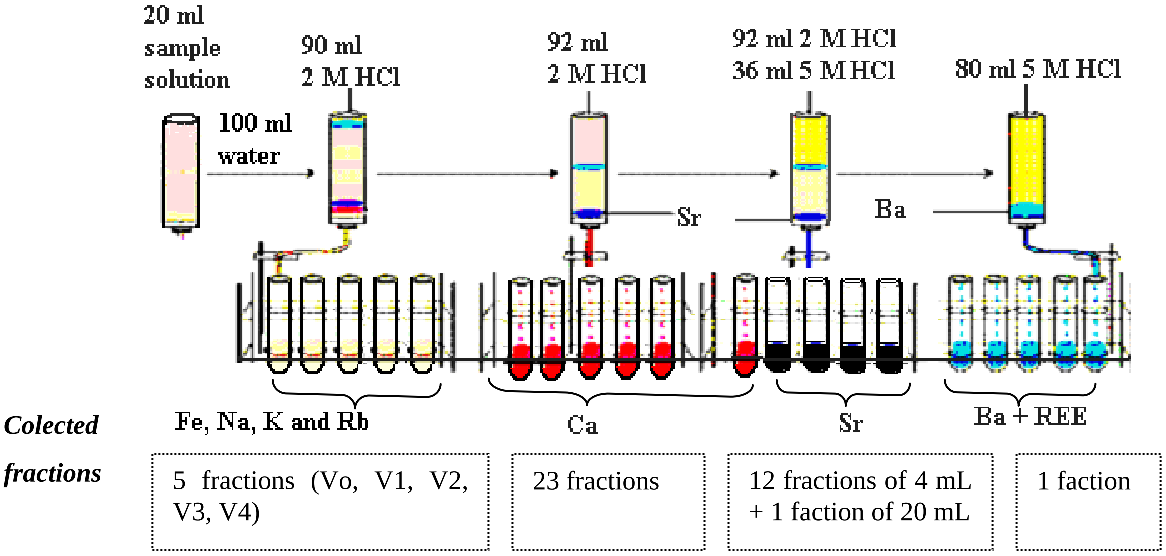


Fig 3.3: Chemical separation between Sr and Ca in cation exchange column (Dowex W50-x8 resin) in the first experiment

Results of chemical separation of 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 (Fig. 3.4).

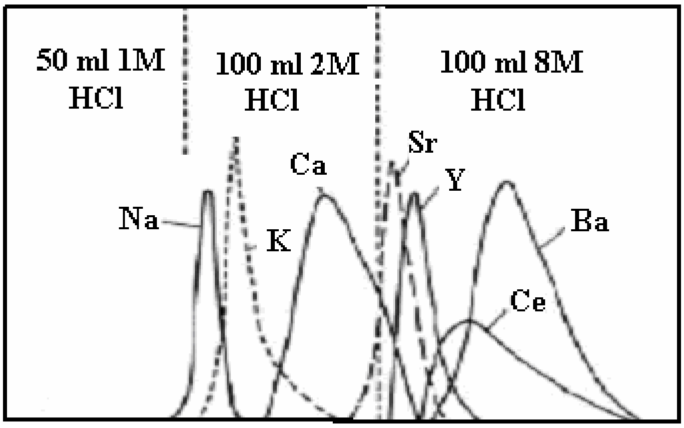


Fig. 3.4: Elution curves for various elements from cation exchange columns with hydrochloric acid (Crock et al., 1984)

The concentration of Sr and Ca in the each collected fraction of cation exchange column were analysed by ICP-OES (Spectro Sciros CCD, Spectro Analytical Instruments GmbH, Kleve, Germany) to determine Sr and Ca-content in different fractions. The collected small fractions from cation exchange using Dowex W50-X8 resin were selected carefully to obtain the most pure Sr solution. The collected fractions from number 24 until 34 and N1 contained high concentrations of Sr and very low concentrations of Ca (Fig. 3.5 and Table A. 3.2).

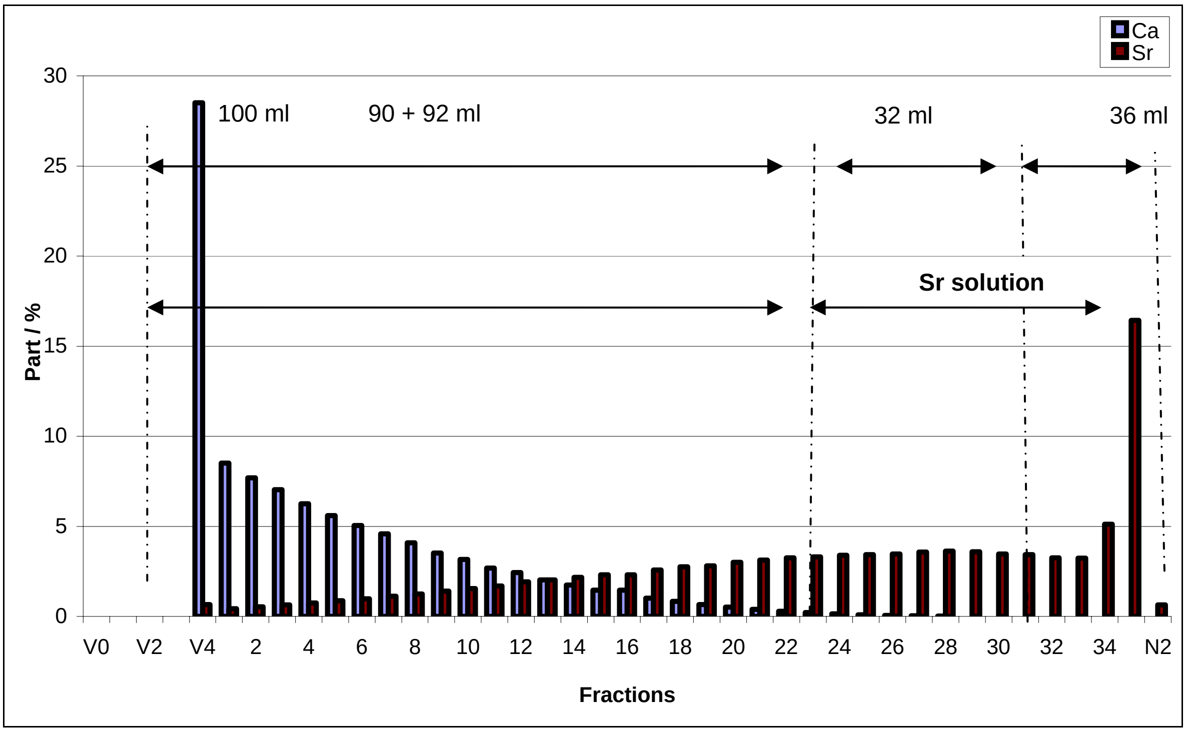


Fig. 3.5: Ca and Sr content in different fractions using the cation exchange resin Dowex W50x8 for the separation between Ca and Sr (Ex. 1)

B *The second experiment*

The method was repeated as described in the previous experiment. Excepting for the number of collected fractions. In this experiment, only five fractions were collected instead of forty one collected factions in previous experiment. Depending on the result of first experiment, all fractions containing the high concentrations of Sr and very low concentrations of Ca were collected together in one combined fraction not as separate fractions as illustrated in Table 3.2. The fractions coming before those containing the main part of Sr were collected in three fractions (V0, V1, and V2), while the fractions coming after it were collected in one fraction (V4). The obtained fractions were analysed by ICP-OES (Spectro Sciros CCD, Spectro Analytical Instruments GmbH, Kleve, Germany). Sr was separated in all analysed samples using this method.

Table 3.2: Steps to chemical separation between Sr and Ca in cation exchange column

Step	Added material			Collected solution
	Type	Concentration	Quantity	
1	Samples solution Little distilled water		20 ml To clean the tube	Vo
2	Distilled water		20 ml	
3			20 ml	
4			20 ml	
5			20 ml	
6			20 ml	
7	HCl	2 Mol/L	90 ml	V1
8			92 ml	V2
9			32 ml	Sr solution taken to measure Sr isotope ratio
10	HCl	5 Mol/L	36 ml	
11			80 ml	V4
12	Distilled water		20 ml	
13			20 ml	
14			20 ml	
15			20 ml	
16			20 ml	

Results of chemical separation of Sr

This method gave good recoveries (Table A. 3.3). It is possible to collect about 68% of Sr with only a low percentage of Ca (about 0.28% of total Ca) as it is shown in (Fig. 3.6).

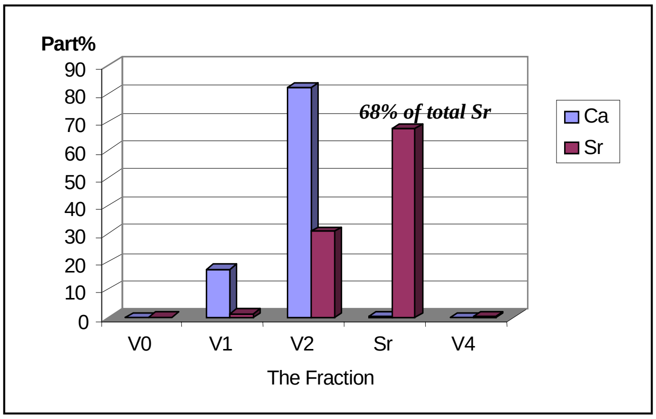


Fig. 3.6: Ca and Sr content in different collected fractions using the cation exchange resin Dowex W50x8 for the separation between Ca and Sr (Ex. 2)

III Measurements of $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ by TIMS

After Sr was isolated from its matrix, the determination of Sr isotope ratios was performed by double filament technique on a Multicollector Thermal Ionisation Mass Spectrometer (Finnigan TRITON, Thermo Element GmbH, Bremen, 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 dropwise on a 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 ionisation 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). ^{87}Sr isotopes usually interfere with ^{87}Rb. It is possible to overcome this problem by determining the signal for another isotope of the interfering element and by using the natural abundance information, by subtracting the appropriate signal from the analyte isotope signal. Rubidium interferences were determined simultaneously by monitoring ^{85}Rb. So, if ^{85}Rb appears, the $^{87}\mathrm{Sr}^+$ ion current can be corrected using the known $^{87}\mathrm{Rb}/^{85}\mathrm{Rb}$ ratio. The ^{87}Sr is corrected for ^{87}Rb by a simultaneous measurement of the ^{85}Rb (m/z=85) signal and using an $^{87}\mathrm{Rb}/^{85}\mathrm{Rb}$ value of 0.385705. However, a correction was only necessary in a few cases. Since the ratio $^{86}\mathrm{Sr}/^{88}\mathrm{Sr}$ 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.

$$R(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_{'true'} = R(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_{meas} \cdot \left(\frac{R(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_{'true'}}{R(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_{meas}} \right)^{\gamma}$$

$$\gamma = \left[\ln\left(\frac{M\left(^{87}\mathrm{Sr}\right)}{M\left(^{88}\mathrm{Sr}\right)} \right) \Big/ \ln\left(\frac{M\left(^{86}\mathrm{Sr}\right)}{M\left(^{88}\mathrm{Sr}\right)} \right) \right]$$

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 ionisation 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 (The SRM 987 ($SrCO_3$, isotopic) from the National Institute of Standards and Technology (NIST) was used for method validation). 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.

3.3.2 Measurements of $R(^{234}U/^{238}U)$- and $R(^{235}U/^{238}U)$ in rock phosphates and P-fertilisers by thermal ionisation mass spectrometry

The natural U is a mixture of three alpha emitting radionuclides (^{234}U, ^{235}U and ^{238}U). These natural isotopes each have a different half-life and activity (Table 3.3). Quantities of U isotopes, as well as other radioactive elements, are measured in units of mass (grams) or radioactivity (curies or becquerels), depending on the type of equipment available or the level that needs to be measured. Consequently, U isotope ratios are expressed either as atomic ratio (abundance ratio) or as activity ratio. If U isotope ratios were measured using alpha spectrometry, $R(^{234}\mathrm{U}/^{238}\mathrm{U})$ isotope activity ratio in the sample can be determined depending on α-particle energy spectrum, while $R(^{234}\mathrm{U}/^{238}\mathrm{U})$ atomic ratio can be measured using mass spectrometry depending on their masses. In very old, undisturbed natural U samples, which are in radioactive or secular equilibrium, the activity of ^{234}U is equal to the activity of ^{238}U, and the $R(^{234}\mathrm{U}/^{238}\mathrm{U})$-activity ratio is about 1 which is equal to an atomic ratio of 5.48×10^{-5}.

Table 3.3: Activities and half-lives and natural abundances of U isotopes (IAEA, 2007, IAEA, 2007^{b}; Kromphorn, 1996)

		^{234}U	**^{235}U**	**^{238}U**
Natural U (atom %)		0.0054	0.72	99.275
% by activity		48.9	2.2	48.9
Half-life		2.457×10^{5}	7.038×10^{8}	4.468×10^{9}
Specific activity (Bq mg^{-1})		2.313×10^{5}	80.011	12.445
Activity in 1 g natural U (Bq)		12.356	568	12.356
Average energy emitted per transformation (MeV Bq^{-1})	Alpha	4.84	4.47	4.26
	Beta	0.0013	0.048	0.01
	Gamma	0.002	0.154	0.001

The advantages of TIMS compared with conventional α-counting methods are: higher precision, smaller sample size and rapid analysis (Yokoyama and Esat 2004, Yokoyama, 1999). The first precise mass spectrometric analyses on ^{234}U were performed by Chen *et al.* (1986). In recent years, quadrupole inductively coupled plasma-mass spectrometry (ICP-QMS)) and high-resolution ICP-MS (HR-ICP-MS) have been increasingly applied for the analysis of long-lived radionuclides including U isotopes. These methods are relatively low cost, but the precision of the isotope ratios is poorer compared with TIMS and Multiple-

Collector ICP-MS (MC-ICP-MS) (Yoshida, 2001). It is reported that TIMS is the most reliable and precise method to determine U isotope ratios. Recently, new instrumental techniques, in particular multicollector ICP-MS, provide an advantage over TIMS in ease and rapidity of isotope analyses, but until now still cannot match TIMS in terms of accuracy of isotope ratio determination, especially for small samples (Taylor *et al.,* 1998; Fujikawa *et al.,* 2000; Howe et al., 2001; Richter and Goldberg 2003; Halicz et al., 2000).

I Sample preparation and testing prior the determination of U isotopes by TIMS

1 Principle of the method

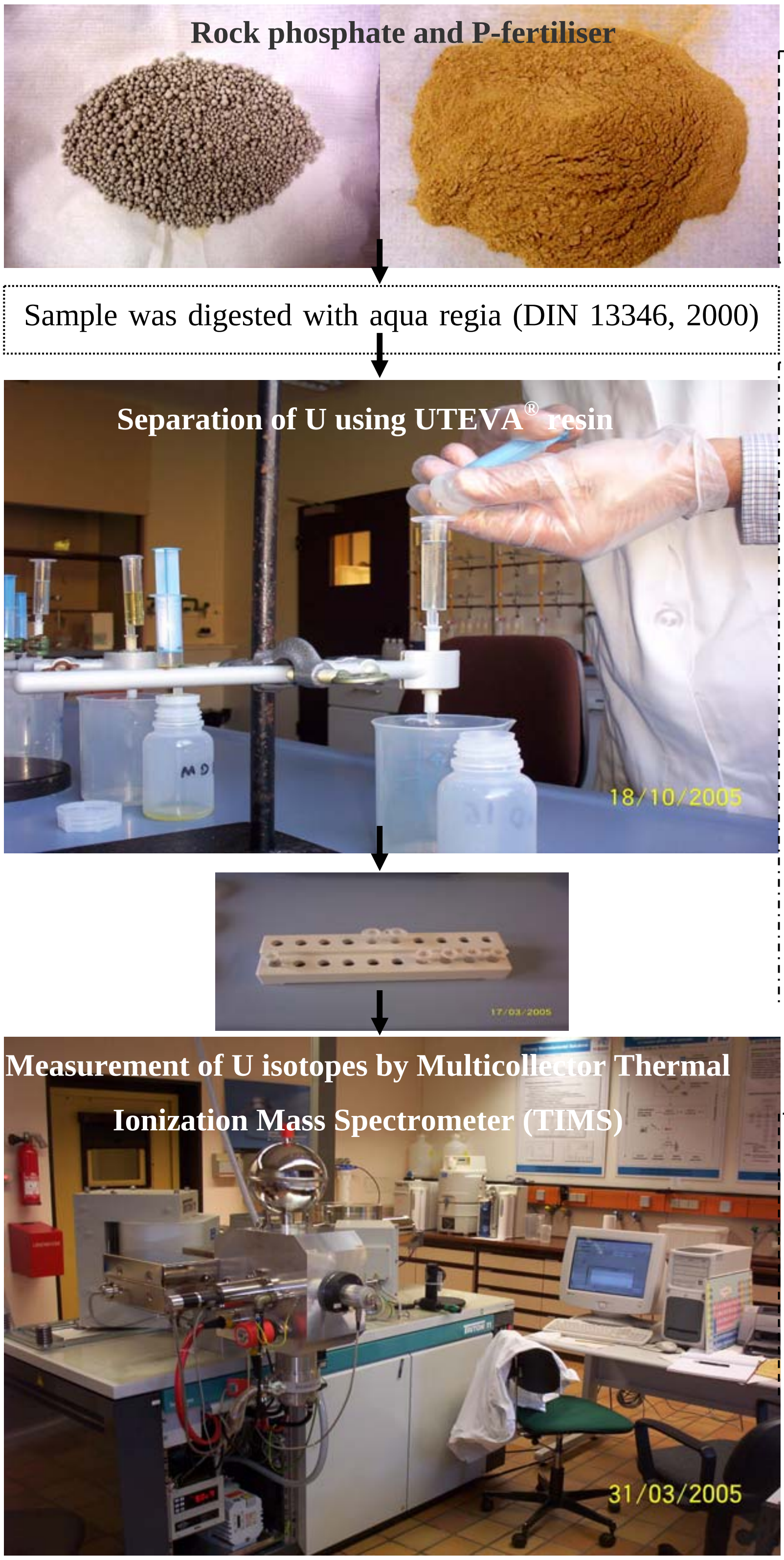
TIMS usually suffers from spectral interferences. In mass spectrometry there will be isobaric overlaps such as ^{238}U and ^{238}Pu, ^{234}Th and ^{234}U. Isobaric interferences are minimized by chemical separations of U prior to introduction of a sample to the mass spectrometer. In the present work, UTEVA® resin columns, manufactured by Eichrom, were utilized to separate U isotopes. The chemical structure of UTEVA® resin is diamyl amylphosphonate (DAAP) ($(C_5H_{11}O)_2C_2H_{11}PO$) as a specific extraction.

UTEVA® resin is able to separate and concentrate U and tetravalent actinides from an aqueous solution, while the trivalent nuclides like Am(III) and Pu(III) are not retained. The principle of this method depends on the formation of a complex between nitrate or chloride ions, actinides and DAP at high nitrate and/or chloride concentrations. The uptake of the actinides increases with increasing nitric acid concentration (Horwitz et al., 1992; Tagami and Uchida 2004) as illustrated in the following equation:

$$UO_2^{2+} + 2X^- + 2E = UO_2X_2E_2$$

Where: X: Cl^- *or* NO_3^-*; E:* diamyl amylphosphonate (DAAP)

From this equation, it can be observed that high chloride and/or nitrate concentration shifts the equilibrium to the right for the sorption of the cations, while at low chloride and/or nitrate concentrations the elution of the cations takes place. Pu(IV), Th(IV), Np(V) and U(VI) are well sorbed at high nitric acid or hydrochloric acid concentrations. U can be eluted from the resin with diluted nitric acid or hydrochloric acid. When the column condition is changed from 5 M HCl to 0.01 M HCl, the equilibrium tends to move to the left side (Yokoyama et al., 1999). In 5 M HCl U(VI) strongly sorbs, while Th(IV) does not, which makes the separation between U and Th possible (Solatie, 2002). U could be eluted from the resin afterwards with weak hydrochloric acid. In the present work, U was separated using UTEVA® resin, after that U isotope ratios was measured by TIMS (Fig. 3.7).



- **2.5 g ground dry matter of rock phosphates or P-fertilisers was weighted**

- **Separation of U was performed using UTEVA® resin (Eichrom, 2000)**
- **The obtained U-containing solution was evaporated to dryness**
- **1 ml H_2O_2 was added to the sample, then the sample was evaporated again**
- **The obtained samples were dissolved in 50 µl 2.5% HNO_3**

$R(^{234}U/^{238}U)$ and $R(^{235}U/^{238}U)$ were measured using Multicollector Thermal Ionization Mass Spectrometer (TIMS)

Fig. 3.7: The scheme for the separation and measurements of U isotopes in rock phosphates and P-fertilisers*

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* These measurements were performed at the Physikalisch-Technische Bundesanstalt (PTB), Department 3.1 Metrology in Chemistry, Inorganic Analysis in Brauschweig.

2 Sample Preparation before the chemical separation of U using UTEVA® resin

A chemical procedure for the isolation of U was performed using UTEVA® resin with little modification of the Eichrom analytical procedure (Eichrom, 2000). The separation and purification of U from samples solution using UTEVA® resin presented here offers a method for U separation using a single extraction column for U isotopic determination by TIMS. Depending on the concentration of U in the samples, 20 to 50 ml of the extraction solutions (aqua regia digests) was evaporated to dryness in crucibles on a sand bath adjusted to 170 ºC. After that 5 ml conc. HNO_3 were added and the obtained solution was evaporated to dryness. The evaporated sample was dissolved in 15 ml of 3M HNO_3 + 0.5M $Al(NO_3)_2$. Aluminium nitrate was used to increase the efficiency of the separation procedure. $Al(NO_3)_3$ was used to complex the phosphates naturally present in the sample. Phosphates form complexes with U and the use of Al^{3+} allows to let U "free" while complexing phosphates. With phosphate concentrations higher than 0.05 M, the affinity of U for UTEVA® starts decreasing. Syringe filter 25 mm with membranes with pore size of 0.2 µm, obtained from VWR International Gmbh Hanover, were used to remove insoluble materials. The filtered solution using polydisc filters and a syringe was loaded into UTEVA resin (Fig. 3.8).

3 U separation from Pu, Am and Th using UTEVA® resin

The U separation and purification is required to make a precise and accurate determination of U isotope ratios by TIMS. In the present work, U separation was performed using UTEVA® resin before the determination by TIMS. In order to remove unwanted interferences in the mass spectrum of U isotopes and to obtain optimal ionisation efficiency the chemical separations of U was performed in following steps:

- Preparation of UTEVA® column: columns were prepared using UTEVA® resin obtained from Eichrom industries. About 0.7 g of resin was weighed then the resin was transferred into 1.5 mL polypropylene columns using 3M HNO_3. Extract-Clean filter columns with two frits at the outlet end obtained from Allech Gmbh were used. They can remove particulate matter down to 20µm from samples. Filter columns were connected with syringe at the tops of columns.
- UTEVA® column was conditioned with 5 ml of 3 M HNO_3 (Fig. 3.8).
- The sample solution was loaded into a UTEVA® column and passed through it (to absorb the U).
- 2 × 5 ml of 3 M HNO_3 were added into the column and allowed to drain (Pu separation).

- 5 ml of 9 M HCl were added into the column in order to convert the resin to the chloride system.
- 20 ml of 5 M HCl-0.05 M oxalic acid were passed through the column (to remove Np, Th and Pu). In the presence of HCl, U is adsorbed onto the resin during the removal of Th and it is not necessary to add a secondary procedure to separate Th from U.
- U was eluted from the columns (isolated) by addition 10 ml of 0.1 M HCl.

The concentration of U in the different fractions was determined using ICP-MS.

This procedure yields essentially quantitative removal of most matrix constituents while recovery of U exceeds 90% using this method.

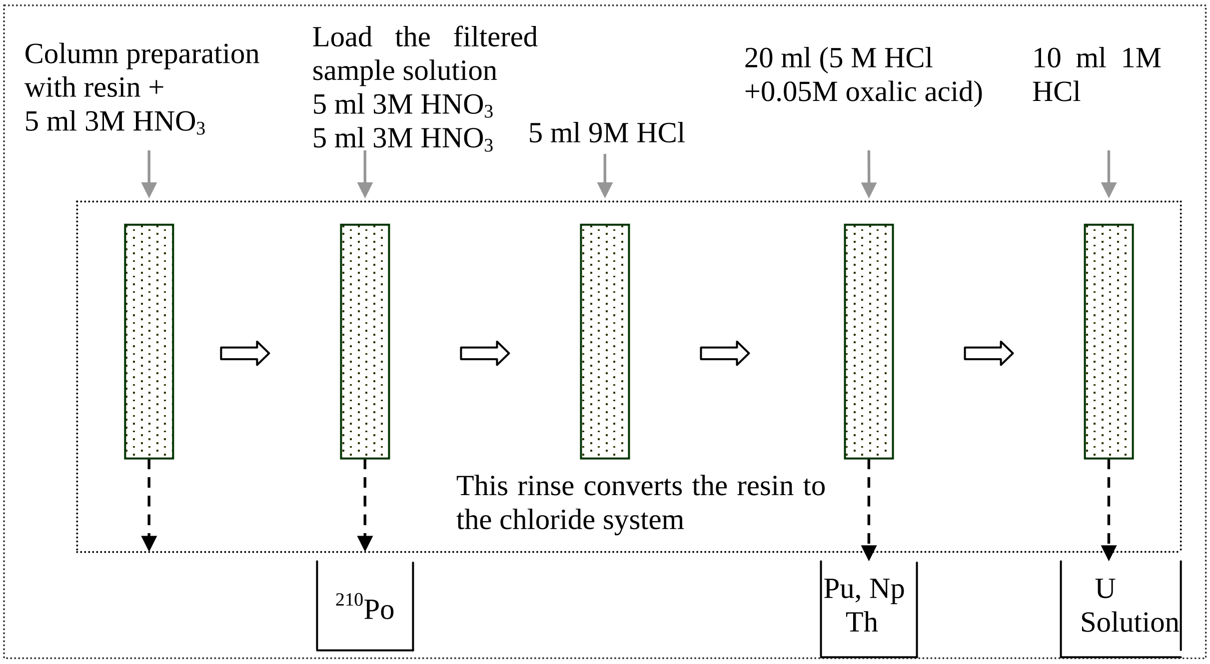


Fig. 3.8: The scheme for separation of U from samples using UTEVA® resin

4 Sample preparation to destroy organic materials

The method described above was tested successfully for P-fertilisers and rock phosphates. However, it was not possible to determine U isotope ratios in organic manure samples using this method. The low concentration of U combined with the presence of organic residue precluded the determination of U isotopes in organic manure. The presence of trace organic residues on the filaments in TIMS affects the ionisation efficiency of U (Sahoo *et al.*, 2004). Therefore, 7.5 g of organic manure sample was ashed at 470 °C overnight to destroy any organic matter present. After ashing, 1 g ashed manure was digested in aqua rqia and then prepared for U separation as it was described for rock phosphates and P-fertilisers.

Results of chemical separation of U isotopes using UTEVA® resin

Samples contaminated with other elements may inhibit or alter the ionisation of analysed elements. A single UTEVA resin was utilised to separate U isotopes from the sample matrix. In the present work, more than 90% of U was eluted with the first 10 ml of 0.1 M HNO_3 (fractions X3 and X4 in Fig. 3.9). The separated solutions were free from most of the matrix elements.

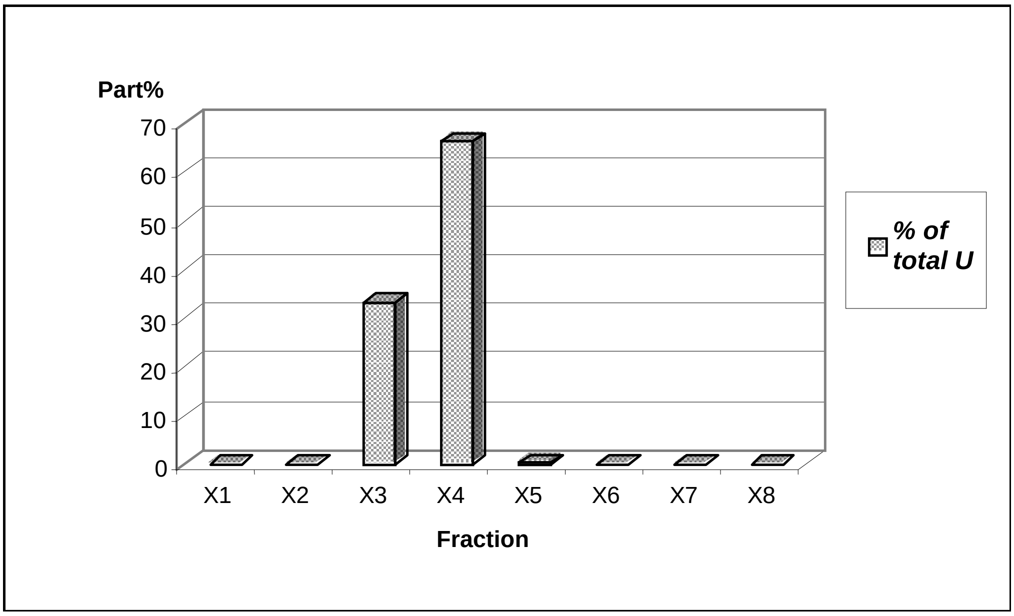


Fig. 3.9: The distribution of U among different fractions using UTEVA® resin

II Measurements of U isotopes by TIMS

After the separation of U, the solution was evaporated to dryness at 60-70 °C. The dry residues were redissolved in 1 ml H_2O_2 (30%) and again evaporated to dryness to remove the organic residues. The dry residues were then dissolved in 50 µl 2.5% HNO_3. 4 µL of this sample solution was used to determine U isotopes using TIMS. Only for two samples with a particularly low U content (<2 mg kg^{-1}) Multiple-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) was needed in order to successfully determine U isotopes.

3.5 Calculation and statistical analysis

The goal of this study was to identify the sources of rock phosphates and P-fertilisers. To this end, U and Sr isotope ratios as well as heavy metal contents in rock phosphates and different types of P-containing fertilisers were analysed. The significance of differences in the contents of P_2O_5, heavy metals, Sr isotope ratio and U isotope ratios in different rock phosphates were determined by analysis of variance (ANOVA). In order to identify the sources of rock phosphates by their heavy metal patterns, pattern recognition methodologies like discriminant analysis, feature extraction (principal components analysis and factor analysis) and hierarchical cluster analysis were applied.

3.5.1 Cluster analysis

In order to determine if rock phosphate samples collected from the same origin can be classified depending on their composition, cluster analysis was used. The cluster analysis' objective is to sort cases (people, things, events, etc) 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. There are a number of different algorithms and methods for grouping objects of similar kind into respective categories. Only hierarchical cluster analysis, using Average Linkage (Between Groups) was used. In this method, the distance between two clusters is defined as the average of the distances between all pairs of individuals (Everitt, 1993).

3.5.2 Discriminant function analysis

In order to check if it is possible to discriminate among rock phosphate samples depending on their content of heavy metals, discriminant function analysis (DA) was used. The objective of DA is the investigation of differences among groups and the classification of cases into groups. Also, DA is used to determine which variables discriminate between two or more naturally occurring groups.

DA is broken into a two-step process: (1) testing the significance of a set of discriminant functions; (2) classification. There are several tests of significance, but only Wilks' lambda was used here. The smaller the lambda for an independent variable, the more that variable contributes to the discriminant function. Lambda varies from 0 to 1, with 0 meaning group means differ, and 1 meaning all group means are the same. The F test and Wilks' lambda show which variables' contributions are significant. Once group means are found to be statistically significant, classification of variables is undertaken. DA automatically determines some optimal combination of variables so that the first function provides the most overall discrimination between groups; the second provides second most, and so on. The first function picks up the most variation, the second function picks up the greatest part of the unexplained variation, etc. With more than two groups one can obtain more than one discriminant function. One can find a total of K-1 (number of groups minus 1) or p (number of predictor variables) orthogonal discriminant functions, whichever is smaller (Jonson and Wichern, 2002; Everitt and Dunn 2001).

3.5.3 Principal components and factor analysis

In order to determine which metal can be used to identify the sources of the samples as well as to identify a limited number of factors, which explain a significant part of the variance, principal components and factor analysis were used.

The main applications of factor analytic techniques are: (1) To reduce the complex data sets with numerous number of variables to a limited number of factors or components (2) to detect structures in the relationships between variables, which help to classify variables. Therefore, factor analysis was applied as a data reduction or structure detection method. Principal components analysis (PCA) was used to form a subset of uncorrelated theoretical variables called principal components (PC) that adequately explain the variation in the original variable set. This method uses linear transformation of original variables to create a new set of uncorrelated variables so that the original values are re-projected onto a new set of orthogonal axes. The method is a three-step procedure, whereby (i) input data are standardized (ii) the correlation matrix is computed (iii) Eigenvalues and eigenvectors from the variance- covariance matrix are extracted. PC is obtained by projecting the multivariate datavectors on the space spanned by the eigenvectors. The eigenvector associated with the largest eigenvalue has the same direction as the first PC and shows the largest variance of the projected data. The eigenvector associated with the second largest eigenvalue determines the direction of the second PC, displays the next largest variance and is orthogonal to the first, and so on (Jonson and Wichern, 2002).

All statistical analyses were performed by SPSS version 12.0 for windows (SPSS Inc., Chicago, IL, USA).

The rock phosphate samples were grouped and classified using cluster analysis and discriminant analysis based on heavy metals content. The idea behind this step was that if the different rock phosphate samples of same origin have a similar composition of heavy metals, these samples should be classified together in one group using cluster analysis or discriminant analysis. Moreover, if the rock phosphate samples of different origin have a different composition of heavy metals, these samples should be classified into different groups. If so, it will be possible to identify the source of particular rock phosphates by their heavy metal patterns.

The importance of each element as an indicator for origin was determined as follows: (1) Natural relationships among heavy metals were investigated by determining the correlation among different metals in order to classify the heavy metals depending on their correlations and associations with each other. (2) Principal components and factor analysis were applied to reduce the number of variables and to identify the metals which can be used for fingerprinting.

3.5.4 Calculation of isotope ratios in P-fertilisers or rock phosphates used to produce compound fertilisers in order to trace back the origin of P-components in compound fertilisers

The use of isotope ratios of one element for examining the origin of P-components in compound fertilisers and organo-mineral fertilisers is possible if isotope ratios of this particular element in different raw materials are known. When a mixture consists of two different sources with different isotope ratio, the isotope ratio of the mixture reflects the relative contribution from each source. Stable isotope ratios have increasingly been used to determine the relative contribution of several sources to a mixture in ecological and geochemical research. For example, mixing mass-balance models, which were used to estimate various food sources in animal diets by determinations of isotope ratios in their tissues (Phillips and Gregg, 2001), can be used to determine the proportions of each source in the mixture such as compound fertilisers.

With one isotope system and two sources, the following system of mass balance equations can be solved to determine the proportions (f_A, f_B) of source isotopic signatures (α_A, α_B), which coincide with the observed signature for the mixture (α_M). Isotopic composition of the mixture (α_M) equals the weighed average of the isotopic composition of the mixture constituents. For two mixture constituents, this results in the following equations:

$$\alpha_M = f_A\alpha_A + f_B\alpha_B \ldots\ldots\ldots\ldots\ldots\ldots\ldots A$$

$$1 = f_A + f_B \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots B$$

Substituting f_B in equation (A) gives the following equation:

$$\alpha_M = f_A\alpha_A + (1 - f_A)\alpha_B$$

Where: f_A, f_B denote the fraction of source A, B respectively. α_A and α_B are the isotopic compositions of the components A and B. α_M is the isotopic composition of the mixture.

This system of equations can be extended to include more than two sources. For example, with two isotopes e.g. (^{13}C, ^{15}N) and three sources (A, B and C), according to Phillips and Gregg (2003) the following equations pertain:

$$\alpha^{15}N_M = f_A\alpha^{15}N_A + f_B\alpha^{15}N_B + f_C\alpha^{15}N_C$$

$$\alpha^{13}C_M = f_A\alpha^{13}C_A + f_B\alpha^{13}C_B + f_C\alpha^{13}C_C$$

$$1 = f_A + f_B + f_C$$

In compound (NPK) fertilisers, the Sr or U isotope ratio of the mixture (NPK) depends on the relative contribution from each source. In this context, the Sr and U isotope ratio of P-fertilisers or rock phosphates which were used to produce the compound fertilisers can be calculated if Sr and U isotope ratios as well as the amounts of Sr and U from each source (except P) are known.

4 Results

The main objective of this work was to identify and characterise the origin of rock phosphates and P-containing fertilisers using their heavy metal pattern and Sr and U isotope ratios. In the first two subchapters (4.1 and 4.2), microelement (Mn, Zn, Cu, B and Mo) and heavy metal (As, Be, Cd, Co, Cr, Ni, Pb, Sb, Se, Sr, Ti, Tl and U) concentrations in rock phosphates and P-fertiliser samples are reported. The concentrations of U and Sr in different P-containing fertilisers are studied in more detail in subchapters 4.3 and 4.4. Results of multivariate statistical analysis, including discriminate analysis, cluster analysis and principal component analysis, are summarised in subchapter 4.5. Results of Sr and U isotope ratio measurements in different types of P-containing mineral fertilisers are described in subchapters 4.6 and 4.7.
All data reported in the following chapters is referred to the original substance.

4.1 Phosphorus and microelements in rock phosphates from different origin

Phosphorus was present in high quantity in all samples (Fig 4.1 and Table A. 2.1). The total phosphorus values (expressed in P_2O_5%) ranged from 24.6% up to 38.8% (Table A. 2.2). The concentration of P_2O_5 was significantly higher in rock phosphates from the Russian Kola Peninsula (38.8%), Senegal (36.6%) and Togo (36.4%), than in rock phosphates from the USA (33.1%), Israel (33.1%) and Morocco (33.4), Tunisia (27.8%) and Syria (24.6%).

In addition, all rock phosphate samples contained considerable concentrations of microelements (Mn, Cu, Zn, B, Mo) (see tables in appendix A. 2.1 and A. 2.2). The concentration of Mn in rock phosphates from Algeria, Morocco, Syria, Tunisia and Israel was significantly lower (with concentration values ranging from 5.27 to 35.4 mg kg^{-1} original substance) than in rock phosphates from the Russian Kola Peninsula, the USA, and Senegal, with concentration values ranging from 121 to 245 mg kg^{-1}, while it ranged from 46 to 207 mg kg^{-1} in rock phosphates from Togo. The concentration of Cu in rock phosphates from different origin was from 5.70 to 54.6 mg kg^{-1}. Cu ranged in Moroccan rock phosphates from 10.2 to 54.6 mg kg^{-1}, this wide range overlapped with most other samples.

The concentration of Zn was the lowest in rock phosphates from Russian Kola Peninsula with values from 10.5 to 26.7 mg kg^{-1}, while in sedimentary rock phosphates it ranged from 54.0 to 500 mg kg^{-1}.

Average of B concentrations in rock phosphate samples varied, depending on their origins, from 39.0 up to 913 mg kg^{-1}. However, B ranged in Moroccan rock phosphates from 268 to 872 mg kg^{-1}. This range overlapped with most other samples.

The concentration of Mo was significantly lower in rock phosphates from Russian Kola Peninsula (ranging from 0.56 to 1.88 mg kg^{-1}) than sedimentary rock phosphates (ranging from 1.40 to 26.5 mg kg^{-1}), while rock phosphates from Israel have the highest content of Mo (21.1 mg kg^{-1}) within sedimentary rock phosphates.

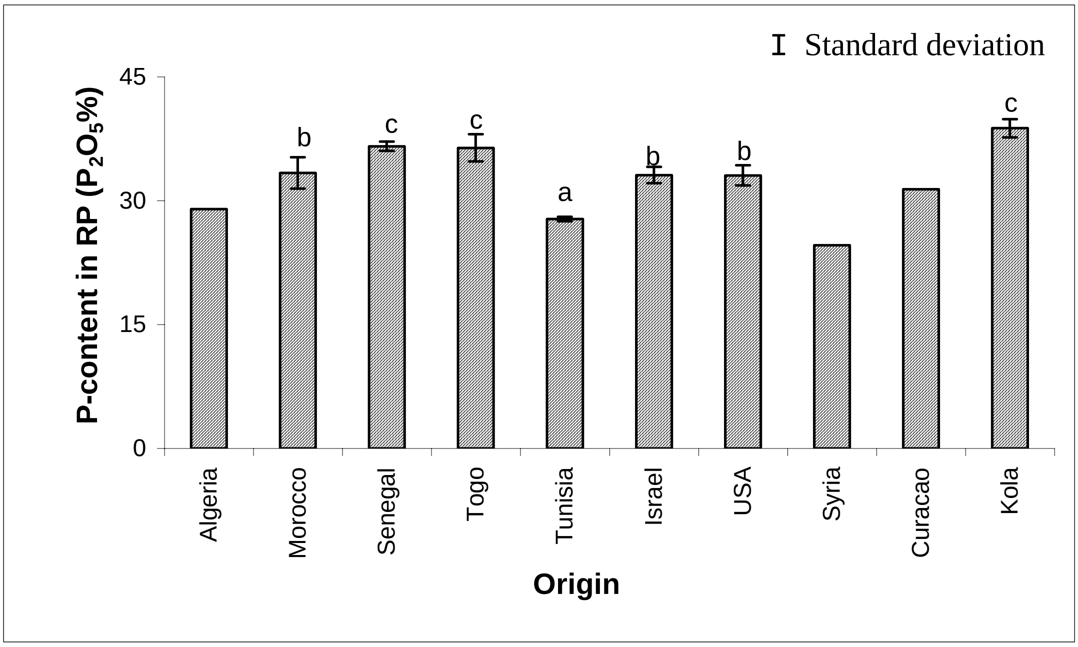


Fig. 4.1: Average of P_2O_5 in rock phosphates from different origin (Different letters denote significant differences between P_2O_5 content in rock phosphates from different origin by Duncan's test at P <0.05, no test performed for Algeria, Syria, Curacao, because n<3).

4.2 Heavy metals in rock phosphates and P-fertilisers from different origin

The rock phosphates of 10 different origin showed considerable variation of As, Be, Cd, Co, Cr, Ni, Pb, Sb, Se Sr, Ti, Tl and U contents according to their geographical origin (Table A. 2.1). As is shown in Table A. 2.3, all these elements were found in detectable amounts in rock phosphate samples, except for Cd in rock phosphates from the Russian Kola Peninsula; Bi in rock phosphates from the Russian Kola Peninsula and some samples from Morocco, Senegal, Israel, Togo and Tunisia; Tl in rock phosphates from the Russian Kola Peninsula, Curacao and some samples from Morocco, Israel and Senegal. In these cases, the concentration was below the limit of quantitation.

In general, the concentrations of As, Cd, Cr, Ni, U were higher in sedimentary rock phosphates of different origin than in igneous rock phosphates from the Russian Kola Peninsula (Table A. 2.2), while Tl and Sr were significantly higher in igneous rock phosphates from the Russian Kola Peninsula than in sedimentary rock phosphates.

The presence of elevated concentrations of Cd is of greatest concern due to its high toxicity. The lowest level of Cd was detected in the rock phosphates from the Russian Kola Peninsula (0.0 to 0.04 mg kg^{-1}), while the highest concentration of Cd was detected in the rock phosphates from Senegal (67.5 to 106 mg kg^{-1}).

Sr content in rock phosphates ranged from 287 to 23016 mg kg^{-1}. Fig. 4.2 shows that the highest concentration was found in rock phosphates from the Russian Kola Peninsula (18596 to 23016 mg kg^{-1}). Within sedimentary rock phosphates it ranged from 287 to 3737 mg kg^{-1}.

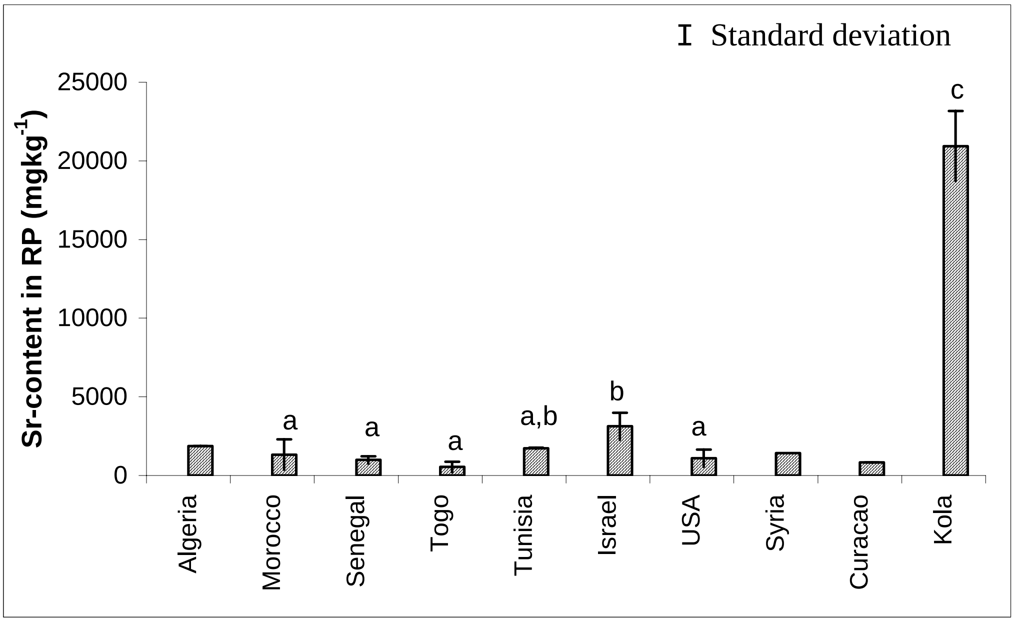


Fig. 4.2: Average content of Sr in rock phosphates from different origin (No test performed for Algeria, Syria, Curacao, because n<3. Different letters denote significant differences between Sr content in rock phosphate from different origin by Duncan's test at P <0.05).

U contents were greater and more variable in sedimentary rock phosphates from different origin compared with igneous rock phosphates from the Russian Kola Peninsula (Fig. 4.3). U contents were significantly lower in rock phosphates from the Russian Kola Peninsula and Tunisia than other origins, and the highest content of this element was found in rock phosphates from Israel.

The concentrations of hazardous elements, including heavy metals and radionuclide (U), not only differed greatly between sedimentary and igneous rock phosphates but also they varied widely within sedimentary rock phosphates of different origin. Therefore, the concentration of heavy metals and radionuclide (U) might discriminate and indicate the origins of rock phosphates.

In this study it was noticed that the concentration of some metals varied widely in rock phosphates even within the same origin. For example: in Moroccan rock phosphates, Sr ranged from 287 to 2958 mg kg^{-1}, U ranged from 71.1 to 245 mg kg^{-1}. Mn in rock phosphates from

Togo ranged from 46.7 to 207 mg kg^{-1}. In rock phosphates from the USA, Zn ranged from 54.9 to 259 mg kg^{-1} and U ranged from 65.5 to 153 mg kg^{-1}.

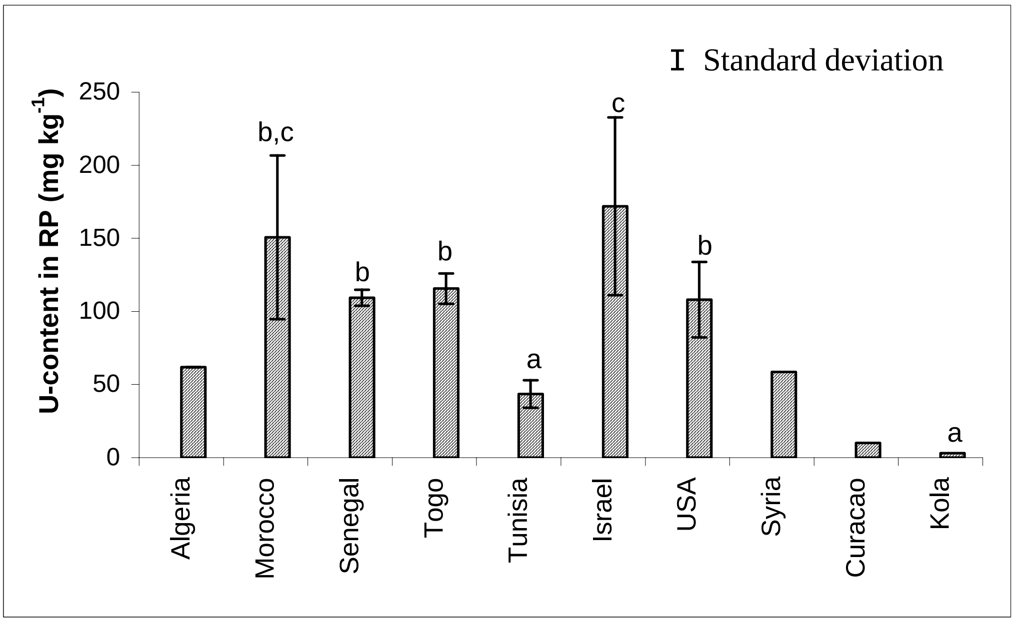


Fig. 4.3: Average concentration of U in rock phosphates from different origin (Different letters denote significant differences between U content in rock phosphates of different origin by Duncan's test at P <0.05, no test performed for Algeria, Syria, Curacao, because n<3).

In five cases, the sample collection allowed for a comparison of microelement and heavy metals contents in P-fertilisers and rock phosphates of the respective origin (Table 4.1, Table 4.2 and Table A. 2.4 in the appendix). From this data it appears that the largest part of several heavy metals present in rock phosphates, such as U, Cd, As, Cr and Co, transfers from rock phosphates to P-fertilisers (Table 4.2). However, heavy metal content in fertilisers is highly variable and depends not only on the heavy metal content of the raw material of different origin (rock phosphate ores), but also on the type of manufacturing process applied for fertiliser production (Mortvedt, 1996; Mortvedt and Beaton, 1995). Due to these variations in the transfer of micro elements and heavy metals from rock phosphates to P-fertilisers, it is very difficult, if not impossible, to trace back the origin of a P-fertiliser based on its elemental pattern alone (see the introduction). As can be seen in Table A. 2.5, a significant part of Sr, B, and Pb were transferred to the (by-product) phosphogypsum. An opposite trend was observed for the concentrations of As, Co, Sb, Tl, which were very low in phosphogypsum.

Table 4.1: Phosphorous and microelement concentrations in P-fertilisers and corresponding rock phosphates as [%]

Country/ Origin	Type of sample	P [%]	Microelements [%]				
			Mn	Zn	Cu	B	Mo
Morocco	Rock phosphate	14.1	0.0010	0.023	0.0028	0.065	0.00046
	P-fertiliser	7.03	0.0044	0.009	0.0013	0.030	0.00029
	Rock phosphate	9.76	0.0014	0.022	0.0024	0.073	0.00028
	P-fertiliser	14.2	0.0014	0.017	0.0021	0.049	0.00025
Syria	Rock phosphate	10.9	0.0007	0.032	0.0006	0.038	0.00060
	P-fertiliser	18.7	0.0014	0.032	0.0006	0.083	0.00061
Israel	Rock phosphate	14.4	0.0009	0.033	0.0013	0.082	0.00265
	P-fertiliser	10.6	0.0004	0.027	0.0017	0.069	0.00181
USA	Rock phosphate	14.5	0.0138	0.008	0.0009	0.041	0.00045
	P-fertiliser	8.60	0.0073	0.006	0.0007	0.018	0.00024

Table 4.2: Heavy metal contents in P-fertilisers and corresponding rock phosphates

Country/ Origin	Type of sample	Heavy metals [mg kg^{-1}]												
		As	Be	Cd	Co	Cr	Ni	Pb	Sb	Se	Sr	Ti	Tl	U
Morocco	Rock phosphate	11.5	1.69	18.3	0.68	208	38.6	4.27	2.77	2.53	950	225	0.16	133
	P-fertiliser	5.58	0.83	6.65	1.34	68.9	22.4	4.23	1.99	1.02	538	140	0.47	63.6
	Rock phosphate	12.0	1.50	22.9	0.74	177	28.0	4.38	2.78	2.54	1001	255	0.09	129
	P-fertiliser	9.80	1.14	15.7	0.66	129	23.0	3.76	2.09	2.23	717	187	0.09	94.7
Syria	Rock phosphate	4.32	0.51	6.10	0.89	266	31.4	3.74	0.99	-	1238	40.4	0.13	58.6
	P-fertiliser	3.12	0.92	7.76	0.58	198	20.5	2.26	0.76	-	891	27.2	0.13	85.4
Israel	Rock phosphate	3.76	0.78	18.9	-	46.9	21.3	3.60	1.12	5.06	2508	209	0.54	129
	P-fertiliser	5.63	0.50	22.0	-	39.2	25.6	4.45	1.25	4.28	1629	138	0.48	99.8
USA	Rock phosphate	5.16	1.41	8.37	2.61	45.0	17.1	9.76	1.99	1.21	1154	394	0.44	121
	P-fertiliser	2.25	0.82	6.17	1.36	32.1	12.3	10.3	1.48	1.42	646	391	0.24	66.4

(-) Concentration lower detection limit.

4.3 U concentration in different types of rock phosphates and P-containing fertilisers

In the present work, U concentrations in sedimentary rock phosphates were greater than in igneous rock phosphates, mineral P-fertilisers, organo-mineral fertilisers and farmyard manures (Table 4.3). The concentration of U in different types of P-containing fertilisers decreased in the following order: Sedimentary rock phosphates of different origin > P-fertilisers made of sedimentary rock phosphates > P-containing mineral fertilisers > Organo-mineral fertilisers > chicken manure > pig manure > igneous RP > dairy cow and calf manures. The U content in sedimentary rock phosphates analysed in the present work was in the range of 27 to 245 mg kg^{-1}, while the U content in igneous rock phosphates from the Russian Kola Peninsula ranged from 3 to 3.35 mg kg^{-1} (Table 4.3). The largest amount of U is transferred into P mineral fertilisers as described in introduction and chapter 4.2, because U tends to go into the acid solution during the production process of P-fertilisers, whereas the by-product (phosphogypsum) has a low U concentration (0.26 to 9.20 mg kg^{-1}) (Table A. 2.5). U concentration in P-containing mineral fertilisers was relatively high, ranging from 56.0 to 129 mg kg^{-1} (Table 4.3).

Table 4.3: Average concentrations and ranges of U and P_2O_5% as well as U/P_2O ratio in different types of P-containing fertilisers

	n	**U [mg kg^{-1}] original substance]**		**P_2O_5 [%]**		**U/P_2O_5**
		Average	Range	Average	Range	
Igneous RP from Kola	6	3.15	3.04-3.35	38.8	37.6-39.9	0.08E-04
Sedimentary RP	53	104	27.0-245	33.2	24.6-37.5	3.42E-04
Straight P fertilisers	9	80.8	56.0-129	22.5	18.0-30.5	3.69E-04
PK-fertilisers	9	53.6	29.0-83.0	14.7	10.0-20.0	3.60E-04
NPK-fertilisers	16	32.4	9.00-44.0	12.2	8.00-15.0	2.68E-04
Organo-mineral fertilisers	4	19.9	7.39-27.6	6.00	4.00-8.00	3.48E-04
Pig manure	3	3.40	2.00-5.25	4.67	3.79-6.23	0.74E-04
Chicken manure	3	3.60	3.00-4.89	3.60	3.26-4.10	1.00E-04
Dairy cow and calf manure	4	1.22	1.15-1.35	1.50	0.95-1.87	0.81E-04

I U concentration in rock phosphates from different origin

The average and range of U concentrations of U of 51 samples of 10 different origin are given in Table 4.4. The average concentration of U in sedimentary rock phosphates increased in the following order: Tunisia < Algeria < Syria < Senegal < USA < Togo < Israel < Morocco. In the literature, the concentration of an element in rock phosphate was compared with average of shale as standard (Van Kauwenbegh, 1997). Similar comparison in this study revealed that all sedimentary rock phosphates were enriched in U over the shale by a factor ranging from 3.11 to 44.6, while U concentration in igneous rock phosphates of the Russian Kola Peninsula was little lower than in shale (Table 4.4). However, it was clear in the present work and in literature data that sedimentary rock phosphates varied widely in their U content, even within the same country such as Morocco and the USA. Ranges of U concentration in samples from Algeria, Morocco, Tunisia, and USA agree well with the ranges of U concentration found in the literature. Only U content in RP7 from Morocco (Khouribga) was higher data obtained by other authors, with values of 245 mg kg^{-1}. U contents in rock phosphates from Senegal and Togo were little higher, while U content in rock phosphates from Syria and the Russian Kola Peninsula was lower than data presented in the literature.

Table 4.4: Average and ranges of U concentration measured in this study in comparison to literature values (Kratz and Schnug, 2006; El-Ghawi *et al.*, 1999; Van Kauwenbegh, 1997)

Origin s=sedimentary, i=igneous, b=biogenic	**n**	**U-content in present work**			**In literature**
		Mean ± Std. dev. [mg kg^{-1}]	**Range [mg kg^{-1}]**	**Enrichment or (depletion) factor [a]**	**Ranges of U [mg kg^{-1}]**
Algeria (s)	5	44.2±10.0	38.0-62.0	13.8	25.0-100
Morocco (s)	8	143±49.4	71.0-245	44.7	70.0-140
Senegal (s)	3	109±5.51	104-115	34.2	64.0-70.0
Togo (s)	5	116±10.5	107-132	36.1	77.0-110
Syria (s)	1	58.6	nd	18.3	75.0-106
Tunisia (s)	6	36.1±7.99	26.7-50.2	11.3	12.0-88.0
Israel (s)	7	140±33.5	120-215	43.8	99.0-155
USA (s)	12	113±30.8	65.5-171	35.3	41.0-200
Curacao (b)	1	9.96	nd	3.11	nd
Russian Kola Peninsula (i)	3	3.15±0.17	3.04-3.35	(1.01)	20.0-40.0

[a] Enrichment or (depletion) factor was determined by comparison with average of U in shale (3.2 mg kg^{-1}) according to Carmichael (1982) cited from Van Kauwenberg, 1997. nd: no data available.

II U/P_2O_5 ratio in different types of P-fertilisers

U concentration by itself is not a sufficient criterion for the quality of a P-fertiliser in terms of heavy metal load. More important is the U/P_2O_5 ratio because this parameter determines how much U is loaded onto a soil at a given P rate. Sedimentary rock phosphates were characterised by high U/P_2O_5 ratio ranging from 1.3 x 10^{-4} to 7.3 x 10^{-4}, while this ratio ranged from 0.078 to 0.085 in igneous rock phosphates from Kola (Table 4.5).

Table 4.5: U and P_2O_5 contents and U/P_2O_5 in rock phosphates from different origin

Country	**Deposit**	**U [mg kg^{-1}]**	**P_2O_5 [%]**	**U/P_2O_5 x 10^{-4}**
Algeria		62.0	29.0	2.13
		38.0		
		39.3		
		40.7		
		41.3		
Morocco		157	35.8	4.39
		118		
		121		
Morocco		146	35.5	4.11
	Spanish Sahara Bu Craa	71.0	32.6	2.18
	Khouribga	152	31.1	4.88
	Khouribga	133	31.9	4.19
	Khouribga	245	33.2	7.37
Senegal	Taiba	115	37.1	3.10
	Taiba	104	36.8	2.82
	Taiba	109	36.0	3.03
Africa	Togo	107	37.1	2.88
	Togo	132	37.3	3.54
	Togo	120	33.5	3.58
	Togo	109	36.7	2.97
	Togo	110	37.5	2.93
Syria		58.6	24.6	2.38
Tunisia	Gafsa	50.2	28.0	1.79
	Gafsa	36.9	27.6	1.34
		36.2		
		26.7		
		36.2		
		29.9		
Israel	Nahal Zin	129	32.4	3.98
	Oron	215	33.8	6.36
	Arad	120		
		121		
		132		
		131		
		132		
USA		121	32.7	3.70
		117	35.4	3.30
	Pebble phosphate	153	31.9	4.80
	Pebble-phosphate	114	33.1	3.44
Florida		122	33.2	3.68
		123	34.2	3.60
		106		
		171		
		65.5	34.2	1.92
North Florida	Pebble-phosphate	70.5	31.7	2.23
South Florida	Pebble-phosphate	110	32.4	3.40
North Carolina		80.4	32.0	2.51
Curacao		9.96	31.4	0.32
Russia	Russian Kola Peninsula	3.35	39.9	0.08
	Russian Kola Peninsula	3.07	37.6	0.08
	Russian Kola Peninsula	3.04	38.9	0.08

It ranged from 0.33 to 1.38 in farmyard manures (Table 4.6). The U/P_2O_5 in animal manures was lower than organo-mineral fertilisers, and lower than in P-fertilisers or rock phosphate (except igneous rock phosphate from the Russian Kola Peninsula).

Table 4.6: P_2O_5 and U concentration and U/P_2O_5 ratio in farmyard manures and organo-mineral fertilisers

Farmyard manures	Sample ID	Dry matter [%]	U [mg kg^{-1} dry matter]	P_2O_5 [%]	U/P_2O_5 x 10^{-4}
Chicken (Poultry)	Chic. 1	13.9	3.98	3.26	1.22
	Chic. 2	13.1	3.00	3.27	0.92
	Chic. 3	33.3	4.89	4.10	1.19
Dairy and beef cattle	Cow2	21.1	1.15	1.87	0.61
	Cow3	22.0	1.34	1.50	0.90
	Cow4	16.0	1.30	0.95	1.36
Pigs	G1	13.5	3.04	3.73	0.81
	G2	26.4	2.00	6.23	0.33
	G3	21.3	5.25	3.79	1.38
Organo-mineral fertilisers	OMF 1	nd	24.8	4.00	6.19
	OMF 2	nd	7.39	5.00	1.48
	OMF 3	nd	19.8	7.00	2.83
	OMF 4	nd	27.6	8.00	3.45

nd: not determined.

III Determination the origin of P-fertilisers from different manufacturers based on U/P_2O_5 ratio

As can be seen in Table 4.7, U/P_2O_5 not only varies between different types of fertilisers (mineral/ organic/ organo-mineral), but it may also vary between fertilisers produced by different manufacturers. Comparing the ratios shown in Table 4.7 to those of rock phosphates (Table 4.3 and Table 4.5), it can be assumed that igneous rock phosphates (e. g. Russian Kola Peninsula) were used by Ruhr-Stickstoff AG (Bochum), while sedimentary rock phosphates were used by other manufacturers.

Table 4.7: Content of N, P_2O_5, K_2O and U as well as U/P_2O_5 in different types of mineral P-fertilisers from different manufacturers

Manufacturer	**Type**	**Sample ID**	**N [%]**	**P_2O_5 [%]**	**K_20 [%]**	**U [mg kg^{-1}]**	**U/P_2O_5 *10^{-4}**
BASF (Ludwigshafen)	P-fertiliser	P 8		18		74.8	4.16
		P 9		20		73.0	3.65
	PK-fertiliser	PK 9		16	16	52.0	3.25
	NP-fertiliser	NP 3	20	20		73.0	3.65
	NPK-fertiliser	NPK 1	11.5	8.5	18	39.5	4.65
		NPK 2	11.5	8.5	18	39.8	4.68
		NPK 3	13	13	21	35.5	2.73
		NPK 4	12	12	20	30.0	2.50
		NPK 5	15	15	15	40.0	2.67
		NPK 13	11.5	8.5	18	28.0	3.29
		NPK 15	15	15	15	43.0	2.87
		NPK 16	24	8	8	24.9	3.11
	NPK Mg Bo Cu Mn	Mix. 2	16	8	12	23.6	2.95
	NPK Mg Mn Zn	Mix. 3	15	9	15	28.3	3.14
	NPK S-fertiliser	Mix. 4	13	13	21	38.0	2.92
Guano-Werk AG	NP-fertiliser	NP 4	11	52		163	3.12
	NPK-fertiliser	NPK 6	10	15	20	44.2	2.93
		NPK 7	6	12	18	28.7	2.39
		NPK 8	10	15	120	47.1	3.13
Hoechst	NPK-fertiliser	NPK 9	13	13	21	30.8	2.31
		NPK10	12	12	17	42.3	3.50
Ruhr-Stickstoff AG (Bochum)	NPK-fertiliser	NPK 11	13	13	21	10.5	0.81
		NPK 12	15	15	15	27.0	1.80
	NP-fertiliser	NP 2	20	20		32.0	1.60

IV *Relation of U concentration and amount of phosphate component in P-containing mineral fertilisers*

The analysis of U contents in different types of fertilisers showed that U concentrations in N or K mineral fertilisers (without P) were much lower than those in P- containing mineral fertilisers (less than 0.48 mg kg^{-1}) (Table A. 1.5). The relationship of U concentration and P concentration in mineral P-fertilisers can be described by a linear regression function with a positive correlation (Fig. 4.4). This is in agreement with Righi et al. (2005). Barisic et al. (1992) found that the U content in P-fertilisers depends on the phosphate component, with a high correlation (r=0.99, n=22) between ^{238}U and the phosphate component in P-fertilisers (rock phosphate from Morocco and Senegal was used). Decreasing the phosphate percentage in the fertiliser generally decreased the U content. However, the level of positive correlation between U and P_2O_5 was higher when looked at separately for just one manufacturer (e.g. BASF) than the "overall correlation" calculated over different manufacturers (Fig. 4.4). The reason for this is the fact that the origins of the rock phosphate ore are not the same for all manufacturers. Another reason may be the different manufacturing processes used by different manufacturers.

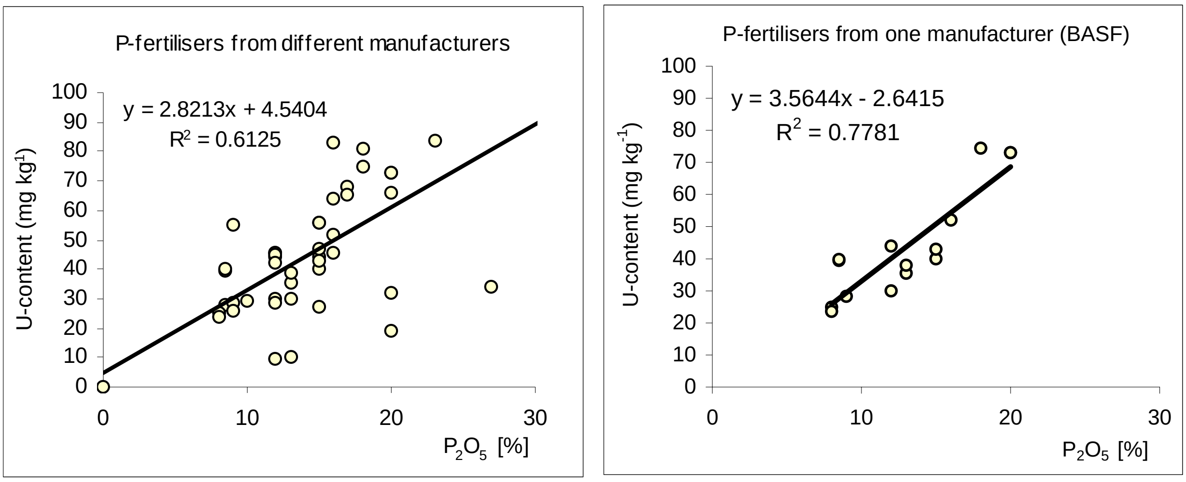


Fig. 4.4: Relationship between phosphorus and U in different P-fertilisers, described by a linear regression function

V *U/P_2O_5 in old and new collections of P- containing mineral fertilisers*

In the present work, two sets of P-containing mineral fertilisers of different origin were compared. Most of the first set was collected between 1975-1985 including 4 straight P-fertilisers, 1 PK-fertiliser and 8 NPK-fertilisers. The second set was collected after 1995 and included 4 straight P-fertilisers, 8 PK-fertilisers and 16 NPK-fertilisers. U content was slightly higher in the new samples for all types of fertilisers (P, PK, NPK) compared to the old samples (Fig. 4.5), i.e. U appeared to be enriched in the new ones. This comparison between old and new collections show that the new samples contained 13.6% to 70.2% more than old samples.

There are two possible reasons for this:

1. The high-grade quality of rock phosphate deposits is being depleted worldwide over the time and lower quality grade sources are used. Lower grade rock phosphates as sources for P-fertilisers could increase the heavy metals in the fertilisers day by day.
2. During the time slot 1975-1985 U was removed in several factories for nuclear fuel.

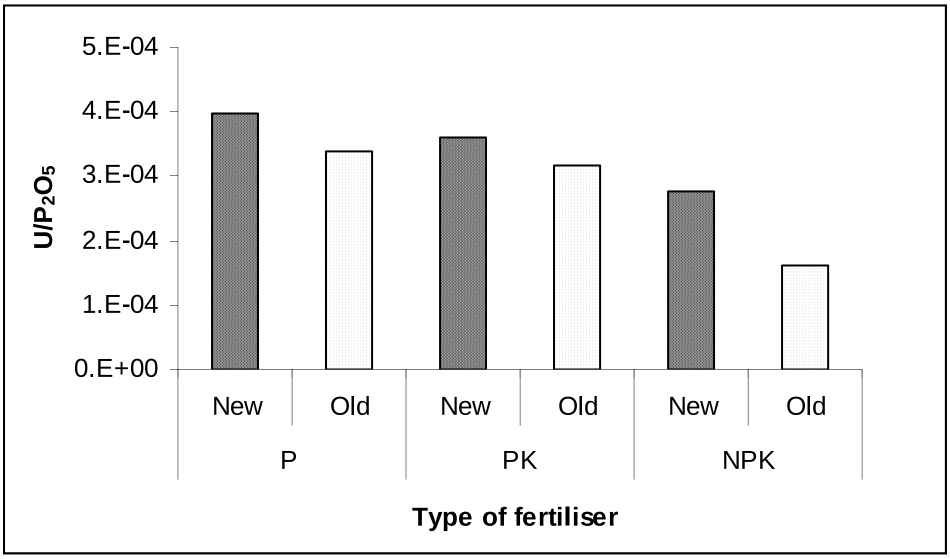


Fig. 4.5: U/P_2O_5 in old and new collections of P-containing fertiliser samples

4.4 *Sr concentration in different types of rock phosphates and P-containing fertilisers*

Inorganic P-fertilisers contained more Sr than organic fertilisers such as farmyard manures (Table 4.8). The highest concentration of Sr was found in igneous rock phosphates from the Russian Kola Peninsula. In general, Sr concentrations decreased in the following order: Igneous RP from the Russian Kola Peninsula > sedimentary RP of different origin > P-fertilisers > compound mineral fertilisers (PK, NPK) > organo-mineral fertilisers > pig manure > chicken manure > dairy cow and calf manure. However, wide variations of Sr concentration were found even within the same type of fertilisers such as straight P-fertilisers, P-containing mineral fertilisers and sedimentary rock phosphates of different origin. The ratio Sr/P_2O_5 varied widely depending on the type of rock phosphate, it was about 41.2 x 10^{-4} in sedimentary rock phosphate while it was about 537 x 10^{-4} in igneous rock phosphate from the Russian Kola Peninsula.

Table 4.8: Concentration of P_2O_5 and Sr and Sr/P_2O_5 ratio in different P-containing fertilisers

Type of sample		**Sr [mg kg^{-1}]**		**P_2O_5 [%]**		**Sr/P_2O_5 x 10^{-4}**
	n	**Average ± Std. Dev.**	**Range**	**Average ± Std. Dev.**	**Range**	
Igneous RP from Russian Kola Peninsula	6	20821±1654	18596-23016	38.8 ± 1.1	37.6 - 39.9	537
Sedimentary rock phosphates	53	1369±1172	287-3737	33.2 ± 3.1	24.6 - 37.5	41.2
P-fertilisers of sed. origins	9	909±638	383-2302	19.8 ± 4.3	18.0 - 30.5	45.8
PK	9	500±257	210-1104	14.7 ± 2.9	10.0 – 20.0	34.0
NPK	16	422±786	120-3361	12.2 ± 2.6	8.00 – 15.0	34.5
Organo-mineral fertilisers	4	217±138	52-376	6.00 ± 1.8	4.00 – 8.00	36.2
Pig manure	3	123±18.0	104-140	4.70 ± 1.5	3.80 - 6.60	26.3
Chicken manure	3	62.5±22.2	43.9-87.0	3.60 ± 0.5	3.30 - 4.20	17.3
Dairy Cows and Calf manure	4	43.4±18.2	17.0-57.0	1.50 ± 0.4	0.90 - 1.90	28.9

I *Sr concentration in rock phosphates from different origin*

All samples were enriched in Sr compared to shale (Table 4.9). Sr content in igneous rock phosphates from the Russian Kola Peninsula was higher than in sedimentary rock phosphates from different origin. It was very high in rock phosphates from the Russian Kola Peninsula, ranging from 18 595 up to 30 000 mg kg^{-1}. This result was confirmed by literature data, which agrees well with the ranges of Sr concentration found in this study (Table 4.9).

The difference between igneous and sedimentary rock phosphates is described clearly in the hierarchical cluster analysis based on total Sr-concentration (Fig. 4.6). However, this parameter did not allow for further differentiation within the sedimentary rock phosphates.

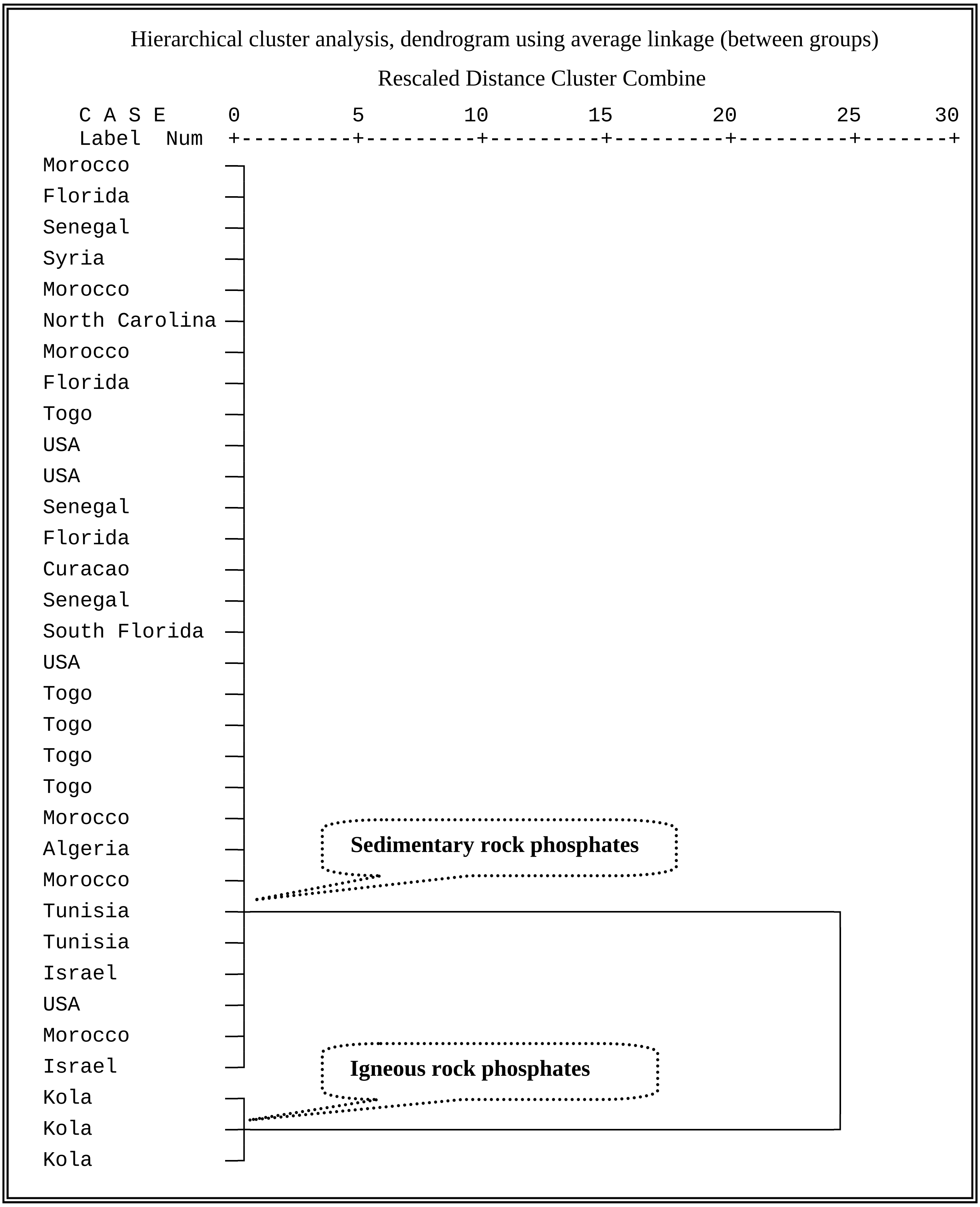


Fig. 4.6: Grouping of rock phosphates from different origin by hierarchical cluster analysis based on total Sr-content

Table 4.9: Comparison of Sr-content [mg kg^{-1}] in rock phosphate samples from different origin analysed in this study with data from literature (Hayumbu *et al.*, 1995; Kpomblekou and Tabatabai, 1994; Heiland, 1986; [c] Kharikov and Smetana, 2000)

The country	**In present work**				**Range of literature data**
	Average	**Range**	**Enrichment factor** [a]	**Sr/P_2O_5 x 10^{-4}**	
Algeria	1876	1829 - 1974	4.69	64.7	1753-2800
Morocco	1331	287-2958	3.33	8.80-89.1	701- 1438
Senegal	922	418 - 1224	2.31	20.5-33.0	587
Africa	544	349-1146	1.36	9.31-34.2	-
Tunisia	1731	1705- 1812	4.33	60.9-63.7	1724 - 4100
Israel	3123	1876- 3737	7.81	77.4-111	120-2700
USA	1104	451-2601	2.76	19.1-81.3	417-1176-
Curacao	831	831	2.08	26.5	-
Russia	20939	18596- 23016	52.4	495-592	22880 - 30000
Finland	<5000	<5000	12.5		1347
Syria	1423	1423	3.56	50.3	1900

[a] was determined in comparison to shale, based on an average Sr content in shale of 400 mg kg^{-1}.

A particularly large variation of Sr content was found in sedimentary rock phosphates from Morocco, even within the same deposit (Khouribga). In this deposit, Sr content ranged from 700 to 2958 mg kg^{-1}. This example illustrates quite clearly that it is not possible to identify the origin of sedimentary rock phosphates depending on Sr concentration in the samples only.

II Relation of Sr concentration and amount of phosphate component in P-containing mineral fertilisers

The analysis of Sr and P_2O_5 contents in different types of P-containing mineral fertilisers revealed that the amount of Sr in samples was largely dependent on the amount of phosphate in the samples. In general, decreasing the phosphate percentage in the fertiliser decreased the Sr content (Fig. 4.7). However there are some exceptions to this rule, because the amount of Sr in P-fertilisers also depends largely on the concentration of Sr in their raw materials (rock phosphate). High amounts of Sr are transferred from rock phosphate to P-fertilisers.

In the present study, a positive correlation was noticed between Sr and P_2O_5 in P-containing fertilisers produced from one manufacturer (e.g., BASF or Ludwigshafen). However, no such correlation could be shown when P-fertilisers from different manufacturers were included in the calculation (Fig. 4.7).

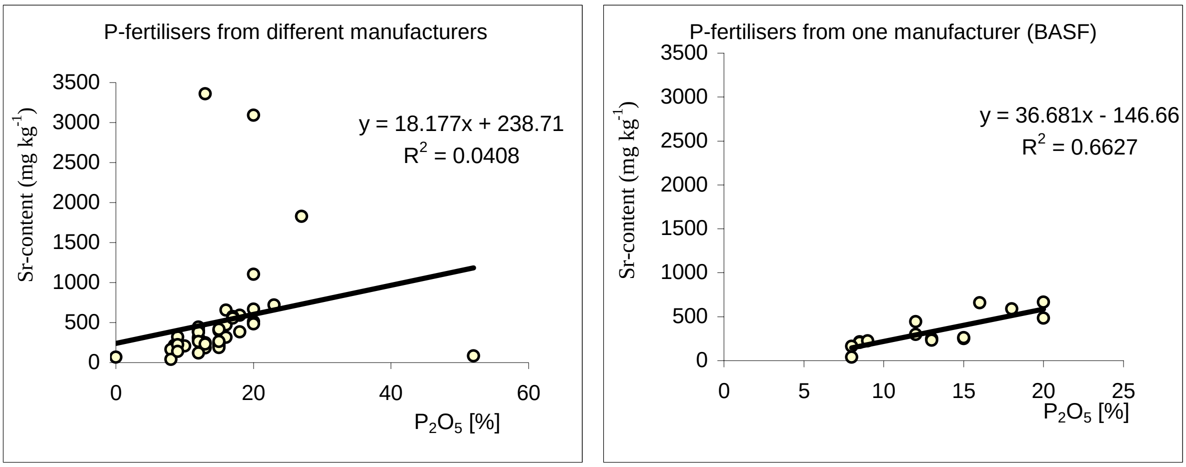


Fig. 4.7: Relationship between phosphorus and Sr in different P-fertilisers

III *Determination of the origin of P-fertilisers from different manufacturers based on* Sr/P_2O_5

Sr/P_2O_5 ratio of fertilisers produced by Ruhr-Stickstoff AG (Bochum) was compared to that of fertilisers produced by other manufacturers (Table 4.10). The Sr/P_2O_5 in different fertilisers from BASF, Guano-Werk AG and Hoechst ranged from 1.61 x 10^{-4} to 41.1 x 10^{-4}, while it ranged from 155 x 10^{-4} to 259 x 10^{-4} in samples from Ruhr-Stickstoff AG (Bochum), except for NPK 12 with a value of 12.7 x 10^{-4}. It is assumed that BASF, Guano-Werk AG and Hoechst used low Sr content rock phosphates (sedimentary) to produce P-fertilisers, while Ruhr-Stickstoff AG (Bochum) often used high Sr content rock phosphates (e.g. from the Russian Kola Peninsula) to produce fertilisers. Sr/P_2O_5 was low only in one sample of Bochum (NPK 12), it is assumed that this sample was produced from sedimentary rock phosphates.

Table 4.10: N, P_2O_5, K_2O and Sr contents and Sr/P_2O_5 ratio in different types of P-containing mineral fertilisers from different manufacturers

Manufacturer	**Type of fertiliser**	**Samples ID**	**N**	**P_2O_5**	**K_20**	**Sr**	**Sr/P_2O_5 10^{-4}**
			---------[%]----------			**[mg kg^{-1}]**	
BASF Ludwigshafen	P-fertiliser	P 8		18		591	32.8
		P 9		20		667	33.4
	PK-fertiliser	PK 9		16	16	658	41.1
	NP-fertiliser	NP 3	20	20		484	24.2
	NPK-fertiliser	NPK 1	11.5	8.5	18	216	25.4
		NPK 2	11.5	8.5	18	208	24.4
		NPK 3	13	13	21	250	19.2
		NPK 4	12	12	20	297	24.7
		NPK 5	15	15	15	250	16.7
		NPK 13	11.5	8.5	18	173	20.4
		NPK 15	15	15	15	263	17.5
		NPK 16	24	8.0	8	167	20.7
	NPK S-fertiliser	Mix. 2	13	13	21	234	18.0
	NPK, Mg, Mn, Zn-fertiliser	Mix. 3	15	9.0	15	224	24.9
	NPK Mg, B, Cu, Mn-fertiliser	Mix. 4	16	8.0	12	39.0	4.88
Guano-Werk AG	NP-fertiliser	NP 4	11	52		83.7	1.61
	NPK-fertiliser	NPK 6	10	15	20	223	14.8
		NPK 7	6	12	18	379	31.6
		NPK 8	10	15	120	209	14.0
Hoechst	NPK-fertiliser	NPK 9	13	13	21	185	14.2
		NPK10	12	12	17	263	21.9
Ruhr-Stickstoff AG (Bochum)	NPK-fertiliser	NPK 11	13	13	21	3361	258
		NPK 12	15	15	15	190	12.7
	NP-fertiliser	NP 2	20	20		3093	155

The main results of the previous chapters (4.1 to 4.4) can be summarised as follows:

1 Rock phosphate samples contained different amounts of a number of toxic heavy metals such as U, Cd, Ni, Co, Pb and Cr depending on their origin. However, it was obvious that a single element could not discriminate between different sedimentary rock phosphate origins because:

(I) It was found that many elements vary significantly between two or more origins, but no element varied significantly among all origins.

(II) Sometimes the average concentration of a certain element varied significantly between two different origin. Nevertheless, this element could not be used to distinguish rock phosphate samples of these two origins, because its concentration also varied widely between different samples of the same origin. For example, Sr concentration in sedimentary rock phosphates of different origin varied from 120 to 4100 mg kg^{-1}, but also a large variation was noticed in sedimentary rock phosphate of one origin and even within the same deposit. E.g., in rock phosphate from Morocco, deposit Khouribga, Sr concentration ranged from 700 to 2958 mg kg^{-1}. Therefore it is not possible to identify the origin of sedimentary rock phosphate depending on Sr concentration in the samples only.

2 The amounts of U and Sr and other heavy metals in P-containing mineral fertiliser samples are largely related and dependent on the origin of their raw material (rock phosphate), the amount of phosphate components in the samples, and on the manufacturing processes of P-fertilisers.

3 It is very complex to trace back the origin of P-fertilisers with regard to the sedimentary rock phosphates from which they were produced using heavy metal patterns, because the amount of heavy metals that are transferred to the fertiliser products from the raw material vary considerably based on the method of production. So the origin of P mineral fertilisers cannot be controlled and identified using heavy metal patterns.

4 U/P_2O_5 and Sr/P_2O_5 in P-fertilisers can be used only to check if this fertiliser was produced from sedimentary rock phosphates or from the Russian Kola Peninsula (igneous rock phosphates) because the concentration of Sr and U vary greatly between each other.

5 Based on U/P_2O_5 and Sr/P_2O_5, it can be concluded that the rock phosphates used by BASF, Guano-Werk AG and Hoechst Manufacturers are of the sedimentary type, containing high levels of U as well as a high U/P_2O_5 ratio. Most of the rock phosphates used in Ruher Bochum are of the igneous type, containing low level of U and low U/P_2O_5 as well as high levels of Sr and high Sr/P_2O_5. However, this parameter did not allow for further differentiation within the group of sedimentary rock phosphates.

4.5 *Fingerprinting the geographical origin of rock phosphates according to their content of heavy metals using multivariate statistical analysis*

In order to make a fingerprint of rock phosphates with respect to their content of heavy metals, the following steps were performed:

- The samples were classified depending on their chemical composition using hierarchical cluster analysis and discriminant analysis.
- Elements with a high discriminating power were determined using discriminant analysis.
- Distributions and natural relationships between metals in rock phosphates of different origin were studied using correlation and cluster analysis.
- Elements which can be used as indicators of the origins of rock phosphate samples were determined using principal component and factor analysis.

4.5.1 *Classification of rock phosphates using discriminant analysis and hierarchical cluster analysis*

In order to determine which variables (elements) have higher discriminate power, ANOVA and Wilkes' Lambda tests were used. It is well known that the variable (element) with the smallest Wilkes' Lambda and the highest F-value is the most important variable. It is therefore best suited to discriminate among different rock phosphate origins. As can be seen in Table 4.11, Sr had the smallest Wilkes’s Lambda, so it was the most important variable for the discrimination function and had the highest discriminating power. The discriminating power generally decreased in the following order: Sr>Cd>Be>Bi>Mn>Cu>Pb>Cr>U>Zn> As>Ti>Sb>B>Tl>Co>Mo>Ni>Se. The number of discriminant functions computed was 9. The first and second functions together account for 88.8% of the variability, the first function alone accounts for 72.2% of the variability. The first discriminant function is related mostly to Sr which can be seen by the correlation between first discriminant function and Sr (Table A. 2. 10). The second function alone accounts for 16.7% of the variability. However, correlations between this function and all tested elements were low. The third function accounts only for 5.5% of the variability (Table A. 2.10). The classification of rock phosphate samples based on the first and second function (Fig. 4.8) showed that the first discriminate function separated the rock phosphates in two groups of samples. Sedimentary rock phosphate samples were located on one side and igneous rock phosphate samples were located on the other side due to high variation between elemental composition in sedimentary rock phosphates and igneous rock phosphates from the Russian Kola Peninsula (Chapter 4.1 and 4.2). Moreover, all igneous rock phosphates were correctly classified when the cross validation was applied (Table 4.12). From these results, it can be concluded that elemental patterns, like the obtained results for U/P_2O_5 and Sr/P_2O_5, are helpful and have high discriminating power to distinguish between igneous rock phosphates from the Russian Kola Peninsula and sedimentary rock phosphates of different origin. However, classifications of sedimentary rock phosphates are meaningless. The procedure cannot be reliably performed for sedimentary rock phosphates. 100% of samples were successfully classified without cross validation. Only 67.7% of total samples were correctly classified when the cross validation was applied. Moreover, rock phosphates from Syria, Algeria, Curacao, 50% of Morocco, and 10% of from the USA were wrongly classified (Table 4.12). These rates of misclassification did not offer good discrimination of sedimentary rock phosphate samples and therefore another type of statistical analysis should be selected.

The same results were obtained by hierarchical cluster analysis, i.e. igneous rock phosphates from the Russian Kola Peninsula, and biogenic rock phosphates from Curacao tended to one side, and the other sedimentary rock phosphates were located on the other side (Fig. 4.9). Twenty-seven samples (about 81% of total samples) of different origin were correctly classified depending on their origins (rock phosphate samples of the same origin were classified together in one sub-cluster). Only 6 samples (RP5, RP7 and RP9 of Morocco, RP34 and RP35 from Israel, RP28 North Carolina) were classified wrongly (about 19% of total samples). One prominent example are the samples from Morocco. As mentioned above, rock phosphate samples of this origin display a wide range of element concentrations, which makes it particularly difficult to classify them based on their heavy metal pattern.

Generally, it was possible to distinguish between igneous rock phosphates from the Russian Kola Peninsula and sedimentary rock phosphates by heavy metal pattern. In Fig. 4.9, it appears that in comparison to discriminate analysis, hierarchical cluster analysis not only distinguishes between igneous rock phosphates from the Russian Kola Peninsula and sedimentary rock phosphates, but it also distinguishes samples from Togo and samples from Senegal. Most samples from USA and from Morocco were classified in separate clusters but not all. In addition, one sample from Morocco and another from North Carolina were classified together with Tunisian samples, which makes it particularly difficult to classify samples from USA, Morocco and Tunisia based on their heavy metal pattern. The use of discriminate analysis and hierarchical cluster analysis showed that it was complex to distinguish among all sedimentary rock phosphate origins. The reason for this was that heavy metals content in sedimentary rock phosphates varied greatly within the same country and even within the same deposit.

Table 4.11: The discriminating strength of each variable for the identification the origin of rock phosphates based on Wilks' Lambda test and univariate F- test

Element	Wilks' Lambda	F	Sig.	Element	Wilks' Lambda	F	Sig.	Element	Wilks' Lambda	F	Sig.
Sr	0.016	136	0.000	**Pb**	0.208	8.4	0.000	**Sb**	0.243	6.9	0.000
Cd	0.116	16.7	0.000	**Cr**	0.217	7.9	0.000	**B**	0.246	6.7	0.000
Be	0.150	12.5	0.000	**U**	0.221	7.8	0.000	**Tl**	0.311	4.9	0.001
Bi	0.183	9.8	0.000	**Zn**	0.222	7.7	0.000	**Co**	0.355	3.99	0.003
Mn	0.191	9.3	0.000	**As**	0.222	7.7	0.000	**Mo**	0.370	3.7	0.005
Cu	0.191	9.3	0.000	**Ti**	0.239	7.0	0.000	**Ni**	0.415	3.1	0.013
								Se	0.483	2.4	0.045

Note: The smaller the Wilks' lambda, the more important the variable the to discriminate the origin of rock phosphate.

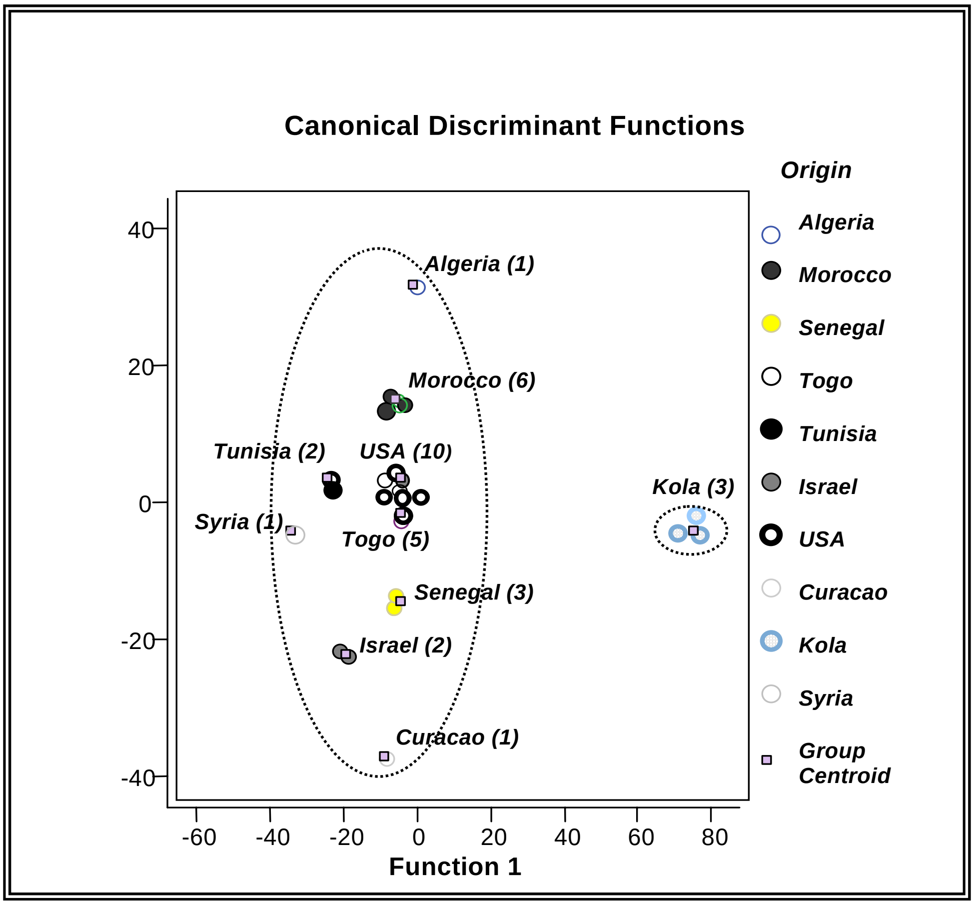


Fig .4.8: Classification of rock phosphate samples based on the first two canonical discriminant functions (Variables included: As, B, Be, Bi, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, U and Zn).

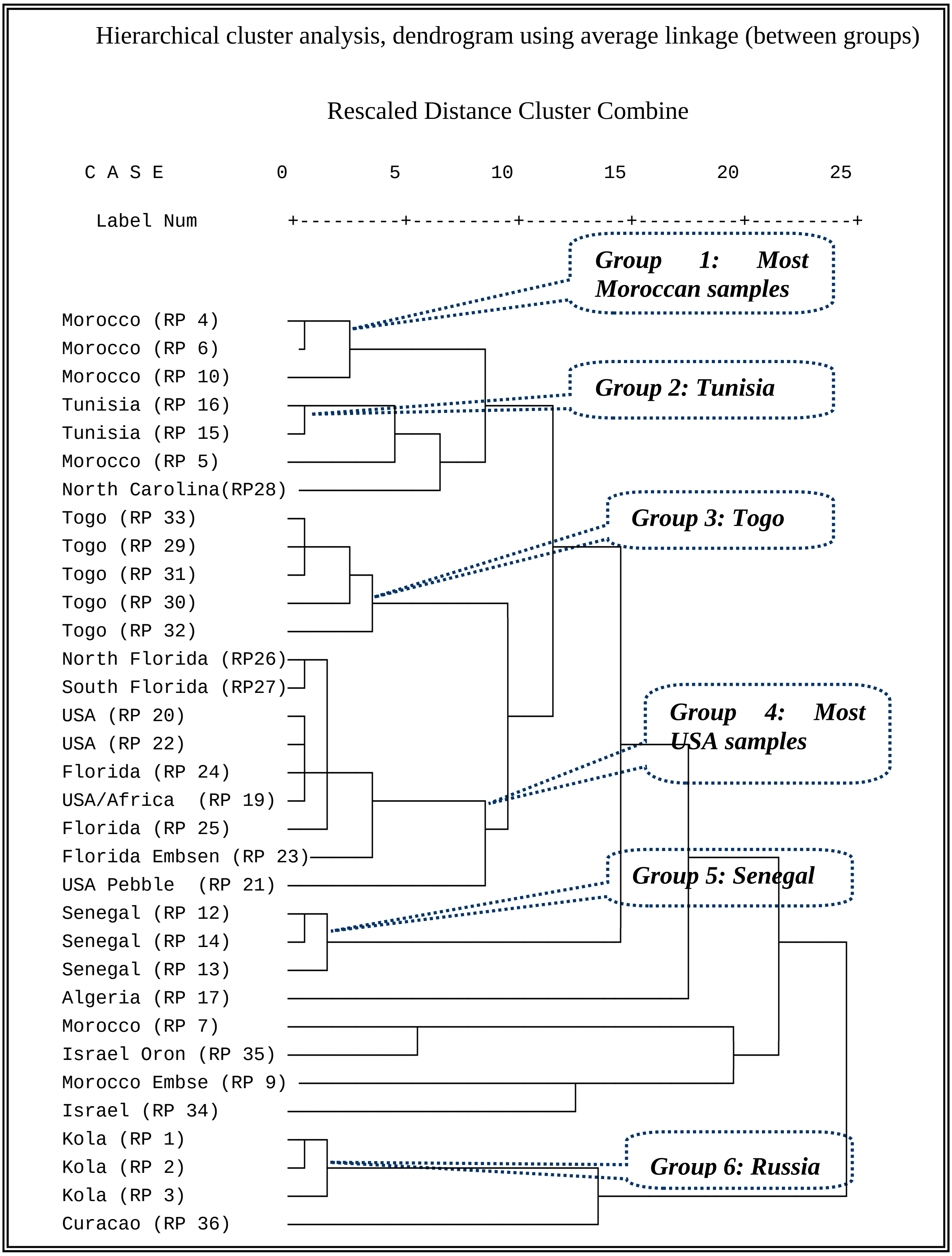


Fig. 4.9: Hierarchical cluster analysis of rock phosphate samples from different origin (Variables included: As, B, Be, Bi, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, U and Zn).

Table 4.12: Classification results of discriminate analysis with cross validation

	Origin	**Predicted Group Membership**										**Total**
		Algeria	**Morocco**	**Senegal**	**Togo**	**Tunisia**	**Israel**	**USA**	**Curacao**	**Kola**	**Syria**	
Cross-validated Count %	**Algeria**	**0**	100	0	0	0	0	0	0	0	0	100
	Morocco	16.7	**50**	0	0	0	0	33.3	0	0	0	100
	Senegal	0	0	**100**	0	0	0	0	0	0	0	100
	Togo	0	0	20	**80**	0	0	0	0	0	0	100
	Tunisia	0	0	0	0	**100**	0	0	0	0	0	100
	Israel	0	0	0	0	50	0	0	50	0	0	100
	USA	0	0	0	10	10	0	**80**	0	0	0	100
	Curacao	0	0	100	0	0	0	0	**0**	0	0	100
	Kola	0	0	0	0	0	0	0	0	**100**	0	100
	Syria	0	0	0	0	100	0	0	0	0	**0**	100

Cross validation is done only for those cases in the analysis. In cross validation, each case is classified by the functions derived from all cases other than that case, 100.0% of original grouped cases classified correctly, 67.6% of cross-validated grouped cases classified correctly.

4.5.2 Natural relationships among heavy metals in different rock phosphates as *determined by cluster analysis*

In order to reduce the number of variables (heavy metals), heavy metals were classified in groups based on patterns of correlation among the heavy metals. A hierarchical cluster analysis was run, applying Average Linkage (Between Groups) of agglomeration and Pearson correlation as the similarity measure. In this case, elemental cluster analysis allows us to determine the associations among different elements (Fig. 4.10). The resulting data could then be applied to characterise the rock phosphates of different origin by their content of different heavy metals.

Heavy metals were grouped into four clusters:

- Cluster 1: Bi, Co, Mn, and Pb. The first level of association was between the pair Pb-Bi, which had high significant levels of correlations ($R > 70$, $P < 0.05$). The pair Pb-Bi at the same time forms a cluster with the pair Mn-Co. These elements were significantly higher in samples from the USA and Togo than in other sedimentary rock phosphates, except for Mn and Co in samples of Senegal.
- Cluster 2: included Se and Tl. Se and Tl concentrations in all samples were lower than 9.16, 2.23 mg kg$^{-1,}$ respectively, except for rock phosphate from Algeria (2.95, 27.9 mg kg^{-1} respectively). But no test was performed for Algeria because n<3.
- Cluster 3: A wide range of elements such as As, B, Be, Cd, Cr, Cu, Mo, Ni, Sb, U and Zn belonged to the same major cluster (C3). There were also positive correlations among these elements and high significant levels of correlations ($R > 70$, $P < 0.05$) were

found between U and Ni (Table A. 2.6). The first level of association was between U and Ni, which was associated with B in the next stage and later forms a cluster with the pair Cr-Zn. Finally As, Be, Cd, Cu, Mo and Sb were added, forming Sub-cluster 3 (C3). All elements in this cluster, except for Cu, Sb, were significantly lower in rock phosphate from the Russian Kola Peninsula than sedimentary rock phosphates.

- Cluster 4: includes Ti and Sr. The correlation among the elements in this cluster was positive. Ti and Sr, which belong to Cluster 4, were correlated negatively with all elements in Cluster 3. Ti and Sr were significantly higher in rock phosphates from the Russian Kola Peninsula than sedimentary rock phosphates. High significant levels of correlations ($R > 70$, $P < 0.05$) were found between Ti and Sr.

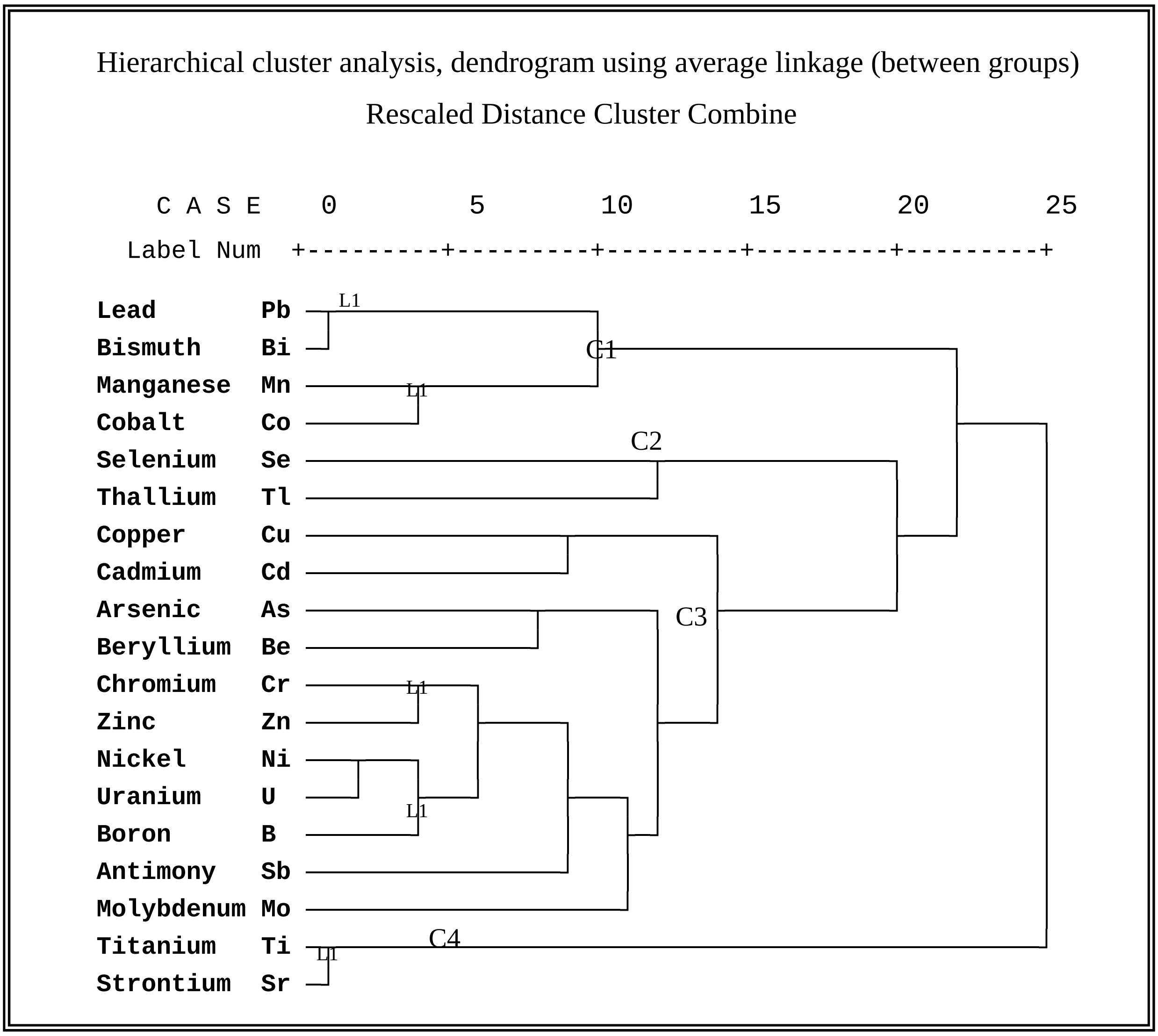


Fig. 4.10: Dendrogram of hierarchical cluster analysis for the heavy metals in rock phosphate samples (L1: the first level of associations, C n: number of the sub-cluster).

4.5.3 Determination of heavy metal pattern by principal component analysis (PCA)

A PCA was performed including all analysed elements in this study (As, B, Be, Bi, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, U and Zn). The number of significant principal components was selected on the basis of the Kaiser criterion. According to this criterion, SPSS extracted only factors with Eigenvalues of 1 or higher (StatSoft, 2003). Based on this criterion, only the first five principal components (PCs) were extracted for analysis (Table 4.13). As indicated in Table 4.13, heavy metal concentrations can be reduced to 5 components which account for 82.0% of the total variance. The PC1 accounted for 31.7% of the variability, PC2 accounted for 20.1%, PC3 accounted for 13.3%, PC4 accounted for 10.0%, PC5 accounted for 6.89% of the variability.

Table 4.13: Results of the rotated component matrix for rock phosphate samples including loading matrix and proportions of variance for each component

	Component*				
	1	**2**	**3**	**4**	**5**
Be	0.747	0.453	0.031	-0.185	-0.240
B	0.770	-0.003	0.296	0.016	0.416
Ti	-0.492	-0.334	0.394	0.516	0.128
Cr	0.804	-0.359	-0.164	0.094	-0.171
Mn	-0.489	0.440	0.641	-0.199	0.216
Co	0.024	0.673	0.543	-0.235	0.173
Ni	0.836	-0.220	0.251	0.280	0.045
Cu	0.437	-0.350	0.723	-0.059	-0.177
Zn	0.775	-0.433	0.173	-0.294	0.158
As	0.481	0.306	-0.140	0.263	-0.525
Se	0.167	-0.391	-0.558	-0.156	0.450
Sr	-0.660	-0.475	0.287	0.273	0.127
Mo	0.530	-0.102	-0.242	0.067	0.571
Cd	0.417	-0.084	0.287	-0.816	-0.084
Sb	0.581	0.356	0.084	0.489	0.025
Tl	0.050	0.307	-0.607	-0.264	0.035
Pb	0.092	0.893	-0.041	0.142	0.125
Bi	-0.104	0.914	-0.067	0.097	0.219
U	0.857	0.168	0.062	0.400	0.077
Explained Variance	**31.7%**	**20.1%**	**13.3%**	**10.0%**	**6.90%**
Sum	**31.7%**	**51.8**	**65.1**	**75.2**	**82.0**

Extraction Method: Principal Component Analysis.

* 5 components with eigenvalues larger than 1 were extracted.

First principal component (PC1)

Variables (heavy metals) were represented using the first two PCs (Fig. 4.11) and the first three PCs (Fig. 4.12). There were high loadings on PC1 (>0.48) for U, Ni, Zn, Cr, Be, Mo, Sb, As and B (Fig. 4.11 and Table 4.13). The result is in agreement with cluster analysis which placed all these elements into one cluster (see Fig. 4.10). There were positive correlations among these elements (Table A. 2.13). The loadings for B, Cr, Ni, U and Zn on PC1 were more than 0.75, while Sr, Mn, and Ti, which correlated positively among each other, displayed a negative loading on PC1 (Table 4.13). The first component reflected the difference between igneous and sedimentary rock phosphates. While sedimentary rock phosphates were characteristically higher in B, Be, Cr, Ni, Mo, Sb, U and Zn concentrations than igneous rock phosphates, Sr and Ti were higher in igneous rock phosphates than sedimentary rock phosphates (Table 4.14).

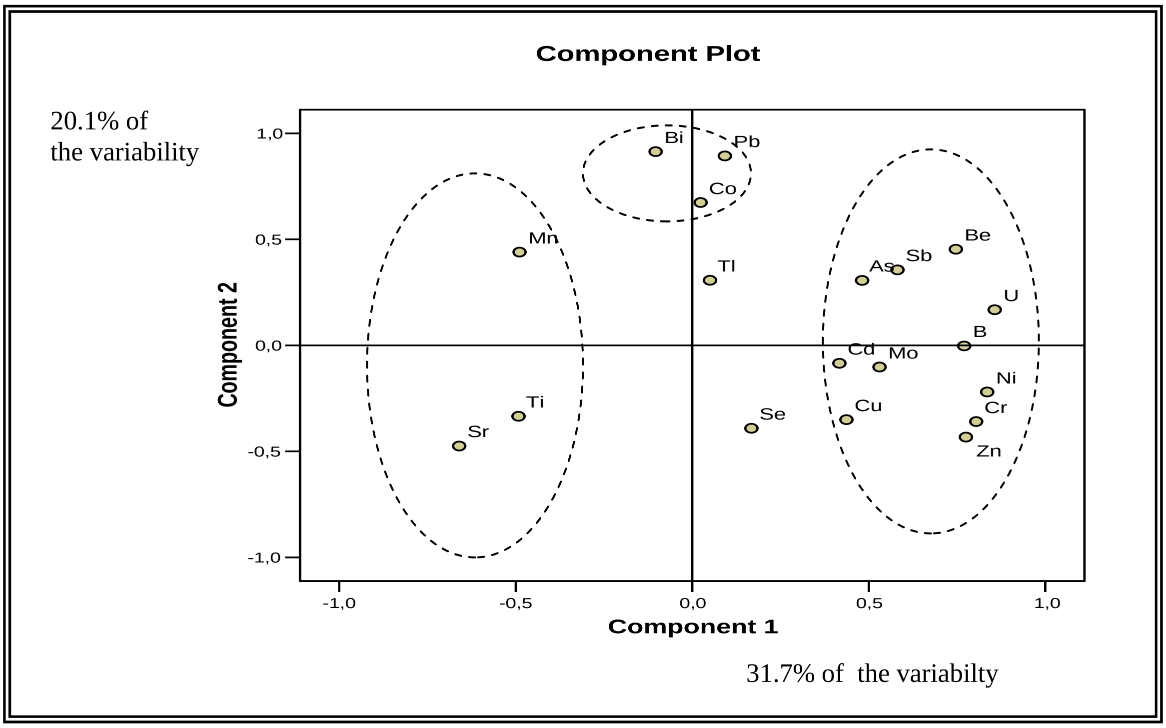


Fig. 4.11: Plot of the rotated component matrix for heavy metals using the first two components of five components with an eigenvalue larger than 1

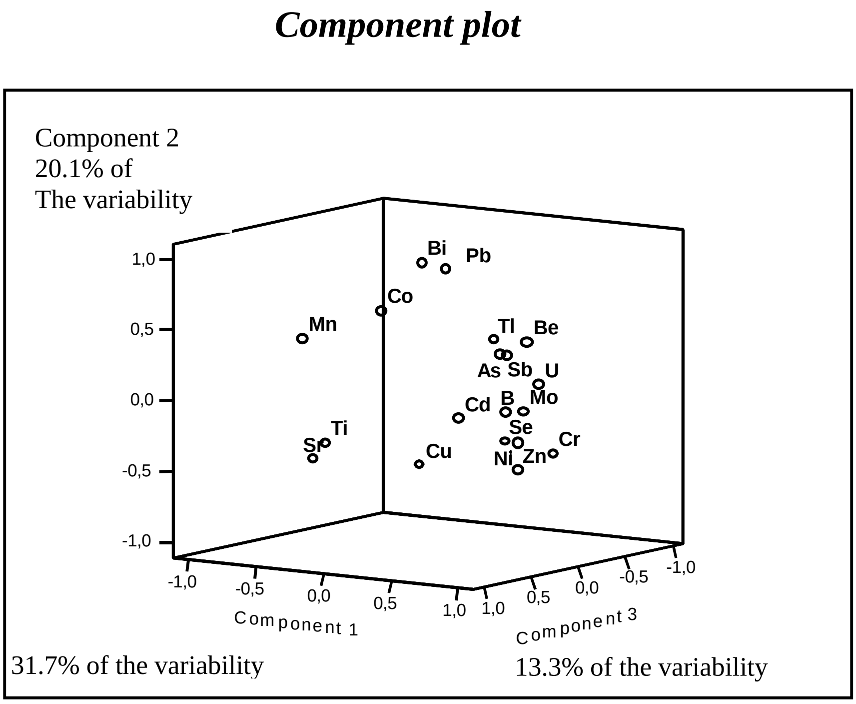


Fig. 4.12: Plot of the rotated component matrix for heavy metals using the first three components of five components with an eigenvalue larger than 1

Table 4.14: Ranges of heavy metal concentrations in rock phosphates analysed by ICP-MS, suitable as indicators for the characterisation of rock phosphates

Element	Sedimentary rock phosphates [mg kg^{-1}]	Igneous rock phosphates [mg kg^{-1}]
Sr	287-3737	18596-23016
Ti	209- 603	744 - 922
Be	0.78 - 2.46	0.08 - 0.26
Cd	3.22 - 106	0.00 - 0.40
Cr	41.9 - 238	0.80 - 1.33
Ni	8.83 - 96.7	4.69 - 7.32
Mo	2.85 - 26.5	0.56 - 1.88
U	36.9 - 245	3.04 - 3.35
Zn	54.9 - 434	10.5 - 26.7

Elements above the line tend to be higher in igneous rock phosphates, while those below tend to be higher in sedimentary rock phosphates.

Second principal component (PC2)

PC2 was highly loaded (>0.49) by Bi, Pb and Co (Fig. 4.12 and Table 4.13). Significant positive correlations among these elements were found (Table A. 2.13). This component reflects differences between 2 groups of sedimentary rock phosphate origins. The concentrations of Bi, Pb and Co were lower in rock phosphates from Middle East and Northern Africa than in rock phosphates from the USA. Rock phosphates from the USA contained the greatest concentration of Bi, Pb, Co (Table 4.15).

Table 4.15: Range of Bi, Pb and Co in rock phosphates from different origin

	Origins	**Pb**	**Bi**	**Co**
			------[mg kg^{-1}]------	
	Algeria	7.52	0.05	0.74
Group 1	Morocco	4.27 - 8.84	0.0 - 0.04	0.55 - 1.38
(Middle East,	Tunisia	4.69 - 5.30	0.0 - 0.04	0.63 - 0.86
Northern Africa)	Israel	3.60 - 6.16	0.0	0.47 - 1.28
	Syria	3.70	0.07	0.89
Group 2	USA	9.76 - 14.70	0.10 - 0.20	0.72 - 6.7

Elements in the group 2 tend to be higher than group 1

Third principal component (PC3)

Cu and Mn were positively correlated with the third component, while Tl and Se were correlated negatively with the third component (Fig. 4.13 and Table 4.13). Like PC2, this component reflects the difference between two groups of origins. The first group includes Algeria and Tunisia, while the second group includes Senegal, Togo and the Russian Kola Peninsula because Cu and Mn are significantly lower in rock phosphates from Algeria and Tunisia than in rock phosphates from Senegal, Togo and the Russian Kola Peninsula, while Tl and Se are significantly higher in rock phosphates from Algeria and Tunisia than in rock phosphates from Senegal, Togo and the Russian Kola Peninsula (Table 4.16).

Fourth principal component (PC4)

Cd is associated with the fourth component. The concentration of Cd is highest in rock phosphates of Senegal (67.5 to 106 mg kg^{-1}) while it is the lowest in rock phosphates from the Russian Kola Peninsula (0 to 0.04 mg kg^{-1}) (Fig. 4.13). Cd concentration in other origins ranged from 5.6 up to 54 mg kg^{-1}. So Cd can be used to distinguish rock phosphates from the Russian Kola Peninsula of other origin, in addition it can be used to distinguish rock phosphates from Senegal of other origins.

Table 4.16: Average concentration of Cu, Mn, Tl and Se in RP from different origin

	Origin	**Cu**	**Mn**	**Tl**	**Se**
		[mg kg^{-1}]			
Group 1	Algeria	8.20	17.5	2.95	27.9
	Tunisia	10.8	19.7	0.84	8.95
Group 2	Senegal	49.0	209	0.00	1.05
	Togo	37.0	126	0.69	2.00
	Kola	29.0	206	0.00	3.30

Cu and Mn in the group 2 tend to be higher than group 1, while Tl and Se in the group 1 tend to be higher than group 2.

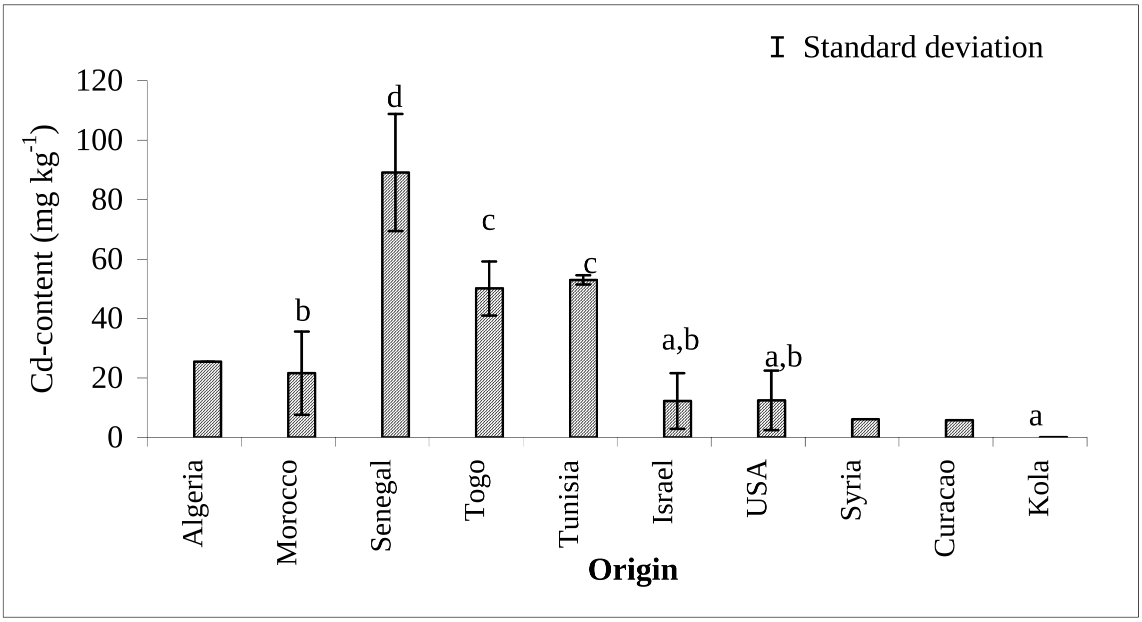


Fig. 4.13: Average concentration of Cd in rock phosphates from different origin (Different letters denote significant differences between Cd content in rock phosphate from different origin by Duncan's test at P <0.05, No test was performed for Algeria, Syria, Curacao, because n<3).

Fifth principal component (PC5)

PC5 is related to Mo. The concentration of Mo was the highest in rock phosphates from Israel and the lowest in rock phosphates from the Russian Kola Peninsula. The origin of samples from Israel and the Russian Kola Peninsula can be distinguished by their Mo concentration.

The main results of fingerprinting the geographical origin of rock phosphates using multivariate statistical analysis (chapter 4.5) can be summarised as following:

- It was possible to distinguish igneous rock phosphates of the Russian Kola Peninsula from sedimentary rock phosphates by several heavy metals (Be, Cd, Cr, Mo, Ni, Sr, Ti, U and Zn); but it was a complex task to identify the origin of all sedimentary rock phosphates.
- Heavy metal patterns allow to identify geographic origin of some rock phosphate samples, however, this is not possible in all cases.
- Because about 19% and 32% of the samples were wrongly classified by cluster analysis and discriminant analysis respectively, PCA seems to be a more useful tool to differentiate between different geographical origins and to determine the metals that can be used to identify the geographical origin of samples.
- Based on PCA, it is possible to distinguish between samples from the USA and other (Middle East and Northern Africa), and between Senegal and other, also between (Algeria and Tunisia) and (Senegal, Togo and the Russian Kola Peninsula).

4.6 Sr isotope ratios in rock phosphates and P-containing fertilisers

4.6.1 Sr isotope ratio in rock phosphates as a tool to identify their geographical origins

R(^{87}Sr/^{86}Sr) in rock phosphates were analysed using TIMS (Finnigan TRITON). The hierarchical cluster analysis based on this ratio divided the rock phosphate samples into two main groups: igneous rock phosphate from the Russian Kola Peninsula in the first group and sedimentary rock phosphates in the second group. The second group divided into three sub-clusters. The first sub-cluster included all samples from Middle East and Northern Africa (Algeria, Syria, Tunisia, Israel, and Morocco), the second sub-cluster included samples from the USA, samples from Togo and Senegal were located separately (Fig. 4.14). The lowest *R*(^{87}Sr/^{86}Sr) (from 0.70339 to 0.7035) was found in igneous rock phosphates from the Russian Kola Peninsula (Table 4.17). It was followed by rock phosphates from Senegal and Togo (from 0.70686 to 0.70742). Rock phosphates from Middle East and Northern Africa (Morocco, Israel, Tunisia, Algeria and Syria) showed Sr isotope ratios from 0.70781 to 0.70803. Rock phosphates from the USA had Sr isotope ratios between 0.70883 to 0.70896.

Table 4.17: *R*(^{87}Sr/^{86}Sr) for rock phosphates and P-fertilisers from different origin

The origin	**Nr of Sample**	***R*(^{87}Sr/^{86}Sr) in RP**	**Mean of R(^{87}Sr/^{86}Sr) in RP**	***R*(^{87}Sr/^{86}Sr) in P-fertilisers**	***R*(^{87}Sr/^{86}Sr) in phosphogypsum**
Algeria	RP 17	0.707 97	0.707 97	0.708 01	
Morocco	RP 5	0.708 03	0.707 95 c	0.708 48	0.708 10
	RP 4	0.708 01			
	RP 10	0.707 81			
Florida	RP 23	0.708 92	0.708 90 b	0.709 09	0.70534
	RP 25	0.708 96			
	RP 24	0.708 83			
	RP 20	0.708 89			
Togo	RP 33	0.707 42	0.707 42		
Israel	RP 34	0.707 92	0.707 92	0.707 90	
Tunisia	RP 15	0.708 01	0.708 01		
Senegal	RP 12	0.706 86	0.706 86		
Syria	RP 18	0.707 90	0.707 90	0.707 91	
Russian Kola Peninsula	RP 2	0.703 45	0.703 42 a	0.703 54	
	RP 1	0.703 39		0.703 38	
	RP 3	0.703 43		0.703 48	

Mean values followed by different letters are significantly different by Duncan's test at P<0.0001

Measurement uncertainty according to the ISO guide, using a coverage factor k = 2 was from 0.00026 to 0.00028 for all samples.

Sr isotope ratio differences among these four groups were statistically significant (P<0.0001) by Duncan's test. The differences in isotope ratio between these groups (Table 4.18) are significantly larger than the minimum detectable difference of $4*10^{-5}$ which is limited by the measurement uncertainty (see material and methods).

Table 4.18: Ranges of Sr isotope ratios in rock phosphates and P-fertilisers

Origin of samples		**USA**	**Middle East, Northern Africa**	**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-fertiliser		0.709 09	0.707 90- 0.708 48		0.703 38- 0.703 54
R(^{87}Sr/^{86}Sr) in phosphogypsum		0.705 34	0.708 01		

Measurement uncertainty (U) using a coverage factor k = 2 was 0.00028 for all samples.

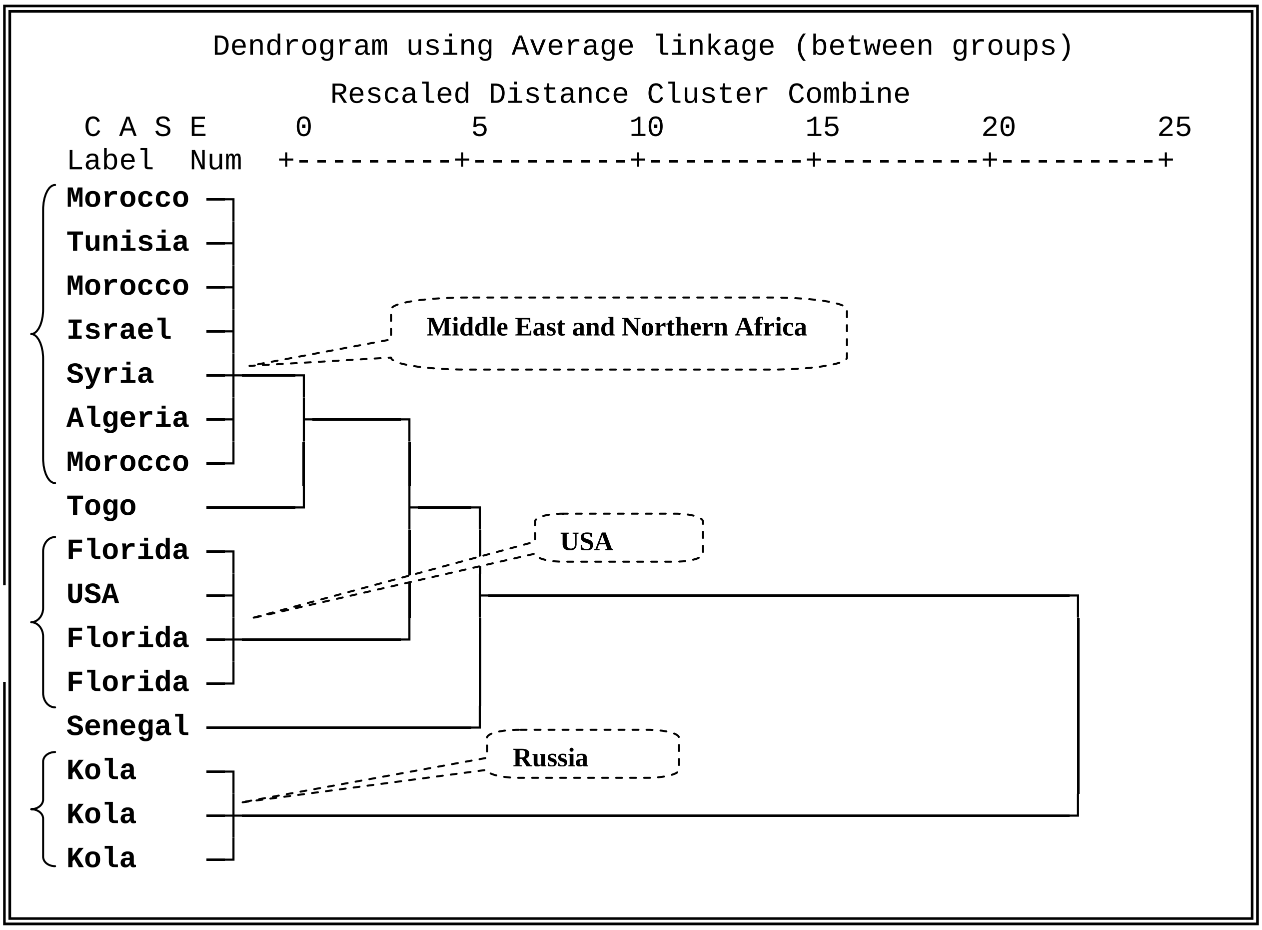


Fig. 4.14: Hierarchical cluster analysis of rock phosphate samples based on Sr isotope ratio

5.6.2 Transfer of *R*(^{87}Sr/^{86}Sr) from rock phosphates to P-fertilisers

This chapter examines if the natural abundance of *R*(^{87}Sr/^{86}Sr) in P-fertilisers varies depending on the rock phosphate from which they were produced. It was observed that ^{87}Sr/^{86}Sr- isotope ratio was similar in P-fertilisers and rock phosphates in the case of Israel and Syria (Fig. 4.15). However, for other origins it was slightly higher in P-fertilisers (up to 0.00048) than in their corresponding rock phosphates.

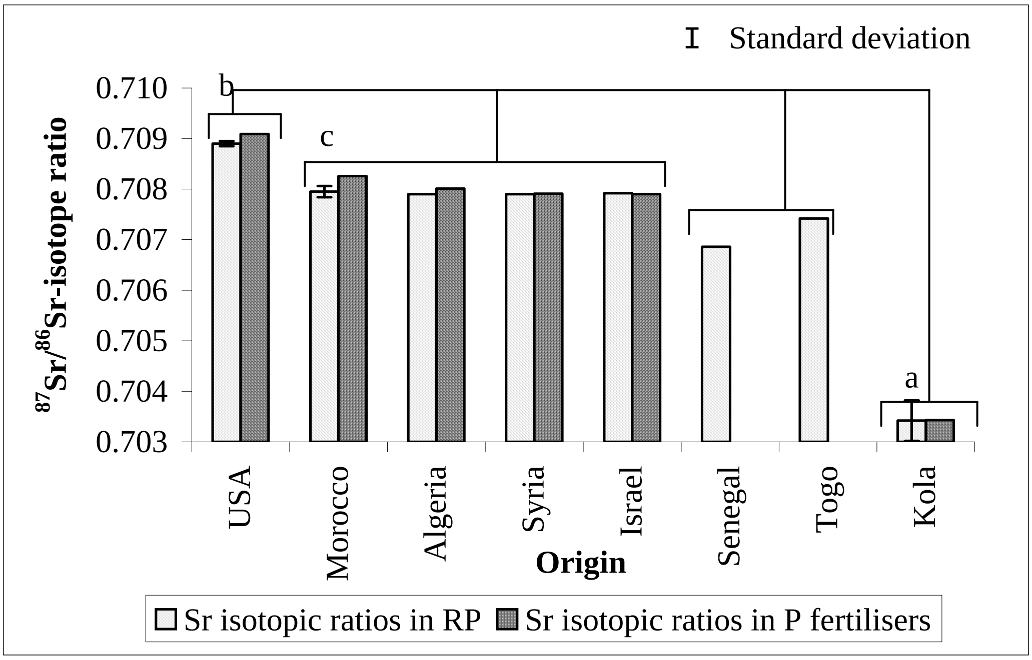


Fig. 4.15: Average *R*(^{87}Sr/^{86}Sr) in P-fertilisers and rock phosphates from different origin. Different letters denote significant differences between Sr isotope ratios in rock phosphates from different origin by Duncan's test at $P<0.0001$. No test was performed for Senegal, Togo because $n<3$.

A small increase of ^{87}Sr in P-fertilisers may be due to isotopic effects during production processes of P-fertilisers. Kinetic isotope effects may occur due to the fact that lighter isotopes (with low atomic mass) form bonds that are more easily broken. Therefore, the lighter isotopes react faster than heavier isotopes and can, in the case of a non- quantitative reaction, be enriched in the product (Kendall and Caldwell, 1998; Criss, 1999). If ^{86}Sr (light isotope) reacted with sulphuric acid only slightly faster than ^{87}Sr (heavy isotope) during the manufacturing processes of P-fertilisers (Fig. 4.16), the *R*(^{87}Sr/^{86}Sr) would slightly increase in P-fertilisers as a result, while the ratio of the remaining Sr in phosphogypsum would decrease. This is only one possible explanation, however, it is beyond of the scope of this study to prove this hypothesis. The data given in Table 4.17 only partly supports this theory. While

R(^{87}Sr/^{86}Sr) in phosphogypsum was lower than that in rock phosphate from the USA, this is not true for the Moroccan samples analysed in this study. Unexpectedly, in this case the *R*(^{87}Sr/^{86}Sr) in the Moroccan P-fertiliser and phosphogypsum was higher than in the rock phosphate samples from that country. Possibly the Moroccan P-fertilisers and phosphogypsum were produced from rock phosphates which came from another deposit than the rock phosphates analysed 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}Sr/^{86}Sr).

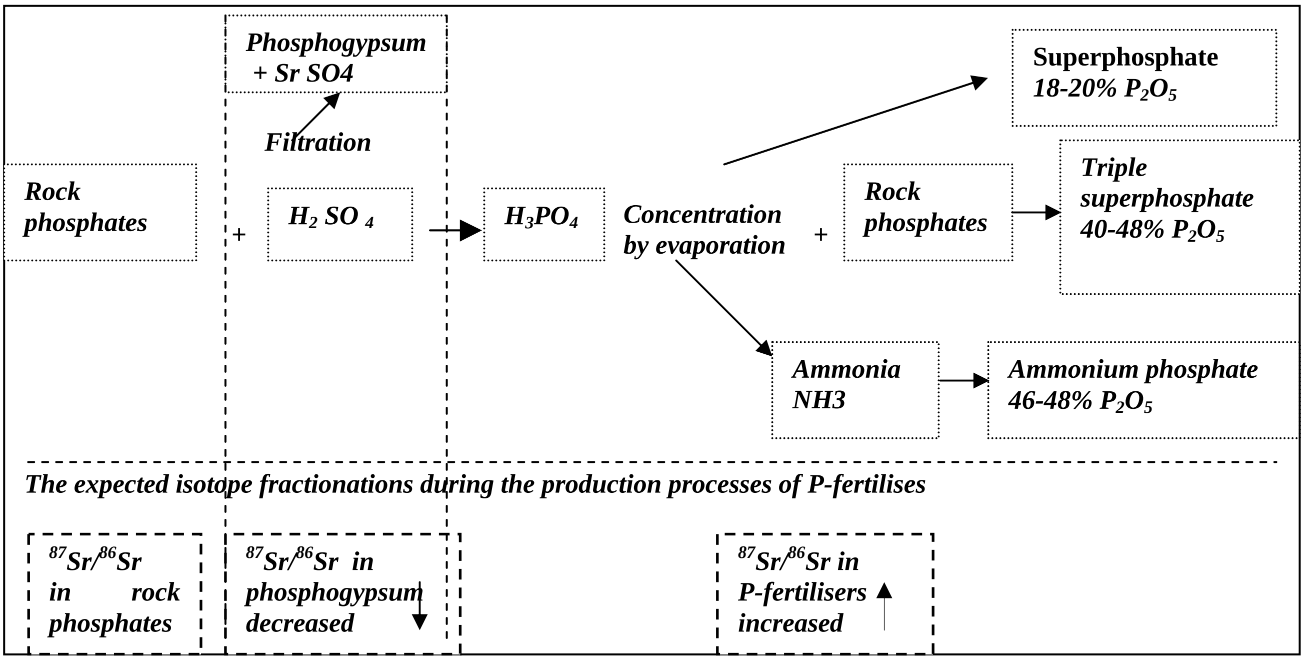


Fig. 4.16: Flow chart for phosphate fertiliser production by sulphuric acid attack (modified after Kratz and Schnug, 2005) and the expected change of Sr isotopes during production processes.

Generally, there was a high significant correlation (r = 0.989, $P<0.05$) between Sr isotope ratio in rock phosphates and in P-fertilisers produced of the same origin (Fig. 4.17), and significantly different values were found in rock phosphates and P-fertilisers of different provenance regions. Sr isotope ratios in P-fertilisers thus reflected the origin of rock phosphate from which P-fertilisers were produced. Therefore, rock phosphates and straight P-fertilisers of the same origin were classified together based on *R*(^{87}Sr/^{86}Sr) and Sr content (Fig. 4.18).

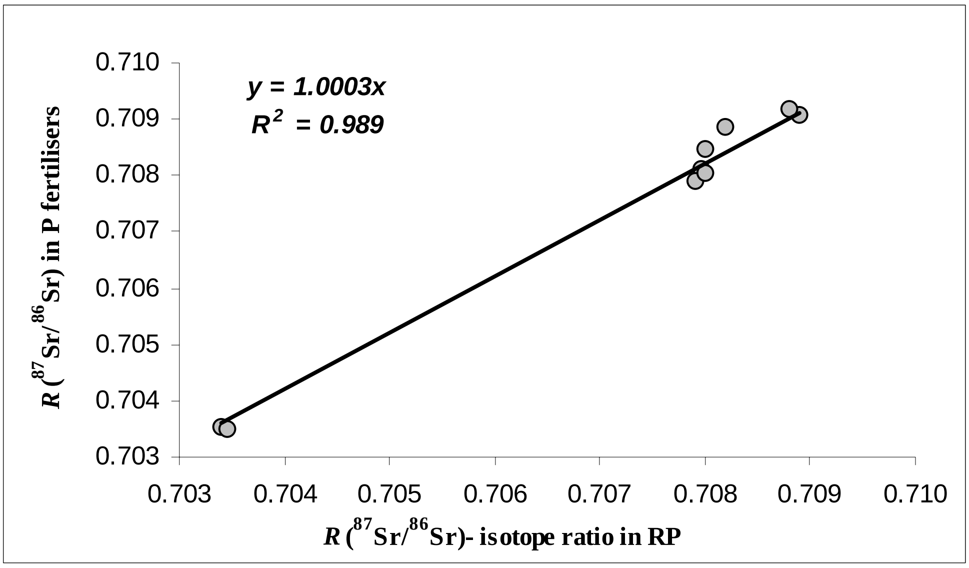


Fig 4.17: Relationship between Sr isotope ratio in rock phosphates and P-fertilisers of the same origin

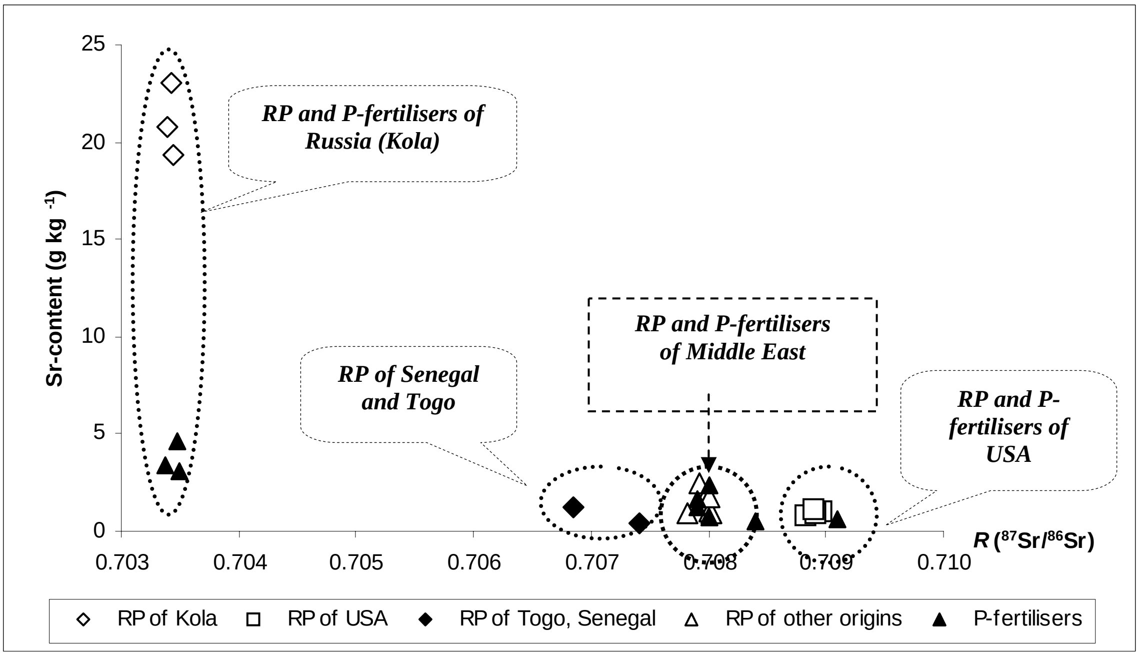


Fig. 4.18: Sr content versus *R*(^{87}Sr/^{86}Sr) for rock phosphates and P-fertilisers from different origin

4.6.3 Natural Sr isotope ratio variation as a tool to trace backs the origin of P-fertilisers of different manufacturers

I Natural Sr isotope ratio in different types of P-containing fertilisers

In compound mineral fertilisers, no significant differences were observed between Sr isotope ratios in the different types of P-containing fertilisers (PK, NP, NPK). However, the average of *R*(^{87}Sr/^{86}Sr) in K containing fertilisers (PK and NPK) was little higher than in fertilisers which did not contain K (Table 4.19).

Table 4.19: Sr isotope ratio, Sr- and P- content in different types of P-containing mineral fertilisers of different manufacturers

Type of fertilisers	**Sample ID**	**P_2O_5** [%]	**Sr-content** [mg kg^{-1}]	**Manufacturer**	***R*(^{87}Sr/^{86}Sr)**	**Average of *R*(^{87}Sr/^{86}Sr) ± Std. dev**
PK	PK 3	16	472	S.I. Düngephosphate	0.708 37	0.708 155 a ±0.00030406
	PK 10		1956	Unknown	0.707 94	
NP	NP 1	27	1829	Hoechst	0.707 91	0.707526 a ±0.00228745
	NP 2	20	3093	Ruhr-Stickstoff AG (Bochum)	0.703 49	
	NP 3	20	484	BASF	0.708 64	
	NP 4	52	84.0	Guano-Werke AG	0.708 92	
	NP 5	9	322	Unknown	0.708 67	
NPK	NPK 1	8.8	216	BASF	0.708 98	0.7076 535 a ±0.00204492
	NPK 2	8.8	208	BASF	0.708 99	
	NPK 3	13	250	BASF	0.708 78	
	NPK 4	12	297	BASF	0.709 12	
	NPK 5	15	250	BASF	0.708 76	
	NPK 15	15	263	BASF	0.709 27	
	NPK 16	8	166	BASF	0.709 15	
	NPK 6	15	222	Guano-Werke AG	0.708 89	
	NPK 7	12	379	Guano-Werke AG	0.708 53	
	NPK 8	15	209	Guano-Werke AG	0.708 95	
	NPK 9	13	185	Hoechst	0.708 49	
	NPK 10	13	263	Hoechst	0.708 24	
	NPK 11	13	3361	Ruhr-Stickstoff AG (Bochum)	0.703 38	
	NPK 12	15	190	Ruhr-Stickstoff AG (Bochum)	0.705 27	
	NPK 13	8.5	173	Unknown	0.709 04	
	NPK 14	12	120	Unknown	0.707 64	
	NPK 17	nd	380	Unknown	0.707 96	
	NPK 18	nd	5000	Unknown	0.703 54	
	NPK 19	nd	97.0	Unknown	0.706 61	
	NPK 20	nd	4627	Unknown	0.703 48	

Mean values followed by different letters are significantly different by Duncan's test at P<0.0001.

Measurement uncertainty (U) using a coverage factor k = 2 was 0.00027 for all samples.

nd: not determined.

The high $R(^{87}Sr/^{86}Sr)$ in K containing fertilisers was probably due to the high $R(^{87}Sr/^{86}Sr)$ in K-fertilisers (Table 4.20): In the present work, $R(^{87}Sr/^{86}Sr)$ in two K-fertilisers was 0.721 and 0.730. Similar Sr isotope ratios for K-fertilisers were found by Borg and Banner (1996) as well as by Vitoria and Otero (2004). The highest $R(^{87}Sr/^{86}Sr)$ reported was in KCl with a value of 0.83518 (Böhlke and Horan, 2000). The enrichment of K-fertilisers in ^{87}Sr, which results in the high $R(^{87}Sr/^{86}Sr)$, may be attributed to the high Rb/Sr in K-feldspar minerals (Jones and Jenkyns, 2001; Banner, 2004; Åberg (1994).

Table 4.20: Sr concentrations and $R(^{87}Sr/^{86}Sr)$ in K-fertilisers

K	**In present study**		**In the literature**		
	Sr [mg kg^{-1}]	$R(^{87}Sr/^{86}Sr)$	Sr [mg kg^{-1}]	$R(^{87}Sr/^{86}Sr)$	References
K_2SO_4	4.0	0.72056		0.715	Vitoria and Otero, 2004
KCl			77	0.835	Böhlke and Horan, 2000
K-fertilisers (unknown)	28	0.72979	18	0.740	Borg and Banner, 1996

Measurement uncertainty (U) using a coverage factor k = 2 was 0.00027.

II *Determining the origin of P-fertilisers of different manufacturers based on $R(^{87}Sr/^{86}Sr)$*

The collections used in this study contained compound fertiliser samples (NP, PK, NPK) from various producers. As can be seen in Table 4.21, in some cases there was a relationship between producer and $R(^{87}Sr/^{86}Sr)$. The most obvious example were the samples produced by Ruhr-Stickstoff AG (Bochum): Their Sr isotope ratio was significantly lower than that of fertilisers produced by other manufacturers (Fig. 4.19). Based on the findings reported above it can be assumed that Ruhr-Stickstoff AG (Bochum) used igneous rock phosphates from the Russian Kola Peninsula, which are characterised by a particularly low Sr isotope ratio, for their production. $R(^{87}Sr/^{86}Sr)$ in P-containing fertilisers NP2 and NPK11 produced by Ruhr-Stickstoff AG (Bochum) were 0.70349 and 0.70338 respectively, which agreed well with $R(^{87}Sr/^{86}Sr)$ in igneous rock phosphates from the Russian Kola Peninsula ranging from 0.70339 to 0.70345. One sample (NPK12) displayed an intermediate $R(^{87}Sr/^{86}Sr)$, ranging between the typical values for igneous rock phosphates and sedimentary rock phosphates, with value of 0.70527.

$R(^{87}Sr/^{86}Sr)$ isotope ratio in P-containing fertilisers produced by other manufacturers (Hoechst AG, BASF and Guano Werk) ranged from 0.70791 to 0.70927, these ratios agreed well with $R(^{87}Sr/^{86}Sr)$ in sedimentary rock phosphates from the USA, Middle East and Northern Africa which ranged from 0.70810 to 070896. It is clear that it was possible to distinguish if certain manufacturer used sedimentary rock phosphates or igneous rock phosphates to produce P-containing fertilisers. However, within manufacturers that used sedimentary rock phosphates to produce P-containing fertilisers, this tool was not sufficient to trace back the origin of sedimentary rock phosphates used in the production of P-fertilisers.

Table 4.21: Sr-content and *R*(^{87}Sr/^{86}Sr) in P-containing mineral fertilisers of different manufacturers

Manufacturer	**N**	**Sr-content/ [mg kg^{-1}]**		**^{87}Sr/^{86}Sr-isotope ratio**	
		Average	Std. Dev.	Average	Std. Dev.
Hoechst AG	3	759 a	927	0.708 2 a	0.00029
R-S- Bochum	3	2215 a	1758	0.704 0 b	0.00106
BASF	8	267 a	96.0	0.709 0 a	0.00021
Guano Werk	3	204 a	178	0.708 8 a	0.00023
Other (manufacturer not declared)	10	1314 a	1928	0.707 2 a	0.00207

Mean values followed by different letters are significantly different by Duncan's test at P<0.0001.

Measurement uncertainty (U) using a coverage factor k = 2 was from 0.00027 to 0.00028.

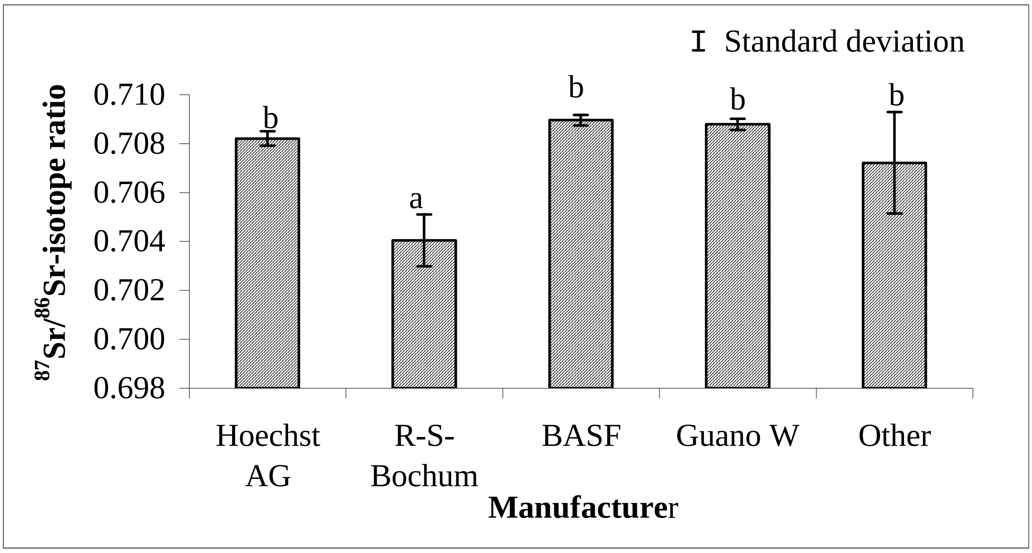


Fig. 4.19: Sr isotope ratio in P-containing mineral fertilisers from different manufacturers. Different letters denote significant differences between Sr isotope ratios in P-fertilisers from different manufacturers by Duncan's test at P<0.0001.

IV Determination of the origin of P-fertilisers in organo mineral fertilises based on $R(^{87}Sr/^{86}Sr)$

The organo-mineral fertilisers had different isotope ratios ranging from 0.7082 to 0.71877 (Table 4.22). Sr isotope ratio in organo-mineral fertilisers depends on the relative contribution from each source. It is clear that OMF 2 had the highest Sr isotope ratio (Fig. 4.22) and the lowest concentration of Sr compared to other organo-mineral fertilisers. This can be explained by the high K content and high K/P_2O_5 ratio in OMF 2, which, as described above (chapter 4.6.3), brings in a high Sr isotope ratio. In order to calculate initial Sr isotope ratio in P-fertilisers or rock phosphates used for organo-mineral fertilisers production, the Sr content and Sr isotope ratio for other components such as farmyard manures and K-fertilisers must be known. Therefore, some farmyard manures as well as K-fertilisers were also analysed for these parameters.

Table 4.22: Sr concentration, P/K ratio and Sr isotope ratio in organo-mineral fertilisers

Organo-mineral fertiliser samples		**K/P**	**Sr- content [mg kg^{-1} fresh matter]**	**$R(^{87}Sr/^{86}Sr)$**
OMF 1	NPK + Mg 5+4+5 +3	1.25	376	0.708 2
OMF 2	NPK + Mg 9+5+13+4	2.60	52.0	0.718 8
OMF 3	NPK + Mg 8+7+12+2	1.70	270	0.708 9
OMF 4	NPK + Mg 8+8+10+2	1.25	173	0.709 8

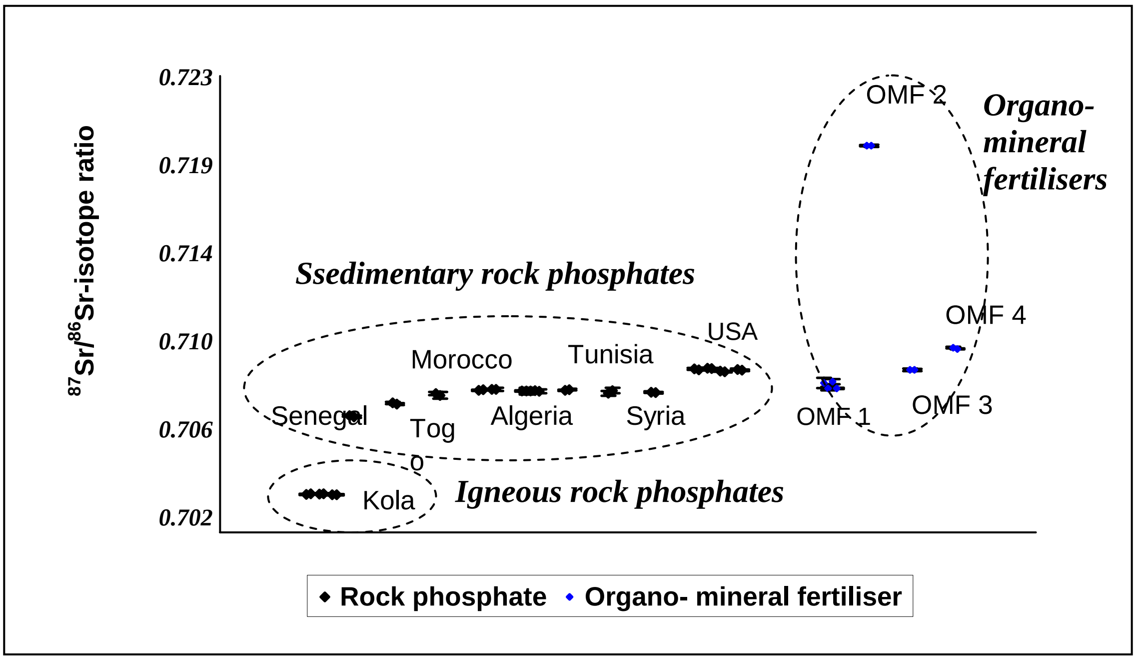


Fig. 4.20: Sr isotope ratio in organo-mineral fertilisers and rock phosphates from different origin

Average $R(^{87}Sr/^{86}Sr)$ in pig manure, with a value of 0.7077, was significantly lower than $R(^{87}Sr/^{86}Sr)$ in chicken and dairy cows and calf manure, with values of 0.7091 and 0.7094, respectively (Table 4.23). Pig manure had a significantly higher concentration of Sr with an average of 123 mg kg^{-1} than chicken manure, and dairy cow and calf manure with an average concentration of Sr 62.5 and 43.4 mg kg$^{-1,}$ respectively. In general, these variations may be due to Sr concentration and Sr isotope ratio in animals' diets.

Table 4.23: P- and Sr-content and Sr isotope ratios in different animal manures

Farmyard Manures	**Nr. of Sample**	**Dry matter [%]**	**P-content [g kg $^{-1}$ fresh matter]**	**Sr-content/ [mg kg^{-1} fresh matter]**	**Average of Sr-content [mg kg^{-1}]**	**$R(^{87}Sr/^{86}Sr)$**	**Average of $R(^{87}Sr/^{86}Sr)$**
Chicken	Chic. 1	13.9	14.5	56.4	62.47 ± 22.23 a	0.708 6	0.709 1± 0.00045 a
	Chic. 2	13.1	14.5	43.9		0.709 5	
	Chic. 3	33.3	18.2	87.1		0.709 0	
Dairy Cow and Calf	Cow1	21.1	7.23	57.5	43.43 ± 18.17 a	0.711 2	0.709 4± 0.00081 a
	Cow2	22.0	8.31	45.6		0.709 8	
	Cow3	nd	6.67	53.4		0.708 5	
	Cow4	16.0	4.24	17.2		nd	
Pig	G1	13.5	16.9	140	123 ± 18.08 b	0.707 2	0.707 7± 0.00072 b
	G3	26.4	27.7	104		0.707 3	
	G2	21.3	16.6	125		0.708 5	

Mean values followed by different letters are significantly different by Duncan's test at P<0.0001.

Uncertainty values were from 0.00028 to 0.0003, nd: not determine.

V *Isotopic-mixing model as a tool to determine Sr isotope ratio in P-fertilisers or rock phosphates used for organo-mineral fertilisers or compound fertiliser production*

Sr isotope ratio in compound mineral fertilisers depends on the relative contribution from each source as was mentioned previously in Chapter 3.4. In order to calculate initial Sr isotope ratio in P-fertilisers or rock phosphates used for PK-fertiliser production, the following equations, which were explained in Chapter 3.4, can be used:

$$\alpha_M = f_k\alpha_k + f_p\alpha_p \ldots\ldots\ldots \mathbf{A}$$

$$1 = f_k + f_p \ldots\ldots\ldots\ldots\ldots \mathbf{B}$$

Substituting f_p in equation (A) gives the following equation:

$$\alpha_p = (\alpha_M - f_k\alpha_k)/(1- f_k)$$

Where: f_k *and* f_P: equals to the fraction of Sr come from K-component and P- component respectively.

α_k and α_p: are the isotopic compositions of K and P-fertilisers respectively.

α_M: isotopic compositions of the compound fertilisers.

In order to calculate Sr isotope ratio in the original P-fertiliser using these equations, the concentration of Sr and Sr isotope ratio in applied K-fertilisers should be known. As was reported in Table 4.20, Sr concentration and Sr isotope ratio in K-fertilisers ranged from 4 to 85 mg kg^{-1}, and 0.72 to 0.83 respectively.

In NPK-fertilisers there are three sources for Sr. Therefore, Sr isotope ratio in the P-component (α_p) can be calculated using the following equation

$$\alpha_M = f_k\alpha_k + f_p\alpha_p + f_n\alpha_n$$

$$1 = f_k + f_p + f_n$$

$$\alpha_p = [\alpha_{M-} (f_k\alpha_k + f_n\alpha_n)](1- f_k + f_n)$$

Where: f_k, f_P and f_n: denote the fraction of Sr coming from K, P, and N-component.

α_k, α_p and α_n: Sr isotope ratio in K, P and N -component respectively.

α_M: Sr isotope ratio of the compound fertilisers.

This equation can be extended to include more than three sources of raw materials mixed together such as organo-mineral fertilisers.

In order to calculate the contribution of different raw materials to the mixture, n different isotope ratios are required to calculate the contributions of n+1 different raw materials to compound fertilisers, as was discussed in chapter 3.4.

Sr isotope ratio in original P-fertilisers can only be calculated if the exact concentration of Sr and Sr isotope of each of the components (except P) is known. The main problem is that in organo-mineral fertilisers the exact Sr isotope ratios and Sr contents for each component of compound fertilisers are not available. In organo-mineral fertilisers Sr is derived from various materials. Sr isotope ratio varied not only between different materials (components), but also even within one material (component), it was from 0.7033 to 0.7090 in rock phosphates and P-fertilisers depending on their origin; from 0.72 to 0.84 in K-fertilisers; from 0.7083 to 0.713 in Mg-lime, and from 0.707 to 0.711 in animal farmyard manures depending on type of animal manure. As a result, it is too complex to determine the origin of the rock phosphate or P-containing fertilisers used for the production of organo-mineral fertilisers using Sr isotope ratio only.

4.7 U isotope ratios in rock phosphates and P-containing fertilisers

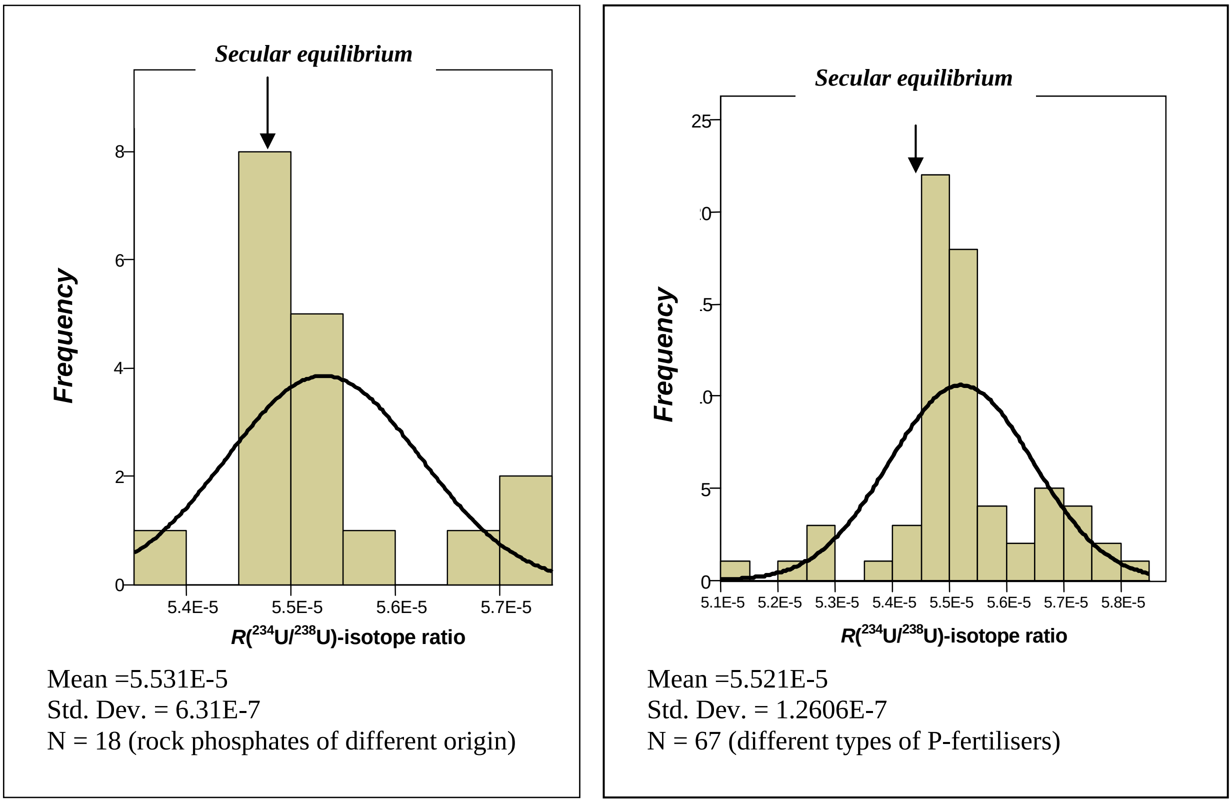
4.7.1 Natural R(^{234}U/^{238}U) in rock phosphates from different origin and P-fertilisers

A characteristic of a U series is that after about 5 half-lives of ^{234}U, the system is in secular equilibrium. ^{234}U is the nuclide with the longest half-life in U decay series; this means that all U daughters in the decay system are at secular equilibrium after 5 half-lives of ^{234}U. In secular equilibrium, *R*(^{234}U/^{238}U) equals 5.48 E-5. *R*(^{234}U/^{238}U) in rock phosphates varied from 0.00536 to 0.00573, and most of the rock phosphate samples were around the secular equilibrium value (Table 4.24 and Fig. 4.22). The same results were found for all types of P-containing fertilisers including straight P-fertilisers, NP, PK, NPK, farmyard manures and organo-mineral fertilisers (Fig. 4.21).

Table 4.24: *R*(^{234}U/^{238}U) in rock phosphates and P-fertiliser samples

Origins	**R(^{234}U/^{238}U) in rock phosphates**			**R(^{234}U/^{238}U) in P-fertilisers**	
	Sample ID	**R(^{234}U/^{238}U)**	**Average**	**Sample ID**	**R(^{234}U/^{238}U)**
Morocco	RP 8	5.493E-05	5.493E-05 a	P 5	5.495E-05
	RP 5	5.511E-05		P 4	5.546E-05
	RP 10	5.467E-05			
	RP 6	5.498E-05			
Algeria	RP 17	5.478E-05	5.478E-05	P 1	5.471E-05
Senegal	RP 12	5.520E-05	5.520E-05		
Tunisia	RP 15	5.526E-05	5.526E-05		
USA	RP 25	5.580E-05	5.676E-05 b	P 3	5.802E-05
	RP 23	5.717E-05			
	RP 20	5.732E-05			
	RP 24	5.676E-05			
Togo	RP 32	5.526E-05	5.535E-05		
	RP 33	5.544E-05			
Israel	RP 34	5.465E-05	5.465E-05	P 2	5.409E-05
Syria	RP 18	5.361E-05	5.361E-05	P 6	5.468E-05
Russian Kola	RP 3	5.486E-05	5.488E-05 a		
	RP 2	5.483E-05			
	RP 1	5.496E-05			

Mean values followed by different letters are significantly different by Duncan's test at P<0.0001.



Mean =5.531E-5
Std. Dev. = 6.31E-7
N = 18 (rock phosphates of different origin)

Mean =5.521E-5
Std. Dev. = 1.2606E-7
N = 67 (different types of P-fertilisers)

Fig. 4.21: Frequency histogram of $R(^{234}U/^{238}U)$ in fertiliser samples of different types (rock phosphates, P-containing fertilisers, farmyard manures and organo-mineral fertilisers)

U decay chains are typically at secular equilibrium in closed systems older than 1 x 10^6 y, so it can be concluded that the deposits from which most samples originate are at least of that age or older. $R(^{234}U/^{238}U)$ can be used as an indicator for secular equilibrium or disequilibrium in natural samples. Data on $R(^{234}U/^{238}U)$ in rock phosphates from different origin are plotted in Fig. 4.22. $R(^{234}U/^{238}U)$ in rock phosphates from the USA was significantly higher than in samples from all other geographical origins (Fig. 4.22). This disequilibrium (enrichment in ^{234}U) indicates the more recent formation of rock phosphates in the USA compared with other origins. So, $R(^{234}U/^{238}U)$ can be used to distinguish the samples from the USA from other samples (Fig. 4.23). This difference between rock phosphates of USA and other rock phosphates is described in the hierarchical cluster analysis based on $R(^{234}U/^{238}U)$ (Fig. 4.24). However, this parameter did not allow for further differentiation within other origins.

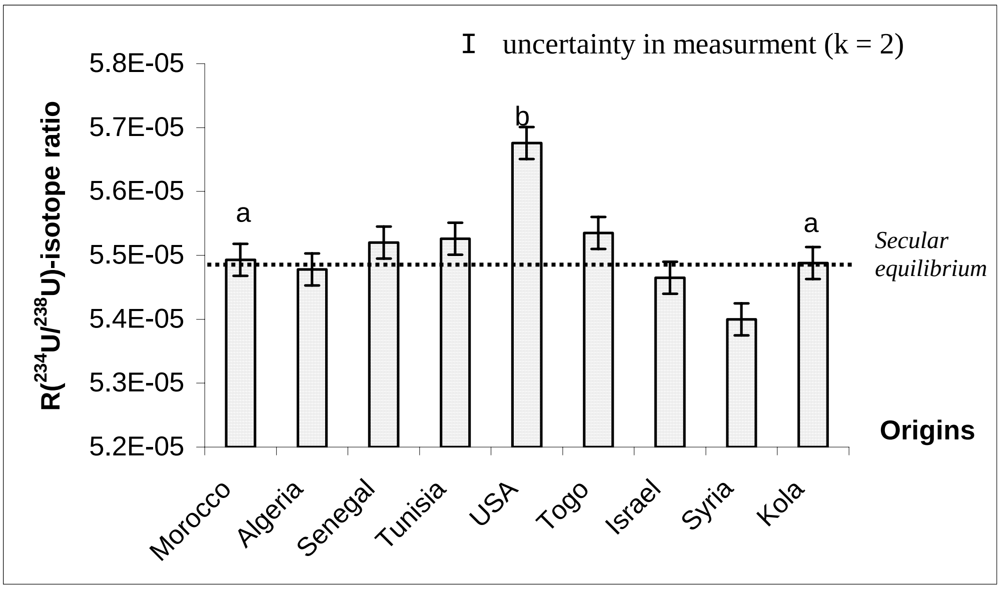


Fig. 4.22: *R*(^{234}U/^{238}U) showing *R*(^{234}U/^{238}U) disequilibrium in rock phosphates from the USA compared with other origin (different letters denote significant differences between U isotope ratio in rock phosphate of different origin by Duncan's test at P<0.0001). Error bars on data points indicate plus/minus uncertainty using a coverage factor k = 2.

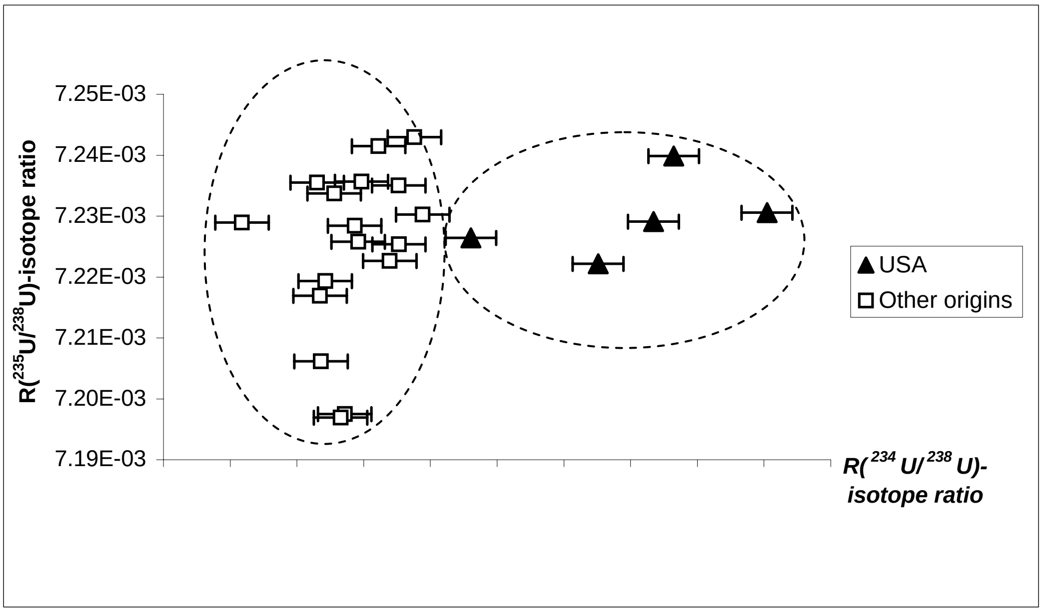
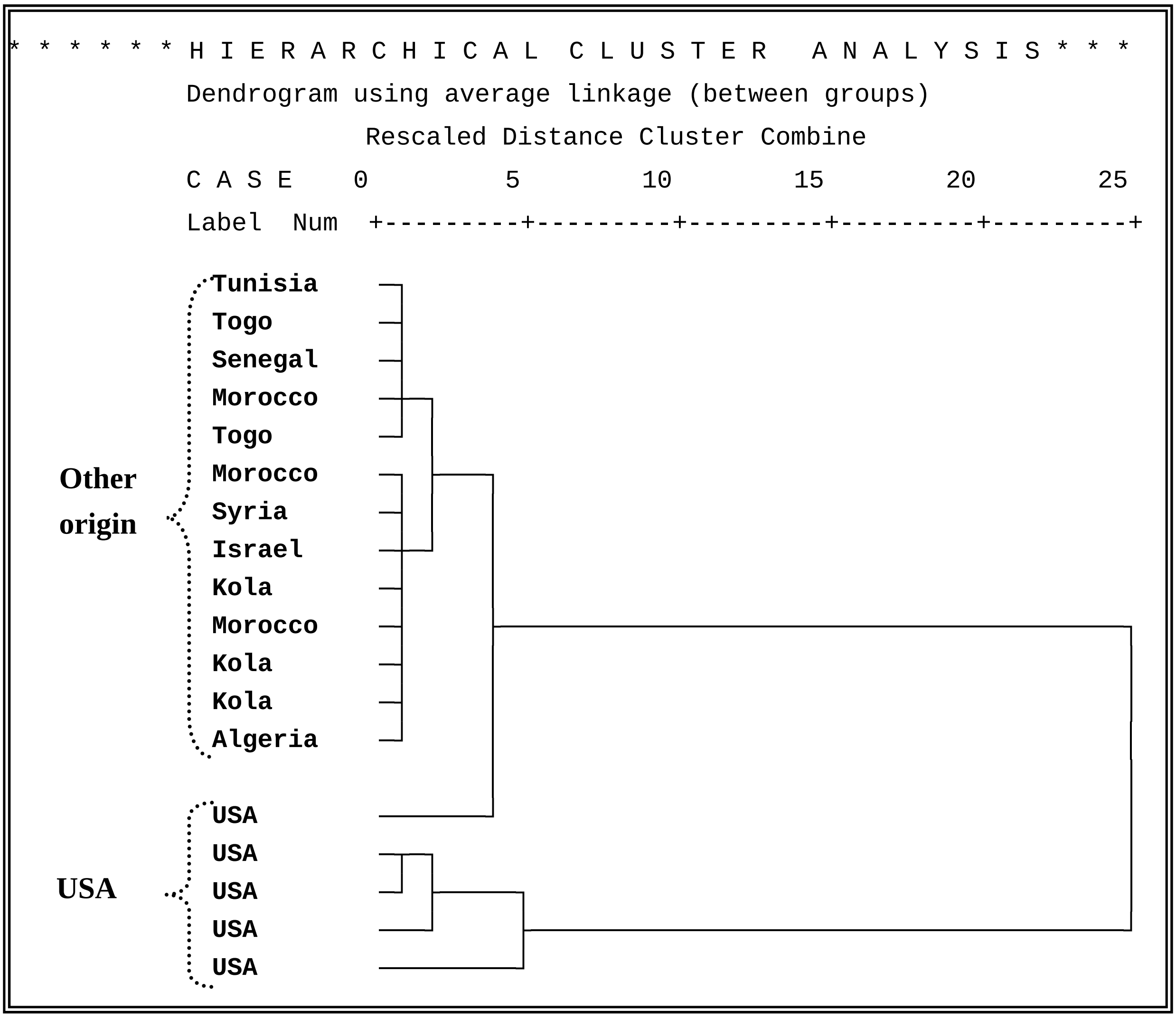


Fig. 4.23: *R*(^{234}U/^{238}U) versus *R*(^{235}U/^{238}U) in rock phosphates from USA and other origins. Error bars on data points indicate plus/minus uncertainty using a coverage factor k = 2.



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* * * * * * H I E R A R C H I C A L   C L U S T E R   A N A L Y S I S * * *
            Dendrogram using average linkage (between groups)
                        Rescaled Distance Cluster Combine
            C A S E     0         5        10        15        20        25
            Label  Num  +---------+---------+---------+---------+---------+
```

Fig. 4.24: Hierarchical cluster analysis of rock phosphate samples based on $R(^{234}U/^{238}U)$

4.7.2 *Transfer of $R(^{234}U/^{238}U)$ from rock phosphates to P-fertilisers*

The acid attack breaks the near secular equilibrium between U and its daughters in the mineral. During the acidulation process, radionuclides are partitioned according to their solubility. ^{238}U and ^{234}U tend to go to the acid solution, whereas the Ra and Po in the uranium decay chain tend to go to the by-product phosphogypsum (Rutherford *et al.*, 1995; Erdem et al, 1996). So while the condition of secular equilibrium between ^{238}U and Ra is disturbed during the wet process of P-fertiliser production (Saueia and Mazzilli, 2006; DaConceição and Bonotto, 2006), this is generally not the case for the condition of secular equilibrium between ^{238}U and ^{234}U (Fig. 4.25). A reason for this is the fact that the differences in mass between U isotopes (dm/m) are relatively small (see introduction). The second reason is the fact that nearly the complete amount of U present in rock phosphates is transferred to P-fertilisers. Therefore it can be expected that $R(^{234}U/^{238}U)$ in P-containing mineral fertilisers reflect $R(^{234}U/^{238}U)$ in their raw material (rock phosphate).

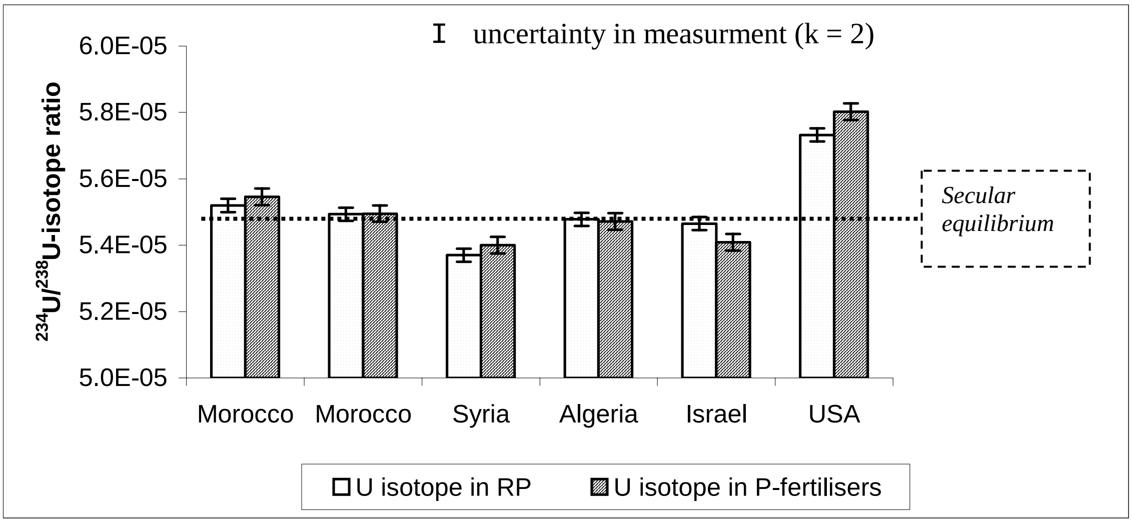

Fig. 4.25: *R*($^{234}U/^{238}U$) in rock phosphate and P-fertiliser samples from different origin. Error bars on data points indicate plus/minus uncertainty using a coverage factor k = 2.

The relationship between *R*($^{234}U/^{238}U$) in rock phosphate and *R*($^{234}U/^{238}U$) in P-fertilisers can be described by a linear function (Fig. 4.26). In this work *R*($^{234}U/^{238}U$) in rock phosphates and P-fertilisers from the USA was significantly higher than *R*($^{234}U/^{238}U$) in rock phosphates and P-fertilisers from other origins. So *R*($^{234}U/^{238}U$) in P-fertilisers allows to distinguish between P-fertilisers produced of rock phosphates from USA and P-fertilisers produced of rock phosphates from other origins (Fig. 4.27).

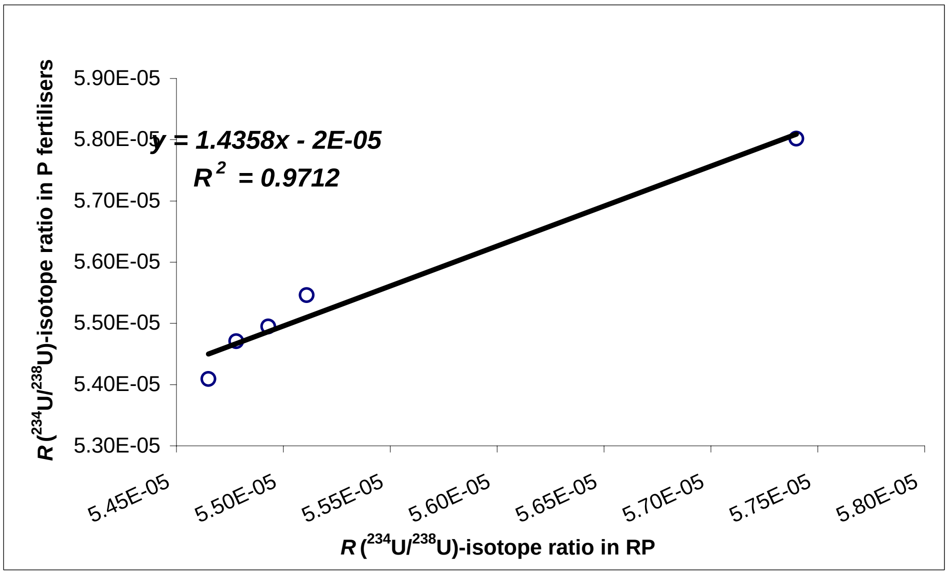

Fig. 4.26: The relationship between *R*($^{234}U/^{238}U$) in rock phosphate and *R*($^{234}U/^{238}U$) in P-fertilisers

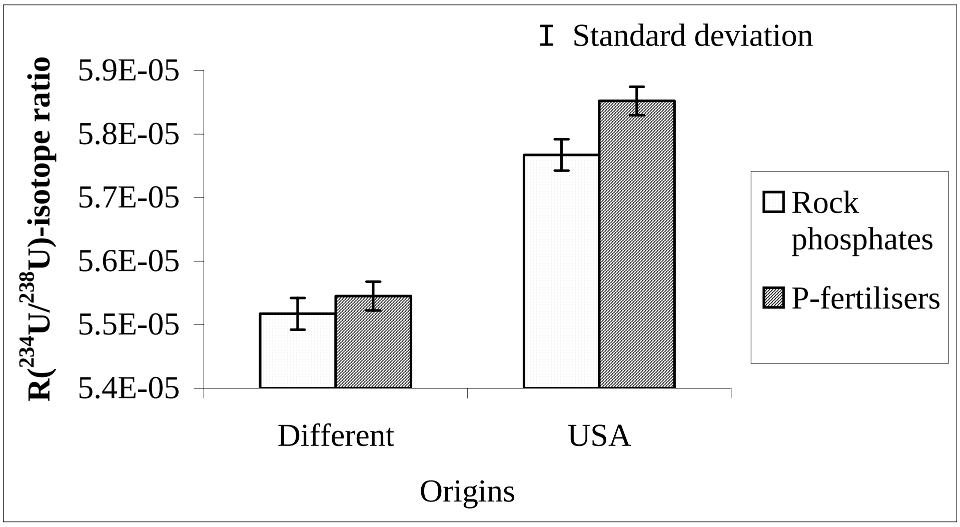

Fig. 4.27: Average $R(^{234}U/^{238}U)$ in rock phosphates and P-fertilisers from the USA and other origins

4.7.3 Determination of the origin of P-fertilisers of different manufacturers based on natural $R(^{234}U/^{238}U)$

$R(^{234}U/^{238}U)$ in the various types of P-containing mineral fertilisers (NP, PK, NPK) fabricated by different manufacturers did not show significant differences among each other (Table 4.25). Ratios ranged from 5.36 x10^{-5} to 5.8 x 10^{-5}, with most of the samples around the secular equilibrium (Fig. 4.28). However, it can be seen clearly that P-containing fertilisers manufactured in different manufacturers had different U isotope ratios (Fig. 4.29). The reason for this is the fact that the origins of the rock phosphate ore were not the same for all manufacturers. $R(^{234}U/^{238}U)$ in P-fertilisers manufactured by BASF was similar to $R(^{234}U/^{238}U)$ in rock phosphates from the USA, which indicates that this type of rock phosphates was used for fertiliser production. However, $R(^{234}U/^{238}U)$ did not allow for further differentiation within the origins of rock phosphates used by other manufacturers. Therefore, $R(^{234}U/^{238}U)$ can be used to distinguish the rock phosphate and straight P-fertiliser samples from the USA from other samples. Also, it can be determined if the manufacturer used rock phosphate from this origin to produce P-fertilisers or P-containing fertilisers.

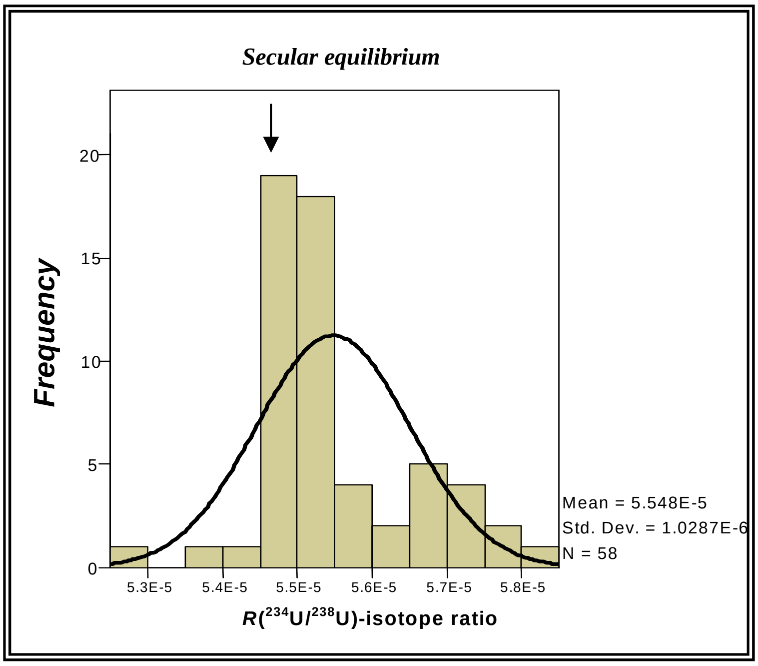

Fig. 4.28: Frequency histogram of *R*(^{234}U/^{238}U) in rock phosphates P-containing mineral fertilisers.

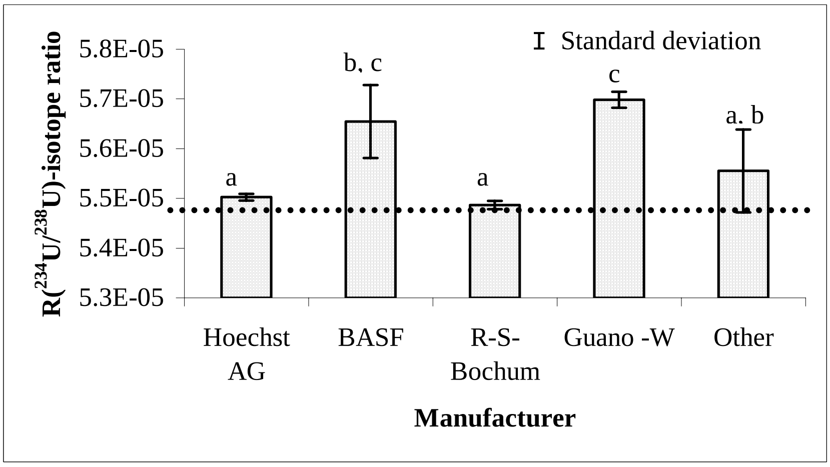

Fig. 4.29: *R*(^{234}U/^{238}U) in P-containing mineral fertilisers of different manufacturers. Different letters denote significant differences between U isotope ratios in rock phosphates from different origin by Duncan’s test at P<0.0001.

Table 4.25: U isotope ratios in P-containing fertilisers from different manufacturers

Type	**Sample**	**P_2O_5 [%]**	**Manufacturer**	**$R(^{234}U/^{238}U)$**			**$R(^{235}U/^{238}U)$**		
				$R(^{234}U/^{238})$	Uncertainty	Average	$R(^{235}U/^{238}U)$	Uncertainty	Average
PK	PK 3	16	S.I. Düngephosphate	5.523E-05	1.1E-07	5.54E-05 ± 0.04E-05	7.2361E-03	6.9E-06	7.23E-03 ± 0.005E-03
	PK 5	20	S.I. Düngephosphate	5.587E-05	1.3E-07		7.2402E-03	8.4E-06	
	PK 6	20		5.513E-05	1.2E-07		7.2309E-03	8.3E-06	
NP	NP 1	27	Hoechst	5.500E-05	1.2E-07	5.63E-05 ± 0.14E-05	7.2333E-03	7.6E-06	7.23E-03 ± 0.007E-03
	NP 2	20	Ruher Bochum	5.488E-05	1.3E-07		7.2207E-03	8.0E-06	
	NP 3	20	BASF	5.781E-05	1.2E-07		7.2290E-03	7.3E-06	
	NP 4	52	Unknown	5.609E-05	1.2E-07		7.2383E-03	7.9E-06	
	NP 5	9	Unknown	5.776E-05	1.2E-07		7.2343E-03	7.5E-06	
NPK	NPK 1	8.8	BASF	5.578E-05	1.3E-07	5.56E-05 ± 0.11E-05	7.2410E-03	7.1E-06	7.21E-03 ± 0.094E-03
	NPK 2	8.8	BASF	5.548E-05	1.2E-07		7.2240E-03	7.9E-06	
	NPK 3	13	BASF	5.663E-05	1.1E-07		7.230E-03	1.3E-05	
	NPK 4	12	BASF	5.704E-05	1.2E-07		7.2254E-03	7.6E-06	
	NPK 5	15	BASF	5.683E-05	1.2E-07		7.2149E-03	7.7E-06	
	NPK 6	15	Guano	5.272E-05	1.0E-07		6.8333E-03	6.4E-06	
	NPK 7	12	Guano	5.687E-05	1.3E-07		7.2298E-03	8.2E-06	
	NPK 8	15	Guano	5.710E-05	1.4E-07		7.2277E-03	9.1E-06	
	NPK 9	13	Hoechst	5.510E-05	1.1E-07		7.2381E-03	7.1E-06	
	NPK 10	13	Hoechst	5.497E-05	1.1E-07		7.2157E-03	7.7E-06	
	NPK 11	13	Ruher Bochum	5.478E-05	1.2E-07		7.2187E-03	7.4E-06	
	NPK 12	15	Ruher Bochum	5.494E-05	1.1E-07		7.2344E-03	8.7E-06	
	NPK 13	8.5	Unknown	5.553E-05	1.3E-07		7.2332E-03	8.3E-06	
	NPK 14	12	Unknown	5.507E-05	1.1E-07		7.2235E-03	8.1E-06	
	NPK 15	15	BASF	5.624E-05	1.3E-07		7.2381E-03	7.5E-06	
	NPK 16	8	BASF	5.655E-05	1.5E-07		7.227E-03	1.1E-05	
	NPK 17		Unknown	5.462E-05	1.1E-07		7.2341E-03	8.4E-06	
	NPK 18		Unknown	5.522E-05	1.0E-07		7.2534E-03	7.5E-06	

No significant differences were found by ANOVA test at $P<0.05$.

4.7.4 *$R(^{234}U/^{238}U)$ in farmyard manures and organo-mineral fertilisers*

The differences between $R(^{234}U/^{238}U)$ in organo-mineral fertilises were not significant. Therefore, the determination of the origin of P-component in organo-mineral fertilises based on $R(^{234}U/^{238}U)$ was not possible. $R(^{234}U/^{238}U)$ in different types of fertiliser samples (rock phosphates, P-containing mineral fertilisers, farmyard manures and organo-mineral fertilisers) ranged from 5.1×10^{-5} to 5.77×10^{-5}. Secular equilibrium of U isotopes ^{234}U and ^{238}U was observed in most samples. The differences between $R(^{234}U/^{238}U)$ in farmyard manures of different animals were not significant (Table 4.26). The $R(^{234}U/^{238}U)$ was not sufficient to identify the type of farmyard manures. $R(^{234}U/^{238}U)$ in all animal manures was less than secular equilibrium (5.48 x 10^{-5}) and less than in organo-mineral fertilisers (5.1 x 10^{-5}).

The depletion of ^{234}U in animal manures indicated that ^{234}U tend to stay in animal body or in their milk little more than ^{238}U. Pillonel et al. (2003) found that cheese samples from different origin showed a $^{234}U/^{238}U$ ratio higher than 1, in contrast to values generally found in soil and vegetation. U isotope fractionation and the ^{234}U enrichment of milk require more investigations.

Table 4.26: $R(^{234}U/^{238}U)$ in farmyard manures and organo-mineral fertilisers

Farmyard manure	**Nr. of sample**	**P_2O_5 [%]**	**U [mg kg^{-1} fresh matter]**	**Average of U [mg kg^{-1} fresh matter]**	**$R(^{234}U/^{238}U)$ E-05**	**Average $R(^{234}U/^{238}U)$ (E-05)**
Chicken	Chic. 1	3.26	3.98	3.96 a	5.132	5.348 a
	Chic. 2	3.27	3.00		5.464	
	Chic. 3	4.10	4.89		5.449	
Cows	Cow3	1.50	1.34	1.26 a	5.405	5.353 a
	Cow2	1.87	1.15		5.451	
	Cow4	0.95	1.30		5.203	
Pigs	G1	3.79	5.25	3.43 a	5.280	5.339 a
	G2	3.73	3.04		5.268	
	G3	6.23	2.00		5.468	
Organo-mineral fertilisers	OMF 1	4.00	24.8	19.9 b	5.536	5.519 b
	OMF 2	5.00	7.39		5.489	
	OMF 3	7.00	19.9		5.539	
	OMF 4	8.00	27.6		5.513	

Mean values followed by different letters are significantly different by Duncan’s test at P<0.0001.

4.7.5 *$R(^{235}U/^{238}U)$ as tool to detect contamination with anthropogenic U*

$R(^{235}U/^{238}U)$ can be used to distinguish natural from anthropogenic U while it is useless as an indicator of origin of different materials such as rock phosphates and P-containing fertilisers. In Fig. 4.30, $R(^{235}U/^{238}U)$-isotope ratio in eight P-fertilisers and eight rock phosphates of same origin are compared. The natural $R(^{235}U/^{238}U)$ in different samples from different origin ranged around 0.72%. The differences in *R*(^{235}U/^{238}U) between P-fertilisers and rock phosphates were very small. Obviously, there was no (or only a very slight) shifting of *R*(^{235}U/^{238}U) during the production process. The differences in *R*(^{235}U/^{238}U) between P-fertilisers and rock phosphates of one origin were lower than the minimum detectable difference of 2.1E-10^{-5}. Measurement uncertainties by applying a coverage factor *k* =2 for P-fertiliser samples ranged from 9.9E-06 to 1.8E-05, while for rock phosphates they ranged from 9.9E-06 to 2.1E-05. So if there was any shifting of *R*(^{235}U/^{238}U) during the production process at all, it was too small to be detected by analytical technique applied in this study.

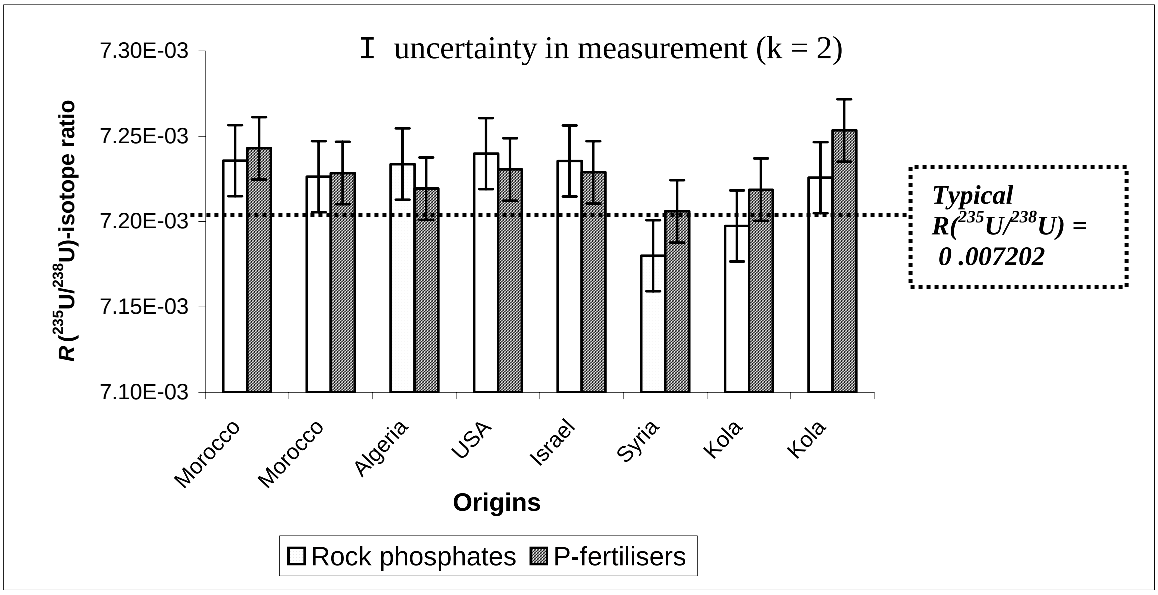

Fig. 4.30: *R*(^{235}U/^{238}U) in rock phosphate and P-fertiliser samples from different origin. Uncertainties were calculated according to the ISO guide to the expression of uncertainty in measurement, using a coverage factor *k*=2.

The determination of *R*(^{235}U/^{238}U) in 64 fertiliser samples including rock phosphates, P-fertilisers and P-containing fertilisers such NP, PK, NPK showed that the average of *R*(^{235}U/^{238}U) was 0.007 20, ranging from 0.007 181 to 0.007 253, which is close to the natural U isotope ratio. The overall distribution of data is illustrated clearly in a histogram (F.g. 4.31). However there was one sample where ^{235}U/^{238}U-isotope ratio was 0.0068 33, indicating that ^{235}U was significantly depleted relative to ^{238}U (Fig. 4.32). The most obvious reason for this finding is the pollution with anthropogenic uranium.

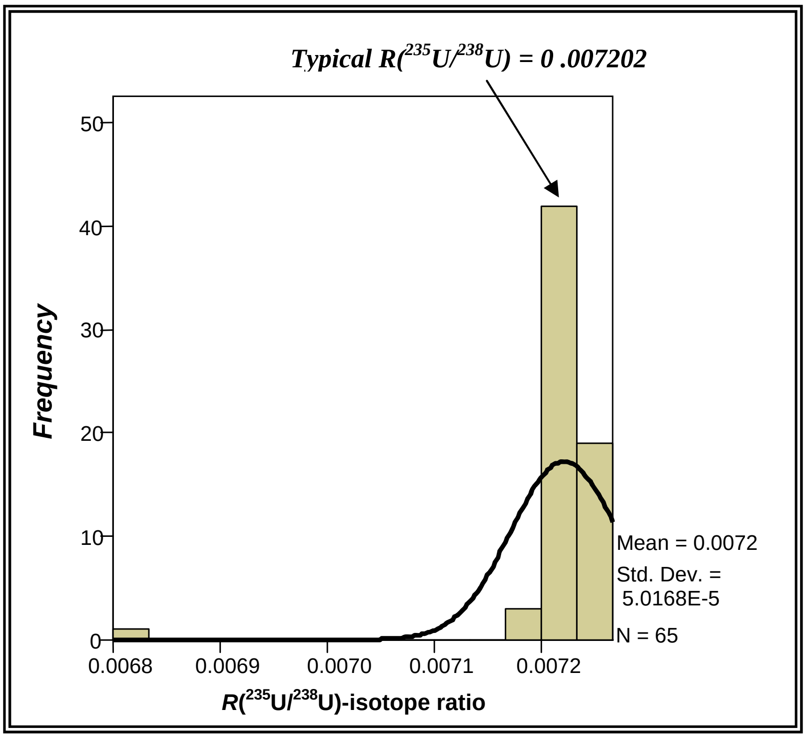

Fig. 4.31: Frequency histogram of $R(^{235}U/^{238}U)$ in 65 fertiliser samples of different type (rock phosphates, P-containing fertilisers, farmyard manures and organo-mineral fertilisers).

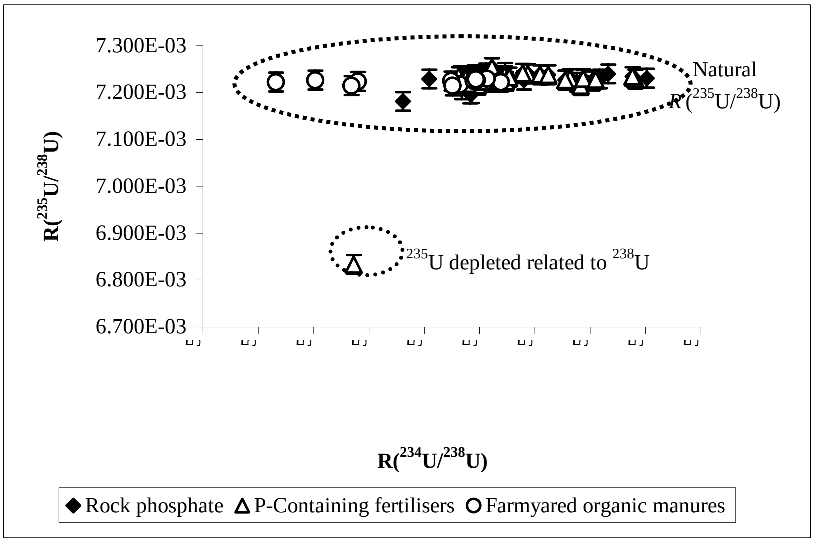

Fig. 4.32: $R(^{235}U/^{238}U)$ versus $R(^{234}U/^{238}U)$ in different rock phosphates, P-containing fertilisers and farmyard manure samples. Error bars on data points indicate plus/minus uncertainty using a coverage factor k = 2.

5 Discussion

Soil pollution with heavy metals and radionuclides is a serious problem; these toxic elements at high levels can pose a significant threat to human health and ecological systems. In general, the remediation of metal polluted soil is a difficult and expensive task. In order to avoid the accumulation of heavy metals in cultivated soil, rock phosphates and P-containing fertilisers, which are an important source of heavy metals in cultivated soils, should be selected which are characterised by their low content of toxic heavy metals and high level of phosphorous. The main objective of this research work was to identify and characterise the origin of rock phosphates and P-containing fertilisers using heavy metal patterns as well as Sr and U isotope ratios. These investigations were based on the hypothesis that the heavy metal patterns and the ratio between radiogenic and non-radiogenic isotopes can vary in rock phosphate samples from different origin. The discussion of the results of this thesis starts, therefore, with a discussion of the heavy metal content in rock phosphates from different origin and heavy metal patterns as an indicator of rock phosphate and P-fertiliser origins (Chapter 5.1). In the following chapter (Chapter 5.2), the high precision measurements of Sr isotope ratios to identify the origin of rock phosphates and P-containing fertilisers are discussed. Two main objectives based on the high precision measurements of U isotope ratio are considered in Chapter 5.3, determining the origin of rock phosphates and P-containing fertilisers based on $R(^{234}\mathrm{U}/^{238}\mathrm{U})$, and monitoring the pollution with anthropogenic U based on $R(^{235}\mathrm{U}/^{238}\mathrm{U})$. Subsequently, fingerprinting the origin of rock phosphates and P-containing fertilisers with regard to U and Sr isotope ratios together is discussed in chapter 5.4.

5.1 Fingerprinting the origin of rock phosphates and P-fertilisers by their heavy metal pattern

5.1.1 Identifying the origin of rock phosphate to reduce the heavy metals and radionuclides in P-fertilisers and to avoid environmental pollution

It was obvious in the present work that the concentration of U and other toxic heavy metals in P-containing fertilisers was higher than in fertilisers without P. This result was in agreement with Kratz and Schnug (2005) and Senesi and Polemio (1981). Also, it was found that the amounts of U, Sr and other heavy metals in P-containing mineral fertilisers were largely related to the origin of their raw material (rock phosphate), the amount of phosphate in the samples, and on the manufacturing processes of P-fertilisers (chapter 4.2). The positive correlation between U concentrations and the amount of phosphate (%P_2O_5) in P-fertilisers indicated that U concentration in P-containing mineral fertilisers depends on the amount of phosphate (%P_2O_5). The large variation of these heavy metal concentrations within a particular type of P-containing fertilisers indicated that amounts of U and Sr are largely related to the origin of their raw material (rock phosphate). This result agreed well with report by Charter et al. (1995), Mortvedt (1987), and Kratz and Schnug (2005). Therefore, as it was expected, it is possible to decrease the amounts of heavy metals and radionuclides in mineral P-fertilisers by the selection of rock phosphates from origins which are characterised by low impurities of heavy metals.

Furthermore, it was concluded in this study that the amounts of heavy metals, which can be loaded into soil with P-fertilisers, vary widely depending on the origin of rock phosphates. Therefore, the long continued application of rock phosphates or P-fertilisers from different origin add varying amounts of heavy metals to the soils.

For example, U loading into agriculture land with P-fertilisers at the same rate of P was decreased in the following order: Israel > Morocco > USA > Togo > Senegal > Syria > Algeria > Tunisia > Curacao > Russian Kola Peninsula. The required number of years to add 1 kg U/ha is from 43 to 704 (years) when sedimentary rock phosphates from different origin are applied, while it is 2778 years when igneous rock phosphates from the Russian Kola Peninsula are applied (Table 5.1).

For Sr, the number of years it take to add 1 kg Sr to the soil at a given P rate decreased in the order: Russian Kola Peninsula > Israel > Algeria > Syria > Morocco > USA > Senegal > Curacao > Togo > Tunisia (Table 5.1). For this reason, in the Ukrainian soils, after more than 10 years of fertilisation with phosphate from the Russian Kola Peninsula, the Sr level increased between 1991-1994. At high Sr level, Sr poses dangers for animals and humans.

Table 5.1: Number of years to add 1 kg U or Sr ha^{-1} with an annual rate of 20 kg P ha^{-1} for rock phosphates from different origin

	Algeria	**Morocco**	**Senegal**	**Syria**	**Togo**	**Tunisia**	**Israel**	**USA**	**Curacao**	**Kola**
U [mg per kg P]	479	1017	671	537	716	352	1163	733	71	18
Years to add 1 kg U at P rate of 20 kg ha^{-1}	104	49	75	93	70	142	43	68	704	2778
Sr [g in kg P]	14.5	8.93	6.10	130	3.44	1.40	21.0	7. 60	5.95	121
Years to add 1 kg Sr at P rate of 20 kg ha^{-1}	3.4	5.6	8.2	3.8	15	36	2.4	6.6	8.4	0.4

The wide variation of heavy metal concentrations in P-fertilisers results in the addition of varying amounts of heavy metals to the soils. This could be one reason for the disagreements in the literature about the impact of heavy metals present in P-fertilisers on agricultural soil. E.g., several studies indicated that the application of phosphate fertilisers to cultivated soil did not significantly affect on U accumulation in soil (Hamamo et al., 1995; Jones and Jenkyns, 1991). However, other studies indicated that the application of P-fertilisers for a long period could elevate the heavy metals and U content in the surface layer of soil. The accumulation of heavy metals and radionuclides in soils through regular P-fertilisers use has been observed in many countries (Tekeda et al., 2006; Stojanovic et al., 2006; Conceicao and Bonotto, 2006; Kharikov and Smetana, 2000; El-Bahi et al., 2004; Zielinski et al., 2006).

As the heavy metals at high concentrations are toxic to humans, animals and plants, the transfer of these toxic metals to the human food chain must be avoided wherever possible. Lowering the heavy metal and U content in P-fertilisers is a possible way to reduce the heavy metal input to farmland. This can be achieved by using rock phosphates with a low heavy metal and U content (usually igneous rock phosphates). In the present work the rock phosphate from the Russian Kola Peninsula contained the lowest amount of U. Stephan (2000) found that P-containing fertilisers produced from Finnish rock phosphate contained lower amounts of ^{238}U than P-containing fertilisers produced from other origins.

The second method to reduce U and other toxic metals in P-containing fertilisers is by extraction of heavy metals and U from the phosphoric acid during the production process. When the rock phosphates contain a high U content, the U can be recovered as by product. Thus, the P-fertiliser produced by this method will have low U content. But the extraction of heavy metals and U is currently very expensive and low cost technologies are not yet fully developed (Kratz and Schnug, 2005; Zafar et al., 1996; Bunus 1994). The expensive extraction of U and other toxic metals from P-fertilisers increases the production cost for P-fertilisers, the costs to farmers, and the cost of food production in general, meaning that these technologies have been of more scientific than commercial interest until now. As a result, the selection of rock phosphates with low contents of U and other toxic metals will be more important in the future.

5.1.2 Factors affecting U concentration in rock phosphates and P-containing fertilisers

Rock phosphates contain naturally occurring radionuclides (NOR) such as ^{238}U, ^{235}Th and ^{40}K (Schnug et al., 1996). ^{238}U is of particular interest due to: (1) the chemical and radiological toxicity of U and its daughters, especially radon-222, (2) their long half-lives, (3) the enrichment of U in sedimentary rock phosphates (4) the concentration of U in P-fertilisers during the production processes. Phosphate ores contain significant concentrations of U (^{238}U and ^{235}U) and their decay products (daughters) such as ^{234}U, radon or radium. Therefore, controlling and reducing the load of U and other toxic heavy metals and radionuclides to cultivated soil with fertilisers especially P-containing fertilisers is essential for sustainable agriculture production, to keep the human environment clean, and to minimize toxic heavy metals in human diet.

In the present work, igneous rock phosphates from the Russian Kola Peninsula contained 3.04 to 3-35 mg kg^{-1} U, which was significantly lower than U content in sedimentary rock phosphates and mineral P-fertilisers (Fig. 5.1). The same results were found by Kratz and Schnug (2006); El-Ghawi *et al*. (1999); Van Kauwenbegh (1997) and Karkunen and Vermeulen (2000).

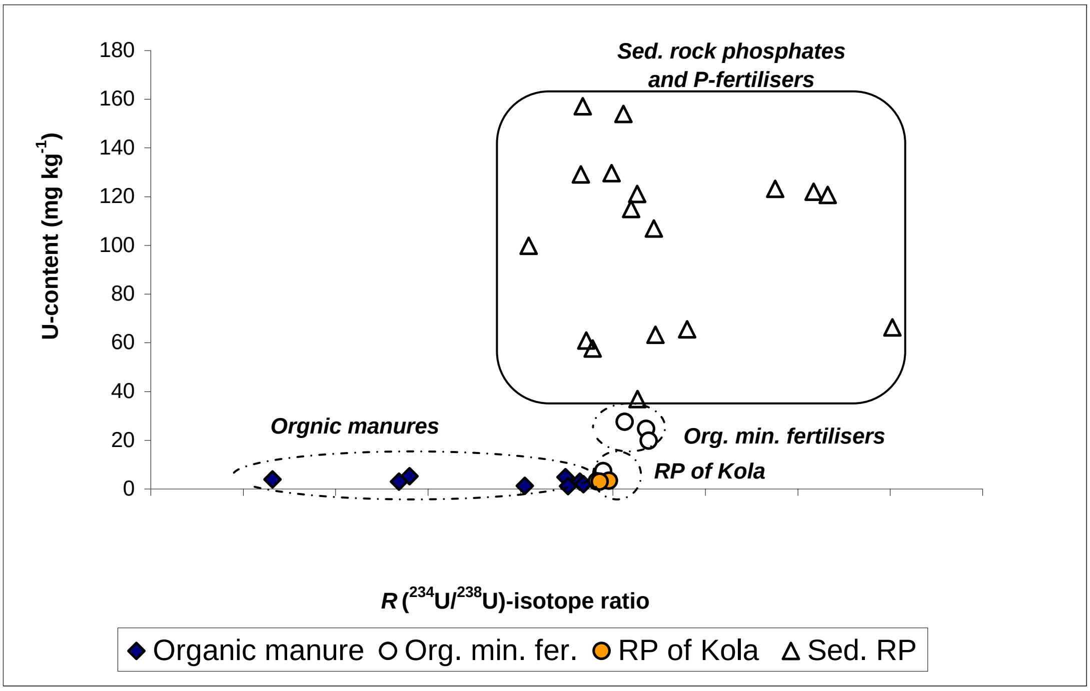

Fig. 5.1: $R(^{234}U/^{238}U)$ versus U concentration for different kinds of P-containing fertilisers

The significant enrichment of sedimentary rock phosphates in U was first discovered in 1906 by Strutt (Baturin and Kocheov, 2001) and it was reported by several authors (i.e. El-Arabi and Khalifa, 2002; Scholten and Timmermans, 1996). This enrichment is due to several factors, the most important are:

- U content in sedimentary rock phosphate deposits is usually higher than that of igneous rock phosphates because the hexavalent U in oxidizing conditions (uranyl ion $(UO_2)^{2+}$) is relatively soluble while Th is extremely insoluble (Calstern and Thomas, 2006). This discrimination is apparently related to the relative solubility of uranyl ion, leading to the U enrichment in seawater, compared to extreme insolubility of Th compounds (WHO, 2001). Uranyl ion $(UO_2)^{2+}$ easily complexes with carbonate and phosphate. Therefore, sedimentary rock phosphates contain high U concentration and low Th concentration.

- U can substitute for Ca in apatite as U^{4+} because the radius of U^{4+} is almost identical with that of Ca^{2+} with values of 0.97 Ǻ and 0.99 Ǻ respectively (Da Conceicao¸ Bonotto 2006; Fourati and Faludi 1988). As the uranyl (U^{6+}) is much larger, it can only be fixed in the exterior part of the structure by various adsorption processes (Khater el al., 2001).

However, large variations in U content within sedimentary rock phosphates based on the origin of sample were found in the present work (Table 4.4). Rock phosphates from Tunisia, Algeria and Syria had lower U contents, ranging from 26.7 to 62.0 mg kg^{-1}, compared with other sedimentary rock phosphates from Morocco, Senegal, Togo, Israel and USA ranging from 65.2 to 245 mg kg^{-1}. Moreover, large variations of U concentration were noticed even within the same origin, e.g. in Moroccan rock phosphates U content ranged from 71.0 to 245 mg kg^{-1} (Table 4.3).

U concentration in rock phosphates depends not only on the origin of samples but also it was reported that it can be affected by the deposit age and various layers. For example Baturin and Kocheov (2001) found that the average U concentration is from 4 to 48 mg kg^{-1} in Precambrian and Cambrian deposits, 20 to 90 mg kg^{-1} in Paleozoic and Jurassic deposits, 40-130 mg kg^{-1} in Late Cretaceous- Paleogene deposits, 30-130 mg kg^{-1} in Neogene deposits, and 30-110 mg kg^{-1} in Quaternary (including Holocene) deposits.

5.1.3 Heavy metal pattern as indicator to rock phosphate origins

Numerous articles cover the content of heavy metals and naturally occurring radionuclides in rock phosphates and commercial P-fertilisers from different origin. Several studies indicated that the concentrations of these impurities in rock phosphates vary considerably depending on their origins (Mortvedt and Beaton, 1995; Schnug *et al.*, 1996; Van Kauwenberg, 1997; Kharikov and Smetana, 2000, Mustonen, 1985). In the present work, a number of rock phosphate samples and commercial P-containing fertilisers from different origin were analysed for their content of microelements (Mn, Zn, Cu, B and Mo) and hazardous elements (As, Be, Cd, Co, Cr, Ni, Pb, Sb, Se, Sr, Ti, Tl and U) to investigate the suitability of the heavy metal pattern to identify the origin of rock phosphates and P-fertilisers. The results showed that the range of toxic heavy metal and radionuclide concentration in marketable rock phosphates from different origin was very broad. However, it was found that no single element could be used to discriminate the origins of rock phosphates (Chapter 4.1). The application of multivariate statistical analysis in the present study showed that two groups of samples could be distinguished using discriminate analysis, sedimentary rock phosphates in the first group and igneous rock phosphates in the second group (Chapter 4.5). The same results were found using cluster analysis. That means that heavy metal patterns can be used to distinguish between igneous rock phosphates from the Russian Kola Peninsula and sedimentary rock phosphates. The difference between sedimentary and igneous rock phosphates was also reflected by the first component of the PCA (Chapter 4.5). Sedimentary rock phosphates contained significantly higher concentrations of potentially hazardous elements (As, B, Be, Cd, Cr, Ni, Mo, Sb, U and Zn) than igneous rock phosphates and there were positive correlations among these elements in rock phosphate samples, while the igneous rock phosphates contained higher concentrations of Sr and Ti than sedimentary rock phosphates, there were also positive correlations among these elements in rock phosphates.

Within the group of sedimentary rock phosphates, heavy metal concentrations varied broadly depending on the origin of sample. However, using discriminate analysis within sedimentary rock phosphates, only 67.4% of the analysed rock phosphate samples were classified correctly (Table 4.12). Other samples were wrongly classified. That means that it is not possible to use discriminate analysis to determine the origin of all sedimentary rock phosphate samples.

The results obtained by hierarchical cluster analysis showed that twenty-seven samples (about 81% of total samples) from different origin were correctly classified depending on their origins (rock phosphate samples of the same origin were classified together in one sub-cluster). But, only all samples from Togo and Senegal within sedimentary rock phosphates were correctly classified (chapter 4.5.1). Most samples from USA and Morocco were classified in separate sub-clusters but not all samples. In addition, one sample from Morocco, and another from North Carolina were classified together with Tunisian samples in one sub-cluster, which makes it so complex to distinguish among these origins based on HCA.

Based on PCA, some further differentiation within the group of sedimentary rock phosphates appeared possible (Table 5.2): The result of PCA revealed that the rock phosphates from the USA contained higher concentrations of Bi and Pb than rock phosphates of other origins (i.e. Middle East and Russia). Rock phosphates from Algeria contained high concentrations of Tl and Se and low concentrations of Mn and Co. Rock phosphates of Senegal had the highest content of Cd. The high Cd content in the rock phosphates of Senegal was reported by Schnier et al (1987) and Isermann (1982).

Table 5.2: Groups of rock phosphates to be distinguished and elements that can be used to identify their origins based on PCA

Discriminated regions		Discriminating elements
1	2	
Russian Kola Peninsula	Sedimentary rock phosphates	Sr, Cd, U, Ti, Cr, Zn, Be, Ni, Mo
The USA	Middle East and Northern Africa	Bi, Pb, Co
Senegal	Other origin	Cd
Algeria and Tunisia	Senegal, Togo, Kola	Cu, Mn, Tl, Se

PCA seemed to be more suitable than discriminate analysis and cluster analysis. However, it is complex to identify all sedimentary rock phosphate origins by their heavy metal patterns for the following reasons:

1- Some samples are chemically identical, but they are not of the same origin. The results of cluster analyses and discriminate analysis showed that about 19, and 32.3% respectively, of all rock phosphate samples were wrongly classified.

2- The concentration of potentially hazardous elements in sedimentary rock phosphates can vary widely between the rock phosphate deposits of a given country (within a particular origin) and within a given deposit, e.g., Sr concentration in the Moroccan deposit at Khouribga ranged from 700 to 2958 mg kg^{-1} (Table A. 2.1), and U from 133 to 245 mg kg^{-1} (Table 4.4).

In general, heavy metal pattern allowed to distinguish three main geographical origins (Middle East and Northern Africa, the USA, Russian Kola Peninsula). It was not surprising to find a large variation of heavy metal concentrations between igneous rock phosphates from Kola Peninsula and sedimentary rock phosphates from different origin because they are different types of rocks. However, it was found a large variation of heavy metal concentrations within sedimentary rock phosphates. Furthermore, the concentrations of these metals varied not only from origin to another and from deposit to another, but sometime a large variation of their concentration even within the same deposit. These variations can be due to the fact that, sometime various layers of deposit may be formed during different geological ages. Riggs (1989) found that the concentration of heavy metals varied considerably within the North Carolina phosphates based on their age (Table 5.3). There are several other factors affect the chemical composition of sedimentary rock phosphate e.g. grain size and specific surface area, cationic exchange capacity, mobilisation of element, organic and inorganic matter, pH, temperature etc.

Table 5.3: Average concentration of some heavy metals [mg kg^{-1}] in North Carolina phosphates formed at two different ages (Riggs et al., 1989)

	As	Cd	Co	Cr	Cu	Mo	Ni	Zn	Pb	Se
Miocene	19	13	5	120	17	109	19	143	22	8
Holocene	122	1	6	125	15	7	10	61	29	6

5.1.4 Heavy metal pattern as indicator to the origins of P-fertilisers

It was possible in the present work to use U/P_2O_5 and Sr/P_2O_5 ratios to determine if one manufacturer used igneous rock phosphates from the Russian Kola Peninsula or sedimentary rock phosphates from different origin due to the large variation between these two groups (Chapters 4.3 and 4.4). However, it was a difficult task to trace back (fingerprint) the origin of P-fertilisers made of sedimentary rock phosphates based on heavy metal patterns. It was noticed in the present work that the amount of heavy metals (such as Cd, Sr and U) in P-containing fertilisers related to the amount and origin of the P component in the fertiliser sample. However it was not possible to trace back the origin of P-fertilisers produced of sedimentary rock phosphates depending on heavy metal patterns because elemental composition of a rock phosphate and P-fertilisers made of that particular rock might differ considerably depending on the manufacturing processes also. It was noticed in the present work, that the greatest amount of As, Cd, Co, Cr and U end up in fertilisers produced from the crude phosphates, which was in agreement with data obtained from the literature (Chapter 2.1.5), the remaining amount of the heavy metals are mainly present in the phosphogypsum. Also, considerable amounts of B, Sr, and Pb were noticed in the by-product (phosphogypsum). However, the distribution of different metals between P-fertilisers and the phosphogypsum was not uniform, i.e. the ratio of certain heavy metal concentrations in P-fertilisers to their concentrations in their raw materials (rock phosphate) varied broadly. Due to this variable ratio of heavy metal concentrations between rock phosphate and P-fertilisers during the production process, heavy metal patterns are very limited in their suitability to identify the sources of P-fertilisers, especially when the fertilisers are made of sedimentary rock phosphates. Furthermore, heavy metals in compound fertilisers (such as NP, PK, NPK, organo-mineral fertilisers) are derived of many sources such as rock phosphate, P mineral fertilisers, potassium salts, nitrogen compounds, sulphur, organic manure, limestone, etc. So it is complex, if not impossible, to determine the amount of heavy metals from each component, and it is not possible to determine the amount or concentrations of heavy metals in the P-component alone.

5.1.5 Influence of declining quality of rock phosphates on U content in P-fertilisers

In the present work, U concentrations in P-containing fertilisers collected after 1995 was a little higher than U concentrations in the P-containing fertilisers collected between 1975-1985 (Fig. 4.5). This indicates that the quality and grade of marketable rock phosphate was declining within this period.

The world production of rock phosphates increased rapidly from 23.4 million tons in 1950 to 166 million tons (the peak) in 1988, which is about 2% more than that in 2004 as illustrated in Fig. 5.2. Then the production of rock phosphates, which peaked in 1988, shows a downward trend up to 119 million tons in 1994. Thereafter rock phosphate production increased slightly up to 144 million tons in 1998. Since 1998, the annual global production of rock phosphate has been around some 140 million tons of rock phosphate which is equivalent to about 40 million tons of P_2O_5. Commercial rock phosphate deposits contain a wide range of U and other heavy metals depending on their origin. Therefore the qualities of rock phosphate are highly influenced by their origin.

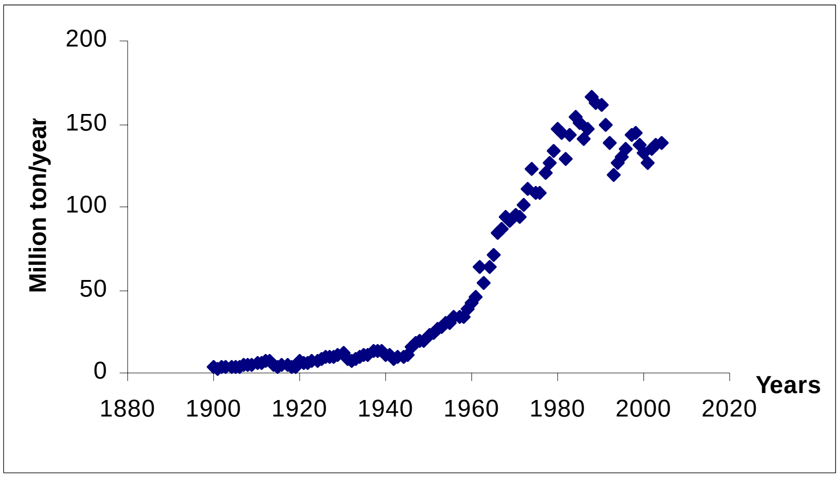

Fig. 5.2: World production of rock phosphates (Jasinski, 2007).

Production to meet the global needs for rock phosphate came from different deposits but the number of rock phosphate deposits of high-grade rock phosphate, particularly those containing low amounts of toxic heavy metals, worldwide is limited. The stores of high-grade quality are being depleted, i.e., higher grade and quality rock phosphate from central Florida is becoming depleted and the production of high quality and grade rock phosphate of central Florida has been declining due to the moving away from the central district (Van Kauwenbergh, 1997). The decline in quality of rock can pose the problem that the high quality rock phosphates may be replaced by low quality rock phosphates, which have higher contents of U and other toxic heavy metals. As a result, P-fertilisers may be affected by declines in rock phosphate quality and the levels of toxic heavy metals could increase in P-fertilisers in future.

Furthermore, the production of the high-grade rock phosphates quality with low impurity content from the Russian Kola Peninsula in 1988-1989 was about 36 x 10^6 tons, which comprises about 24.4% of the world production. This production had fallen sharply from 36 million tons in 1988-1989 to an estimated 19 million tons in 1990. In 1995, it decreased to 8 million tons. From 2003 to 2006, the production was 11 x 10^6 tons (about 7.43 to 7.79% of world production). As the production from the Russian Kola Peninsula rock phosphates was decreased, their export to Europe and other countries was decreased also. Prior to the break-up of the former Soviet Union (FSU), about 3x 10^6 tons/year of rock phosphate of Russian Kola Peninsula was exported, mostly to Eastern Europe, while it decreased to about 0.85 x 10^6 tons/year in 1996 (Jasinski, 2007; Van Kauwenbergh, 1997). Instead of the high-grade rock phosphates with low impurity content, lower grade rock phosphates with higher impurity content rock phosphates may be mined. This could be the reason to increase the level of U in P-fertilisers with time. In general the high-grade rock phosphate from some sources are becoming depleted and the quality of rock phosphate that is utilised on worldwide is lower.

The second possible reason for decreasing U content in P-containing fertilisers collected between 1975-1985 might be the removal of U as nuclear fuel because of high U prices. But today most of the U in rock phosphate is not recovered and it remains in the final P-fertilisers. The recovery of U from phosphate is affected by the market price of U.

As it clear in Fig. 5.3 that U price reached the peak during 1975-1980 when U price exceeded 250 \$/kg U_3O_8 (equal to about 110 US \$/lb U_3O_8). This price encouraged the U recovery from phosphoric acid plants on industrial scale. Several companies enter the business by 1981 (MccCREADY et al., 1981).

Global peace movements and anti nuclear campaigns triggered by the Three Mile Island meltdown and by the Chernobyl disaster (the worst nuclear reactor accident) on April 26, 1986 caused the world U market to fall in, resulting in U prices well below the profitability threshold to collect it from rock phosphates during fertilisers manufacturing. In addition to these accidents which raised the concerns about the safety of nuclear power plants, the overproduction of U during 1975-1985 and the end of the Cold War in 1989 led to large amounts of enriched U from military stockpiles in Russia and the United States being sold on commercial markets (Geoscience Australia, 2006). These factors together contributed to depressed U prices. As U recovery costs were higher than U price, most of U recovery plants have been closed (Kratz and Schnug 2005, WISE, 2002).

U price tended to increase since 2002 because of an increased demand of U to generate electricity in nuclear power reactors increase, and to manufacture of radioisotopes for medical and other applications increase too. U spot price reached 112 $ /kg U in May 2006 (IAEA, 2007[c]) and 95$ /lb U in March 2007 (equal to 209 $ /kg U) (Uxc, 2007). As U prices continue to increase, U recovery form phosphoric acid could again become economically viable (McMurray, 2005) and U recovery form phosphoric acid could be renewed.

U is the key element for sustainable production of the energy in nuclear power plants. However, the conventional U reserves are around 3.5 Mio t U and it will sufficient to meet current demand till about 2050 (McMurray, 2005, Kratz and Schnug 2005). Worldwide U resources associated with rock phosphates deposits are estimated at approximately 9 million t U. Four countries, Jordan (0.1 million t U), Morocco (6.9 million t U), Mexico (0.15 Mio t U) and the USA (1.2 million t U), accounting for more than 90% of the estimated resources associated with sedimentary rock phosphate deposits (IAEA, 2001). The production of large quantity of rock phosphates each year (about 140 Mio t per year) makes it a significant source of U. Thus, theoretically at the current global rate of consumption, U in rock phosphates could meet the global demand for about 220 to 324 years (Kratz and Schnug 2005).

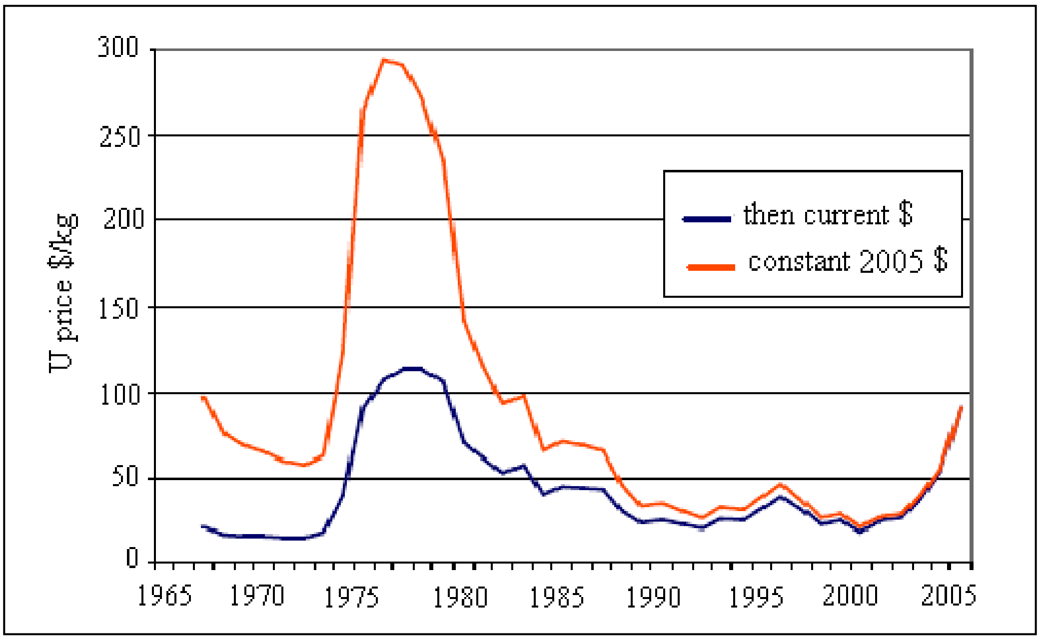

Fig. 5.3: U prices from 1967 to 2005 (IAEA, 2007[c])

5.2 *Use of Sr isotopes to identify the origin of rock phosphates and P-fertilisers*

Isotope ratios may be a possible solution not only to identify the origin of rock phosphates but also to trace back the origin of rock phosphates used in the production of different P-containing fertilisers. It is well known that the magnitude of the isotopic fractionation depends on the mass of the isotopes. These fractionations are very small for heavy elements such as Sr and U. In the present work, the shift of $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ during the production process of P-fertilisers was so small that it can be ignored. The most important difference between heavy metal patterns and isotope ratios is that for heavy elements such as Sr and U the shift of isotope ratio during the production processes of P-fertilisers is so small that it can be ignored, unlike the transfer of heavy metals from rock phosphates to P-fertilisers. Sr isotope ratios in P-fertilisers reflected the isotopic composition of rock phosphate from which they were produced. Therefore natural $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ may identify the origin of both rock phosphates and P-fertilisers.

As the differences of isotope ratio in natural samples are relatively small, high precision measurements of isotope ratios are required in this type of study. High precision measurements of U and Sr isotope ratios can be performed using TIMS. Sr was separated from its matrix to avoid isobaric interference between $^{87}\mathrm{Sr}$ and $^{87}\mathrm{Rb}$, then $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ was measured by TIMS. The accuracy of the measurement in the present work were calculated according to the ISO guide to the expression of uncertainty in measurement, all samples were calculated using a coverage factor $k=2$. The accuracy was from 0.00026 to 0.00028 for sedimentary rock phosphates, 0.00026 to 0.00027 for igneous rock phosphates, 0.00026 to 0.00028 for P-fertilisers, 0.00027 for K- fertilisers, 0.00026 to 0.00027 for PK and NPK, 0.00027 for farmyard manure, and 0.00027 to 0.00030 for organo-mineral fertilisers.

5.2.1 *Identifying the origin of rock phosphates and P-fertilisers using the Sr isotope ratio and total Sr concentrations*

In the present work, significant differences of Sr isotopes analysed by TIMS seem to be suitable to classify rock phosphates from different sources into four different classes using cluster analysis and an ANOVA test (Fig. 5.4). The lowest $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ and the highest Sr concentrations were found in the first group (from 0.70339 to 0.7035), which includes igneous rock phosphates from the Russian Kola Peninsula, and this result is in agreement with Bizzarro et al. (2003). It was followed by the second group involving rock phosphates from Senegal and Togo (from 0.70686 to 0.70742). The third group includes rock phosphates from Middle East and Northern Africa (Morocco, Israel, Tunisia, Algeria and Syria) with Sr isotope ratios from 0.70781 to 0.70803. The last group comprises rock phosphate from the USA with a Sr isotope ratio value from 0.70883 to 0.70896.

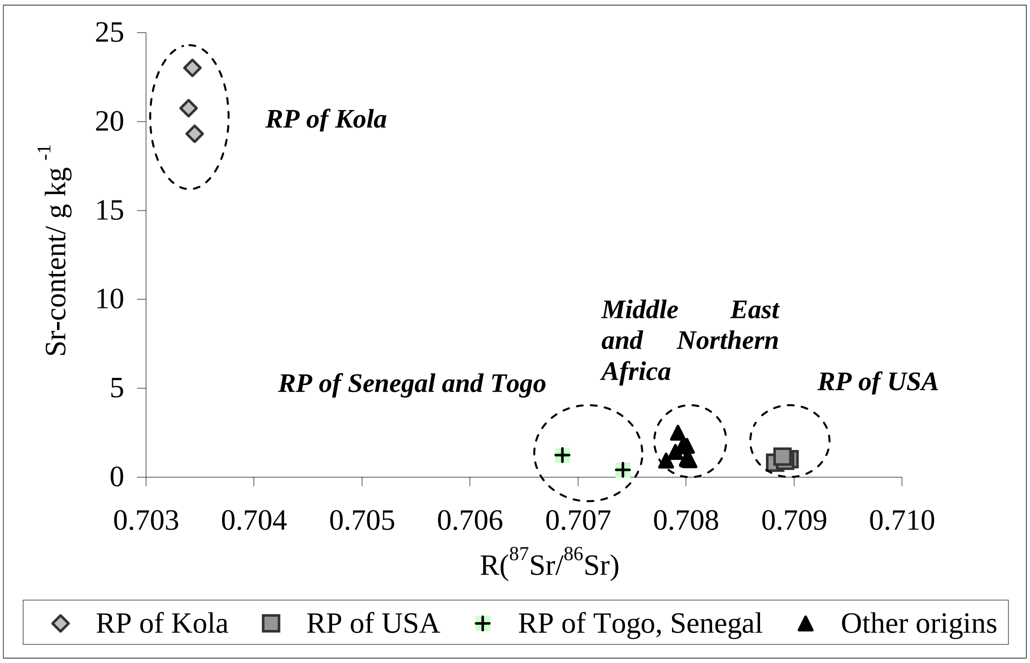

Fig. 5.4: $R(^{87}Sr/^{86}Sr)$ versus Sr concentration for rock phosphate samples from different origin

5.2.2 Factors affecting the Sr isotope ratio in rock phosphates

The variations in $R(^{87}Sr/^{86}Sr)$ of rock phosphates from different origin are a result of:

1. *Rb-Sr System*: The $^{87}Sr/^{86}S$-isotope ratio increases with time due to ^{87}Rb decay to ^{87}Sr. Sr isotope ratio depends on the age of ores or samples, Rb/Sr ratio and $R(^{87}Sr/^{86}Sr)$ at time of formation (Fortunato et al., 2003; Barbaste et al., 2002; Koch et al., 1995) as discussed in the previous chapter 2.2 Since the igneous rock phosphate from the Russian Kola Peninsula (Sr rich-rock) contains high levels of Sr (about 20939 mg kg^{-1}), the Rb/Sr ratio is very low and as a result $^{87}Sr/^{86}Sr$ will be low. In our study, $R(^{87}Sr/^{86}Sr)$ was 0.07033 in rock phosphate from the Russian Kola Peninsula , which is in agreement with Bizzarro et al. (2003). He found that igneous minerals (apatites and carbonates) yield $R(^{87}Sr/^{86}Sr)$ compositions ranging from 0.7025 to 0.7031.
2. *The initial* $R(^{87}Sr/^{86}Sr)_0$: Sr isotope ratio in marine sediments depends on the Sr isotope ratio of seawater because initial Sr isotope ratio in sedimentary rock phosphates at the time of formation is equal to Sr isotope ratio in seawater from which they were formed at this period. As the Sr isotope ratio in seawater changed during the geological ages (Fig. 5.5), rock phosphate of different geological age will have different Sr isotope ratios. E.g., in the present work, rock phosphate samples from the USA, which are formed in Miocene

(Shields and Stille, 2000), have significantly higher Sr isotope ratios than other samples (older samples).

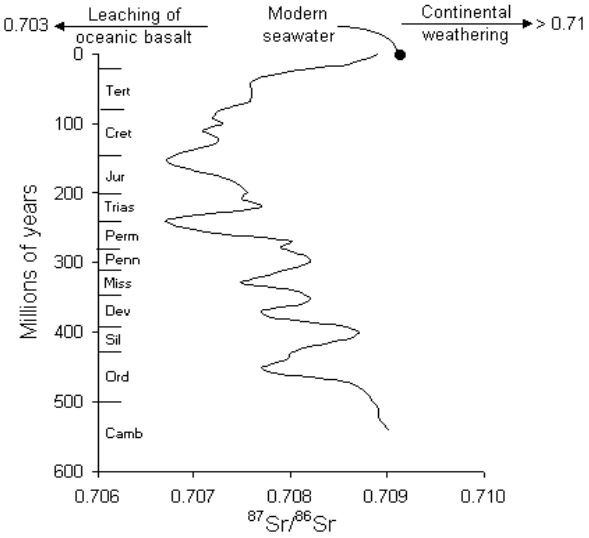

Fig. 5.5: Sr isotope ratio in sedimentary rocks throughout Phanerozoic time *(modified from Veizer, 1989)*

In marine carbonate rocks, Sr isotope ratio in rocks reflects the isotope ratio of seawater from which they were precipitated (Ehrlich et al., 2001; Kohn and, Cerling 2002). *R*(^{87}Sr/^{86}S) in seawater is about 0.709 at the present day (Veizer, 1989; Åberg, 1994). This ratio is uniform through the ocean. The *R*(^{87}Sr/^{86}Sr) is incorporated into the minerals such as phosphates, carbonates, sulphates, and some salts often without isotopic fractionation (Hess *et al*., 1986). Therefore, the *R*(^{87}Sr/^{86}Sr) of carbonate sediments forming today is the same as that of the seawater in which they formed (Veizer, 1989). This ratio in seawater has varied during the geological time. By measuring the Sr isotope ratios in apatite (which is the main constituent of sedimentary rock phosphates) from older geological formations, it is possible to log the Sr isotopic variations in seawater with time. It can be seen that *R*(^{87}Sr/^{86}Sr) decreases from the early Carboniferous to the late Jurassic. From the late Jurassic up to the present day *R*(^{87}Sr/^{86}Sr) increases (Fig. 5.5). If seawater interchanges chemically with rocks, which are rich in Rb, its ratio of *R*(^{87}Sr/^{86}Sr) will increase, whereas if it interchanges with rocks having a low Rb/Sr, the *R*(^{87}Sr/^{86}Sr) will be pulled down again. The mixing of different Sr sources (each with its own characteristic Sr isotope composition) controls the Sr isotope composition of seawater. Sr isotope ratio in seawater is about 0.709, it is intermediate between the continental crust average (0.716) and oceanic basalt (0.703). Seawater Sr isotope variations with time reflect temporal changes in the mass fluxes of the various sources of Sr to the ocean

(Dickin, 1995; Hess *et al.,* 1986; Åberg, 1994). The increasing Sr isotope ratio in sea water between 40 m. yr to the present (Fig. 5.6) is due also to the high isotope ratio in the large rivers, e.g., ^{87}Sr/^{86}S is 0.7109 in Amazon rivers, 0.7183 in Orinoco rivers and 0.7127 in Himalayan rivers, so average of Sr isotope ratio in rivers is about 0.711 (Hess *et al.,* 1986; Veizer, 1989). This rapid and steady increase in ^{87}Sr in the late sedimentary may lead to variations in Sr isotope ratio in rock phosphate depending on the geographic origin of the sample.

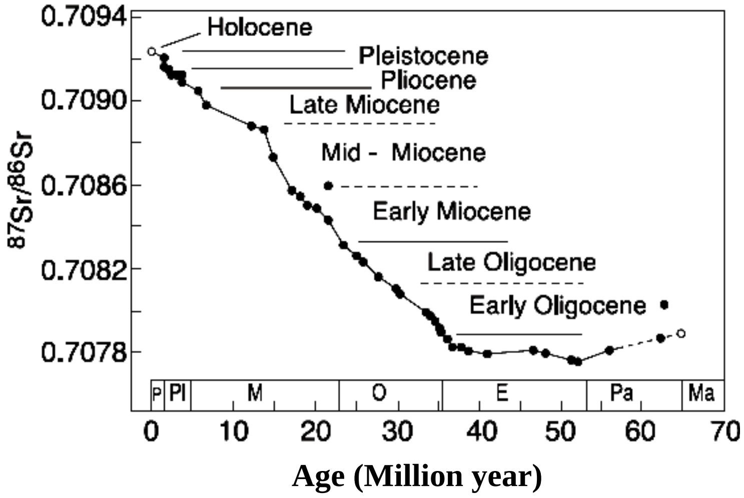

Fig. 5.6: The *R*(^{87}Sr/^{86}Sr) curve in seawater over last 70 million year (Banner, 2004)

3. Mass fractionation of Sr isotopes: Mass fractionation based on mass differences is very small for heavy isotopes unlike the light stable isotopes H, C, N or O (see chapter 2.3.4). Therefore, the influence of this factor on Sr isotope variation in sedimentary rock phosphates is very small.

5.2.3 Tracing back the origin of P-fertilisers of different manufacturers based on R(^{87}Sr/^{86}Sr)

Significantly different values of Sr isotope ratios were found in rock phosphate and P-fertilisers of different provenance regions and the relationship of Sr isotope ratio in rock phosphate and in P-fertilisers can be described by a linear regression function with a high positive correlation (Chapter 4.6). Thus, Sr isotope ratio in straight P-fertilisers thus reflects the origin of rock phosphate from which P-fertilisers were produced (Table 5.4).

Table 5.4: Comparison between discriminating ability of heavy metal pattern and Sr isotope ratio to distinguish the origin of rock phosphates and P-fertilisers

Parameter measured	**Statistical analysis**	**Discriminated origins**		**Type of discriminated samples**
		Igneous and sedimentary	**Within sedimentary rock phosphates**	
HM Pattern	DA	Yes	No	Rock phosphates
	HCA	Yes	Togo and Senegal	Rock phosphates
	PCA	Yes	Middle East and North Africa, the USA, Senegal	Rock phosphates
U/P_2O_5	ANOVA	Yes	No	Rock phosphates + straight P-fertilisers
Sr/P_2O_5	ANOVA	Yes	No	Rock phosphates + straight P-fertilisers
Sr isotopes	Cluster + ANOVA	Yes	The USA, Middle East and North Africa, Kola, Senegal and Togo	Rock phosphates + straight P-fertilisers
Sr isotopes + Sr content	ANOVA	Yes	The USA, Middle East and North Africa, Kola, Senegal and Togo	Rock phosphates + straight P-fertilisers

In compound mineral fertilisers, it was possible to use Sr isotope ratio in compound mineral fertilisers to check if the samples were produced from igneous rock phosphates from the Russian Kola Peninsula or from sedimentary rock phosphates from different origin due to the large variation of Sr concentration and isotopic composition between these two groups. However, Sr isotope ratio alone cannot be used to trace back the origin of P-component in compound fertilisers within sedimentary rock phosphates (Chapter 4.6). The largest amount of Sr came from the P-component because P-containing fertilisers have significantly higher Sr concentrations than non-P containing fertilisers (such as K- and N-fertilisers) (Table 5.5). Therefore, Sr isotope ratio in compound mineral fertilisers is primary related to the P-component and less to other components such as N and K.

Table 5.5: Sr- content and isotope ratio for different type of fertilisers measured in this study in comparison to literature values (Böhlke and Horan, 2000; Borg and Banner, 1996; Vitoria and Otero, 2004)

Type of fertilisers	**Description**	**In present work**		**In literature**	
		Sr-content/ [mg kg^{-1}]	**R(^{87}Sr/^{86}Sr)**	**Sr-content/ [mg kg^{-1}]**	**R(^{87}Sr/^{86}Sr)**
Rock phosphate	Different origin	287-23016	0.70339-0.70896	120-30000	No data
P-fertilisers	Triple super phosphate P-fertilisers	383-2302	0.70348-0.70919	2400 520	0.7088 0.7089
NP-fertilisers	Diammonium phosphate Ammonium polyphosphate	83.7-3093	0.70349-0.70892	1290 9	0.70859 0.7096
PK-fertilisers	-	210-1104	0.70794-0.70837	No data	No data
NPK-fertilisers	NPK	120-3361	0.70338-0.71927	212	0.703-0.71573
K-fertilisers	K-fertilisers Potassium chloride Potassium sulphate	28-85	0.72056-0.72979	18 77 No data	0.74 0.83518 0.715
N-fertilisers	Urea +Ammonium nitrate Unknown Ammonium nitrate	0.18	No data	2 0.11	- 0.7095 0.7079
N S-fertilisers	$NH_4NO_3SO_4$ Ammonium sulphate	No data	No data	< 1	0.7085 0.7085
Farmyard manure of different animals		17-140	0.7072-0.7102	No data	No data
Organo-mineral fertilisers		52-376	0.70821-0.71877	No data	No data

In organo-mineral fertilisers Sr isotope ratio alone cannot be used to determine the origin of the P-component. Sr-isotope ratio in organo-mineral fertilisers related to the relative contribution of several components, Sr isotope ratio in each component may vary considerably. For example, Sr isotope ratio in rock phosphates varies depending on their origin, Sr isotope ratio in farmyard manures vary according to the animal type. The potassium chloride and K-fertilisers have the highest $R(^{87}Sr/^{86}Sr)$ from 0.74 to 0.8352 (Fig. 5.7), which may be due to the high Rb/Sr in K-feldspar minerals (Jones and Jenkyns, 2001; Banner, 2004). It was noticed that the higher the K/P ratio in organo-mineral fertilisers, the higher the Sr isotope ratios. K-fertilisers have the highest Sr isotope ratio as mentioned above and this result is in agreement with Vitoria and Otero (2004) and Böhlke and Horan (2000).

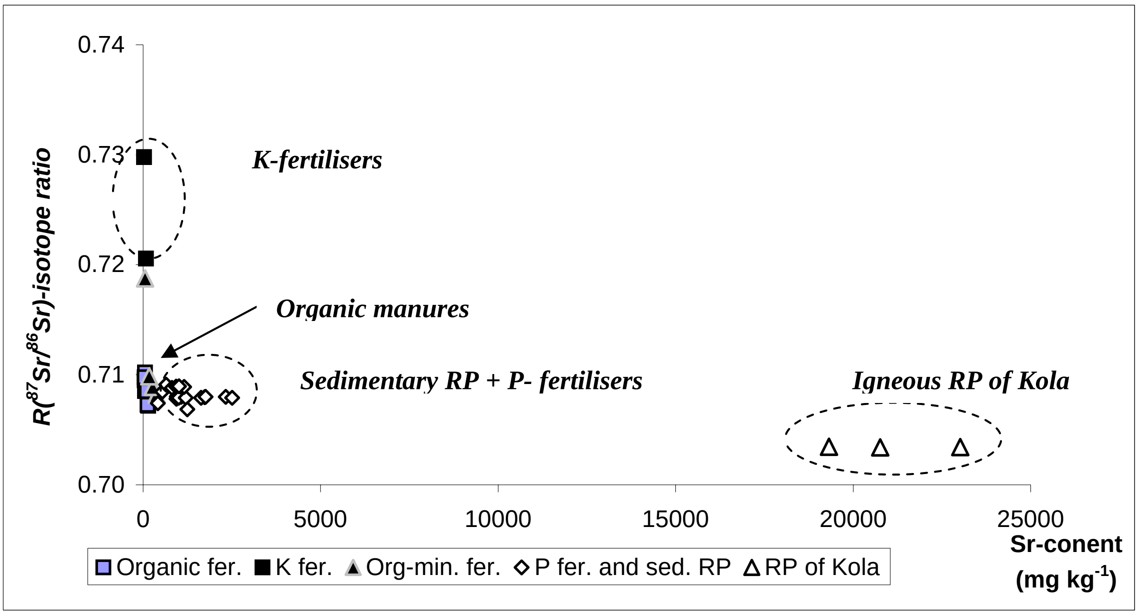

Fig. 5.7: $R(^{87}Sr/^{86}Sr)$ versus Sr-concentration for different kind of P-containing fertilisers
fer. = Fertiliser

5.3 Use of U isotopes to identify the origin of rock phosphates and P-fertilisers and as an indicator of natural or anthropogenic U

All isotopes of U are radioactive, ^{235}U and ^{238}U are parent isotopes for two separate radioactive decay series, which produce a series of unstable isotopes called daughter elements and yield the stable isotopes of radiogenic ^{207}Pb and ^{206}Pb, respectively (Chapter 2.2).

^{234}U is one of 14 daughters included in the natural ^{238}U-series. The ratio between ^{234}U to its parent has been used in many studies in earth and environmental science, geology, oceanography, hydrology, and science-based archaeology (Calsteren and Thomas, 2006). This ratio is interesting in this study because the changes of isotope ratios of $R(^{234}U/^{238}U)$ during the application of chemical processes are usually negligible. The isotope effect is so small not only because the relative masses differences between this isotopes dm/m is small but also due to the fact that nearly the complete amount of U present in rock phosphates is transferred to P-fertilisers during the production process. That means, with the isotopic fingerprint method, information about the origin of samples can be obtained even in P mineral fertilisers. In the present work, U was separated from its matrix using UTEVA® resin. The accuracy of the method (uncertainties), described in this work for R(^{234}U/^{238}U), was (U=1.8E-07) for sedimentary rock phosphate, (U=2.5E-07) for igneous rock phosphates, (U=1.7E-07) for P-fertilisers, (U=1.3E-07) for PK and NPK, (U=1.9E-07) for farmyard manure, and (U=2.2E-07) for organo-mineral fertilises.

U exists in the environment naturally but at low concentrations (i.e. in soil, water, fertilisers, etc.), which can be elevated due to human activities, for example recently U has been added to the environment by nuclear power plants. The ^{235}U/^{238}U-isotope ratio can be used as an indicator of natural or anthropogenic sources of U. The accuracy of the method (uncertainties) described in present work for the determination of R(^{235}U/^{238}U) in different types of samples was ranged from 1.0E-6 to 1.8E-5).

5.3.1 Identifying the origin of rock phosphates and P-fertilisers using R(^{234}U/^{238}U) and total U concentrations

It can be concluded from results obtained in chapter 4.7.1 that it is possible to use U concentration data combined with the R(^{234}U/^{238}U) to distinguish rock phosphates from the Russian Kola Peninsula and from the USA from other samples (Fig. 5.8). The enrichment of sedimentary rock phosphates in U compared with igneous rock phosphates was mentioned and explained in chapter 5.1. ^{234}U and ^{238}U was in secular equilibrium in most samples except in samples from the USA. Other studies confirm that natural U activity values in rock phosphates and P-fertilisers are generally about secular equilibrium in most cases (Table 5.6).

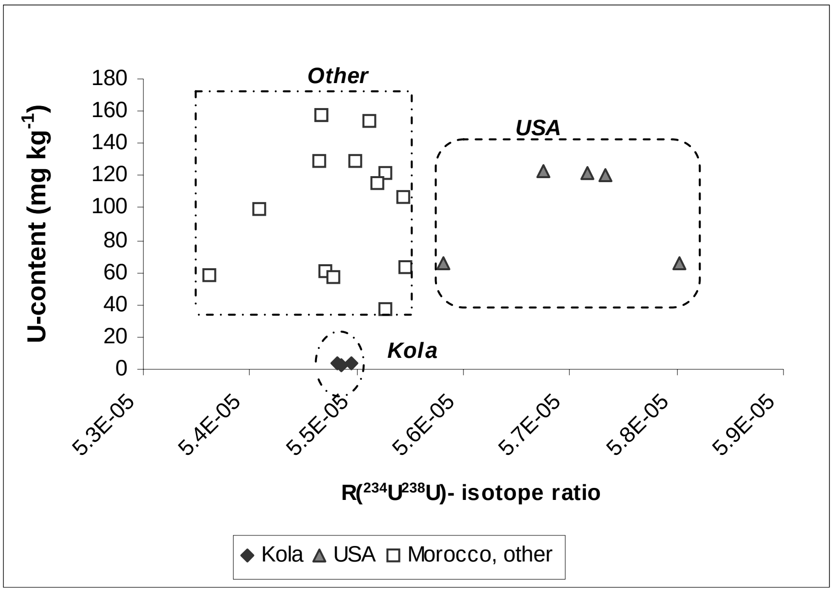

Fig. 5.8: R(^{234}U/^{238}U) versus U concentration for different rock phosphate samples

Table 5.6: $R(^{234}U/^{238}U)$-activity ratio for some rock phosphates and P-fertilisers (Da Conceicao and Bonotto, 2006; Zielinski *et al.*, 2006, Makweba and Holm, 1993; Uchida *et al.*, 2000)

Samples	**$R(^{234}U/^{238}U)$ activity ratio in literature**
Triple super phosphate 0-46-0	0.99 - 1.023
Ammonium polyphosphate 10-34-0	0.99
Commercial P-fertilisers	~ 1.00
Phosphogypsum	0.98-1.07
Rock phosphates from Abu-Tartor	1.0054
Wet rock phosphates from Abu-Tartor	0.96
Rock phosphates from Tapiar, Brazil	0.85-0.87
Rock phosphates from Minjingu	1.057-1.076
TSP from Tanga fertiliser manufacturer	1.053-1.089
SSP	1.077-1.087

Most samples had activities ratio about 1 because one gram of natural U in secular equilibrium has an activity of 0.67 µCi. Of this activity, about 48.9% is attributable to ^{234}U, 2.2% to ^{235}U, and 48.9% to ^{238}U (ATSDR, 1999; WHO, 2001; Rosamilia *et al.*, 2004). The activity of ^{234}U is almost equal to the activity of ^{238}U, therefore $^{234}U/^{238}U$-activity ratio is about 1 in natural U. However, this ratio may have small variations depending on the age, type and geographic origin of the sample.

The variation of $R(^{234}U/^{238}U)$ in sedimentary rock phosphates is based on the age of samples because $R(^{234}U/^{238}U)$ shows a disequilibrium value of about 1.15 in seawater. U enters the apatite lattice at the time of sedimentary rock phosphate formation with an initial $R(^{234}U/^{238}U)_0$ close to that of modern seawater of about 1.15 which means that sedimentary rock phosphates at the time of their formation have the same ratio. Since all radionuclides following ^{238}U have shorter half-lives than the mother nuclide (^{238}U), the undisturbed decay series reach to the secular equilibrium after millions of years (Scholten and Timmermans, 1996). The activity ratio of $R(^{234}U/^{238}U)$ decreases towards the secular equilibrium unity value with a half-life of ^{234}U of $2.48*10^5$ yr. With increasing age, the $R(^{234}U/^{238}U)$ decreases, until secular equilibrium is reached (Dickin, 1995). A state of secular equilibrium will be achieved after about five half-lives of ^{234}U (Fig. 2.9). Therefore, the recent phosphates have a $R(^{234}U/^{238}U)$ very close to present seawater, while $R(^{234}U/^{238}U)$ activity ratio is about 1 in the sedimentary rock phosphates older than the dating limit of the $R(^{234}U/^{238}U)$ method (about 8×10^5 yr) (Banner, 2004; Kolondy, 1992). In the present work, most rock phosphate samples were near secular equilibrium ($^{234}U/^{238}U = 5.48E-05$), meaning that most samples were older than 5 x 2.48 x 10^5 = 12.4 * 10^5, except for rock phosphates from the USA.

In igneous rock phosphate ^{234}U was in radioactive equilibrium with ^{238}U. This result was in a good agreement with Sato and Endo (2001), who found that $R(^{234}U/^{238}U)$ was around the secular equilibrium in different volcanic rocks.

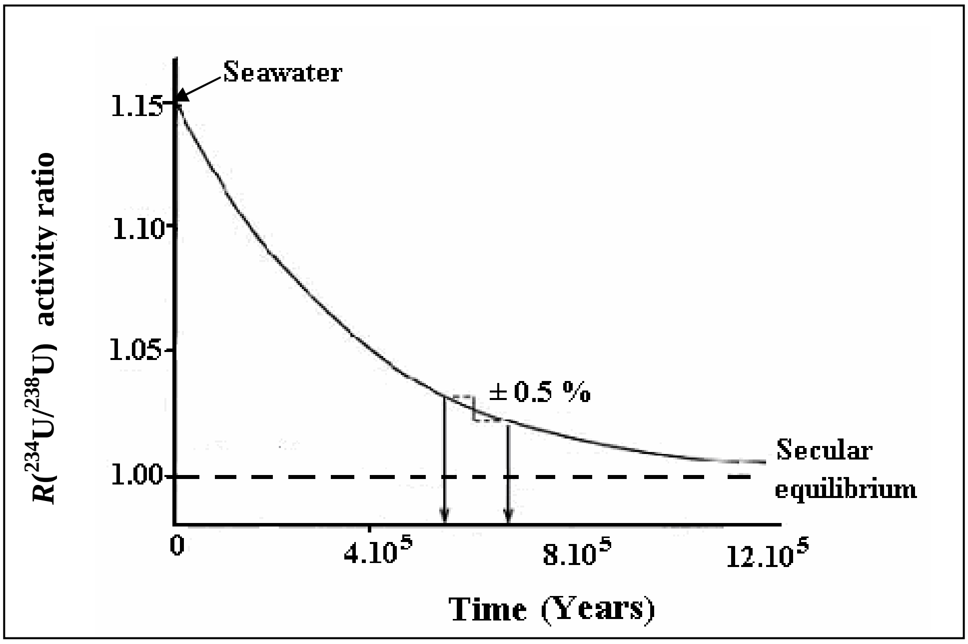

Fig. 5.9: Plot of $R(^{234}U/^{238}U)$ activity ratio against time showing the return to secular equilibrium after isolation from seawater. Arrows show the effect of typical α counting errors on age uncertainty (Dickin, 1995)

5.3.2 Tracing back the origin of P-fertilisers of different manufacturers based on R*(^{234}U/^{238}U)*

$R(^{234}U/^{238}U)$ can be used to check if a certain fertiliser was manufactured from the USA or from other origins. However, $R(^{234}U/^{238}U)$ did not allow for further differentiation within the other origins. Sedimentary rock phosphates are enriched in ^{238}U and all its daughters, including ^{234}U, ^{226}Ra ^{230}Th, ^{210}Po. While the daughter-parent ratios in ^{238}U series have been used in environmental, archaeological and geological researches, the $R(^{234}U/^{238}U)$ is the most important in this work because $R(^{234}U/^{238}U)$ transfers from rock phosphates to P-fertilisers during the production process of P-fertilisers without change. The acid attack breaks the near secular equilibrium between the ^{238}U and daughters (except for ^{234}U) in the mineral (Bolivar 1996). The varied properties of these daughter isotopes lead to their fractionation during P-fertiliser production. Reviews of fractionation of U isotopes have been published by several authors (e.g. Righi et al., 2005; Fukuma et al., 2000). They found a different ability of U and its daughters to fractionate through the wet acid process. U tends to go into the acid solution (about 86% of ^{238}U transfer to the phosphoric acid), whereas 80-90 % of Ra and Po tend to be bound to the by-product phosphogypsum (Righi et al., 2005; Mazzilli et al., 2000). Therefore, ^{226}Ra/^{238}U activity ratios should be clearly higher in phosphogypsum than in the phosphoric acid (DaConceição and Bonotto, 2006; Karkunen and Vermeulen, 2000; Bolivar 1996; Barisic et al., 1992) due to the preferential leaching of ^{226}Ra relative to ^{238}U, ^{234}U and ^{235}U to phosphogypsum.

5.3.3 R(^{235}U/^{238}U) as an indicator to natural or anthropogenic U

^{235}U is a particular important and valuable isotope because under certain conditions it can readily be split or fission, and release huge amount of energy. In order to use U as fuel in nuclear power plants and most reactors, enrichment of ^{235}U from 0.72% to about 3% is required for civilian nuclear power reactors, while highly enriched of ^{235}U to (>90%) is required for nuclear weapons. Enrichment processes remove ^{234}U and ^{235}U from natural U, the remaining by-product is called depleted U (DU). Enrichment processes yielded huge quantities of DU. DU and natural U have the same chemical properties, but DU contains less ^{234}U and less ^{235}U: about 0.0006% ^{234}U, 0.2% ^{235}U and 99.8% ^{238}U, by mass (WHO, 2001; Rosamilia *et al.*, 2004; Brand and Schnug, 2005). The total radioactivity of U depends on the ratio of isotopes. As half-life of ^{238}U is the longest, it emits less radiation during a given time period than other U isotopes. Thus, ^{238}U emits fewer alpha particles per second than does ^{235}U. Therefore, the same weight of enriched U is more radioactive than natural U, and natural U is more radioactive than depleted U (ATSDR, 1999). Thus enrichment of ^{235}U> 90% generates alpha activity 100 time that of natural U (Ribera et al., 1996).

Depletion or enrichment of ^{235}U can be used as a characteristic fingerprint to distinguish between natural, enriched and depleted U (Fig. 5.10). Therefore, the variation in R(^{235}U/^{238}U) has been used as indicators of natural or anthropogenic sources of U (Sansone *et al.*, 2001). ^{235}U/^{238}U-isotope ratio for natural U is about 0.007205. This value drops to about 0.002 in the case of the depleted U (Danesi *et al.*, 2003).

An anthropogenic source of U can be detected by slight change of R(^{235}U/^{238}U) (Rokop et al., 1996). In the rock phosphates and P-fertiliser samples analysed in the present work, the average of R(^{235}U/^{238}U) is 0.007 20 ± 0.000 01, ranging from 0.007181 to 0.007253. However there was one sample where R(^{235}U/^{238}U) was 0.0068 33, indicating that ^{235}U was significantly depleted relative to ^{238}U. In this sample, a lower amount of total U as well as depletion of ^{235}U compared with other similar type of samples, which have the same amount of N, P and K was found. Furthermore, this sample contained detectable amounts of ^{236}U.

^{236}U ($t_{1/2}$ = 2.3 × 107 year) occurs in nature at ultra-trace abundances. $R(^{236}U/^{238}U)$ ranges in natural U from 1.2E-11 to 5.6E-10. A significant amount of ^{236}U is present in DU and in almost all anthropogenic U associated with nuclear fuel or weapons materials because ^{236}U is generated by neutron capture on ^{235}U. $R(^{236}U/^{238}U)$ was 2.06E-5 in present sample. Thus the isotopic composition of this sample (the presence of ^{236}U and non natural $^{235}U/^{238}U$) indicates that this sample could be contaminated with anthropogenic U.

It is a widely practised procedure to recover U during the wet-process phosphoric acid as an alternative or secondary sources of U (Chpter 5.1), which is then used as fuel in nuclear plant. The high U content in sedimentary rock phosphates made it profitable to extract U as by product of phosphate production. Many plants recovered the U from phosphoric acid on an industrial scale due to the high price of U (MacCready et al. 1981; Awadalla and Habashi, 1986). Recovery of U from phosphoric was carried out in eight plants in the USA (6 in Florida and 2 in Louisiana) (Stoica et al., 1997). Other plants have also been built in Canada, Spain, Belgium, Israel, Brazil and Taiwan (WISE, 2006, Fukuma et al., 2000). Thus, fertiliser obtained from these plants will have low U content but the U isotopes should remain constant and not change. Therefore, the recovery of U from phosphoric acid could be the reason for the decrease in total amount of U but not for ^{235}U depletion. Most of the U recovery plants have been closed because the current U market price lower than operating costs for the U recovery plants (Chapter 5.1).

In a variety of processes for producing nuclear fuels, low level toxic and radioactive waste solution that contain nutrients is separated as a by-product. Sometime these low radioactive wastes are used as fertilisers e.g., ammonium nitrate and ammonium hydroxide. These wastes could be contaminated by small amounts of anthropogenic U (WISE, 2006). It was reported that this Ammonium nitrate can be used safely as a fertiliser depending on the national regulations because it contains low amount of radioactive components (U and ^{226}Ra) (IAEA, 1999; WISE, 2007).

The reason for a lower $R(^{235}U/^{238}U)$ in this sample could be related to the use of nitric acid or ammonia from nuclear wastes, which are contaminated by low levels of anthropogenic U, as source for N during the production process of NPK. In the present sample, less than 3.4 mg U kg^{-1} anthropogenic U was found, which confirms that this sample was polluted (contaminated) only with small amount of U.

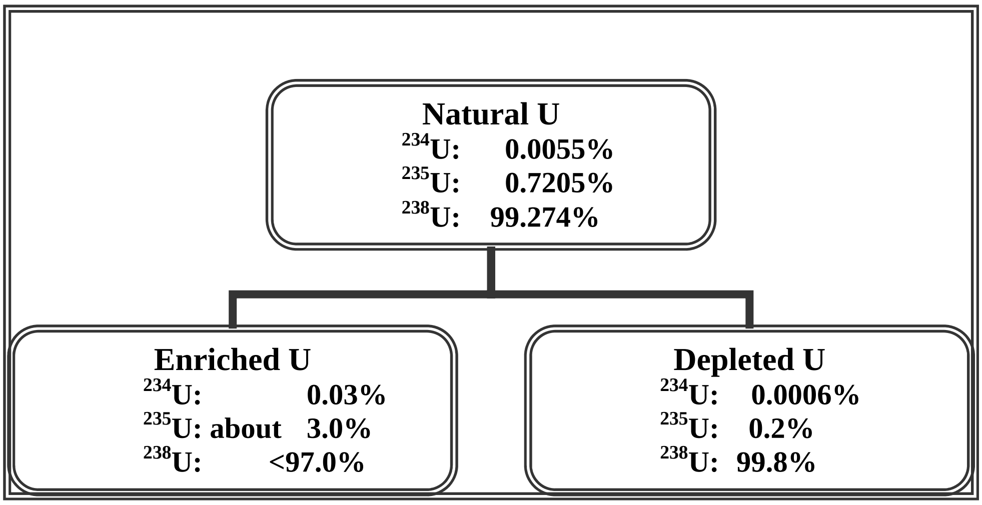

Fig. 5.10: U isotopic composition in natural, depleted and enrichmed U (WHO, 2001; ATSDR, 1999).

5.4 *Application of Sr and U isotope ratios together to identify the sources of phosphorus in compound mineral fertilisers*

In chapter 5.2 and 5.3, the separate use of either Sr or U isotope ratio to identify the origin of rock phosphates and straight P-fertilisers allows to distinguish several groups (Table 5.7). But the use of a single parameter such as Sr or U isotope ratio does not help much to distinguish the origin of the P-component in compound fertilisers.

Table 5.7: Groups of rock phosphates, straight P-fertilisers and compound fertilisers to be distinguished based on $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ and $R(^{234}\mathrm{U}/^{238}\mathrm{U})$

Parameter measured	**Discriminated origins**	**Type of discriminated samples**
Sr isotopes	Russian Kola Peninsula, The USA, Senegal and Togo, Middle East and North Africa	Rock phosphates + straight P-fertilisers
Sr isotopes + Sr content	Russian Kola Peninsula, P- The USA, Senegal and Togo Middle East and North Africa	Rock phosphates + straight P-fertilisers
U isotope	The USA	Rock phosphates, straight P-fertilisers
U isotopes + U content	The USA, Kola	Rock phosphates + straight P-fertilisers

In compound mineral fertilisers Sr isotope ratio can be used to check if the P-component came from igneous rock phosphates from the Russian Kola Peninsula or from other sedimentary rock. While $R(^{234}U/^{238}U)$ can be used to check if the P-component came from rock phosphates from USA or from other origins. Therefore an attempt was made to combine these two parameters to improve the results.

In the first step rock phosphates from different origin were classified based on U and Sr isotopes together. The result of the application of Sr and U isotope ratios together to identify the sources of rock phosphate allow to distinguish four rock phosphate groups (Fig. 5.11)

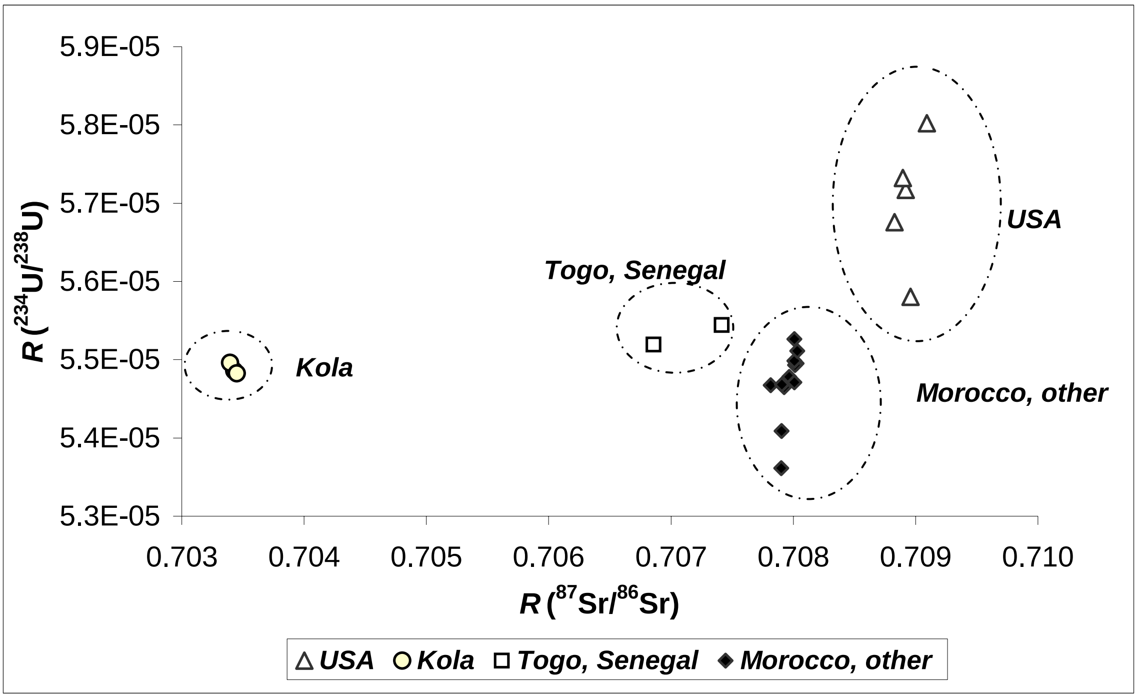

Fig. 5.11: $R(^{234}U/^{238}U)$ versus $R(^{87}Sr/^{86}Sr)$ for rock phosphates from different origin

In second step, this parameter combination was applied to a collection of fertilisers produced by different manufactures to test if it would be possible to determine the origin of the rock phosphates these manufactures used for their P-fertilisers production Also four groups can be distinguish when rock phosphates and 35 P-containing compound mineral fertilisers were classified (Fig. 5.12). The comparison between these groups and group formed in Fig. 5.11 showed that the origin of the P-component in compound fertilisers are distinguishable when their $R(^{87}Sr/^{86}Sr)$ values are plotted against $R(^{235}U/^{238}U)$.

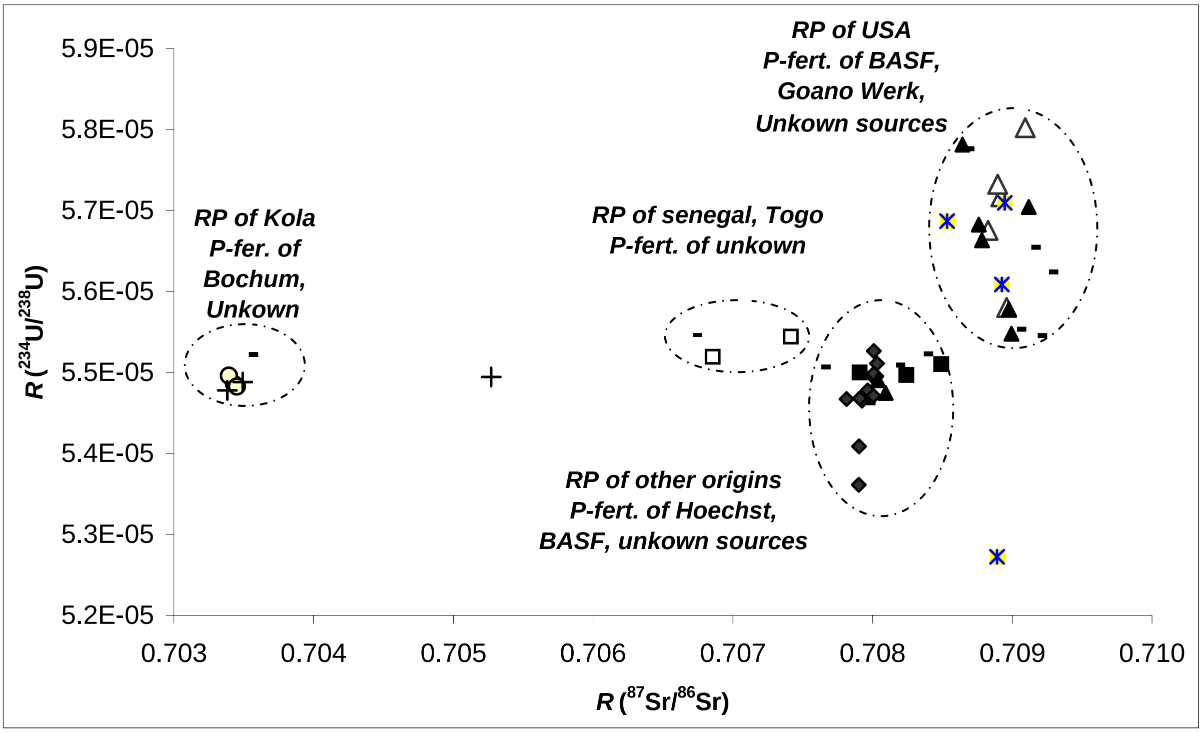

Fig. 5.12: $R(^{234}U/^{238}U)$ versus $R(^{87}Sr/^{86}Sr)$ for P-fertilisers and rock phosphates from different origin

The results of high precision determination of $R(^{234}U/^{238}U)$ and $R(^{87}Sr/^{86}Sr)$ showed that Hoechst AG manufacturer use sedimentary rock phosphates from Middle East and Northern Africa to produce P-compound mineral fertilisers, R-S- Bochum often use igneous rock phosphates from the Russian Kola Peninsula, BASF use sedimentary rock phosphates from Middle East and Northern Africa and from the USA, Guano Werk use sedimentary rock phosphates from the USA (Table 5.8).

Table 5.8: The origins of rock phosphates used in different manufacturers to produce P-fertilisers based on $R(^{87}Sr/^{86}Sr)$ and $R(^{234}U/^{238}U)$

Manufacturer	Total (n)	The origin
Hoechst AG	3	Middle East and Northern Africa
Ruhr Bochum	3	Russian Kola Peninsula
BASF	8	The USA, Middle East and Northern Africa
Guano Werk	3	The USA
Other (manufacturer not declared)	10	All origins

Only two samples did not classify, the first one was NPK 12, Sr isotope ratio in this sample showed intermediate values of $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ in igneous rock phosphate and $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$-isotope ratio in sedimentary rock phosphate, meaning that this sample might be a mixture of igneous and sedimentary rock phosphates. The second exception was for one sample with anthropogenic U. Therefore, isotope ratios did not allow us to determine the origin of this sample also.

Limitations and possibilities of U and Sr isotope ratio in rock phosphates and P-fertilisers for tractability

In general, the use of isotope ratios is a promising tool to identify the origin of both rock phosphates and P-fertiliser samples. It is better than total heavy metal contents. However the high precision measurement of U and Sr isotope ratio requires that: the analyte element should be isolated from the matrix, so that the pre-treatment and high quality chemical separation of analyte element is time-consuming. Also it requires expensive mass spectrometers (TIMS or MC-ICP-MS), which are not available in most agricultural institutes.

In conclusion, the approach using isotope ratio techneque seems quite promisinig, Sr and U isotope ratios have been shown to be a good indicators of severel geographical origin of both rock phosphates and P-fertilizers and therefore to be useful tool to control the origin of rock phosphates used in different manufacturers. In this study four groups of samples were distinguishable using U and Sr isotope ratios. However, more origin of rock phosphate samples could be identified with increasing the number variables (isotope ratio for other elements such as $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$, $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$, etc). With isotope ratio for several elements (more than 3), the discrimination could be improved using multivariate statistical analysis such as discriminate analysis and principal component analysis.

6 Summary/Zusammenfassung

The aim of this study was to investigate the use of heavy metals as well as Sr and U isotope ratios as a fingerprinting method to identify the origin of rock phosphates and P-fertilisers. Three sets of samples were analysed for their content of heavy metals as well as Sr and U isotope ratios. Different discriminating parameters including heavy metal pattern for 17 elements, U/P_2O_5 and Sr/P_2O_5 as well as $R(^{234}U/^{238}U)$ and $R(^{87}Sr/^{86}Sr)$ were used to characterise and identify the origin of rock phosphates and P containing fertilisers. $R(^{235}U/^{238}U)$ was used as indicator to anthropogenic U in investigated samples.

I The investigation of heavy metal pattern as a fingerprinting method yielded the following results:

- Sedimentary rock phosphates and P-containing fertilisers are characterised by a higher content of numerous hazardous radioactive elements such as ^{235}U and ^{238}U and their daughters as well as the non-radioactive toxic heavy metals such as Cd, Cr, Sr, Zn, etc. compared with non P-containing fertilisers. However, rock phosphates vary considerably in their content of these toxic elements depending on their geographical origins.
- Heavy metal patterns can be used to distinguish rock phosphates from the Russian Kola Peninsula and sedimentary rock phosphates from different origin that Sedimentary rock phosphates are characterised by a significantly higher content of Be, Cd, Cr, Ni, Mo, U, compared with igneous rock phosphates, while an opposite trend was found for Sr and Ti they were higher in igneous rock phosphate compared with sedimentary rock phosphates. Also rock phosphates from the Middle East and Northern Africa can be distinguished from samples from the USA based on the concentration of Bi, Pb and Co. Rock phosphates from Senegal have the highest Cd content.
- The concentration of U, Sr and other heavy metals in P-containing mineral fertilisers depends on the concentration of phosphate component (P_2O_5%) in fertilisers, origin of rock phosphates and manufacturing process.
- Sr/P_2O_5, U/P_2O_5 can be used to check if P-fertilisers were produced from igneous rock phosphates from the Russian Kola Peninsula or from sedimentary rock phosphates from different origin.
- The origin of P-containing fertilisers can not be controlled and identified using heavy metal patterns especially within sedimentary rock phosphates in most cases because:
  1. the amount of heavy metals that are transferred from rock phosphate to the P-fertiliser

vary considerably based on the production process.

2 The compound mineral fertilisers and organo-mineral fertilisers have heavy metals from different sources such as rock phosphates, P-fertilisers, potassium salts, nitrogen compounds, sulphur, etc. So it is complex, if it not impossible, to determine the amount of heavy metals from each component.

II The investigation of Sr isotope ratios as a fingerprinting method revealed the following results:

- The application of isotope ratio technique as "fingerprinting method" for the purpose of identifying the origin of rock phosphates and P-containing fertilisers showed that the most important difference between isotope ratios and heavy metal patterns is the fact that the latter are changed by application of a chemical process, whereas changes of isotope ratios are usually negligible. Sr isotope ratios, like the isotope ratios for the other heavy metals, are not changed significantly in the course of chemical processing, they will remain practically constant in P-fertilisers because the relative mass differences of heavy isotopes is relatively small.
- Significant differences of ^{87}Sr/^{86}Sr-isotopes analysed by thermal ionisation mass spectrometry revealed to be suitable for classifying rock phosphates from different sources into four different groups: the lowest ^{87}Sr/^{86}Sr- isotope ratio was found in the first group (R(^{87}Sr/^{86}Sr): 0.70339 to 0.7035), which includes igneous rock phosphates from the Russian Kola Peninsula. The second group involved rock phosphates from Senegal and Togo (R(^{87}Sr/^{86}Sr): 0.70686 to 0.70742). The third group included rock phosphates from Middle East and Northern Africa (R(^{87}Sr/^{86}Sr): 0.70781 to 0.70803) and the last one comprised rock phosphates from the USA (R(^{87}Sr/^{86}Sr): 0.70883 to 0.70896).
- R(^{87}Sr/^{86}Sr), Sr/ P_2O_5, U/ P_2O_5 in P-containing fertilisers such as (P-fertilisers, NP, PK and NPK) can be used to determine if they were produced from igneous rock phosphates from the Russian Kola Peninsula or from sedimentary rock phosphates from different origin.

III The investigation of R(^{234}U/^{238}U) as a fingerprinting method revealed the following results:

- R(^{234}U/^{238}U) was at secular equilibrium in most samples except in rock phosphates from the USA, where it was found to be significantly higher than in all samples from other geographical origins. This disequilibrium indicates the more recent formation of rock phosphates in the USA compared with other origins. Thus the ratio of ^{234}U/^{238}U –isotope ratio seems only suitable to distinguish phosphates as well as straight P-fertilisers of the

USA from others. Also compound fertilisers.

- The joint analysis of $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ and $R(^{234}\mathrm{U}/^{238}\mathrm{U})$ in P-fertilisers of different manufacturers permits a very satisfactory discrimination of their origins. $R(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$ together with $R(^{234}\mathrm{U}/^{238}\mathrm{U})$ can be used to determine if P-containing fertilisers were produced from phosphates from USA or from igneous rock phosphates from the Russian Kola Peninsula or from the Middle East and Northern Africa or form the Senegal and Togo. Furthermore it is possible to predict if igneous rock phosphates of Russian Kola Peninsula and sedimentary rock phosphates were mixed together to produce P containing fertilisers.

The investigation of $R(^{235}\mathrm{U}/^{238}\mathrm{U})$ as an indicator to natural or anthropogenic U revealed the following results

- $R(^{235}\mathrm{U}/^{238}\mathrm{U})$ was around the natural value of 0.007 20 ± 0.000 01 ranging from 0.007 18 to 0.007 25 in all natural rock phosphates and P-containing fertiliser samples. Except for one sample, a significantly lower $R(^{235}\mathrm{U}/^{238}\mathrm{U})$ of 0.0068 was found. U isotope ratio of this sample was located outside the natural range of U isotope ratio. This evidence indicates to the anthropogenic U in this sample. It is concluded that $R(^{235}\mathrm{U}/^{238}\mathrm{U})$ can be used to distinguish the anthropogenic pollution with U.

Zusammenfassung

Ziel dieser Studie war es, die Eignung von Schwermetallmustern sowie von Strontium (Sr)- und Uran (U)-Isotopenverhältnissen als Fingerprint-Methode zur Identifizierung der Herkunft von Rohphosphaten und Phosphor-Düngemitteln zu untersuchen. Drei Probenserien wurden auf ihren Gehalt an Schwermetallen sowie ihre Sr- und U-Isotopenverhältnisse analysiert. Als diskriminierende Parameter zur Kennzeichnung der Herkunft der Rohphosphate und P-Düngemittel wurden die Schwermetallmuster für 17 Elemente, die U/P_2O_5 -und Sr/P_2O_5 – Relation sowie die Isotopenverhältnisse $R(^{234}U/^{238}U)$ und $R(^{87}Sr/^{86}Sr)$ verwendet. Das Isotopenverhältnis $R(^{235}U/^{238}U)$ wurde als Indikator für anthropogen modifiziertes Uran in den untersuchten Proben genutzt.

I Die Untersuchung der Schwermetallmuster auf ihre Eignung als Fingerprint-Methode erbrachte folgende Resultate:

- Sedimentäre Rohphosphate und P-haltige Düngemittel sind durch einen höheren Gehalt an zahlreichen gefährlichen radioaktiven Elementen wie ^{235}U und ^{238}U und deren Tochternuklide sowie nicht radioaktiven giftigen Schwermetallen wie Cd, Cr, Sr, Zn etc. gekennzeichnet als P-freie Düngemittel. Allerdings variieren die Rohphosphate in Abhängigkeit von ihrer geographischen Herkunft beträchtlich hinsichtlich ihrer Elementgehalte.
- Schwermetallmuster können genutzt werden, um magmatische Rohphosphate von der russischen Halbinsel Kola von sedimentären Rohphosphaten unterschiedlicher Herkunft zu unterscheiden. Die untersuchten sedimentären Rohphosphate waren durch höhere Gehalte an Cd, Cr, Ni, Mo und U gekennzeichnet als magmatische Rohphosphate, während letztere höhere Gehalte an Sr und Ti aufwiesen. Darüber hinaus ließen sich Rohphosphate aus dem Mittleren Osten und Nordafrika anhand der Gehalte an Bi, Pb und Co von solchen aus den USA unterscheiden. Rohphosphate aus Senegal zeichneten sich durch die höchsten Cd-Gehalte aus.
- Die Konzentration von U, Sr und anderen Schwermetallen in P-haltigen Mineraldüngern waren abhängig vom Phosphatgehalt sowie von der Herkunft der verwendeten Rohphosphate und dem Herstellungsverfahren.
- Die Relationen Sr/ P_2O_5 und U/ P_2O_5 konnten genutzt werden, um zu überprüfen, ob zur Herstellung der P-Düngemittel Rohphosphate von der russischen Halbinsel Kola oder solche sedimentärer Herkunft verwendet wurden.
- Die Herkunft der zur Herstellung von P-haltigen Düngemitteln verwendeten

Rohphosphate (insbesondere im Fall sedimentärer Rohphosphate) lässt sich nicht zuverlässig anhand von Schwermetallmustern identifizieren und kontrollieren, weil :

1 der Anteil an Schwermetallen, welcher im Produktionsprozess aus dem Rohphosphat ins Düngemittel transferiert wird, je nach Herstellungsverfahren beträchtlich variieren kann und

2 die Schwermetalle in mineralischen Mehrnährstoffdüngern und organo-mineralischen Düngemitteln aus mehreren unterschiedlichen Quellen wie Rohphosphaten, P-Düngemittel, Kaliumsalzen, Stickstoffkomponente, Schwefelkomponente etc. stammen können und es kaum möglich ist, den Anteil an Schwermetallen von jedem Bestandteil festzustellen.

II Die Untersuchung des Sr Isotopverhältnisses auf seine Eignung als Fingerprint-Methode erbrachte folgende Resultate:

- Als wichtigster Unterschied zwischen den Parametern „Isotopenverhältnis“ und „Schwermetallmuster“ wurde die Tatsache identifiziert, dass letztere durch die Anwendung eines chemischen Prozesses (nämlich das nasschemische Herstellungsverfahren für Dünger) geändert werden, während Änderungen der Isotopenverhältnisse normalerweise vernachlässigbar gering sind. Das ergibt sich im Fall des Sr-Isotopenverhältnisses daraus, dass die relativen Massenunterschiede bei schweren Isotopen wie Sr verhältnismäßig klein sind, so dass im Verlauf des chemischen Prozesses keine Massenfraktionierung stattfindet.
- Mithilfe der Thermionen-Massenspektrometrie (TIMS) analysierte Unterschiede im ^{87}Sr/^{86}Sr-Isotopenverhältnis erlaubten die Identifizierung von vier Rohphosphat-Gruppen unterschiedlicher Herkunft: Das niedrigste Verhältnis (R(^{87}Sr/^{86}Sr): 0.70339 bis 0.7035) wurde bei den magmatischen Rohphosphaten (Herkunft: Kola) gefunden. Die zweite Gruppe setzte sich aus Rohphosphaten von Senegal und Togo zusammen (R(^{87}Sr/^{86}Sr): 0.70686 bis 0.70742). Die dritte Gruppe umfasste Rohphosphate vom Mittlere Osten und von Nordafrika (R(^{87}Sr/^{86}Sr): 0.70781 bis 0.70803), die vierte enthielt Rohphosphate aus den USA (R(^{87}Sr/^{86}Sr): 0.70883 bis 0.70896).
- Die Kombination der Parameter R(^{87}Sr/^{86}Sr), Sr/P_2O_5 und U/ P_2O_5 in P-haltigen Düngemitteln (P, NP, PK und NPK) ermöglichte die Unterscheidung magmatischer Rohphosphate (Kola) von sedimentären Rohphosphaten.

III Die Untersuchung von *R*(^{234}U/^{238}U) auf seine Eignung als Fingerprint-Methode erbrachte folgende Resultate:

- *R*(^{234}U/^{238}U) war in den meisten Proben im radioaktiven Gleichgewicht. Eine Ausnahme waren die Rohphosphate aus den USA, in denen ein deutlich höheres Isotopenverhältnis vorlag als in allen anderen Herkünften. Dieses Ungleichgewicht ist als Indikator für die jüngere Entstehungszeit der US-amerikanischen Rohphosphate zu deuten und erlaubt es, sowohl die US-amerikanischen Rohphosphate als auch aus diesen hergestellte P-Dünger von solchen anderer Herkunft zu differenzieren.
- Die gemeinsame Analyse von *R*(^{87}Sr/^{86}Sr) und *R*(^{234}U/^{238}U) in P-Düngemitteln unterschiedlicher Hersteller ermöglichte eine sehr zufriedenstellende Unterscheidung ihrer Herkunft. Auf diese Weise ließ sich bestimmen, ob die P-haltigen Düngemittel aus Rohphosphaten aus den USA, von der Kola-Halbinsel, aus dem Mittleren Osten bzw. Nordafrika oder aus Senegal bzw. Togo hergestellt wurden. Ausserdem war es möglich festzustellen, ob für die Herstellung des Düngemittels eine Mischung aus magmatischen (Kola-) und sedimentären Rohphosphaten verwendet wurde.

Die Untersuchung von *R*(^{235}U/^{238}U) als Indikator für die Verwendung von natürlichem oder anthropogen modifiziertem Uran erbrachte folgendes Ergebnis:

- Mit einer Ausnahme lag das Verhältnis *R*(^{235}U/^{238}U) mit einer Spannweite zwischen 0.007 18 bis 0.007 25 in allen untersuchten Rohphosphaten und Düngern nahe am Wert für natürliches Uran, der allgemein mit 0.007 20 ± 0.000 01 angegeben wird. In einer Probe wurde jedoch mit einem Wert von 0.0068 ein erheblich niedrigeres Verhältnis gefunden. Dies ist als deutlicher Indikator für eine Verunreinigung der betreffenden Probe mit anthropogen modifiziertem Uran anzusehen.

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8 Glossary

Atomic mass unit (u): This unit is based on the standard which is exactly one twelfth the mass of a neutral atom carbon12 (u 71.660 * $10.^{27}$ kg.)

Atomic number (Z): The number of protons in the nucleus of an atom.

Alpha particle: A positively charged particle emitted from the nucleus of an atom having the same charge and mass as that of a helium nucleus (two protons and two neutrons)

Becquerel (Bq): The unit of radioactive equal to 1 disintegration per second. $3.7*10^{10}$ = 1 Curie

Beta particle A beta is a high-speed particle, identical to an electron, emitted from the nucleus of an atom

Curie (Ci): A unit of radioactivity. One curie is defined as 3.7×10^{10} (37 billion) disintegrations per second

Daughter product (s): The nuclide (s) formed by radioactive decay of a different parent nuclide. In the case of radium 226, for example, there are 10 successive products, ending in the stable isotope lead 206

Decay (radioactive): The change of one radioactive nuclide into a different nuclide by the spontaneous emission of elfa, beta, or gamma rays, or by electron capture. The end product is a less energetic, more stable nucleus. Each decay process has a definite half life

Decay chain: A series of nuclides in which each member decays to the next member of the chain through radioactive decay until a stable nuclide has been formed

Deposit: Ore or mineral deposit is used to designate a natural occurrence of a useful mineral, or an ore, in sufficient extent and degree of concentration to invite exploitation.

Disequilibrium: If any member radionuclide is departing from, or being added to, the decay series system by any process other than radioactive decay, a state of radioactive disequilibrium exists (activity ratio #1)

Enriched uranium. U in which the ^{235}U isotope concentration has been increased to greater than the 0.711 percent ^{235}U (by weight) present in natural uranium.

Gamma ray: High-energy, short-wavelength electromagnetic radiation emitted from the nucleus of an excited atom. Gamma rays are identical to X rays except for the source of the emission.

Half life: the time in which one half of the atoms of a particular radioactive substance disintegrates into another nuclear form. Each radioactive isotope has a characteristic half life, e.g. ^{238}U = $4.468 * 10^{9}$ years

Ionisation: The process of adding one or more to, or removing one or more electrons from, atoms or molecules, thereby creating ions. High temperatures, electrical discharges, or nuclear radiation's can cause ionisation

Ionising radiation: Ionising radiation is radiation with enough energy so that during an interaction with an atom, it can remove tightly bound electrons from their orbitals, causing the atom to become charged or ionised. Examples are gamma rays, alpha particles, and beta particles

Isotope: isotopes of a given element have same atomic number (same number of protons in their nuclei) but different atomic weights (different number of neutrons in their nuclei)

Isotope effect: The different masses cause isotopes to behave differently in physical and chemical processes

Mass number (m): The sum of the total number of protons and neutrons in an atom, ion or molecule

Nonradiogenic Stable Nuclides: These atoms have all been present since the (big Bang) so their overall abundance is not a function of time

Non-ionising radiation: it is radiation without enough energy to remove tightly bound electrons from their orbitals around atoms. Examples are microwaves and visible light.

Radioactive material: Radioactive Material is any material that contains radioactive atoms

Radioactivity: Radioactivity is the spontaneous transformation of an unstable atom and often results in the emission of radiation. This process is referred to as a transformation, decay, or disintegration of an atom

Radioisotope: An unstable isotope of an element that decays or disintegrates spontaneously, emitting radiation

Radiogenic: The radiogenic stable nuclides are continuously formed by decay of radioactive parent nuclide, e.g. strontium isotope ratios (^{87}Sr/^{86}Sr) are considered radiogenic, because of the decay of 87Rb to produce

Shale: It is a fine-grained sedimentary rock. The average metal compositionhas been considered as background standard for the calculation of metal depletion or enrichment factor in sedimentary rock

Secular equilibrium or radioactive secular equilibrium: Relationship in a parent/progeny radionuclide system where the half-life of the parent is much longer than that of the progeny; with time, the radioactivity of the parent becomes equal to that of the progeny within the series (e.g., ^{226}radium to ^{222}radium). The radioactive decay chain is said to be in secular equilibrium if the activities of the member radionuclides are equal to the activity of their long-lived parent (activity ratio = 1)

Specific activity: Total activity of a given radionuclide per unit mass or volume. Examples are Bq/g or mCi/mL

Yellow cake: (a) Sludge of uranium oxide concentrate formed during the final step of the milling process.

(b) Applied to certain uranium concentrates produced by mills. It is the final precipitateformed in the milling process. Usually considered to be ammonium diuranate, $(NH_4)_2U_2O_7$, or sodium diuranate, $Na2U_2O_7$, but the composition is variable,and depends on the precipitating conditions.

(c) A common form of triuranium octoxide, U_3O_8, is yellow cake, which is the powder obtained by evaporating an ammonia solution of the oxide.

9 Appendix

A. 1: Description of samples

Table A. 1.1: Rock phosphates and P-fertilisers analysed for heavy metals content and for their U and Sr isotope ratios (collected between 1975-1985)

Origin	Type	No. of samples	Deposit
Russia	Rock phosphate	RP 1, RP 2*and RP 3*	Russian Kola Peninsula
Morocco	Rock phosphate	RP 4+, RP 5*, RP 6- and RP 14, (RP 8*)	Khouribga
		RP 9 and RP 10*	
		RP 11	Spanish Sahara Bu Craa, W-Sahara.
Senegal	Rock phosphate	RP 12*, RP 13 and RP 14	Taiba
Tunisia	Rock phosphate	RP15* and RP 16	Gafsa
Algeria	Rock phosphate	RP 17*	
Syria	Rock phosphate	RP 18*	
USA/Africa	Rock phosphate	RP 19	
USA	Rock phosphate	RP 20*, RP 21 and RP 22	
		RP 23*, RP 24* and RP 25*	Florida,
		RP 26	North Florida.
		RP 27	South Florida
		RP 28	North Carolina
Togo	Rock phosphate	RP 29, RP 30, RP 31, RP 32 and RP 33*	
Israel	Rock phosphate	RP 34*	Nahal Zin
		RP 35	Oron.
Curacao	Rock phosphate	RP 36	Curacao
Algeria	P-fertilisers	P 1*	
Syria	P-fertilisers	P 2*	
USA	P-fertilisers	P 3*	
Morocco	P-fertilisers	P 4*, P 5*	
Israel	P-fertilisers	P 6*	Nahal Zin
Morocco	Phosphogypsum	GP 1+	
Togo	Phosphogypsum	GP 2 and GP 3	
USA	Phosphogypsum	GP 4 and GP 4+	Florida

* Sample was selected for U and Sr isotope ratios analysis.

\+ Sample was selected for Sr isotope ratio analysis

\- Sample was selected for U isotope ratios analysis

Table A. 1.2: Rock phosphates analysed for their content of U and Sr (collected after 1995)

Probe Nr,	**Description of sample**	**Country/ Origin**	**Sr [mg kg^{-1}]**	**U [mg kg^{-1}]**
RP-N 1	Rock phosphate	Algeria	1829	38.0
RP-N 2	Rock phosphate	Algeria	1877	39.3
RP-N 3	Rock phosphate	Algeria	1974	40.7
RP-N 4	Rock phosphate	Algeria	1942	41.3
RP-N 5	Rock phosphate	Israel -Arad	1991	119
RP-N 6	Rock phosphate	Israel- Arad	1976	121
RP-N 7	Rock phosphate	Israel	2059	132
RP-N 8	Rock phosphate	Israel	2057	1301
RP-N 9	Rock phosphate	Israel	2069	132
RP-N 10	Rock phosphate	Morocco	1630	114
RP-N 11	Rock phosphate	Morocco	895	119
RP-N 12	Rock phosphate	Morocco	924	121
RP-N 13	Pebble- Rock phosphate	Florida	654	106
RP-N 14	Rock phosphate	Florida	451	172
RP-N 15	Rock phosphate (Pebble-Phosphate)	Badische Anilin- & Soda- Fabrik (Ludwigshafen a, Rhein)	449	108
RP-N 16	Rock phosphate Pebble		816	118
RP-N 17	Rock phosphate	Tunisia Gafsa	1752	36.2
RP-N 18	Rock phosphate	Tunisia Gafsa	1735	26.7
RP-N 19	Rock phosphate	Tunisia Gafsa	1746	35.9
RP-N 20	Rock phosphate	Tunisia Gafsa	1812	29.9
RP-N 21	Apatit -Konzentrat	Russia/ Kali-Chemie A,G, Werk Brunsbüttelkoog i,H	19949	2.83
RP-N 22	Kola-Apatit-Konzentrat		21342	2.14
RP-N 24	Hyper	dhg, Dünger	1648	106
RP-N 25	Hyperphos-Kali 20/20		1104	18.8
RP-N 26	Roh-P/Hyperphosphat		1970	82.0
RP-N 28	teilaufgeschl, Rock phosphate 23 Handelsname Cederan-P23	BASF	723	79.5

Table A. 1.3: The selected farmyard manures and P-containing fertiliser samples for U, Sr isotope ratio analysis

Type of samples		**Nr. of samples**	**Total samples**
Farmyard manures	Chicken	Chic. 1*, Chic. 2* and Chic. 3*	3
	Dairy Cows and Calf	Cow1-, Cow2* and Cow3*, Cow4 +	3
	Pigs	G2*, G 3* and G1*)	3
Organo-mineral fertiliser samples		OMF (1, 2, 3, 4) *	4
Mineral fertilisers	P-fertilisers	KDM (53, 54, 55, 56)*	4
	K-fertilisers	MD 5-, MD 7-	2
	PK	KDM (34)* MD 38-, 36+, 61+	3
	NP	KDM (27, 57, 58, 59, 60)*	5
	NPK	NPK (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16)* MD (39, 42)* , (24, 41)-	20

+ Sample was selected for U isotope ratios analysis, - Sample was selected for Sr isotope ratio analysis, * Sample was selected for U and Sr isotope ratios analysis.

Table A. 1.4: The organic fertiliser samples used for U, Sr isotope ratio analysis

Nr. of samples	**Type**	**Trade name**	**Notes**
OMF1*	Org. fertilisers NPK- with Mg 5+4+5 (+3)	Tannendünger	Made of: Cacao shells, Chicken manure, calcium phosphate, potassium sulphate and lime
OMF2*	Org. fertilisers NPK with Mg 9 + 5 + 13 (+4)	Erdbeerdünger plus Guano (chloridarm) Spezialdünger auch für Obst, Beeren und Feingemüse	Basic materials: lake bird guano, grape/cluster core pellet, urea, di-ammonium phosphate, potassium sulphate and kieserite ($MgSO4.H2O$)
OMF3*	Org. fertilisers NPK with Mg 8 + 7 + 12 +(+2)	Tomatendünger für alle Arten von Tomaten	Made of: Cacao shells, Chicken manure, urea, calcium phosphate, potassium sulphate, lime and kieserite
OMF4*	Org. fertilisers NPK with Mg 8 + 8 + 10 (+2)	Erdbeerdünger mit echtem Guano	Contents materials: original Guano, nature fertiliser, prepared vegetable substances, nature lime and mineral fertilisers.

* Sample was selected for U and Sr isotope ratios analysis

Table A. 1.5: Different types of mineral fertilisers collected after 1995 analysed for their content of U and Sr and U and Sr isotope ratios

Type	**Samples ID**	**Description**	**Trade name**	**Manufacturer/ Sources**	**N [%]**	**P_2O_5 [%]**	**K_20 [%]**	**MgO [%]**	**Sr [g kg^{-1}]**	**U [mg kg^{-1}]**	**Sr/ P_2O_5**	**U/ P_2O_5**
Straight P-fertiliser	P 6 *	Super phosphate 18%				18			383	80.8	21.3	4.49
	P 7 *	Super phosphate 18%				18			512	66.1	28.5	3.67
	P 8 *	Super phosphate 18%	Cederan Superphosphat	BASF(Ludwigshafen)		18			591	74.8	32.8	4.16
	P 9 *	Super phosphate 20%	Cederan Stall-Super	(BASF)		20			667	73.2	33.4	3.65
	P 10	Novaphos 23							695	75.3		
	P 11	Novaphos		S,I, Düngephosphate		23			720	83.8	31.3	3.64
PK	PK 1	Hyperphos-Kali 20/20				20	30		1104	18.8	55.2	0.94
	PK 2	PK: 16+16				16	16		472	61.1	29.5	3.82
	PK 3 *	PK: 16+16		S,I, Düngephosphate		16	16		474	64.0	29.6	4.00
	PK 4	PK: 15+20				15	20		402	55.9	26.8	3.73
	PK 5 *	PK: 15+20		S,I, Düngephosphate		15	20		415	56.2	27.7	3.73
	PK 6 *	PK: 10+20				10	20		210	29.1	21.0	2.90
	PK 7	PK: 10+19				12	19	4	318	45.5	26.5	3.79
	PK 8	PK: 12+19	Cederan	BASF		12	19		444	44.5	37.0	3.71
	PK 9	PK: 16+16	Cederan	BASF		16	16		658	52.5	41.1	3.25
NP	NP 1 *	NP: 1.5+27	Granuphos	Hoechst	1.5	27			1829	34.2	67.7	1.26
	NP 2 *	NP: 20+2	Rustica	Ruhr-Stickstoff AG (Bochum)	20	20			3093	32.2	155	1.60
	NP 3 *	NP: 20+2		BASF	20	20			484	73.2	24.2	3.65
	NP 4 *	NP:11+52	EN-PE-KA 11+52+0	Guano-Werke AG	11	52			83.7	163	1.61	3.12
	NP 5 *	NP: 9+9		Super-Phosphate	9	9			322	55.4	35.8	6.11
P Mg	P Mg 1	P Mg-Novaphos 17+7				17		7	578	68.1	340	4.00
	P Mg 2	P Mg-Novaphos 17+7		S,I, Düngephosphate		17		7	557	65.5	32.8	3.85
	P Mg 3		Camaphos			16		4	318	45.5	19.9	2.84
K	K 1 -	K (without P)							28.0	0.48		
	K 2 -	K (without P)							85.0	0.07		
P K Mg fertiliser	Com. 1	PK Mg: 12+19+4				12	19	4	385	45.5	32.1	3.79
	Com 2	PK Mg: 12+19+4		S,I, Düngephosphate		12	19	4	400	45.0	33.3	3.75

Table A. 1.5 continued

Type	Sample ID	Description	Trade name	Manufacturer/ Sources	N [%]	P_2O_5 [%]	K_20 [%]	MgO [%]	Sr [g kg^{-1}]	U [mg kg^{-1}]	Sr/ P_2O_5	U/ P_2O_5
NPK	NPK 1*	NPK	Nitrophoska, (Volldünger)	BASF	11.5	8.5	18		216	39.5	25.4	4.65
	NPK 2*	NPK-	Nitrophoska (Volldünger)	BASF	11.5	8.5	18		208	39.8	24.4	4.68
	NPK 3*	NPK	Nitrophoska (Volldünger)	BASF	13	13	21		250	35.5	19.2	2.73
	NPK 4*	NPK	Nitrophoska blau (Volldünger chloridfrei)	BASF	12	12	20		297	30.2	24.7	2.50
	NPK 5*	NPK: 15:15:15	Nitrophoska (Volldünger)	BASF	15	15	15		250	40.9	16.7	2.67
	NPK 6*	NPK:10+15+20	EN-PE-KA 10+15+20 violett	Guano-Werke AG	10	15	20		223	44.2	14.8	2.93
	NPK 7*	NPK: 6+12+18	EN-PE-KA 6+12+18 grün	Guano-Werke AG	6	12	18		379	28.7	31.6	2.39
	NPK 8*	NPK Cu: 10+15+20+2	EN-PE-KA 10+15+20+2 blau	Guano-Werke AG	10	15	20		209	47.1	14-0	3.13
	NPK 9*	NPK:13+13+21	Volldünger Rotkorn 13:13:21	Hoechst	13	13	21		185	30.8	14.2	2.31
	NPK 10*	NPKMg: 12+12+17+2	Spezial-Volldünger Blaukorn	Hoechst	12	12	17	2	263	42.3	21.9	3.50
	NPK 11*	NPK: 13+13+21	Rustica	Bochum	13	13	21		3361	10.5	259	0.81
	NPK 12*	NPK: 15+15+15	Rustica	Bochum	15	15	15		190	27.3	12.7	1.80
	NPK 13*	NPK:	Nitrophoska		11.5	8.5	18		173	28.0	20.4	3.29
	NPK 14*	NPK: 10+12+18	Am-Sup-Ka Gartendünger	Chem, Düngerf, Rendsb	10	12	18		120	9.44	10.0	0.79
	NPK 15*	NPK: 15+15+15	Nitrophoska	BASF	15	15	15		263	44.0	17.5	2.87
	NPK 16*	NPK: 24+8+8	Nitrophoska	BASF	24	8	8		166	24.9	20.7	3.11
Other	MIX. 1	N Mg Cu (without P)	Rustica		20			7	69	0.18		
	MIX. 2	NPKMg 16+8+12+5	Compo/Triabon (Vollvorratsdünger mit Crotodur)	BASF	16	8	12	5	39	23.6	4.88	2.95
	MIX. 3	NPK Mg Mn Zn	Compo/Nitrophoska permanent (Isodor Langzeitdünger mit Kaliumsulfat für Intensivkulturen und Zieranlagen)	BASF	15	9	15	2	224	28.3	24.9	3.14
	MIX. 4	NPKS 13+13+21 (+2)	Nitrophoska	BASF	13	13	21		234	38.5	18.0	2.92
	MIX. 5	NPK S Mg 13+9+16 (+4+3)	Nitrophoska-Magnesium	BASF	13	9	16	4	139	25.6	15.4	2.84

BASF: BASF (Ludwigshafen), Hoechst: Farbwerke Hoechst AG, (Frankfurt/Main), Bochum: Ruhr-Stickstoff AG (Bochum), Ludwigshafen a, Rhein: Badische Anilin- & Soda- Fabrik (Ludwigshafen a, Rhein). - Sample was selected for Sr isotope ratio analysis; * Sample was selected for U and Sr isotope ratios analysis.

Table A. 2.1: P_2O_5, microelements and heavy metal concentrations in rock phosphates of different origin

Country/ Origin	**Sample Nr.**	**Deposit**	**P_2O_5 [%]**	**Micro elements [mg kg^{-1}]**					**Heavy metals [mg kg^{-1}]**													
				Mn	**Zn**	**Cu**	**B**	**Mo**	**As**	**Be**	**Bi**	**Cd**	**Co**	**Cr**	**Ni**	**Pb**	**Sb**	**Se**	**Sr**	**Ti**	**Tl**	**U**
Algeria	RP 17	-	29.0	17.5	154	8.20	293	3.23	3.92	1.48	0.05	25.5	0.74	189	14.8	7.52	1.14	27.9	1876	257	2.95	62.0
Morocco	RP 9	Embesn	35.5	5.30	476	18.3	836	19.7	3.71	1.14	0.00	36.6	0.55	238	45.2	6.65	1.60	40.4	1833	341	0.37	146
	RP 10	-	35.8	9.40	183	33.4	268	3.84	11.9	2.03	0.00	3.22	0.65	211	40.9	8.84	2.35	2.02	937	340	0.00	157
	RP 11	Sahara Bu Craa	32.6	35.4	128	10.2	512	2.85	12.1	1.21	0.00	41.0	0.61	118	10.9	5.71	0.93	1.65	287	372	0.00	71
	RP 4	Khouribga	31.2	8.60	221	24.9	650	5.13	10.4	1.51	0.00	17.5	0.63	191	34.1	5.02	3.21	2.12	1020	265	0.15	152
	RP 6	Khouribga	31.9	11.8	231	27.6	647	4.57	11.5	1.69	0.00	18.3	0.68	208	38.6	4.27	2.77	2.53	950	225	0.16	133
	RP 7	Khouribga	33.2	19.8	434	54.6	872	11.5	14.8	2.46	0.04	12.8	1.38	335	78.4	7.30	3.31	3.90	2958	663	0.11	245
Syria	RP 18	-	24.6	22.5	322	8.30	442	6.02	4.32	0.51	0.07	6.10	0.89	266	31.4	2.90	0.99	2.00	1238	40.6	0.13	58.6
Senegal	RP 12	Taiba	37.1	241	488	52.1	727	6.24	1.31	1.96	0.04	106	4.32	156	33.6	6.40	1.98	1.20	1224	346	0.0	115
	RP 13	Taiba	36.8	215	398	48.6	867	3.31	3.05	1.88	0.00	67.5	4.50	118	45.1	6.50	1.65	1.10	753	335	0.0	104
	RP 14	Taiba	36.0	172	445	47.5	867	4.06	2.11	2.03	0.04	93.9	3.89	141	35.2	7.00	1.9	0.86	999	345	0.0	109
Togo	RP 33	-	37.1	157	211	40.2	610	10.3	13.0	2.18	0.09	53.4	2.95	89.4	36.0	9.50	0.84	2.13	418	265	1.07	107
	RP 31	-	37.3	123	198	36.0	450	7.66	11.9	1.88	0.07	52.7	2.71	83.6	27.9	11.0	0.84	2.01	400	316	0.81	132
	RP 32	-	33.5	46.7	224	34.8	518	5.10	14.6	1.56	0.05	34.3	1.85	147	33.4	12.0	1.45	1.99	1146	342	0.10	120
	RP 29	-	36.7	207	208	39.7	588	10.8	14.4	2.02	0.09	52.6	2.87	85.9	33.8	9.10	1.00	1.75	406	265	1.16	109
	RP 30	-	37.5	96.4	259	38.0	618	8.67	13.7	2.13	0.00	57.6	2.32	99.4	32.7	8.40	0.81	2.13	349	251	0.30	110
Tunisia	RP 16	Gafsa	28.0	12.1	288	9.60	437	7.21	1.83	1.36	0.00	54.1	0.63	141	20.8	4.70	0.42	9.16	1705	250	1.05	50.2
	RP 15	Gafsa	27.6	27.4	329	12.0	362	4.05	2.15	1.81	0.04	51.9	0.86	190	17.4	5.30	0.51	8.74	1757	301	0.63	36.9
Israel	RP 34	Nahal Zin	32.4	9.30	328	13.2	822	26.5	3.76	0.78	0.00	18.9	0.47	46.9	21.3	3.60	1.12	5.06	2508	209	0.54	129
	RP 35	Oron	33.8	6.50	499	46.2	913	15.7	9.08	1.19	0.00	5.65	1.28	214	96.7	6.20	2.00	4.94	3737	603	0.0	215

Table A. 2.1 continued

Country	**Sample Nr.**	**Deposit**	**P_2O_5 [%]**	**Micro elements mg kg^{-1}**					**Heavy metals mg kg^{-1}**													
				Mn	**Zn**	**Cu**	**B**	**Mo**	**As**	**Be**	**Bi**	**Cd**	**Co**	**Cr**	**Ni**	**Pb**	**Sb**	**Se**	**Sr**	**Ti**	**Tl**	**U**
USA	RP 20	-	32.7	138	77.6	8.50	412	4.50	5.16	1.41	0.15	8.37	2.61	45.0	17.1	9.80	1.99	1.21	1154	394	0.44	121
	RP 19	-	35.4	154	138	16.3	545	6.13	8.28	1.66	0.12	24.4	2.72	65.8	20.3	11.0	1.56	1.36	675	363	0.46	117
	RP 21	Florida	33.1	162	66.5	7.90	611	8.20	13.90	1.98	0.15	5.75	6.70	58.1	27.9	14.0	3.45	2.03	1082	356	1.95	114
	RP 23	Florida	33.2	239	100	7.60	751	8.88	8.11	1.70	0.20	5.27	3.25	41.9	22.4	15.0	2.27	1.62	926	328	0.7	122
	RP 24	-	34.2	176	102	7.60	563	4.80	6.03	1.55	0.14	12.5	3.19	51.7	17.9	12.0	1.89	1.34	814	408	0.63	123
	RP 25	Florida	34.2	184	54.9	8.10	339	10.2	4.91	1.50	0.13	5.43	2.45	57.0	8.83	14.0	1.46	1.43	1013	409	0.43	65.5
	RP 26	North Florida	31.7	145	72.5	7.90	484	6.36	3.79	1.36	0.10	6.55	2.54	59.7	12.9	11.0	1.52	1.21	1025	433	0.21	70.5
	RP 27	South Florida	32.4	121	109	9.00	520	3.40	2.97	1.55	0.13	12.1	1.64	64.2	11.8	12.0	1.63	1.26	788	447	0.18	110
	RP 28	Carolina	32.0	16.3	259	9.10	396	9.26	15.8	1.89	0.05	35.8	0.72	127	21.0	5.90	1.22	4.22	2601	429	2.23	80.4
	RP 22	Pebble phospahte	31.9	149	65.3	8.80	403	5.07	7.62	1.40	0.14	9.17	2.48	55.7	16.9	13.0	1.98	1.42	959	361	0.33	153
Curacao	RP 36	-	31.4	174	210	19.2	39.0	1.40	7.68	0.06	0.03	5.82	2.63	15.7	11.7	4.10	0.25	1.15	831	333	0.0	9.96
Russia	RP 1	Kola	39.9	203	14.9	26.4	354	1.12	0.95	0.14	0.00	0.00	1.35	0.80	4.69	5.50	0.17	3.41	21204	922	0.0	3.35
	RP 2	Kola	37.6	171	10.5	26.2	229	0.56	1.07	0.08	0.00	0.00	1.46	0.53	4.69	3.20	1.08	3.32	18596	877	0.0	3.07
	RP 3	Kola	38.9	245	26.7	34.8	222	1.88	0.96	0.26	0.00	0.40	1.60	1.33	7.32	2.90	0.10	3.19	23016	744	0.0	3.04

Table A. 2.2: Averages ± Std. and ranges of P_2O_5 and microelements [mg kg^{-1}] in rock phosphates of different origin

Element	**Origin**	**Algeria**	**Morocco**	**Senegal**	**Syria**	**Togo**	**Tunisia**	**Israel**	**USA**	**Curacao**	**Kola**
	n	1	6	3	1	5	2	2	10	1	3
P_2O_5%	Average	29.0	33.4±1.9 b	36.6±0.56 c	24.6	36.4±1.65 c	27.8±0.26 a	33.1±0.98 b	33.1±1.22 b	31.4	38.8±1.1 c
	Range	29.0	31.2-35.8	36.0-37.1	24.6	33.5-37.5	27.6-28.00	32.4-33.8	31.6-35.4	31.4	37.6-40.0
Mn	Average	17.5	15.0±11 a	209±34.8 c	7.37	126±60.6 b	19.75±11a	7.91±2 a	148±56.6 b,c	174	206±37 c
	Range	17.5	5.27-35.4	172-241	7.37	46.7-207	12.1-27.4	6.48-9.34	121-239	174	171-245
Zn	Average	154	279±142 c,d	444±45 e	322	220±23.7 b,c	308 ±29 c,d,e	414±121 d,e	104±60 a,b	210	17.4±8.4 a
	Range	154	128-476	398-488	322	198-259	288-329	328-499	54.9-259	210	10.5-26.7
Cu	Average	8.20	28.2±15 b	49.4±2.4 c	5.75	37.7±2.3b,c	10.8±1.7 a	29.7±23 b	9.09±2.6 a	19.2	29.0±4.9 b
	Range	8.20	10.2-54.6	47.5-52.6	5.75	34.8-40.2	9.62-12.0	13.2-46.2	8.54-16.3	19.2	26.2-34.8
B	Average	293	631±222 b,c	820±80.8 c,d	376	557±71.5b	399±53 a,b	867±64 d	502±123 b	39.0	268±74 a
	Range	293	268-872	727-876	376	450-618	362-437	822-913	339-611	39.0	222-354
Mo	Average	3.23	7.90±6.5 a,b	4.54±1.5 a,b	6.02	8.50 ±2.28 a,b	5.63±2.2 a,b	21.1±7.6 c	6.68±2.3 a,b	1.40	1.19±0.66 a
	Range	3.23	2.85-11.5	3.31-6.24	6.02	5.10-10.8	4.05-7.21	15.7-26.5	3.40-10.2	1.40	0.56-1.88

Mean values followed by different letters are significantly different by Duncan’s test at $P < 0.05$.

Table A. 2.3: Averages ± Std. and ranges of heavy metals [mg kg^{-1}] in rock phosphates from different origin

Element	Origin	Algeria	Senegal	Morocco	Syria	Togo	Tunisia	Israel	USA	Curacao	Kola
	n	1	3	6	1	5	2	2	10	1	3
As	average	3.92	2.16±0.87 a	10.7±3.7 b,c	4.32	13.52 ± 1 c	1.99±0.23 a	6.42±3.76 a,b	7.66±4.2 b	7.68	0.99±0.07 a
	range	3.92	1.31-3.05	3.71-14.8	4.32	11.9-14.6	1.83-2.15	3.76-9.08	2.97-8.28	7.68	0.95-1.07
Be	average	1.48	1.96±0.08 c	1.67±0.5 c	0.51	1.95±0.24 c	1.59±0.3 c	0.99±0.29b	1.60±0.21 c	0.06	0.16±0.09 a
	range	1.48	1.88-2.03	1.10-2.46	0.51	1.56-2.18	1.36-1.81	0.78-1.19	1.36-1.98	0.06	0.08-0.26
Bi	average	0.05	0.03±0.02a,b	0.007±0.01 a	0.07	0.06±0.03 b	0.02±0.03a,b	0.0 a	0.13±0.04 c	0.03	0.0a
	range	0.05	0-0.04	0-0.04	0.07	0-0.09	0-0.04	0.0	0.1-0.2	0.03	0.0
Cd	average	25.5	89±19.6 d	21.6±14 b	6.10	50±9 c	53±1.6 c	12.3±9.4 a,b	12.5±10 a,b	5.82	0.133±0.23 a
	range	25.5	67.5-106	3.22-36.6	6.10	34.3-53.4	51.9-54.1	5.65-18.9	5.27-35.8	5.82	0.0-0.04
Co	average	0.74	4.24±0.3 d	0.75±0.3 a	0.89	2.54±0.4 b,c	0.75±0.16 a	0.88±0.6 a,b	2.83±1.5 c,d	2.63	1.47±0.1a,b,c
	range	0.74	3.89-4.5	0.55-1.38	0.89	1.85-2.95	0.63-0.86	0.47-1.28	0.72-6.7	2.63	1.35-1.46
Cr	average	189	138±19b,c	217±71 d	266	101±26b,c	165±35 c,d	130±118 b,c	62.6±23.8 b	16.0	0.89±0.4 a
	range	189	118-156	118-335	266	83.6-147	141-190	46.9-214	41.9-65.8	16.0	0.53-1.33
Ni	average	14.8	37.97±6.2 b,c	41.4± 22 b,c	31.4	32.8±2.98b,c	19.1±2.4 a,b	59.0±53 c	17.7 ±5 a,b	11.7	5.57±1.5 a
	range	14.8	33.6-45.1	10.9-78.4	31.44	27.9-36.0	17.4 –20.8	21.3-96.7	8.80- 27.9	11.7	4.69-7.32

Mean values followed by different letters are significantly different by Duncan’s test at P <0.05.

Table A. 2.3: contained

Element	**Origin**	**Algeria**	**Senegal**	**Morocco**	**Syria**	**Togo**	**Tunisia**	**Israel**	**USA**	**Curacao**	**Kola**
	n	1	3	6	1	5	2	2	10	1	3
Pb	average	7.52	6.63±0.3 a	6.30±1.7 a	3.74	9.97±1.4 b	4.99±0.43 a	4.88±1.8a	11.7±2.6 b	4.05	3.88±1.4 a
	range	7.52	6.36-7.01	4.27-8.84	3.74	8.40-11.5	4.69-5.30	3.60-6.16	5.90-14.7	4.05	2.88-5.53
Sb	average	1.14	1.84±017 b,c	2.40±0.9 c	0.99	0.99±0.27a,b	0.46±0.06 a	1.56±0.62b,c	1.90±0.63b,c	0.25	0.45±0.55 a
	range	1.14	1.65-1.98	0.93-3.31	0.99	0.81-1.45	0.42-0.51	1.12-2.00	1.22-3.45	0.25	0.10-1.08
Se	average	27.9	1.05±0.17 a	8.80±15.5 a	-	2.00±0.16 a	8.95±0.3 a	5.00±0.09 a	1.70±0.9 a	1.15	3.31±0.11 a
	range	27.9	0.86-1.2	1.65-40.4	-	1.75-2.13	8.74-9.16	4.95-5.06	1.21-4.22	1.15	3.19-3.41
Sr	average	1876	992±236 a	1331±937 a	1423	544±338 a	1731±37 a,b	3123±869 b	1104±546 a	831	20939±2222 c
	range	1876	753-1224	287-2958	1423	349-1146	1705-1757	2508-3737	788-2601	831	18596-23016
Ti	average	257	342±6 b	368±155b	40.40	288±39 b	275±36 b	406±279 b	380±39 b	333	847±93 a
	range	257	335-346	225-663	40.40	251-342	250-301	209-603	328-447	333	744-877
Tl	average	2.95	0 a	0.13±0.14 a	0.14	0.69±0.47 a	0.84±0.3 a	0.27±0.38 a	0.76±0.72 a	0	0 a
	range	2.95	0	0-0.37	0.14	0.10-1.16	0.63-1.05	0-0.44	0.18-2.23	0	0
U	average	61.8	109±5.5 b	151±56 b,c	58.59	116±10 b	43.6±9.4 a	172±61 c	108±27 b	9.96	3.15±0.17 a
	range	61.8	104-115	71.1-245	58.59	107-120	36.9-50.2	129-215	65.5-153	9.96	3.04-3.35

Mean values followed by different letters are significantly different by Duncan’s test at P <0.05.

Table A. 2.4: Heavy metal concentrations in P-fertiliser and in their respective rock phosphate

Country/ Origin	Type of sample	P [g kg^{-1}]	Micro elements [mg kg^{-1}]					Heavy metals [mg kg^{-1}]												
			Mn	**Zn**	**Cu**	**B**	**Mo**	**As**	**Be**	**Cd**	**Co**	**Cr**	**Ni**	**Pb**	**Sb**	**Se**	**Sr**	**Ti**	**Tl**	**U**
Morocco	Rock phosphate	141	11.8	231	27.6	647	4.57	11.5	1.69	18.3	0.68	208	38.6	4.27	2.77	2.53	950	225	0.16	133
	P-fertilisers	70.3	44.2	87.7	12.5	302	2.89	5.58	0.83	6.65	1.34	68.9	22.4	4.23	1.99	1.02	538	140	0.47	63.6
	Rock phosphate	97.6	13.6	221	23.7	728	2.76	12.0	1.50	22.9	0.74	177	28.0	4.38	2.78	2.54	1001	255	0.09	129
	P-fertilisers	142	14.1	168	21.0	493	2.50	9.80	1.14	15.7	0.66	129	23.0	3.76	2.09	2.23	717	187	0.09	94.7
Syria	Rock phosphate	109	7.37	322	5.75	376	6.02	4.32	0.51	6.10	0.89	266	31.4	3.74	0.99	-	1238	40.4	0.13	58.6
	P-fertilisers	187	13.9	317	5.90	834	6.08	3.12	0.92	7.76	0.58	198	20.5	2.26	0.76	-	891	27.2	0.13	85.4
Israel	Rock phosphate	144	9.34	328	13.2	822	26.5	3.76	0.78	18.9	-	46.9	21.3	3.60	1.12	5.06	2508	209	0.54	129
	P-fertilisers	106	4.50	273	16.9	685	18.1	5.63	0.50	22.0	-	39.2	25.6	4.45	1.25	4.28	1629	138	0.48	99.8
USA	Rock phosphate	145	138	77.6	8.54	412	4.50	5.16	1.41	8.37	2.61	45.0	17.1	9.76	1.99	1.21	1154	394	0.44	121
	P-fertilisers	86.0	73.3	61.9	6.91	178	2.41	2.25	0.82	6.17	1.36	32.1	12.3	10.3	1.48	1.42	646	391	0.24	66.4

Heavy metal concentrations in P-fertiliser and in their respective rock phosphate (expressed as %)

Country	Type	P	Mn	Zn	Cu	B	Mo	As	Be	Cd	Co	Cr	Ni	Pb	Sb	Se	Sr	Ti	Tl	U
Morocco	Rock phosphate	14.1	0.0010	0.023	0.0028	0.065	0.00046	0.0012	0.00017	0.0018	0.00007	0.021	0.0039	0.00043	0.00028	0.00025	0.095	0.023	0.000016	0.013
	P-fertilisers	7.03	0.0044	0.009	0.0013	0.030	0.00029	0.0006	0.00008	0.0007	0.00013	0.007	0.0022	0.00042	0.00020	0.00010	0.054	0.014	0.000047	0.0064
	Rock phosphate	9.76	0.0014	0.022	0.0024	0.073	0.00028	0.0012	0.00015	0.0023	0.00007	0.018	0.0028	0.00043	0.00028	0.00025	0.100	0.026	0.000009	0.0129
	P-fertilisers	14.2	0.0014	0.017	0.0021	0.049	0.00025	0.0010	0.00011	0.0016	0.00007	0.013	0.0023	0.00038	0.00021	0.00022	0.072	0.019	0.000009	0.0095
Syria	Rock phosphate	10.9	0.0007	0.032	0.0006	0.038	0.00060	0.0004	0.00005	0.0006	0.00009	0.027	0.0031	0.00037	0.00001	-	0.124	0.004	0.000013	0.0059
	P-fertilisers	18.7	0.0014	0.032	0.0006	0.083	0.00061	0.0003	0.00009	0.0008	0.00006	0.020	0.0021	0.00023	0.00008	-	0.089	0.003	0.000013	0.0085
Israel	Rock phosphate	14.4	0.0009	0.033	0.0013	0.082	0.00265	0.0004	0.00008	0.0019	-	0.005	0.0021	0.00036	0.00011	0.00051	0.251	0.021	0.000054	0.0129
	P-fertilisers	10.6	0.0004	0.027	0.0017	0.069	0.00181	0.0006	0.00005	0.0022	-	0.004	0.0026	0.00045	0.00013	0.00043	0.163	0.014	0.000048	0.0100
USA	Rock phosphate	14.5	0.0138	0.008	0.0009	0.041	0.00045	0.0005	0.00014	0.0008	0.00026	0.005	0.0017	0.00098	0.00020	0.00012	0.115	0.039	0.000044	0.0121
	P-fertilisers	8.6	0.0073	0.006	0.0007	0.018	0.00024	0.0002	0.00008	0.0006	0.00014	0.003	0.0012	0.00103	0.00015	0.00014	0.065	0.039	0.000024	0.0066

Table A. 2.5: Heavy metal concentrations in rock phosphate and in phosphogypsum

Country		**Be**	**B**	**Ti**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sr**	**Mo**	**Cd**	**Sb**	**Tl**	**Pb**	**U**
Morocco	Rock phosphate	1.69	647	225	208	11.8	0.68	38.6	27.6	231	11.5	2.53	950	4.57	18.3	2.77	0.16	4.27	133
Khouribga	Phosphogypsum	0.6	216	6.7	15.4	1.10	-	8.88	1.12	8.13	-	1.36	1046	1.07	2.41	-	-	3.44	9.20
Togo	Rock Phosphate	2.18	610	265	89.4	157	2.95	36.0	40.2	211	13	2.13	418	10.3	53.4	0.84	1.07	9.5	107
	Phosphogypsum	0.39	169	21	4.3	6.66	-	8.42	2.04	9.24	0.37	0.93	211	0.54	3.65	0.1	-	6.65	0.67
	Rock phosphate	2.02	588	265	85.9	207	2.87	33.8	39.7	208	14.4	1.75	406	10.8	52-6	1	1.16	9.05	109
	Phosphogypsum	0.29	182	19	3.73	5.55	-	5.12	3.71	9.16	-	0.83	251	0.61	5.29	0.09	-	6.53	0.26
USA	Rock phosphate	1.41	412	394	45	138	2.61	17.1	8.54	77.6	5.16	1.21	1154	4.50	8.37	1.99	0.44	9.76	121
	Phosphogypsum	0.1	49	63.4	1.49	5.88	-	7.64	1.04	3.88	-	-	861	0.14	0.42	-	-	8.49	0.37

Table A. 2.6: The Pearson Correlation among heavy metals in rock phosphates

	Be	B	Ti	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Cd	Sb	Tl	Pb	Bi	U
Be	1																		
B	.485(**)	1																	
Ti	-.54(**)	-.219	1																
Cr	.528(**)	.457(**)	-.235	1															
Mn	-.154	-.131	.275	-.69 (**)	1														
Co	.302	.206	-.097	-.347(*)	.713(**)	1													
Ni	.453(**)	.691(**)	-.056	.730(**)	-.371(*)	-.002	1												
Cu	.265	.418(*)	.166	.382(*)	.119	.163	.643(**)	1											
Zn	.373(*)	.669(**)	-.285	.708(**)	-.374(*)	-.065	.735(**)	.574(**)	1										
As	.518(**)	.134	-.294	.295	-.307	.038	.390(*)	.163	.037	1									
Se	-.108	.079	-.111	.401(*)	-.420(*)	-.375(*)	.097	-.180	.292	-.225	1								
Sr	-.69(**)	-.353(*)	.847(**)	-.376(*)	.297	-.191	-.283	.120	-.360(*)	-.424(*)	-.004	1							
Mo	.158	.579(**)	-.270	.246	-.348(*)	-.143	.440(*)	.031	.471(**)	.170	.332	-.274	1						
Cd	.486(**)	.385(*)	-.438(*)	.271	.069	.252	.166	.468(**)	.620(**)	-.040	.042	-.351(*)	.041	1					
Sb	.500(**)	.508(**)	-.150	.454(**)	-.177	.264	.490(**)	.089	.168	.344(*)	-.104	-.386(*)	.135	-.151	1				
Tl	.272	-.146	-.316	.026	-.172	.070	-.152	-.393(*)	-.129	.238	.356(*)	-.213	.134	.037	-.023	1			
Pb	.456(**)	.071	-.219	-.202	.313	.527(**)	-.068	-.290	-.355(*)	.283	-.192	-.437(*)	.018	-.152	.346(*)	.211	1		
Bi	.292	-.037	-.158	-.381(*)	.451(**)	.533(**)	-.253	-.45(**)	-.45(**)	.109	-.243	-.334	-.041	-.221	.275	.290	.862(**)	1	
U	.614(**)	.700(**)	-.265	.617(**)	-.370(*)	.040	.796(**)	.332	.490(**)	.491(**)	.004	-.53(**)	.495(**)	.042	.731(**)	-.094	.304	.132	1

N= 30. ** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).

Table A. 2.7: Pearson correlation among heavy metals (The positive correlation)

Element	**positive correlation**		
	High correlation (>0.75)	**Medium correlation (0.5-0.75)**	**Low correlation (<0.5)**
Ni	(U)**	(Zn, Cr, Cu, B)**	(Sb, Be)**, (Mo, As)*, Se ,Cd
Cr		(Ni, Zn, U, Be)**	(Sb, B)**, (Se, Cu)*, Cd, Mo, As,Tl
Zn		(Ni, Cr, B, Cu, Cd)**	(U, Mo)**, Be*, Sb, Se, As,
U	(Ni)**	(Sb, Be, B, Cr)**	(Zn, As, Mo)**,Pb, Bi, Co, Cu, Se
Be		(Sb, U, Cr, As)**	(Ni, Pb, Cd, B)** (Zn)*, Co, Cu, Mo, Tl
B		(U, Sb, Ni, Zn, Mo)**	(Cr, Be, Cu)**, Pb, Bi, Co, As, Se, Cd
Sb		(U, Be, B)**	(Ni, Cr|)**, (Pb, As)*, Bi, Co, Cu, Zn, Mo
Cu		(Ni, Zn)**	Cd**, (Cr, B)*, Ti, Sr, Sb, U, Mn, Co, Be, As,Mo
Cd		Zn**	(Cu, Be)**, B, Cr, Mn, Co, Ni, Se, Tl
Mo		B**	(U, Zn,)**,Ni*, Sb, Pb, Bi, Be, Cr, Cu, As, Se
As		Be**	U**, (Sb, Ni)*, Pb, B, Cr, Co, Cu, Zn,Mo, Tl
Pb	Bi**	Co**	Be**, Sb*, U, B, Mn, As, Mo
Mn		Co**	Bi*, Ti, Sr, Pb, Cu, Cd
Co		(Mn, Pb)**	Sb, Bi, Be, B, Cu, As, Cd Tl
Bi	Pb**		Mn*, Sb, U, B, Ti, Co, Mo
Ti	Sr**		Bi, Mn, Cu
Sr	Ti**		Mn, Cu
Se			Tl, Cr*, Ni, Zn, Mo, Cd, , U, B
Tl			Be, Co, As, Se, Cd

*Correlation is significant at the 0.05 level

**Correlation is significant at the 0.01 level

Table A. 2.8: Pearson correlation among heavy metals (the negative correlation)

Element	**Negative correlation**		
	High correlation (>0.75)	**Medium correlation (0.5-0.75)**	**Low correlation (<0.5)**
Ni			Mn*, Sr, Pb, Bi, Ti, Co,Tl
Cr		(Mn)**	(Sr, Bi, Co)*, Pb, Ti
Zn			Bi**, (Sr, Pb, Mn)*, Ti, Co, Tl
U		Sr**	(Mn,)*, Cd, Tl, Ti
Be		Sr. Ti**	Mn, Se
B			Sr*Ti, Mn, Tl, Bi
Sb			Sr*, Cd, Ti, Mn, Se, Tl
Cu			Bi**, Tl*, Se, Pb
Cd			Ti, Sr*, As, Sb, Pb, Bi
Mo			Mn*, Co, Ti, Sr, Co, Bi
As			Sr*, Ti, Mn, Se, Cd
Pb			Sr, Zn*Cu, Se, Cd, Ti, Cr, Ni, Cu
Mn		Cr**	(Zn, Ni, Se, Mo,U)*, B, Be, As, Tl, Sb
Co			Se, Cr*, Ti, Ni, Zn, Sr, Mo
Bi			(Zn, Cr, Cu)**, Se, Mo, Cd, B, Ti, Ni, Sr
Ti		Be**	Cd*, Sb, Pb, U, B, Cr, Bi, Co, Ni, Zn, As, Se, Mo, Tl
Sr		(U, Be)**	(Sb, Pb, B, Cr, Zn, Cd, As)*, Bi, Co, Ni, Se, Mo,Tl
Se			(Mn, Co)*, Cu, As, Be, Ti, Cu, As, Sb, Pb, Bi
Tl			Cu*, Sb, B, Ti, Mn, Ni, Zn, Sr, Sb, U

* Correlation is significant at the 0.05 level.

**Correlation is significant at the 0.01 level

Table A. 2.9: The eigenvalues and the contrubution of each extracted function in variances between rock phosphates

Function	Eigenvalue	% of Variance	Cumulative%	Canonical Correlation
1	970.778(a)	72.2	72.2	0.999
2	224.496(a)	16.7	88.8	0.998
3	73.766(a)	5.5	94.3	0.993
4	30.089(a)	2.2	96.6	0.984
5	17.484(a)	1.3	97.9	0.973
6	16.538(a)	1.2	99.1	0.971
7	7.840(a)	0.6	99.7	0.942
8	3.411(a)	0.3	99.9	0.879
9	1.052(a)	0.1	100.0	0.716

a First 9 canonical discriminant functions were used in the analysis.

Table A. 2.10: The correlations between the discriminant function and the independent variables (structure matrix)

	Function								
	1	2	3	4	5	6	7	8	9
As	-.014	.028	.064	.192(*)	-.127	.011	-.018	.160	.016
Cd	-.021	-.025	.229	-.124	.290(*)	-.130	-.051	.111	-.275
Be	-.034	.059	.143	.117	.262(*)	.033	-.027	.098	.080
Sr	.219	-.066	-.269	-.273	-.140	-.428(*)	-.171	.114	.043
Zn	-.034	-.030	.078	-.060	.062	-.258(*)	.154	-.222	-.147
Cu	.012	-.036	.156	.012	.026	-.248(*)	.092	-.005	.128
Cr	-.035	.058	.032	-.078	-.057	-.247(*)	.180	-.088	-.067
Ni	-.017	-.004	.036	.060	-.002	-.178(*)	.084	-.152	.115
Tl	-.008	.041	.004	-.026	.008	.141	-.296(*)	-.243	-.032
Se	-.001	.036	.003	-.050	-.043	-.029	-.027	-.267(*)	-.199
Mo	-.020	-.012	-.022	.141	.012	-.149	-.073	-.249(*)	.089
Ti	.057	-.015	-.060	.030	.044	-.023	.077	-.084(*)	.014
Bi	-.016	.011	-.050	.088	.111	.370	-.180	.272	.698(*)
Mn	.032	-.061	.048	-.026	.131	.226	-.030	.277	.558(*)
B	-.021	-.006	.050	.089	.175	-.200	.115	-.175	.507(*)
Sb	-.013	.035	.003	.085	.081	.009	.263	-.116	.499(*)
Co	.000	-.039	.064	.007	.141	.171	-.006	.144	.488(*)
Pb	-.010	.027	.023	.169	.140	.281	-.157	.162	.484(*)
U	-.027	.025	.039	.186	.062	-.113	.140	-.197	.408(*)

Pooled within-groups correlations between discriminating variables and standardized canonical discriminant functions Variables ordered by absolute size of correlation within function.

* Largest absolute correlation between each variable and any discriminant function

Table A. 2.11: Classification results of discriminate analysis with cross validation

		Predicted Group Membership										**Total**
	Origin	**Algeria**	**Morocco**	**Senegal**	**Togo**	**Tunisia**	**Israel**	**USA**	**Curacao**	**Kola**	**Syria**	
Cross-validated Count %	**Algeria**	**0**	100	0	0	0	0	0	0	0	0	100
	Morocco	16.667	**50**	0	0	0	0	33.333	0	0	0	100
	Senegal	0	0	**100**	0	0	0	0	0	0	0	100
	Togo	0	0	20	**80**	0	0	0	0	0	0	100
	Tunisia	0	0	0	0	**100**	0	0	0	0	0	100
	Israel	0	0	0	0	50	0	0	50	0	0	100
	USA	0	0	0	10	10	0	**80**	0	0	0	100
	Curacao	0	0	100	0	0	0	0	**0**	0	0	100
	Kola	0	0	0	0	0	0	0	0	**100**	0	100
	Syria	0	0	0	0	100	0	0	0	0	**0**	100

Cross validation is done only for those cases in the analysis. In cross validation, each case is classified by the functions derived from all cases other than that case, 100.0% of original grouped cases classified correctly, 67.6% of cross-validated grouped cases classified correctly.

Table A. 2.12: The correlation between HMs which have high loading in the first components

		U	**Be**	**B**	**Zn**	**Ni**	**Cr**	**Sb**	**As**
U	Pearson Correlation	1	0.613(**)	0.700(**)	0.490(**)	0.796(**)	0.616(**)	0.731(**)	0.491(**)
	Sig. (2-tailed)	.	0.000	0.000	0.004	0.000	0.000	0.000	0.004
	N	33	33	33	33	33	33	33	33
Be	Pearson Correlation	0.613(**)	1	0.485(**)	0.373(*)	0.453(**)	0.528(**)	0.500(**)	0.518(**)
	Sig. (2-tailed)	0.000	.	0.004	0.032	0.008	0.002	0.003	0.002
	N	33	33	33	33	33	33	33	33
B	Pearson Correlation	0.700(**)	0.485(**)	1	0.669(**)	0.691(**)	0.457(**)	0.508(**)	0.134
	Sig. (2-tailed)	0.000	0.004	.	0.000	0.000	0.008	0.003	0.457
	N	33	33	33	33	33	33	33	33
Zn	Pearson Correlation	0.490(**)	0.373(*)	0.669(**)	1	0.735(**)	0.708(**)	0.168	0.037
	Sig. (2-tailed)	0.004	0.032	0.000	.	0.000	0.000	0.350	0.838
	N	33	33	33	33	33	33	33	33
Ni	Pearson Correlation	0.796(**)	0.453(**)	0.691(**)	0.735(**)	1	0.730(**)	0.490(**)	0.390(*)
	Sig. (2-tailed)	0.000	0.008	0.000	0.000	.	0.000	0.004	0.025
	N	33	33	33	33	33	33	33	33
Cr	Pearson Correlation	0.616(**)	0.528(**)	0.457(**)	0.708(**)	0.730(**)	1	0.454(**)	0.295
	Sig. (2-tailed)	0.000	0.002	0.008	0.000	0.000	.	0.008	0.095
	N	33	33	33	33	33	33	33	33
Sb	Pearson Correlation	0.731(**)	0.500(**)	0.508(**)	0.168	0.490(**)	0.454(**)	1	0.344(*)
	Sig. (2-tailed)	0.000	0.003	0.003	0.350	0.004	0.008	.	0.050
	N	33	33	33	33	33	33	33	33
As	Pearson Correlation	0.491(**)	0.518(**)	0.134	0.037	0.390(*)	0.295	0.344(*)	1
	Sig. (2-tailed)	0.004	0.002	0.457	0.838	0.025	0.095	0.050	.
	N	33	33	33	33	33	33	33	33

* Correlation is significant at the 0.01 level (2-tailed). ** Correlation is significant at the 0.05 level (2-tailed).

Table A. 2.13: The correlation between heavy metals in the second component

		Pb	**Co**	**Bi**
Pb	Pearson Correlation	1	0.527(**)	0.862(**)
	Sig. (2-tailed)	.	0.002	0.000
	N	33	33	33
Co	Pearson Correlation	0.527(**)	1	0.533(**)
	Sig. (2-tailed)	0.002	.	0.001
	N	33	33	33
Bi	Pearson Correlation	0.862(**)	0.533(**)	1
	Sig. (2-tailed)	0.000	0.001	.
	N	33	33	33

** Correlation is significant at the 0.01 level (2-tailed).

Table A. 3.1: Steps to chemical separation between Sr and Ca in cation exchange column (Exp. 1)

	The added HCL and water (loaded solution)			**The collected solution**	
Fraction	**Water**	**C (HCl) mol/L**	**V HCl**	**V**	**The number**
1	20 ml solution			82 ml	V0
2	20 ml water				
3	20 ml water				
4	20 ml water				
5	20 ml water			20 ml	V1
6	20 ml water			20 ml	V2
7		2	90 ml	45 ml	V3
				45 ml	V4
8			80 ml	about 4 ml	1 to 21
9			40 ml	about 4 ml	21 to 32
10		5	100	about 4 ml	33 to 36
				20 ml	N1
				64 ml	N2

Table A. 3.2: Ca and Sr concentrations in collected solutions from cation exchange columns (Ex. 1)

The fraction		V ml	%Ca	%Sr	Ca µg/g	Sr µg/g	Ca µg	Sr µg
Solutions	Num.							
H_2O+sample solution	V0	82	0.001	0.00	0.04	0.00	3.5	-0.1
H_2O	V1	20	0	0.00	0.05	0.00	1	0
H_2O	V2	20	0	0.00	0.05	0.00	1	0
2 M HCl	V3	45	0.001	0.00	0.05	0.00	2.5	-0.1
2 M HCl	V4	45	28.51	0.66	502.93	0.12	22632	5.2
2 M HCl	1	4	8.51	0.42	1688.78	0.83	6755.1	3.3
2 M HCl	2	4	7.687	0.53	1525.41	1.06	6101.6	4.2
2 M HCl	3	4	7.028	0.63	1394.68	1.26	5578.7	5.1
2 M HCl	4	4	6.254	0.74	1241.12	1.49	4964.5	6
2 M HCl	5	4	5.596	0.86	1110.57	1.73	4442.3	6.9
2 M HCl	6	4	5.052	0.97	1002.67	1.94	4010.7	7.8
2 M HCl	7	4	4.575	1.12	907.97	2.23	3631.9	8.9
2 M HCl	8	4	4.082	1.24	810.05	2.49	3240.2	10
2 M HCl	9	4	3.522	1.41	698.94	2.82	2795.8	11.3
2 M HCl	10	4	3.16	1.54	627.07	3.08	2508.3	12.3
2 M HCl	11	4	2.682	1.69	532.36	3.37	2129.4	13.5
2 M HCl	12	4	2.435	1.91	483.32	3.82	1933.3	15.3
2 M HCl	13	4	2.024	2.02	401.63	4.05	1606.5	16.2
2 M HCl	14	4	1.744	2.17	346.17	4.33	1384.7	17.3
2 M HCl	15	4	1.448	2.31	287.31	4.62	1149.2	18.5
2 M HCl	16	4	1.448	2.31	287.31	4.62	1149.3	18.5
2 M HCl	17	4	1.01	2.57	200.44	5.15	801.8	20.6
2 M HCl	18	4	0.827	2.76	164.08	5.52	656.3	22.1
2 M HCl	19	4	0.657	2.80	130.50	5.61	522	22.4
2 M HCl	20	4	0.513	3.00	101.87	6.01	407.5	24
2 M HCl	21	4	0.388	3.13	77.09	6.26	308.4	25
2 M HCl	22	4	0.288	3.25	57.25	6.51	229	26
2 M HCl	23	4	0.205	3.31	40.74	6.63	163	26.5
2 M HCl	24	4	0.138	3.39	27.51	6.78	110	27.1
2 M HCl	25	4	0.091	3.43	18.16	6.86	72.6	27.5
2 M HCl	26	4	0.053	3.46	10.51	6.92	42	27.7
2 M HCl	27	4	0.035	3.58	6.97	7.16	27.9	28.6
2 M HCl	28	4	0.02	3.63	3.94	7.25	15.8	29
2 M HCl	29	4	0.005	3.60	1.08	7.20	4.3	28.8
2 M HCl	30	4	0.002	3.46	0.53	6.92	2.1	27.7
2 M HCl	31	4	0.001	3.43	0.29	6.87	1.2	27.5
5 M HCl	32	4	0.001	3.26	0.15	6.51	0.6	26.1
5 M HCl	33	4	0	3.23	0.10	6.46	0.4	25.8
5 M HCl	34	4	0	5.12	0.10	10.25	0.4	41
	N1	20	0.002	16.42	0.12	6.57	2.5	131.5
	N2	80	0.003	0.64	0.07	0.06	5.7	5
	Total		100	100.00			79394.7	799.9
							Ca	Sr
	24…N1						279.8	448.2

Table A. 3.3: The Ca and Sr concentrations in collected solutions from cation exchange columns (Ex. 2)

Fraction	V ml	Ca%	Sr%	Ca µg/g	Sr µg/g	Ca µg	Sr µg
V0	122	0.002	0.042	0.02	0.002	2.30	0.30
V1	90	17.325	1.154	259	0.079	23341	7.10
V2	92	82.386	30.692	1206	2.066	110991	190
Sr	68	0.284	67.795	5.63	6.174	383	**412**
N1	80	0.003	0.316	0.05	0.024	4.40	2.00
Total		00.000	00.000			134721	**619**

Table A. 3.4: Sr-content and Sr isotope ratios in rock phosphates, P-straight fertilisers and phosphogypsium from different origin

Type of sample	Description	ID	Sr-content/ [mg kg^{-1}]	$R(^{87}Sr/^{88}Sr)$	U(R(87), k=2	$R(^{87}Sr/^{86}Sr)$	U(R87), k=2
Farmyard manure	Chicken	Chic. 1	56.4	0.0845936	2.0E-06	0.7086	0.00027
		Chic. 2	43.9	0.0847036	2.3E-06	0.7095	0.00027
		Chic. 3	87.1	0.0846542	3.0E-06	0.7091	0.00027
	Dairy Cows and Calf	Cow1	57.5	0.0847884	2.0E-06	0.7102	0.00027
		Cow3	53.4	0.0845862	2.0E-06	0.7085	0.00027
		Cow2	45.6	0.0847339	6.0E-06	0.7098	0.00027
	Pig	G1	140	0.0844268	2.5E-06	0.7072	0.00027
		G2	125	0.0844354	2.0E-06	0.7073	0.00027
		G3	104	0.0845842	2.7E-06	0.7085	0.00027
Org.-min. fertiliser		MD16	376	0.0845486	1.6E-05	0.70821	0.00030
		MD17	52	0.0858092	3.6E-06	0.71877	0.00027
		MD18	270	0.0846301	4.6E-06	0.70889	0.00027
		MD19	173	0.0847440	2.6E-06	0.70985	0.00027
Rock phosphates	Morocco	RP 8		0.0845275	2.6E-06	0.70801	0.00027
		RP 4	1070	0.0845244	2.3E-06	0.70801	0.00027
		RP 5	951	0.0845272	4.3E-06	0.70803	0.00027
		RP 10	937	0.0845012	9.8E-06	0.70781	0.00028
	Senegal	RP 12	1244	0.0843868	3.7E-06	0.70686	0.00027
	Algeria	RP 17	1731	0.0845193	4.2E-06	0.70797	0.00027
	Tunisia	RP 15	1757	0.0845243	2.8E-06	0.70801	0.00027
	Syria	RP 18		0.0845115	3.0E-06	0.70790	0.00027
	Togo	RP 33	418	0.0844535	4.1E-06	0.70742	0.00027
	USA	RP 25	1013	0.0846378	3.0E-06	0.70896	0.00027
		RP 24	814	0.0846222	2.6E-06	0.70883	0.00027
		RP 23	926	0.0846329	3.1E-06	0.70892	0.00027
		RP 20	1154	0.0846301	3.6E-06	0.70889	0.00027
	Israel	RP 34	2508	0.0845143	9.3E-06	0.70792	0.00028
	Finland	RP 37	<5000	0.0844615	2.4E-06	0.70748	0.00027
	Kola	RP 3	23016	0.0839777	2.0E-06	0.70343	0.00026
		RP 1	20757	0.0839735	2.4E-06	0.70339	0.00026
		RP 2	19314	0.0839803	3.9E-06	0.70345	0.00027
P-fertiliser	Algeria	P 1	2329	0.0845242	3.0E-06	0.70801	0.00027
	Morocco	P 4	538	0.0845806	2.2E-06	0.70848	0.00027
		P 5		0.0845291	2.6E-06	0.70803	0.00027
	Syria	P 6		0.0845123	2.4E-06	0.70791	0.00027
	USA	P 3	646	0.0846538	3.1E-06	0.70909	0.00027
	Israel	P 2	1629	0.0845118	2.8E-06	0.70790	0.00027
	Kola	NPK 17	4627	0.0839861	3.7E-06	0.70348	0.00027
		NPK 18	5000	0.0839940	3.1E-06	0.70354	0.00026
		NPK 11	3361	0.0839746	4.8E-06	0.70338	0.00027
Gypsum	Morocco	GP 2	1046	0.0845357	3.0E-06	0.70810	0.00027
	Florida	GP 4	1688	0.0842059	5.4E-06	0.70534	0.00027

Table A. 3.5: Sr-content and Sr isotope ratios in different types of P-containing

Type	ID	Component	Sr-content [mg kg^{-1}]	$R(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})$	U(R(87), k=2	$\mathrm{R}(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})$	U(R87), k=2
Straight P-fertiliser	P 6	Super pho. 18%	383	0.0846680	2.5E-06	0.70919	0.00027
	P 7	Super pho. 18%	512	0.0845469	9.8E-06	0.70818	0.00028
	P 8	Super pho. 18%	591	0.0845370	3.0E-06	0.70809	0.00027
	P 9	Super pho. 20%	667	0.0845304	3.0E-06	0.70804	0.00027
K-fertiliser	K 1		28.0	0.0871275	2.9E-06	0.72979	0.00027
	K 2		85.0	0.0860250	5.1E-06	0.72056	0.00027
PK	PK 3	16+16	474	0.084571	2.3E-06	0.70837	0.00027
	PK 10		1956	0.0845188	3.7E-06	0.70794	0.00027
NP	NP 1	1.5+27	1829	0.0845150	2.7E-06	0.70791	0.00027
	NP 2	20+2	3093	0.0839878	2.0E-06	0.70349	0.00026
	NP 3	20+2	484	0.0846026	3.4E-06	0.70864	0.00027
	NP 4	11+52	83.7	0.0846363	3.1E-06	0.70892	0.00027
	NP 5	9+9	322	0.0846060	2.8E-06	0.70867	0.00027
NPK	NPK 1		216	0.0846425	2.8E-06	0.70898	0.00027
	NPK 2		208	0.0846446	2.1E-06	0.70899	0.00027
	NPK 3		250	0.0846195	2.7E-06	0.70878	0.00027
	NPK 4		297	0.0846593	2.8E-06	0.70912	0.00027
	NPK 5	15:15:15	250	0.0846166	3.1E-06	0.70876	0.00027
	NPK 6	10+15+20	223	0.0846322	2.2E-06	0.70889	0.00027
	NPK 7	6+12+18	379	0.0845895	2.8E-06	0.70853	0.00027
	NPK 8	10:15:20 Cu: 2	209	0.0846388	2.4E-06	0.70895	0.00027
	NPK 9	13+13+21	185	0.0845847	2.8E-06	0.70849	0.00027
	NPK 10	12:12:17 Mg: 2	263	0.0845549	2.6E-06	0.70824	0.00027
	NPK 12	15+15+15	190	0.0842001	3.1E-06	0.70527	0.00027
	NPK 13		173	0.0846502	2.7E-06	0.70904	0.00027
	NPK 14	10+12+18	120	0.0844832	2.3E-06	0.70764	0.00027
	NPK 15	15+15+15	263	0.0846776	3.2E-06	0.70927	0.00027
	NPK 16	24+8+8	166	0.0846627	3.4E-06	0.70915	0.00027
	NPK 17		380	0.0845214	2.4E-06	0.70796	0.00027
	NPK 18		97	0.0843604	3.0E-06	0.70661	0.00027

Table A. 3.6: U-content and U isotope ratios in rock phosphates, P-straight fertilisers from different origin

Type of sample	Description	Nr	U-content/ [mg kg^{-1}]	R(^{234}U/^{238}U)	U(R(234), k=2	R(^{235}U/^{238}U)	U(R235), k=2
Farmyard manure	Chicken	Chic. 1	3.98	5.132E-05	1.6E-07	7.222E-03	1.1E-05
		Chic. 2	3.00	5.464E-05	1.9E-07	7.217E-03	1.2E-05
		Chic. 3	4.89	5.449E-05	1.7E-07	7.225E-03	1.3E-05
	Dairy Cows and Calf	Cow3*	1.50	5.405E-05	9.9E-08		
		Cow2	1.87	5.451E-05	1.6E-07	7.214E-03	1.0E-05
		Cow4	0.95	5.203E-05	1.6E-07	7.227E-03	1.1E-05
	Pig	G1	5.25	5.280E-05	1.6E-07	7.224E-03	1.1E-05
		G2	3.04	5.268E-05	1.8E-07	7.215E-03	1.2E-05
		G3*	2.00	5.468E-05	1.1E-07		
Org.-min. fertiliser		OMF 1	24.7	5.536E-05	1.5E-07	7.224E-03	9.7E-06
		OMF 2	7.39	5.489E-05	1.8E-07	7.225E-03	1.1E-05
		OMF 3	19.8	5.539E-05	1.6E-07	7.222E-03	1.0E-05
		OMF 4	27.6	5.513E-05	1.6E-07	7.230E-03	1.0E-05
Rock phosphates	Morocco	RP 8	129	5.493E-05	1.6E-07	7.228E-03	9.9E-06
		RP 5	154	5.511E-05	1.7E-07	7.242E-03	1.1E-05
		RP 6	130	5.498E-05	1.6E-07	7.236E-03	1.0E-05
		RP 10	157	5.467E-05	1.6E-07	7.2169E-03	9.8E-06
	Senegal	RP 12	115	5.520E-05	1.7E-07	7.223E-03	1.0E-05
	Algeria	RP 17	57.7	5.478E-05	1.7E-07	7.2337E-03	9.7E-06
	Tunisia	RP 15	36.9	5.526E-05	1.7E-07	7.225E-03	1.1E-05
	Syria	RP 18	58.6	5.361E-05	1.6E-07	7.181E-03	1.0E-05
	Togo	RP 32	121	5.526E-05	1.7E-07	7.235E-03	1.0E-05
		RP 33	107	5.544E-05	1.6E-07	7.2302E-03	9.3E-06
	USA	RP 25	65.5	5.580E-05	1.6E-07	7.2264E-03	9.4E-06
		RP 23	122	5.717E-05	1.7E-07	7.229E-03	1.0E-05
		RP 20	121	5.732E-05	1.9E-07	7.2399E-03	9.9E-06
		RP 24	123	5.676E-05	1.8E-07	7.222E-03	1.0E-05
	Israel	RP 34	129	5.465E-05	1.6E-07	7.2355E-03	9.4E-06
	Kola	RP 1	3.42	5.496E-05	1.8E-07	7.226E-03	1.3E-05
		RP 3	3.04	5.486E-05	2.5E-07	7.198E-03	2.1E-05
		RP 2	3.18	5.483E-05	1.7E-07	7.197E-03	1.0E-05
P-fertiliser	Algeria	P 1	61.0	5.471E-05	1.6E-07	7.219E-03	1.0E-05
	Morocco	P 4	63.3	5.546E-05	1.6E-07	7.243E-03	1.8E-05
		P 5	94.7	5.495E-05	2.2E-07	7.226E-03	1.2E-05
	Syria	P 6	85.4	5.468E-05	1.6E-07	7.206E-03	1.0E-05
	USA	P 3	66.4	5.802E-05	1.7E-07	7.231E-03	1.0E-05
	Israel	P 2	99.8	5.409E-05	1.6E-07	7.229E-03	1.0E-05
	Kola	NPK 18	17.4	5.522E-05	1.0E-07	7.2534E-03	7.5E-06
		NPK 17	10.5	5.478E-05	1.2E-07	7.2187E-03	7.4E-06

All samples analysed using TIMS excpting for two samples (Cow3* and G3*), they analysed by (ICP-MS)

Table A. 3.7: U-content and U isotope ratios in in different types of P-containing

Type	Samples Nr.	Component	U-content [mg kg^{-1}]	R(^{234}U/^{238}U)	U(R(234), k=2	R(^{235}U/^{238}U)	U(R235), k=2
Straight P-fertiliser	P 6	Super pho. 18%	81.0	5.545E-05	1.2E-07	7.2366E-03	7.1E-06
	P 7	Super pho. 18%	66.0	5.509E-05	1.2E-07	7.2327E-03	9.2E-06
	P 8	Super pho. 18%	75.0	5.475E-05	1.3E-07	7.2296E-03	8.0E-06
	P 9	Super pho. 20%	73.0	5.491E-05	1.2E-07	7.2380E-03	7.6E+08
PK	PK 3	16+16	64.0	5.523E-05	1.1E-07	7.2361E-03	6.9E-06
	PK		56.0	5.587E-05	1.3E-07	7.2402E-03	8.4E-06
	PK		29.0	5.513E-05	1.2E-07	7.2309E-03	8.3E-06
NP	P m1	1.5+27	34.0	5.500E-05	1.2E-07	7.2333E-03	7.6E-06
	NP 2	20+2	32.0	5.488E-05	1.3E-07	7.2207E-03	8.0E-06
	NP 3	20+2	73.0	5.781E-05	1.2E-07	7.2290E-03	7.3E-06
	NP 4	11+52	162	5.609E-05	1.2E-07	7.2383E-03	7.9E-06
	NP 5	9+9	55.0	5.776E-05	1.2E-07	7.2343E-03	7.5E-06
NPK	NPK 1		39.5	5.578E-05	1.3E-07	7.2410E-03	7.1E-06
	NPK 2		39.8	5.548E-05	1.2E-07	7.2240E-03	7.9E-06
	NPK 3		35.5	5.663E-05	1.1E-07	7.230E-03	1.3E-05
	NPK 4		30.0	5.704E-05	1.2E-07	7.2254E-03	7.6E-06
	NPK 5	15:15:15	40.0	5.683E-05	1.2E-07	7.2149E-03	7.7E-06
	NPK 6	10+15+20	44.0	5.272E-05	1.0E-07	6.8333E-03	6.4E-06
	NPK 7	6+12+18	28.7	5.687E-05	1.3E-07	7.2298E-03	8.2E-06
	NPK 8	10:15:20 Cu: 2	47.0	5.710E-05	1.4E-07	7.2277E-03	9.1E-06
	NPK 9	13+13+21	30.0	5.510E-05	1.1E-07	7.2381E-03	7.1E-06
	NPK 10	12:12:17 Mg: 2	42.0	5.497E-05	1.1E-07	7.2157E-03	7.7E-06
	NPK 12	15+15+15	27.0	5.494E-05	1.1E-07	7.2344E-03	8.7E-06
	NPK 13		28.0	5.553E-05	1.3E-07	7.2332E-03	8.3E-06
	NPK 14	10+12+18	9.44	5.507E-05	1.1E-07	7.2235E-03	8.1E-06
	NPK 15	15+15+15	43.0	5.624E-05	1.3E-07	7.2381E-03	7.5E-06
	NPK 16	24+8+8	24.9	5.655E-05	1.5E-07	7.227E-03	1.1E-05
	NPK 17		26.6	5.462E-05	1.1E-07	7.2341E-03	8.4E-06
	NPK 18		4.94	5.522E-05	1.0E-07	7.2534E-03	7.5E-06

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