

1. Phosphorus Concentrations in Environmental Samples

1.2 P Concentrations in Mineral Rock Phosphates

Karen Baumann, Dana Zimmer, Rhena Schumann

In nature, phosphorus (P) is almost exclusively found in apatite minerals ($\text{Ca}_5[(\text{F},\text{Cl},\text{OH})(\text{PO}_4)_3]$). Their total P concentrations vary between 2 to 16 % depending on their history of origins (Gwosdz 2006 cited in Killiches 2013, table 1.1). Apatites can be formed marine-sedimentary, magmatic or by guano deposition (Killiches 2013).

The marine sedimentary rock "rock phosphate" is a mixture of apatite and organic compounds. It can be found as nodules, crusts and concretions in marine clay minerals (Richter 1992) and has higher P concentrations compared to magmatic rocks (Killiches 2013). This rock phosphate develops through biological processes (e.g. accumulation of P from animal excrements, bones) or chemical processes such as precipitation from sea water. P-rich marine sedimentary rock is lifted up to the earth's surface by geological processes (Filippelli 2011). Therefore, most of it can be mined in open pits.

At the earth's surface phosphorite is build up, if phosphoric acid from seabird excrements is reacting with underlying limestone (Hintze 1933). This phosphorite is also called "guano" (Quechua: fertilizer). The fine-grained material consists of different phosphates such as apatite, limestone and organic compounds and has total P concentrations of 10 to 20 % (Filippelli et al. 2011).

In magmatic rock (e.g. granite), apatite minerals consist of microliths, microscopic inclusions or crystals in the main components feldspar, quartz and mica and/or they are in druses of granite, developed by precipitation from solution (Roth 1883). Apatite concentrations are less than 1 % (= accessory rock contents) (Fiedler 2001).

Apatites can develop by biomineralisation (e.g. in soil, as dental plaque, in bones or coral skeleton). By this process apatite crystals precipitate well-ordered in reaction compartments (Mann & Ozin 1996). P concentrations of some products can be found in the respective chapter. Hydroxyapatite can be synthesized chemically from CaCl_2 und Na_2HPO_4 in NaOH (Tiselius et al. 1956). High-purity hydroxyapatite can be used for chromatographic

segregation material for biopolymers or for substitution of bones (Tiselius et al. 1956, Damien & Parsons 1991).

In geology and mineralogy, P concentrations in mineral rock phosphates are determined by acid digestion (e.g. Aydin et al. 2009) or X-ray fluorescence analysis (e.g. Fabbri 1971).

Table 1.2-1 TP concentrations (% = g P per 100 g dry matter mineral⁻¹) in apatite minerals and rock phosphates

Matrix	Concen- tration (% P)	Note	Reference
Apatite minerals	general mineral formula: $\text{Ca}_5[(\text{F},\text{Cl},\text{OH})(\text{PO}_4)_3]$	2-16 depending on origin	Killiches (2013)
Phosphorite	marine sediment rock	10-20 typical: carbonate fluorine apatite	Fillippelli et al. (2011)
	Guano (bird excrements on limestone)	carbonate fluorine apatite	Schenker (2012), Hintze (1933)
Magmatic rock	in granite: often inclusion in other minerals	< 1 typical: fluorine apatite	Roth (1983), Fiedler (2001)

References

- Aydin I, Imamoglu S, Aydin F, Saydut A, Hamamci C (2009) Determination of mineral phosphate species in sedimentary phosphate rock in Mardin, SE Anatolia, Turkey by sequential extraction. Microchem J 91: 63-69, DOI: [10.1016/j.microc.2008.08.001](https://doi.org/10.1016/j.microc.2008.08.001)
- Damien CJ, Parsons JR (1991) Bone graft and bone graft substitutes: A review of current technology and applications. J Appl Biomaterials 2: 187-208, DOI: [10.1002/jab.770020307](https://doi.org/10.1002/jab.770020307)
- Fabbri BP (1971) Rapid X-Ray fluorescence determination of phosphorus in geologic samples. Appl Spectrosc 25: 41-43, DOI: [10.1366/00037027177437137](https://doi.org/10.1366/00037027177437137)
- Fiedler HJ (2001) Böden und Bodenfunktionen. In Ökosystemen, Landschaften und Ballungsgebieten. Expert-Verlag, Renningen

- Filippelli GM (2011) Phosphate rock formation and marine phosphorus geochemistry: The deep time perspective. *Chemosphere* 84: 759-766, DOI: [10.1016/j.chemosphere.2011.02.019](https://doi.org/10.1016/j.chemosphere.2011.02.019)
- Hintze C (1933) Handbuch der Mineralogie. Borate, Aluminate und Ferrate. Phosphate, Arseniate, Antimoniate, Vanadate, Niobate und Tantalate. Vol. 1, Section 4 Half 1. Walter de Gruyter & Co-Verlag, Berlin
- Killiches F (2013) [Phosphat: Mineralischer Rohstoff und unverzichtbarer Nährstoff für die Ernährungssicherheit weltweit](#). Federal Institute for Geosciences and Natural Resources (BGR) on behalf of the Federal Ministry for Economic Cooperation and Development (BMZ)
- Mann S, Ozin GA (1996) Synthesis of inorganic materials with complex form. *Nature* 382: 313-318, DOI: [10.1038/382313a0](https://doi.org/10.1038/382313a0)
- Richter D (1992) Allgemeine Geologie. de Gruyter Verlag Berlin, New York. 4th extended ed.
- Roth JLA (1883) Allgemeine und chemische Geologie. Vol. 2, Wilhelm Hertz Verlag, Berlin
- Schenker F (2012) Phosphor und Phosphate. In: Rohstoffe der Erde. Skript
http://www.sgtk.ch/rkuendig/dokumente/Skript_RdE_2012_Seiten_5_1-73.pdf
- ETHZ
- Tiselius A, Hjertén S, Levin Ö (1956) Protein Chromatography on Calcium Phosphate Columns. *Arch Biochem Biophys* 65: 132-155, DOI: [10.1016/0003-9861\(56\)90183-7](https://doi.org/10.1016/0003-9861(56)90183-7)

For citation: Baumann K, Zimmer D, Schumann R (*year of download*) Chapter 1.2 Concentrations in Mineral Rock Phosphates (Version 1.0) in Zimmer D, Baumann K, Berthold M, Schumann R: Handbook on the Selection of Methods for Digestion and Determination of Total Phosphorus in Environmental Samples. DOI: 10.12754/misc-2020-0001