HS 8.1.5
EGU23-4264

# The Input of Phosphate & Vanadium into the Lake Laacher See by Dissolution of Volcanic Rocks (East Eifel, Germany)

**Sascha Rudolph[1*], Sven Philipp[1,2], Michael Pirrung[1], Karl-Heinz Köppen[2], Thorsten Schäfer[1]**

[1] Friedrich-Schiller-University Jena, Institute of Geosciences, Burgweg 11, 07749 Jena, Germany

[2] Wasser und Boden GmbH, Am Heidepark 6, 56154 Boppard-Buchholz, Germany

* Email: sascha.rudolph@uni-jena.de

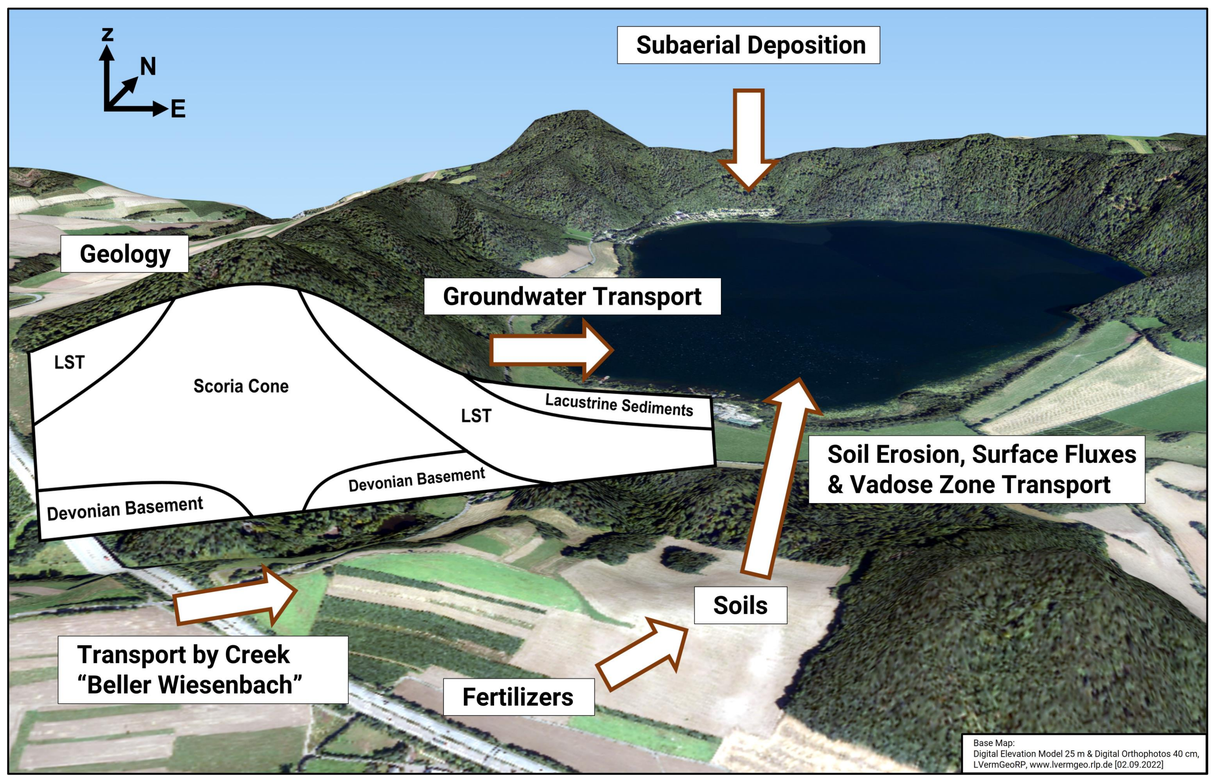
## Motivation

- Laacher See located within the crater of the Laacher See Volcano is affected by eutrophication due to elevated conc. of **lake water P** (avg. **34 µg/l**) [4]
- origin of the nutrient P, especially the role of geogenic input to lake, is unclear
- elevated **V-conc.** (**6.7 - 28.4 µg/l**) correlating to $PO_4^{3-}$ in groundwaters of volcanic rocks in West Eifel stated [11]

## Objectives

- identify sources of geogenic input within the surrounding volcanic rocks
- evaluate the significance of both geogenic and anthropogenic P-sources
- investigate mobility, leaching behavior and equilibrium, and groundwater transport of P in Laacher See area

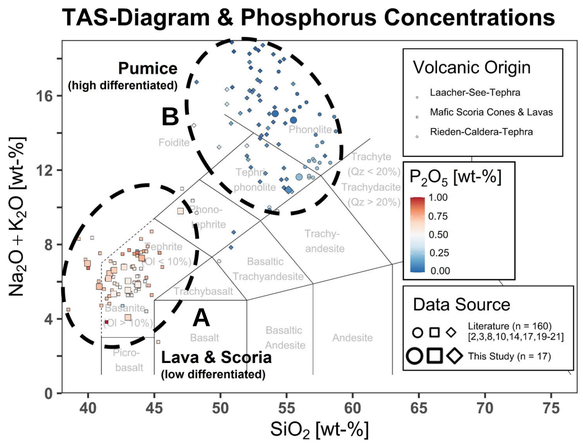
## Paths of Phosphorus Input




## Conclusion & Outlook

- bulk-rock geochemistry points to the significance of volcanic rocks as geogenic P source compared to soils of agricultural lands or **subaerial deposition** (**114 mg $m^{-2}$ $a^{-1}$** [5])
- increased Ortho-$PO_4^{3-}$ conc. in wells close to scoria cones evidence geogenic P input by groundwater to lake
- PHREEQC modelling indicate increased apatite dissolution in acidic conditions induced by $CO_2$-degassing mofettes
- in further studies, batch experiments will be used to determine release potential and kinetics of P dissolution from rocks and sediments and detailed investigation of V
- these input data will be used to quantify geogenic phosphorus input with 1D-transport model by PHREEQC

## Geochemical Behavior of Phosphorus

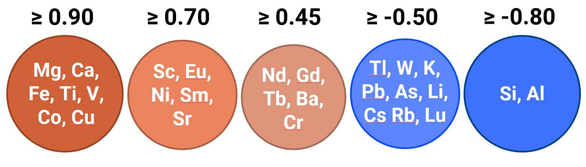



- bulk rock geochemistry measured by X-ray fluorescence (XRF) & Total Digestion with ICP-OES/MS
- two geochemical domains of volcanic rocks occurring near Laacher See area:

A. Basanites & Tephrites
   - represent lava & scoria erupted by prevalent occurring scoria cones
   - **bulk-rock P = 2291 - 3216 mg/kg**

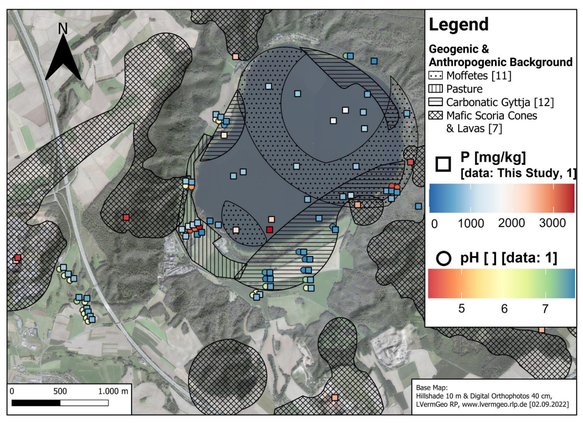
B. Phonolites, Foidites & Tephriphonolites
   - pumice from tephra of the caldera-erupted Laacher See Volcano (LST) and Rieden volcanic complex
   - **bulk-rock P = 113 - 938 mg/kg**

**Pearson Correlation of Elements to P**



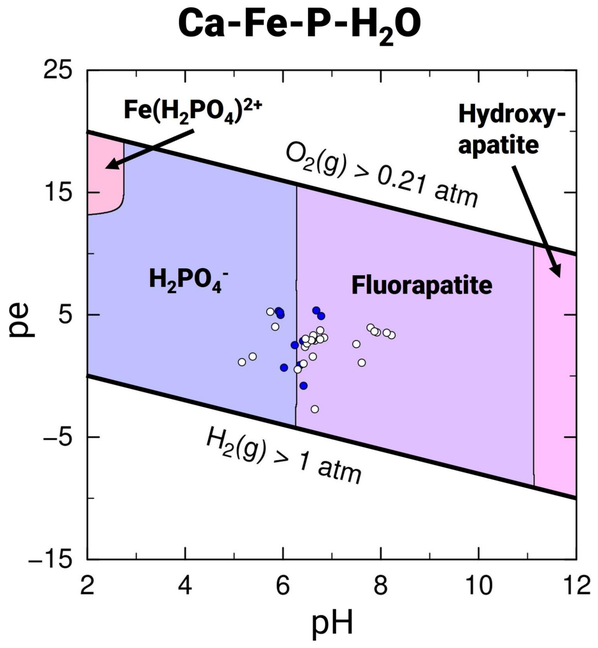

→ P and V occur at higher concentrations in mafic rocks, similar to the behavior of other compatible elements

## Phosphorous in soils and lake sediments




- P-conc. of surface sediments reflects both geogenic (vicinity to P-rich scoria cones) and anthropogenic sources by agriculture (pastures and fertilizers)
- **soil P = 313 - 1260 mg/kg** [1]
- pH of soil equilibrium solution is a further tracer for these backgrounds to determine P-sources:
   - animal excrements increases P-conc. and decreases pH by nitrification on pastures and by smaller degree on fields due to the use of excrements as fertilizer
   - acidic conditions appear by mofettes
   - high pH conditions reflect P-poor lacustrine carbonate sediments
- erosion and surface fluxes control P-conc. in recent lake sediments, as evidenced by high spatial variability of P appearance:
   - **lake sediment P = 586 - 3449 mg/kg**
   - increased P-conc. of lake sediments occur near terrestrial P-rich soils
   - enhanced erosion at morphological steep outcrops of scoria cones increases P-conc. of lake sediments

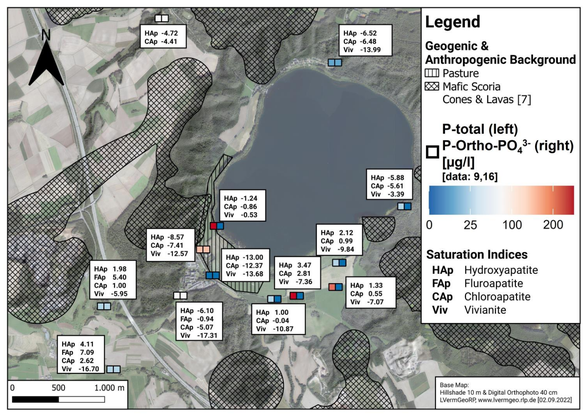
## Leaching of geogenic Phosphorus




- predominance plot of Ca-Fe-P-$H_2O$ system calculated by PHREEQC & PhreePlot [14, 18] displays species occurrence of P at different pe & pH
- pH governs dissolution of igneous P
- fluor- and chlorapatite characterizes lower solubilities at lower pH compared to hydroxyapatite
- mobile $PO_4^{3-}$-phases become predominant related to apatite at **pH ≤ 6.3**
- redox status (pε) has insignificant influence on solubility of $PO_4^{3-}$-species
- acidic conditions in groundwaters caused by mofettes due to solution of degassing $CO_2$ as carbonic acid
- surface waters degas dissolved $CO_2$ to the atmosphere leading to neutral pH

→ significance of mofettes for the dissolution of igneous $PO_4^{3-}$-phases

## Phosphorus transport by groundwater




- P in **groundwaters** near Laacher See:
   - **P(total): ≤ 0.40 mg/l**
   - **P(Ortho-$PO_4^{3-}$): ≤ 0.13 mg/l**
- elevated Ortho-$PO_4^{3-}$ indicate geogenic input by leaching of apatite particularly in the western lake area where inflows from scoria cones appear
- high conc. of total P compared to low Ortho-$PO_4^{3-}$ indicates P input due to pastures and agricultural lands (S area)
- saturation indices (SI) of igneous, primary P-phases (apatite) and the secondary P-phase vivianite were calculated by PHREEQC [18] for groundwaters and surface waters [8,15]
- apatite is undersaturated at wells of elevated Ortho-$PO_4^{3-}$ (assumed as geogenic P input) → $PO_4^{3-}$ solution from apatite is a rate-limited process and not equilibrium-controlled
- creek waters (SW area) characterizes elevated Ortho-$PO_4^{3-}$ conc. caused by apatite leached groundwater from near located springs and strong over-saturated conditions of apatite-phases due to degassing of $CO_2$ and increasing pH on the surface

**References:**

[1] Armbruster, M. & Wiesler, F. (2012). Ermittlung der P-Gehalte entlang von 10 Transekten am Laacher See. LUFA Speyer, 24. (unpublished)
[2] Baudouin, C., & Parat, F. (2015). Role of volatiles (S, Cl, H2O) and silica activity on the crystallization of haüyne and nosean in phonolitic magmas (Eifel, Germany and Saghro, Morocco). *American Mineralogist, 100(10),* 2308-2322. https://doi.org/10.2138/am-2015-5318
[3] Bednarz, U., & Schmincke, H. U. (1990). Evolution of the Quaternary melitite-nephelinite Herchenberg volcano (East Eifel). *Bulletin of Volcanology, 52,* 426-444. https://doi.org/10.1007/BF00268924
[4] Block, U. et al. (2015). Übersicht über die Phosphatthematik am Laacher See. Fachhochschule Bingen, 41.
[5] Borcherding, N. (2019) Ermittlung der atmosphärischen Deposition von Phosphor auf den Laacher See. ANECO Mönchengladbach, 29. (unpublished)
[6] Bogaard, P.v.d. & Schmincke, H.U. (1984). The eruptive center of the late quaternary Laacher see tephra. *Geologische Rundschau, 73,* 933-980. http://doi.org/10.1007/BF01820883
[7] Bogaard, P.v.d. & Schmincke, H.U. (1990). Vulkanologische Karte der Osteifel (Maßstab 1: 50000).
[8] Duda, A. & Schmincke, H.U. (1978). Quaternary basanites, melilite nephelinites and tephrites from the Laacher See area (Germany). *Neues Jahrbuch Mineralogischer Abhandlungen, 132,* 1-33.
[9] Enderlein, S. (2020). Geologisch-mineralogische und hydrogeochemische Analyse des Gebiets "Laacher See Südwest". Friedrich-Schiller-Universität Jena, 125.
[10] Frechen, J. (1976). Siebengebirge am Rhein, Laacher Vulkangebiet, Maargebiet der Westeifel. *Sammlung geologischer Fuhrer 56, 3.*
[11] Goepel, A., Lonschinski, M., Viereck, L., Büchel, G., & Kukowski, N. (2015). Volcano-tectonic structures and $CO_2$-degassing patterns in the Laacher See basin, Germany. *International Journal of Earth Sciences, 104,* 1483-1495. https://doi.org/10.1007/s00531-014-1133-3
[12] Götze, M., Fritsch, S. (2015). Bodenkundliche Kartierung des Einzugsgebietes des Laacher Sees sowie Analyse und Kartierung der limnischen Sedimente. Friedrich-Schiller-Universität Jena, 93.
[13] Härter, L.M. et al. (2020). Vorkommen von Vanadium im Grundwasser der Vulkaneifel. *Grundwasser, 25,* 127-136. http://doi.org/10.1007/s00767-020-00447-x
[14] Karakuzu F. (1982): Bericht zur Diplomkartierung und Diplomarbeit, Teil I: Diplomkartierung "Aufbau und Entstehung der spätquartären Vulkane Dachsbusch und Rothenberg in der Osteifel", Teil II: Diplomarbeit "Petrographie und Geochemie der vulkanischen Gesteine der Vulkane Dachsbusch, Wehr und Rothenberg (Osteifel),. Ruhr-Universität Bochum, 215.
[15] Kinniburgh, D., & Cooper, D. (2011). PhreePlot: Creating graphical output with PHREEQC, 648.
[16] MKUEM – Abteilung Wasserwirtschaft. Wasserportal Rheinland-Pfalz. https://wasserportal.rlp-umwelt.de [17.04.2023]
[17] Müller W. & Schumacher K.-H. (2021). Steinreiche Eifel 3. Görres-Druckerei und Verlag GmbH, Neuwied, 447.
[18] Parkhurst, D. L., & Appelo, C. A. J. (2013). Description of input and examples for PHREEQC version 3—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US geological survey techniques and methods, 6(A43), 497.
[19] Viereck, L. (1984). Geologische und petrologische Entwicklung des pleistozänen Leuzitit Leuzitphonolith-Vulkankomplexes Rieden, Ost-Eifel. In: Institut für Geologie der Ruhr-Universität Bonn (Hrsg.), Bochumer geologische und geotechnische Arbeiten, 337.
[20] Wörner, G. & Schmincke, H.U. (1984). Mineralogical and chemical Zonation of the Laacher See Tephra Sequence (East Eifel, W. Germany). Journal of Petrology, 25(4), 805-835. https://doi.org/10.1093/petrology/25.4.805
[21] Wörner, G., Schmincke, H. U., & Schreyer, W. (1982). Crustal xenoliths from the Quaternary Wehr volcano (East Eifel). *Neues Jahrbuch für Mineralogie-Abhandlungen, 144,* 29-55. http://doi.org/10.1127/njma/144/1982/29