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Contribution of Laser-Induced Breakdown Spectroscopy (LIBS) to the exploration of phosphate sedimentary rocks: Case study of Hyon-S2 borehole, Mons Basin, Belgium

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Since the publication of the EU list of critical materials a decade ago, there has been a renewed interest in mineral exploration in Europe. The Maastrichtian Ciply-Malogne Fm in the Mons Basin hosts one of Europe's largest phosphate deposits, with 600–900 Mt phosphatic ore at a grade of 10 wt% P_2O_5 in average and up to 700 ppm REE (Robaszynski et al., 1986; Jacquemin, 2020). However, relatively little is known about this deposit.

The objective of this work is to test pLIBS (portable Laser-Induced Breakdown Spectroscopy) for fast geochemical analysis of phosphate ores in the Mons Basin. The study was focused on borehole Hyon-S2, which crosscuts the thickest known part of the formation (75 m). The cores were analysed at high resolution, with one analytical spot (~1 mm^2) every 5 cm. The spectral data were extracted and processed using a Python code developed specifically for the project.

The qualitative geochemical profiles of the borehole obtained by LIBS were compared to previous analytical data such as gamma-ray, XRF and ICP-MS analyses (Robaszynski et al., 1986; Jacquemin, 2020). There is a good to excellent agreement between the LIBS profiles and control data for phosphate. Some cyclicity can be observed in LIBS profiles, which opens perspectives for further cyclostratigraphic studies. The lanthanum profile obtained by LIBS also reflects ICP-MS data for this element. These results show that LIBS can reliably detect phosphates and REE in phosphate ores, which is a first step towards quantitative analysis using calibration.

In addition, multi-elemental LIBS profiles also showed silicified horizons that were not visible on the cores as well as peculiar levels that could be associated with stratigraphic markers. This highlights the great potential of LIBS for fast and high-resolution geochemical profiling of cores despite its small analytical spot.

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Morphometric analysis of fossil ear bones as a tool to investigate delphinoid diversity in the southern North Sea during the late Neogene

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In and around the city of Antwerp, Belgium, many paleontological discoveries were done in the context of the construction of fortification belts and the expansion of the harbour. This led to the discovery of a large number of fossil remains of Neogene marine mammals, among others. Because the specimens are generally fragmentary and the fossil record is relatively scarce, a clear overview of the diversity and time range of these extinct species is difficult to obtain. In cetaceans, the ear bones, including the periotic (which houses the inner ear), are more compact than other cranial material, often resulting in a better preservation, although these elements are generally found isolated. In addition, the periotic preserves many diagnostic features, especially concerning delphinoids, the superfamily including delphinids (oceanic dolphins), phocoenids (porpoises), and monodontids (belugas and narwhals). Therefore, these fossils can aid in improving our comprehension of the diversity of delphinoids in the southern North Sea during the late Neogene (Late Miocene and Pliocene). Based on a morphological comparative analysis of 187 fossil periotics from the Antwerp area, recovered mainly from the Kattendijk and

Lillo formations, with identified fossil and modern periotics, combined with a principal component analysis based on 13 measurements, the periotics were divided into morphological groups which, in a second step, were given a family attribution and, in most cases, affinities with one or two genera. At least nine delphinid, three phocoenid, and two monodontid genera were tentatively recognised. Additional support could be obtained for the presence in the southern North Sea during the late Neogene (mainly, but possibly not only, the Pliocene) of close relatives to the modern pilot whales Globicephala spp. and the extinct large dolphin *Hemisyntrachelus*, as well as porpoise species closely related to *Haborophocoena toyoshimai* and *Numataphocoena yamashitai*. Furthermore, a hypothetical extension into the Pliocene of the time range in the southern North Sea of taxa closely related to (or even within) the delphinid genera *Stenella*, *Delphinus*, *Lagenorhynchus*, and *Tursiops*, the phocoenid *Phocoena*, and the monodontids *Delphinapterus* and *Monodon* are proposed. Additional support for several trans-Arctic dispersal events of extinct porpoise lineages between the North Pacific and the northern Atlantic realm is provided, as well as for a more southern distribution for extinct relatives of the beluga and narwhal. The presence of close relatives to the delphinids *Astadelphis gastaldii* and *Arimidelphis sorbinii*, both previously only recorded from the Mediterranean, indicates a possible interchange between the latter sea and the North Sea during the Pliocene. Unfortunately, precise stratigraphic information could be obtained only for a part of the studied periotics. Furthermore, due to their isolated nature, the identifications remain tentative and do not reach the species level. As a result, there is a need to find new in situ material, as well as periotics associated with other cranial elements.

Mineralogical, petrographic and geochemical study of the Musha-Ntunga pegmatite mineralisation in Eastern Rwanda

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Pegmatites are intrusive magmatic rocks with typically very coarse grained minerals. As they tend to form from the last and most evolved portion of a magmatic melt, they can contain significant mineralisation of (incompatible) critical elements, including lithium, tin, tantalum, and niobium (London, 2018). The demand for these critical metals, particularly lithium, has been increasing due to an ongoing energy transition aiming at achieving net zero carbon emissions by 2050. Therefore, a comprehensive understanding of the genesis and evolution of rocks containing these elements, especially in pegmatites, is crucial to ensure a constant supply of these critical resources.

The Musha-Ntunga area in eastern Rwanda, part of the Mesoproterozoic Karagwe-Ankole belt (KAB), contains Li-Sn-Ta-Nb mineralised pegmatites and Sn-mineralised quartz veins. This mineralisation is associated with widespread G4 granitic magmatism, which intruded the KAB metasediments forming intrusive rocks around 1 Ga (Tack et al., 2010; Fernandez-Alonso et al., 2012). In the Musha-Ntunga area, both pegmatite and quartz vein mineralisation occur associated with the Lake Muhazi granitic pluton. The emplacement of the mineralisation is structurally controlled and is related to the reactivation of pre-existing discontinuity regimes (Hulsbosch et al., 2017). Like other pegmatite fields in the KAB, pegmatites in the Musha-Ntunga area exhibit a regional zonation that may be attributed to a single path of fractional crystallisation of a granitic melt. This fractional crystallisation results in the progressive enrichment of incompatible elements, such as Li, Rb, Cs, Nb, Ta, and Sn (Hulsbosch et al., 2013).

This research was carried out in the framework of a Master's thesis and aimed to characterise a representative Li-mineralised pegmatite and the interaction of the pegmatite system with the host rock. Fresh, unweathered drill core samples have been studied using optical microscopy, Cold-CL microscopy, Raman spectroscopy and X-ray diffraction to identify the paragenesis of the pegmatite and the host-rock mineralogy. ICP-OES and ICP-MS were applied to determine changes in the host rock geochemistry related to the intrusion and evolution of the pegmatites.

We were able to divide the crystallisation history of the studied pegmatite into three stages: a primary, a secondary, and a late secondary stage. Primary minerals are interpreted to be associated with the magmatic phase of pegmatite crystallisation, i.e. they crystallised as primary minerals from a Si-saturated and H_2O-rich melt. The minerals include microcline, albite, quartz, muscovite, spodumene, columbite-tantalite, cassiterite, fluorapatite and monazite. Secondary minerals, such as albite, muscovite, quartz, and cassiterite, are linked to the (magmatic-) hydrothermal phase of pegmatite crystallisation, characterised by (magmatic-)hydrothermal overprinting of primary minerals. Later secondary minerals consist of kaolinite, chlorite, and goethite, interpreted to have formed during more recent—potentially supergene—alteration.

While tourmaline is the dominant metasomatic alteration mineral observed in addition to muscovite, a geochemical dispersion halo of at least 5 m, enriched in Cs, Rb, Sn, and Zn is identified in the host rock adjacent to the selected pegmatite intrusion. This suggests that a residual fluid enriched in incompatible elements, released during the pegmatite crystallisation, intruded the host rock. The enrichment of these incompatible elements indicates the extreme fractionation of the pegmatite system.

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Contribution to the characterization of the supergene mineralization of the Bou Skour Cu-Ag(-Pb-Zn) deposit (Anti-Atlas, Morocco)

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This Master's thesis focuses on the supergene mineralization of the polymetallic Bou Skour deposit, located in the Moroccan Anti-Atlas. This mountain range, which marks the northern boundary of the West African craton, is notably rich in polymetallic deposits with exposed inlier revealing the Precambrian basement. The Bou Skour mine is located in the Sidi Flah-Bou Skour inlier, which belongs to Cryogenian magmatic formations in the Saghro massif (Maacha et al., 2011). The deposit, mainly composed of copper associated with silver, lead and zinc, has a mining history dating back to the Middle Ages (Bouabdellah et al., 2016), with significant industrial exploitation from 1958 to 1977 (Maacha et al., 2011). It consists mainly of a system of polymetallic veins that form longitudinal structures with a NW-SE orientation. These veins, known as "Filon Principal", "Filon 1", and "Filon 2", reach widths of up to 20 metres and extend laterally for several kilometres through andesite, granite, and granodiorite (Bouabdellah et al., 2016).

The study aims to understand the weathering processes associated with the deposit, and to identify zones of economic interest. The methods include field sampling, X-ray diffraction for mineralogical identification, petrographic analysis by optical and scanning electron microscopy, and geochemical analyses of whole rock samples and isolated minerals. Results show a complex mineralogy with primary sulphides such as pyrite, chalcopyrite, sphalerite, galena, tennantite-tetrahedrite, arsenopyrite and bornite, as well as significant secondary mineralization, including Fe-Mn oxides, carbonates, arsenates, sulphates and copper silicates. The paragenesis suggests an initial phase of fluid acidification followed by a neutralization phase. The former results from the oxidation of the primary sulphides, while the latter occurs when the fluid interacts with carbonates (e.g. dolomite) and potentially silicates (e.g. chlorite) present in the deposit.

Geochemical data reveal enrichments in rare earth elements, chalcophile metals and metalloids compared to the upper continental crust (UCC) in weathered zones, highlighting the supergene processes in the formation and enrichment of the deposit. The results show significant enrichment in copper, lead, zinc and silver in weathered areas, with copper content reaching up to 5.39 wt% in some whole rock samples, mostly those composed of iron oxides. In summary, analyses of vein samples and mineralized rocks indicate that metal migration and concentration are related to weathering. However, unlike the classic "top-down" pattern of a supergene profile, here the different parts of the profile merge and overlap in a complex way.

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Syn- to late orogenic fluid evolution in the High Ardenne slate belt (Herbeumont, Belgium)

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Near Herbeumont (Belgium), two different types of quartz veins can be identified. Firstly, synorogenic veins were identified within the top-to-north Herbeumont shear zone (Schavemaker et al., 2012), reflecting the main compressional stage of the Variscan orogeny. Secondly, discordant veins were observed within a top-to-south extensional shear zone, attributed to the late orogenic gravitational collapse of the High Ardenne slate belt. These discordant veins are further classified into two types: Type I, where the foliation-parallel shear continues across the 'precursor vein', and Type II, where the shear zone displaces at the level of the 'precursor vein' and is transferred across the 'precursor vein' (Van Baelen & Sintubin, 2022).

The veins were examined by petrographic analysis and the fluid inclusions were analysed by microthermometry and Raman spectroscopy. The characterization of the fluid inclusions within these quartz veins enables to constrain the evolution of the metamorphic fluids circulating in the High Ardenne slate belt in the later stages of the Variscan orogeny.

Synorogenic veins contain aqueous fluid inclusions (H_2O–NaCl–(CO_2–N_2–CH_4)) with an average salinity of 5.2 eq. wt% NaCl and a very low amount of gaseous content. Microthermometry indicates metamorphic conditions ranging from 335 °C to 390 °C and 245 MPa to 250 MPa. Both Type I and Type II veins show an H_2O–NaCl–CO_2–N_2–CH_4 system, with Type II veins displaying an increased presence of N_2. The average salinity for Type I is 4.5 eq. wt% NaCl, while Type II records 3.7 eq. wt% NaCl. Pressure–temperature conditions show Type I veins formed within a range of 305 °C to 380 °C and 220 MPa to 270 MPa, while Type II veins formed between 280 °C to 380 °C and 200 MPa to 270 MPa. Late orogenic discordant veins exhibit high gaseous content in their fluid inclusions, which can be attributed to exhumation releasing the gaseous components in addition to a low saline fluid. In a closed fluid system, as is the case for the High Ardenne slate belt, gaseous species have multiple origins (Kenis et al., 2005). CO_2 is derived from the decarbonization of organic matter, while CH_4 is derived from the maturation of organic matter. The relatively high N_2 content can partially be due to the maturation of organic matter; however, during retrograde metamorphism, N_2 is often the result of the release of nitrogen from NH_4-rich phyllosilicates. A retrograde metamorphic trajectory, suggested by the literature, can be fitted, from synorogenic veins to discordant veins, which correlates well with the increase in N_2 content.

Pressures ranging from 200 MPa to 270 MPa correspond to depths of 7 to 10 km. The occurrence of large blocky quartz crystals indicates open cavity growth. The existence of open cavities at depths of 7 to 10 km can only be the result of very high, up to supralithostatic, fluid pressures, typical for periods of tectonic inversion (Depoorter et al., 2014).

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Linking sedimentary earthquake imprints to ground motions in south-central Alaskan lakes

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Paleoseismology is important for understanding the hazards that earthquakes can cause in Alaska, which is located along the Alaska–Aleutian subduction zone. Its high seismic activity is demonstrated by, among others, two recent damaging events, the 2016 Iniskin and 2018 Anchorage earthquakes. These were two intraslab earthquakes, both of M_w 7.1, but occurring at different depths. Both earthquakes caused strong shaking on the Kenai Peninsula and its surroundings, and five lakes in the area have been investigated to search for earthquake-related imprints. The 2016 Iniskin earthquake triggered turbidites in Skilak and Tustumena Lakes (Singleton et al., 2024), while the 2018 Anchorage earthquake triggered turbidity currents in all five lakes (Chelatna, Eklutna, Kenai, Skilak, and Tustumena Lakes; Van Daele et al., 2019; Singleton et al., 2024). Local ground motions were modelled by combining the ground-motion prediction equation from Montalva et al. (2017) and seismometer station registrations for these five lakes to see if objective ground motion parameters, such as the peak ground acceleration and the peak spectral acceleration for periods of 0.3 s, 1.0 s, and 3.0 s could be linked to the presence or absence of coseismic sedimentary imprints instead of the subjective Modified Mercalli Intensity scale which is typically used for lacustrine paleoseismic studies. The peak ground velocity could not be modelled but was also considered using the USGS shakemaps. A threshold was estimated for these ground motion parameters using the values from Skilak Lake and Kenai Lake, as they experienced, the weakest shaking with deposits and the strongest shaking without any deposit, respectively, as a result of the 2016 Iniskin earthquake. These are 45 %g, 4 cm/s, 10 %g, 5 %g, and 0.65 %g for the PGA, PGV, PSA03, PSA10, and PSA30, respectively. These should however be interpreted with caution because the error margin on the modelled ground motion is large. This large spreading could be attributed to the model itself—as it was not developed specifically for Alaska—or incorrect VS30 estimations for either the stations, the lakes, or both. A separate model could therefore be developed for Alaska so that the modelled shaking parameters are more accurate and precise, which would reduce the large errors and improve our threshold intensities.

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Mantle melting behaviour in low-Mg exoplanets

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As the search for habitable exoplanets becomes more prominent, plenty of exoplanetary research is needed to deepen our understanding of the formation and evolution of all types of exoplanets. Although, as the surface and interior compositions of rocky exoplanets still cannot be directly determined, rocky exoplanets are assumed to have similar refractory element ratios, e.g. low Mg/Si vs. high Mg/Si, as their stars considering they have formed from the same cloud of gas and dust. This assumption allows us to examine different compositions and their effect on the interior of a planet with that composition. The aims of this MSc research are (1) to determine the melting behaviour of non-peridotitic mantles of low-Mg planets, (2) to determine the composition of melts produced in a non-peridotitic mantle and the formation of a secondary volcanic crust, and (3) to get first order constraints on the atmospheric composition.

The selected starting compositions are based on the EH composition of Berthet et al. (2009), as enstatite chondrites are assumed to be one of the potential building blocks of reduced planetary bodies. From the three selected compositions, with a varying molar Ca/Al ratio (0.76, 0.85, and 0.95), synthetic samples are prepared using the following pure oxide powders: SiO_2, Al_2O_3, Fe_2O_3, MgO, $CaSiO_3$, and Na_2SiO_3. High-temperature experiments are run with the samples in a vertical tube gas-mixing furnace at five different temperatures (1300 °C, 1325 °C, 1350 °C, 1375 °C, and 1400 °C), at a fO_2 of FMQ-2

for 50 to 100 hours. Afterwards, the samples are chemically analysed by the Scanning Electron Microscope (SEM), developing a thermodynamic model of mantle melting for various lithological sources. The SEM is also used to obtain backscattered electron (BSE) images to determine the distribution of melt and crystals in the samples. Energy Dispersive X-ray Spectroscopy is used to chemically analyse the experimental products.

The main crystallising phases present in the experimental products are orthopyroxene and quartz. They both occur as anhedral to euhedral crystals within the melt, with quartz occasionally being trapped in orthopyroxene crystals at lower temperatures. The composition of the melt has decreasing amounts of Si and Al, and increasing amounts of Mg with increasing temperatures, i.e. degree of partial melting. The melt composition is also slightly influenced by the increasing Ca/Al ratio in the starting composition, where an increase of Mg and Ca is visible and a decrease in the amounts of Na and Si. However, these are not highly significant differences as they only vary up to 2 oxide% with increasing Ca/Al ratio. Further, the estimated fraction of melt in the samples ranges from 25% to 55%. This wide range is mostly due to the occurrence of melt blobs in certain samples, greatly affecting the estimations. An increasing Ca/Al ratio also increased the melt fraction present in the experiments, although only at higher temperatures. At lower temperatures a more dubious trend is visible. In general, only a minimal influence of the Ca/Al ratio is visible within the samples of this research, causing slightly more CaO and marginally less Al_2O_3 to be present in the melt at higher Ca/Al ratios. Lastly, predictions for volatile saturation in the produced melts show the following general evolution in dominant volatile species: H_2-CH_4 → H_2 → CO → CO-CO_2. An increase in volatile H as H_2O concentration in the melt shifts the atmospheres with reduced oxygen fugacities (IW-3 to IW-6) from a CO-rich to an H_2-CH_4 rich atmosphere. At more oxidized conditions (IW to IW+3) the atmospheres are always CO- to CO-CO_2 rich.

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The **Geologica Belgica 'Master Day'** is an annual event organised by the scientific association *Geologica Belgica Luxemburga Scientia & Professionis* to give recently graduated students in Geosciences the opportunity to present their Master's thesis research in a competitive inter-university context. The 2024 edition of the 'Master Day' took place on 18 October at the Ghent University.

The eight graduates who presented the results of their Master's thesis during the 'Master Day' organized this year in Ghent University. They came from Ghent University, KU Leuven, University of Mons and Université Libre de Bruxelles.