

COMBINING FIELD SPECTROSCOPY AND ELECTRICAL METHODS IN CRITICAL RAW MATERIAL EXPLORATION

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ABSTRACT. An integrated methodology combining electrical resistivity tomography (ERT), induced polarisation (IP), and portable X-ray fluorescence (pXRF) spectroscopy was applied at two contrasting geological settings in Bulgaria within the CleanExplore project (BG-RRP-2.017-0035): the Radulovtsi Cu-porphyry occurrence, Burel ore field, and the Svidnya potassic-alkaline pluton, Western Balkan Mountains. At Radulovtsi, the ERT section delineates a low-resistivity alteration zone above the mineralised body, while an IP chargeability anomaly exceeding 80 ms coincides spatially with the Cu-mineralisation outcrop. Field XRF data define a copper anomaly reaching 0.80%, with positive regression relationships established for resistivity-Cu ($r = 0.49$) and for IP-Cu ($r = 0.41$). At Svidnya, the ERT section distinguishes strongly altered K-alkaline igneous rocks from fresh K-alkaline igneous rocks, while pXRF measurements detect trace CRM-relevant elements (U, Th, Rb, Sr, Ba, Nb) preferentially in less altered domains. The results confirm the effectiveness of the combined non-destructive ERT-IP-pXRF approach for environmentally responsible preliminary CRM exploration.

Key words: critical raw materials (CRM); copper porphyry; alkaline igneous rocks; Bulgaria.

КОМБИНИРАНЕ НА ПОЛЕВА СПЕКТРОСКОПИЯ И ЕЛЕКТРИЧЕСКИ МЕТОДИ В ПРОУЧВАНЕТО НА КРИТИЧНИ СУРОВИНИ

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РЕЗЮМЕ. Интегрирана методология, комбинираща електросъпротивителна томография (ЕСТ), предизвикана поляризация (ПП) и преносима рентгенофлуоресцентна (pXRF) спектроскопия, беше приложена на два контрастни геоложки обекта в България в рамките на проект CleanExplore (BG-RRP-2.017-0035): рудопроявлението при Радуловци от порфирно-меден тип в рудно поле Бурел, и калиево-алкалния плутон при Свидня в Западна Стара планина. При Радуловци ЕСТ разрезът очертава нискосъпротивителна зона на хидротермална промяна над рудоносното тяло, докато аномалия на предизвиканата поляризация, надвишаваща 80 ms, пространствено съвпада с повърхностното разкритие на Cu-минерализацията. Теренните pXRF данни определят медна аномалия, достигаща 0,80%, с установени положителни регресионни зависимости между съпротивление и Cu ($r = 0.49$) и между ПП и Cu ($r = 0.41$). При Свидня ЕСТ разрезът разграничава интензивно променени от слабо изменени калиево-алкални магмени скали, като pXRF измерванията регистрират следи концентрации на елементи от значение за критичните суровини (U, Th, Rb, Sr, Ba, Nb) предимно в по-слабо променените скални разновидности. Резултатите потвърждават ефективността на комбинирания неразрушителен подход ЕСТ-ПП-pXRF за екологосъобразно предварително проучване на критични суровини.

Ключови думи: критични суровини; порфирна медна минерализация; алкални магмени скали; България.

Introduction

The accelerating global transition toward green and digital technologies has significantly intensified the demand for critical and strategic raw materials (CRM), placing considerable pressure on domestic geological exploration capacities within European Union member states. The EU Critical Raw Materials Act (CRMA) mandates that at least 10% of annual raw material consumption be sourced domestically, and requires member states to implement national exploration programmes encompassing geological mapping, geochemical sampling campaigns, and geoscientific surveys, including geophysical investigations. In this legislative context, the development of rapid, cost-effective, and environmentally responsible exploration methodologies capable of delineating prospective mineralisation with minimal surface disturbance represents a priority research objective for the European geoscientific community.

Bulgaria occupies a geologically favourable position within the Balkan metallogenic province, hosting a diverse range of ore deposit types, including copper-porphyry, epithermal gold-silver, skarn, and polymetallic vein systems, as well as potentially CRM-bearing alkaline igneous complexes. Despite this

geological endowment, Bulgaria's potential for critical and strategic raw materials including Bi, Co, Cu, Ga, Ge, Li, Mn, Ni, platinum-group elements, and rare earth elements (REE) for magnets (Nd, Pr, Tb, Dy, Gd, Sm, Ce), remains largely unquantified, primarily due to limited targeted geological investigations and the absence of systematic modern exploration campaigns.

Electrical geophysical methods, and specifically electrical resistivity tomography (ERT) combined with induced polarisation (IP), represent the most widely applied near-surface methods for imaging subsurface geological structures and mapping mineralisation. Their sensitivity to sulphide mineral distributions, hydrothermal alteration zones, and lithological contrasts makes them particularly suitable for CRM exploration targeting. However, a well-recognised limitation of geophysical methods applied in isolation is the inherent ambiguity of subsurface models: a low-resistivity anomaly, for instance, may equally reflect sulphide mineralisation, clay-rich alteration, or elevated pore fluid content (Binley and Slater, 2020). Independent geochemical information is therefore essential for reliable geological interpretation of geophysical cross-sections.

Portable X-ray fluorescence (pXRF) spectroscopy has emerged in recent years as a powerful complementary field tool,

enabling real-time, non-destructive elemental analysis of rocks, soils, and sediments at the point of measurement. The method is particularly well-suited to dynamic exploration workflows, where the ability to modify sampling strategies in response to immediate field results significantly reduces costs and increases targeting efficiency (Lemière and Uvarova, 2019). While pXRF is semi-quantitative and less sensitive than laboratory methods for light elements and many REE, its high sampling density compensates for these limitations by providing spatial coverage that is unachievable through conventional laboratory sampling alone.

The CleanExplore project (Investment № BG-RRP-2.017-0035), funded under Bulgaria's Recovery and Resilience Plan, was conceived to develop and test an integrated exploration methodology combining synchronous field measurements of electrical resistivity, induced polarisation, and elemental composition using portable XRF spectroscopy. The central hypothesis is that these two fundamentally different but complementary methods will mutually reinforce each other, thereby increasing the efficiency, speed, and environmental sustainability of field exploration while reducing costs. The methodology complies fully with the "do no significant harm" principle, as all three methods are non-destructive and non-invasive, eliminating the requirement for drilling or excavation at the preliminary exploration stage.

The present paper describes the CleanExplore project methodology in detail and illustrates its application through two case studies representing contrasting geological settings and mineralisation styles: the Radulovtsi Cu-porphyry occurrence within the Burel ore field, Western Srednogie, and the Svidnya potassic-alkaline pluton in the Western Balkan Mountains. These two sites were selected as illustrative examples because they represent fundamentally different CRM exploration targets – a sulphide-bearing porphyry copper system on the one hand, and an alkaline igneous complex bearing large-ion lithophile and rare earth elements on the other – thereby demonstrating the broad applicability of the combined methodology across contrasting lithological and metallogenic environments. The results presented are preliminary and are intended to demonstrate the operational effectiveness of the integrated approach rather than to provide definitive assessments of the CRM potential of the investigated sites.

Geological Settings

The CleanExplore project encompassed geophysical and geochemical surveys at thirteen sites distributed across Bulgaria (Fig. 1, Table 1), selected to represent a broad range of geological environments and potential CRM targets.

The Radulovtsi Cu-porphyry occurrence, Burel ore field

The Radulovtsi site is located within the Burel ore field, Western Srednogie, which constitutes a northwest-oriented metallogenic strip extending from the town of Bankya westward into the territory of Serbia. Within this structural corridor, a series of small Late Cretaceous ore-bearing paleovolcanoes – the Dragotinski, Zlatushinski, Klisurski, and Radulovski centres – collectively form the so-called Burel Group (Angelov et al., 2010; Marinova et al., 2010). The Radulovtsi ore occurrence is hosted within a subvolcanic intrusion of intermediate composition, comprising quartz-diorite porphyrites in the central portions of the body and andesites in its peripheral parts. The ore

occurrence is classified as a copper-porphyry type, with copper as the principal economic element and gold as a secondary one. This site was selected as a case study because it represents a well-defined sulphide-bearing target, where the IP method's sensitivity to disseminated metallic sulphides and the direct relevance of pXRF copper measurements to the exploration objective provide an optimal setting for evaluating the performance of the combined methodology.

The Svidnya potassic-alkaline pluton, Western Balkan Mountains

The Svidnya site is located in the south-southwestern part of the village of Svidnya, Western Balkan Mountains, where small intrusive bodies of the potassic-alkaline igneous rocks of the Svidnya association crop out. The Svidnya pluton consists of several closely situated small Early Carboniferous bodies emplaced within the Ordovician metasediments of the Grohoten Formation (Angelov et al., 2010; Sachanski and Zareva, 2024). The association is geochemically characterised by significant enrichment in large-ion lithophile elements (LILE) (Ba, Sr, Rb), high-field-strength elements (Zr, Th, U, Nb), and light rare earth elements (LREE) (La, Ce, Nd), with apatite identified as the principal REE-bearing accessory phase (Vladykin et al., 2001). At the contact between the pluton and the Ordovician metasediments, uranium mineralisation and radioactive anomalies have been reported along fault structures (Popov and Popov, 2022). This site was selected as a case study because it represents a fundamentally different CRM target type – an alkaline igneous complex bearing LILE and LREE.

Materials and Methods

Overview of the integrated approach

The methodological innovation of the CleanExplore project consists of the synchronous acquisition of three complementary datasets along common field profiles: electrical resistivity, induced polarisation chargeability, and portable XRF elemental concentrations. This integration is designed to overcome the principal limitation of each method applied independently. Electrical methods provide spatially continuous subsurface imaging but lack direct chemical information and are subject to interpretational ambiguity. Portable XRF provides direct elemental data but only at the surface and at discrete measurement points. Their combination along common profiles enables real-time geochemical ground-truth for geophysical anomaly interpretation, geological interpretation of geophysical cross-sections based on heterogeneous information combining resistivity, IP chargeability, and surface elemental composition, and spatial extrapolation of surface geochemical signatures to depth in accordance with geophysical variability.

The workflow is structured as a dynamic field plan (Robbat et al., 1998) in which initial pXRF reconnaissance scanning guides the positioning and orientation of geophysical measurement profiles, and real-time pXRF results acquired simultaneously with geophysical measurements allow immediate adjustment of sampling density, profile length, and laboratory sample selection priorities. This operational flexibility represents a key advantage over conventional sequential exploration programmes in which geophysical and geochemical datasets are acquired and interpreted independently at different project stages, with laboratory results typically available only weeks to months after field data collection.

The overall methodology is structured in two sequential phases corresponding to the two modules of the CleanExplore project. In the first phase, a conventional approach is applied at ten pre-selected sites, combining geophysical profiling with the collection of samples for laboratory petrological and geochemical analyses. The results of this phase inform the selection of a minimum of two sites for detailed investigation in the second phase, where the novel synchronous measurement approach is applied and geostatistical spatial models of CRM distribution are created.

Module 1 (Months 1–12), field geophysical surveys applying the electrical resistivity and induced polarisation methods were carried out, and samples were collected for laboratory petrological-geochemical analyses at ten pre-selected sites: Sliven (Glushnik), Tvarditsa (Sborishte), Shipka, Teteven (Lesidren), Dimitrovgrad (Parvomay), Sofia (Radulovtsi and

Klisura), Belogradchik, Sandanski (Rupite, Kozhuh and Novo Delchevo), Simitli (Cherniche), and Svoje (Svidnya) (Fig. 1; Table 1). At each site, structural relationships were clarified, and factors favourable for critical and strategic raw material mineralisation were assessed, based on field observations of rock type relationships and geophysical cross-sections. The following laboratory analyses were performed: X-ray diffraction analysis at an external laboratory, petrographic microscopic analyses, and elemental and isotopic analysis by LA-ICP-MS at in-house laboratories. The results of the laboratory petrological-geochemical analyses and the field observations and measurements were analysed in the context of the genesis, controlling factors for mineralisation, and prospectivity of each site. A minimum of two sites were subsequently selected for detailed investigation in Module 2.

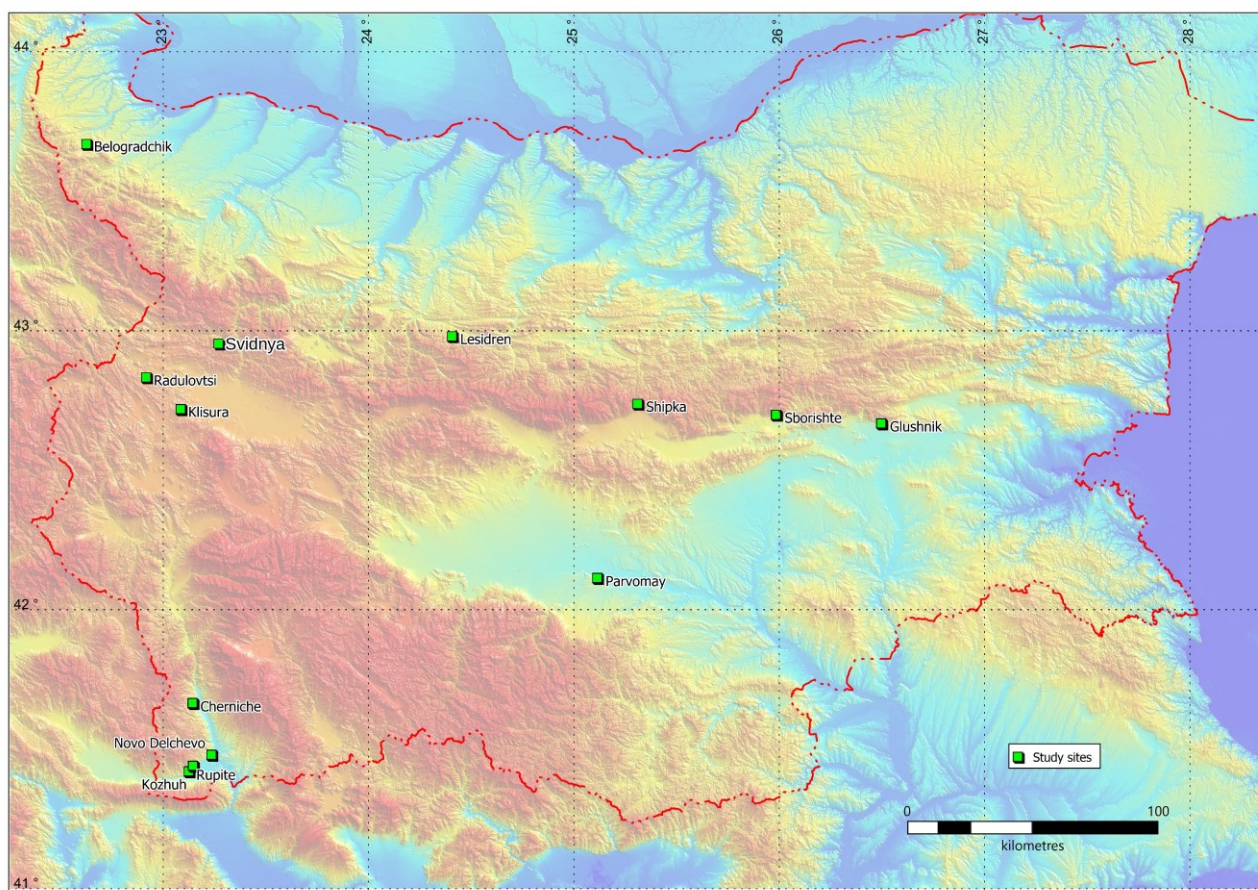


Figure 1. Geophysical surveys at sites of different geological environments across the country employed measurements of electrical resistivity and induced polarisation along profiles

Module 2 (Months 11–19), field activities and laboratory analyses were analogous to those of Module 1, complemented by field measurements with the pXRF spectrometer carried out along the geophysical measurement profile lines and areally. The data from the field geophysical and geochemical profiles were correlated. These data, together with the data from the laboratory analytical activities, were processed and interpreted, and on their basis geostatistical models of the predicted spatial distribution of critical and strategic raw materials were created, both in plan and in cross-section.

Electrical Resistivity Tomography and Induced Polarisation

Field geophysical measurements were carried out using an ABEM Terrameter SAS 1000 multi-electrode system with an ES 10-64C electrode selector, enabling simultaneous acquisition of apparent electrical resistivity and time-domain induced polarisation chargeability data.

At Radulovtsi, a profile of 160 m in length was established with 2 m electrode spacing, employing a Wenner-Schlumberger array configuration selected for its optimal compromise between lateral resolution and depth of investigation. At Svidnya, a profile of 80 m in length was established with 1 m minimum electrode

spacing, employing a dipole-dipole array configuration. Laser levelling was performed at both sites to incorporate accurate surface topography into the inversion models (Marinova et al., 2026).

Table 1. The CleanExplore project investigation sites with target critical raw materials and deposit genetic types.

Sites	Critical raw material	Genetic type
Klisura	Cu, Au, Mo, Ag	Hydrothermal
Radulovtsi	Cu, Au	Hydrothermal
Svidnya	Sr, Zr, Nb, Ce, Y	Magmatic
Glushnik	Mn, Fe	Volcano-sedimentary
Parvomay	Si, Cs	Volcanic
Cherniche	U	Infiltration
Rupite	U	Hydrothermal
Kozhuh	U	Hydrothermal
Novo Delchevo	U	Hydrothermal
Sborishte	U, Pb, Zn, Cu	Hydrothermal
Shipka	Fe	Hydrothermal
Lesidren	Fe	Sedimentary
Belogradchik	Cu, Au	Volcanic

Field X-Ray Fluorescence Spectroscopy

Elemental concentrations were determined in the field using a *Bruker S1 Titan 800* portable X-ray fluorescence spectrometer equipped with a rhodium X-ray tube and a silicon drift detector with a graphene window, enabling detection of a broad range of elements from Mg to U. At Radulovtsi, measurements were performed synchronously with the geophysical survey at each electrode position, yielding 42 measurement points at 2 m intervals along the profile to a total distance of 84 m, corresponding to the section where geochemical data were available for joint interpretation. At Svidnya, measurements were performed at six accessible points with good rock exposure along the 80 m geophysical profile. At each point, the instrument was applied directly to freshly exposed rock or soil surfaces using the factory-calibrated Geochem analytical mode. It is important to note that pXRF results are semi-quantitative, with inherently limited sensitivity for light elements, alkali metals, and most REE, and results are therefore interpreted as qualitative to semi-quantitative indicators rather than definitive elemental concentrations.

Laboratory Petrographic and Geochemical Analysis

Representative rock samples collected along both geophysical profiles were prepared as polished thin sections and examined under transmitted and reflected light using *Leica DM750P* and *Leica DMLP* polarising microscopes equipped with digital cameras, as well as a *Nikon LV100ND* microscope at Svidnya. Elemental and isotopic analyses were performed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) using a *PerkinElmer ELAN DRC-e* mass

spectrometer coupled with a *New Wave UP193FX* laser ablation system at the Geological Institute, Bulgarian Academy of Sciences. X-ray diffraction analyses were performed at an external accredited laboratory on selected samples. Pearson correlation coefficients were calculated for element pairs at both study sites to identify statistically significant geochemical associations and evaluate the coupling between electrical parameters and elemental concentrations along the profiles.

Results

The following section presents selected results from the two illustrative case studies. These results are intended to demonstrate the operational effectiveness and mutual complementarity of the integrated ERT–IP–pXRF methodology rather than to provide definitive assessments of the CRM potential of the investigated sites. Complete datasets from all CleanExplore project sites will be presented in subsequent publications.

Example 1: Sulphide-bearing porphyry system — Radulovtsi Cu-porphyry occurrence

Petrographic context. Petrographic examination of samples from the Radulovtsi subvolcanic body confirms a copper-porphyry mineralisation style with fine disseminated pyrite as the principal ore mineral within quartz-diorite porphyrite. Advanced supergene oxidation is evidenced by malachite veins and iron hydroxide-stained quartz veins, indicating that a significant proportion of the original sulphide assemblage has been partially replaced by secondary copper carbonate and iron oxide minerals under near-surface oxidising conditions. This petrographic context is directly relevant to the interpretation of both the geophysical and geochemical datasets.

Geophysical and geochemical results. The ERT section reveals resistivity values ranging from approximately 80 to in excess of 220 Ωm . A low-resistivity zone (80–130 Ωm) in the upper portion of the section is interpreted as weathered and clay-altered rock corresponding to the supergene oxidation zone, while elevated resistivity values (180–220 Ωm) at greater depths reflect fresher, less altered host rock. The IP chargeability section reveals a prominent high-chargeability anomaly in the central portion of the profile, with values reaching in excess of 80 ms and extending to approximately 30–35 m depth, spatially coincident with the inferred outcrop of the Cu-mineralisation. Field XRF measurements reveal background copper concentrations of 0.01–0.08% in the western half of the profile, with a sharp increase to a maximum of 0.80% from measurement point 72 onwards, defining a well-developed secondary geochemical halo. Statistical analysis yields a Pearson correlation coefficient of $r = 0.49$ ($R^2 = 0.24$) between resistivity and copper content, and $r = 0.41$ ($R^2 = 0.18$) between IP chargeability and copper content along corresponding profile positions. The geochemical correlation matrix reveals a Cu–Fe₂O₃ element association ($r = 0.42$) consistent with a chalcopyrite-pyrite sulphide paragenesis and confirms that copper enrichment is decoupled from the primary lithological framework of the host intrusion (Marinova et al., 2026).

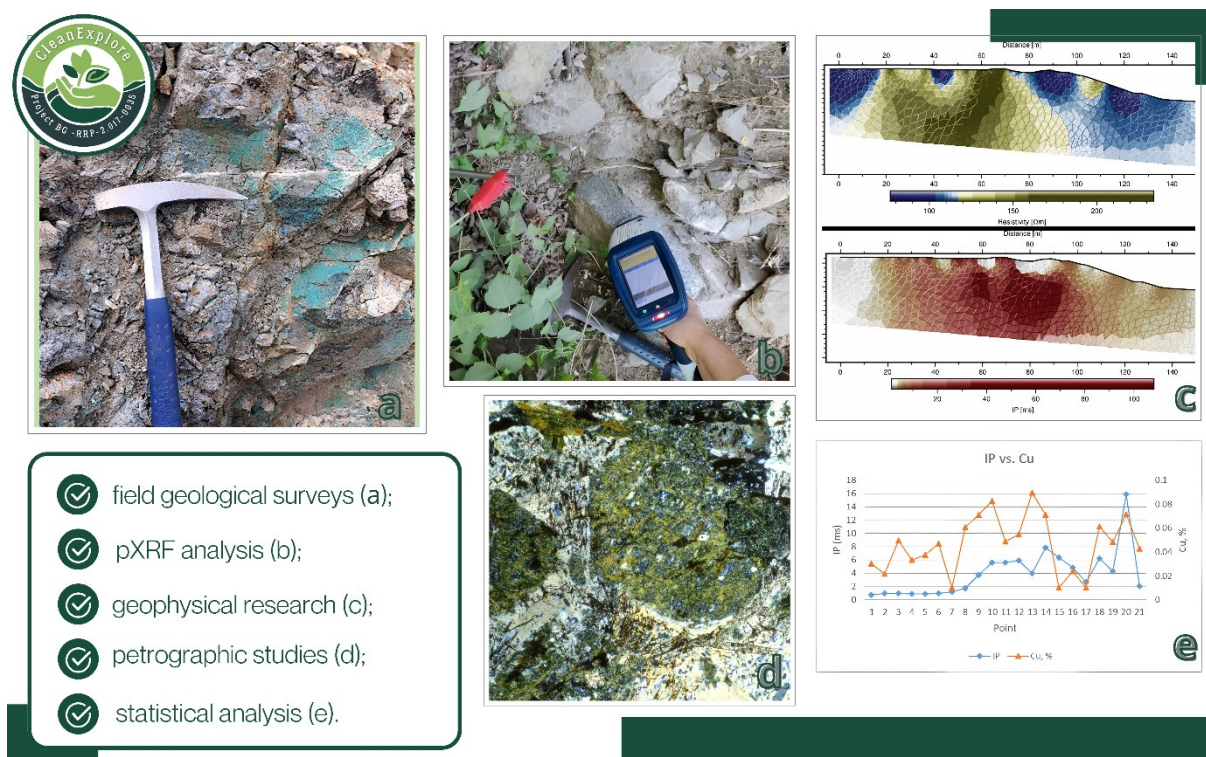


Figure 2. Comprehensive research methodology

Example 2: Svidnya potassic-alkaline pluton, Western Stara Planina

Petrographic context. The geophysical profile at Svidnya intersects melasyenites (shonkinites) and dykes of alkaline syenites displaying varying degrees of hydrothermal and supergene alteration. The primary mineralogy comprises K-feldspar, biotite, augite, amphibole, and abundant accessory apatite identified as the principal REE carrier. The secondary alteration assemblage consists of chlorite-group minerals, fine white mica, clay minerals, carbonates, and iron hydroxides, whose development directly controls both the electrical properties of the rock mass and the surface geochemical signature measurable by pXRF.

Geophysical and geochemical results. The ERT section distinguishes two main subsurface domains:

1. a low-resistivity zone below 600 Ωm from the beginning of the profile to approximately 35 m, corresponding to the most strongly altered portion of the section confirmed by field observation;
2. a higher-resistivity zone of 620–1200 Ωm from 35 m to the end of the profile, reflecting predominantly fresh to weakly altered K-alkaline igneous rock.

The IP model exhibits a heterogeneous pattern reflecting variations in rock composition and alteration intensity. Field pXRF measurements detect trace concentrations of U, Th, Rb, Sr, Ba, and Nb preferentially in less altered rock exposures in the higher-resistivity eastern domain, with pronounced geochemical heterogeneity within the intrusion. Pearson correlation analysis reveals positive correlations among Rb, Th, U, and Ce, consistent with control by felsic mineral phases and late-stage magmatic differentiation. The spatial correspondence between the geophysically delineated fresh rock domain and the

pXRF-detected CRM-relevant element enrichments illustrates the direct utility of combining alteration mapping by ERT with surface geochemical screening by pXRF (Marinova et al., 2026).

Conclusions

The integrated application of electrical resistivity tomography, induced polarisation, and portable X-ray fluorescence spectroscopy within the CleanExplore project demonstrates the practical effectiveness of this combined non-invasive approach for preliminary critical raw material exploration across contrasting geological settings.

At Radulovtsi, the ERT and IP sections successfully delineated the alteration zone and sulphide mineralisation, respectively, while field pXRF measurements defined a well-developed copper geochemical halo and established statistically significant correlations between electrical parameters and copper content. At Svidnya, ERT imaging resolved the alteration pattern within the K-alkaline pluton, and pXRF measurements confirmed preferential enrichment of CRM-relevant elements in less altered rock domains, illustrating the direct complementarity of the two method groups.

The synchronous acquisition workflow proved operationally efficient and fully compliant with the "do no significant harm" principle, supporting its application within the environmentally responsible exploration programmes required under the EU Critical Raw Materials Act. Complete datasets from all thirteen CleanExplore project sites will be presented in subsequent publications.

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