Evaluation of serpentinite composition through X-Ray fluorescence and complementary analytical methods

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ABSTRACT. Serpentinite, metamorphic rocks primarily composed of serpentine-group minerals, pose significant challenges in chemical analysis due to their complex and heterogeneous composition. The variability in mineralogy, including the presence of resistant phases such as chromite and magnetite, complicates sample dissolution and leads to potential inaccuracies in bulk chemical data. Additionally, the high content of structurally bound water in serpentine minerals interferes with gravimetric and thermal analyses, while the presence of elements in multiple oxidation states, such as Fe^{2+} and Fe^{3+}, requires specialized analytical techniques. In this study, we present results from X-ray fluorescence spectroscopy (XRF) analyses conducted on serpentinite samples. XRF offers a non-destructive approach for determining major and some trace elements without requiring acid digestion, making it suitable for routine geochemical screening. However, to overcome the limitations inherent to each method, XRF data are complemented by other techniques, including inductively coupled plasma mass spectrometry (ICP-MS), thermogravimetric analysis (TGA), and alkali fusion or acid digestion protocols. This integrated approach enhances the reliability of the compositional data and supports more accurate interpretation in geological, mineralogical, and environmental studies involving serpentinites.

1 Introduction

1.1 General description of serpentinites

Serpentinite is a metamorphic rock composed predominantly of minerals of the serpentine group, such as lizardite, antigorite and clinohrysotile. These minerals are formed by the hydration and alteration of ultrabasic minerals, such as olivine and pyroxenes, from peridotite, harzburgite or dunite [1]. The rock is variable in color from light to dark green to dark green or blackish, often with silky luster and fibrous or massive texture.

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Chemically, serpentinite is rich in MgO (generally above 35%), with variable contents of FeO, SiO_2, and structural H_2O. Typical density is between 2.5 and 2.7 g/cm^3, and hardness is relatively low (2.5-3.5 on the Mohs scale).

1.1.1 Serpentinization: mechanism of formation

Serpentinization is the geochemical process by which anhydrous ultramafic minerals, in particular olivine and orthopyroxenes, are transformed into hydrated serpentine group minerals in the presence of water. The typical reaction for olivine is as follows:

$$2MgSiO \text{ (olivine)} + 3H_2O + CO \rightarrow MgSiO(OH) \text{ (serpentine)} + MgCO$$

This reaction is exothermic, releasing heat and often molecular hydrogen (H_2), which has important implications for chemotrophic life in underwater environments and prebiotic reactions [2]. The optimum temperature for serpentinization ranges from 200 to 500 °C, and the process is facilitated in fault zones and tectonic plate margins.

1.1.2 Ferrous serpentinite

Ferrous serpentinite is a variant of serpentinite that contains higher proportions of iron, both as Fe^{2+} and Fe^{3+}, distributed in serpentinized minerals or as iron oxides (e.g. magnetite, hematite). In these rocks, primary olivine is often richer in Fe (and poorer in Mg), and serpentinization reactions produce a higher proportion of magnetite.

The chemical composition may include more than 8-10% total iron, and the density is higher than in ordinary serpentinite. Also, the color is often darker, and traces of sulfides, chromium, or nickel may be present.

1.1.3 Alteration of serpentinite

After initial formation, serpentinite continues to undergo transformations by:

- Carbonatization: when exposed to CO_2-rich fluids, serpentinite transforms to talc and magnesite. Typical reaction:

$$2Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow Mg_3Si_4O_{10}(OH)_2 \text{ (talc)} + 3MgCO_3 + 3H_2O \quad (1)$$

- Oxidation: At the surface, under the influence of air and water, oxidation of Fe^{2+} to Fe^{3+} occurs and the formation of goethite, limonite or hematite. These reactions lead to reddish coloration of the rock and its disaggregation.
- Deserpentinization: at high temperatures (between 600-800 °C), during regional metamorphism or subduction, serpentinite loses water and transforms to olivine, enstatite or talc [6].

1.1.4 Importance of serpentinite

Serpentinite is of major geological, economic and ecological importance:

- Geological: it is a marker of subduction processes, continental collision zones and alteration of the upper mantle;
- Economic: may contain chromite, magnetite, asbestos, talc, and even precious elements in some cases (Ni, Co, Pt);
- Ecological: it has the potential to capture CO_2 through mineral carbonation and is being studied for use in geoengineering technologies.

Also, its high reactivity in the presence of water and ability to support chemotrophic microbiomes make serpentinite an essential object of study in astrobiology and experimental geochemistry.

Serpentinite and its ferrous form are rocks with a complex geochemical evolution, involved in primary tectonic cycles and with relevant applications in geology, industry, and environmental protection. The study of serpentinization and alteration reactions has implications for understanding tectonic processes, the geological storage of CO_2, and the origins of life on Earth.

2 Modern methods of mineralogical and geochemical analysis applied to serpentinite and ferrous serpentinite

Serpentinite and its ferrous variant are important metamorphic rocks for understanding tectonic processes, the composition of the Earth's mantle, and geochemical reactions involving hydration and alteration of ultramafic rocks. The analysis of these rocks requires the use of advanced and integrated methods capable of revealing their mineralogical, chemical, structural and microtextural composition. This article presents a synthesis of the primary techniques used for characterizing serpentinites, with an emphasis on their applicability in studying ferrous variants, as well as their limitations and advantages.

2.1 Mineralogical analysis

2.1.1 X-Ray Diffraction (XRD)

X-ray diffraction is the main method for the identification of serpentine minerals (lizardite, antigorite, clinohrysotile), which have characteristic diffractometric patterns. XRD allows differentiation of crystalline phases and estimation of relative proportions. It can also reveal the presence of magnesite, talc, calcite, or iron oxide minerals, characteristic of alteration.

2.1.2 Optical microscopy and petrography

Thin sections analyzed under the optical microscope allow the observation of serpentinization textures, relationships between minerals, the degree of alteration, and the presence of ferriferous neoformations. Colored interferences and specific birefringences help to recognize serpentinites and associations with talc, chlorite, or magnetite.

2.1.3 Electron microscopy (SEM/EDS)

Scanning electron microscopy, in combination with EDS analysis, provides detailed images of microstructures as well as pinpoint chemical identification of minerals. It helps differentiate platy or fibrous serpentinite phases, as well as in highlighting metallic micro-inclusions or oxidation zones.

2.2 Geochemical analysis

2.2.1 X-Ray Fluorescence (XRF)

XRF is widely used for the determination of major oxides and major elements (SiO_2, MgO, FeO/Fe_2O_3, Al_2O_3, CaO, etc.). It is fast and relatively inexpensive, but limited by spectral interferences and the difficulty of determining elements in low concentrations or with close emission lines (e.g. Ag, Rh) [3].

2.2.2 Inductively coupled plasma emission spectrometry (ICP-OES)

This technique is suitable for the determination of Mg, Fe, Fe, Ca, Al, Ni, Cr, Co, but requires prior acid-thermal digestion. It is more sensitive compared to XRF for some transition elements [4].

2.2.3 Inductively coupled mass spectrometry (ICP-MS)

Allows the detection of trace and ultra-trace elements (ppm, ppb), including precious or heavy metals (Ag, Rh, Pt, Pd, REE). It is essential in geodynamic provenance or mineral exploration studies, but can be influenced by isotopic and matrix interferences.

2.2.4 Loss on Ignition (LOI)

LOI is used to estimate the content of volatile compounds (structural H_2O, CO_2 from carbonates, OH-). Serpentinite shows high values (12-16%) due to the presence of OH- and possible inclusions of magnesite, hydromagnesite or calcite [11].

2.3 Complementary techniques

2.3.1 Electron microprobe (EPMA)

Allows the analysis of the element distribution on a micrometer scale, useful for the differentiation of serpentinic phases and the determination of the exact mineral composition in ferrous serpentinites.

2.3.2 Spectroscopy (FTIR, Raman)

FTIR spectroscopy highlights OH vibrations and silicate lattices, useful for confirming the presence of different serpentine species. Raman is used for rapid phase identification in thin sections or altered samples.

2.3.3 Thermal analysis (TG-DTA/DSC)

It allows the highlighting of dehydroxylation and decarbonation steps, relevant for mineral stability and volatile composition estimation.

2.4 Integrated interpretation and applications

A complete characterization of serpentinite requires the integration of mineralogical, geochemical and structural data. This approach is essential for: identifying the source of the protolith (harzburgite, dunite); estimating the degree of serpentinization; determining the subsequent processes (carbonation, oxidation, deserpentinization); evaluating the economic potential (chromite, Ni, precious metals); geoengineering (CO_2 sequestration) and astrobiology studies [5].

Modern methods of serpentinite and ferrous serpentinite analysis allow a complex and accurate characterization of these rocks essential for geology, mineral resources and global processes. The choice of appropriate analytical techniques and integrated interpretation of the data are fundamental for the correct assessment of these complex geochemical systems.

3 Difficulties in serpentinite and ferrous serpentinite analysis: mineralogical, geochemical and interpretative challenges

Serpentinite and its ferrous variant are metamorphic rocks resulting from the hydration of ultramafic rocks such as peridotites and harzburgites. Their mineralogical and geochemical characterization is essential for studies in geodynamics, petrology, mineral exploration and geoengineering. However, the analysis of these rocks is complex and often difficult due to heterogeneous composition, multiple alteration, presence of poorly crystallized minerals and limitations of instrumental methods. The paper details the difficulties encountered in the analysis of serpentinite and ferrous serpentinite, focusing on technical and interpretative aspects, and proposes solutions based on the latest scientific research.

3.1 Challenges in mineralogical characterization

3.1.1 X-ray diffraction (XRD) and the difficulties of serpentine phases

Serpentinite minerals, including lizardite, antigorite and clinohrysotile, have similar structures and very similar diffraction patterns, making it difficult to accurately differentiate them using XRD. Especially in samples with poor crystallinity or complex mixtures, diffraction lines overlap and interpretation becomes uncertain. Also, the preferential orientation of particles in pressed samples can lead to distortion of the relative intensities of the lines, affecting quantitative interpretation.

3.1.2 Optical petrography and interpretive limitations

Thin-section analysis by optical microscopy can reveal typical textures such as "mesh" or "pseudomorphs", but accurate mineral identification is difficult without confirmation by complementary methods. Serpentinite may contain areas of neoformations (chlorite, talc, magnetite), which mask the initial serpentinite phases. In addition, progressive alterations reduce textural clarity, and opaque minerals such as magnetite may block the observation of adjacent phases.

3.1.3 Electron microscopy (SEM) and EDS analysis

Scanning electron microscopy (SEM) allows detailed observation of the morphology and microcrystalline texture of serpentinites. Still, interpretation of elemental composition by EDS is limited by a lack of standardization and low resolution for light elements such as Mg and Si. Also, the distinction between fibrous and platy serpentinites is not always clear without correlation with XRD or TEM.

3.2 Difficulties in quantitative chemical analysis

3.2.1 X-ray fluorescence (XRF)

XRF is widely used to analyze major oxides in serpentinite, but it has significant limitations. Interferences between spectral lines of transition elements, such as Fe, Ni, Co, and overlap with Mg and Al, lead to quantification errors. In addition, the variable matrix composition of serpentinite affects the accuracy of the analysis, requiring specific calibration standards [7]. For ferrous serpentinite, the high Fe content can mask other elements, especially when present only in trace amounts.

3.2.2 Inductively coupled plasma optical emission spectrometry (ICP-OES)

ICP-OES provides higher sensitivity than XRF for Mg, Fe, Cr and Al, but requires complete acid digestion. Resistant phases, such as magnetite and chromite, are not readily dissolved, leading to underestimation of the true Fe and Cr content [8]. Additionally, matrix complexity can lead to interference in the plasma, affecting the spectral lines of certain elements, particularly in the presence of magnesium at high concentrations.

3.3.3 Inductively coupled mass spectrometry (ICP-MS)

ICP-MS is essential for the determination of trace and ultra-trace elements (Ag, Rh, Pt, REE), but is susceptible to isotopic interferences as well as matrix effects that can lead to false positive signals. For example, apparently high values for silver and rhodium (>1000 ppm) have been recorded in ferrous serpentinites, which were subsequently invalidated by multi-method analysis. This problem is accentuated by the presence of interfering elements such as Ba, Sr or Zr, which generate multiple ions.

3.3.4 Loss on Ignition (LOI) and uncertainties

The LOI method is often used for estimating volatile compounds in serpentinite ($H_{(2)}O$, CO_2) but it gives only a rough estimate. Hydroxyls in serpentinites are lost at different temperatures than carbonates, and the presence of clays or adsorbed water leads to overestimates [9]. In addition, for altered samples, LOI can include contributions from secondary phases such as smectite or calcite.

4 Methods and apparatus used to determine the chemical composition of serpentinite

Determination of the chemical composition of serpentinite, including ferrous varieties, is essential for understanding geochemical and petrogenetic processes. In this study, the main analysis was conducted using X-ray fluorescence spectrometry (XRF) with the RIGAKU SUPERMINI spectrograph, a compact and powerful model specifically optimized for determining major oxides and trace elements in silicate rocks [10].

4.1 XRF determinations

X-ray fluorescence is a non-destructive method that uses primary X-rays to excite atoms in a sample, generating secondary radiation characteristic of each chemical element. This signal is measured and interpreted according to the intensity of spectral lines, allowing quantification of the elements present in the sample.

The analyses were performed using the RIGAKU SUPERMINI spectrometer, a WDXRF (Wavelength Dispersive X-ray Fluorescence) type apparatus equipped with a Pd window X-ray tube and scintillation detector for hard X-rays and a proportional detector for soft X-rays.

It offers high accuracy in the determination of major oxides and some trace elements and is ideal for field analysis or laboratories with limited space.

Serpentinite samples were dried, ground below 75 µm, and pressed into pellets using a hydraulic press. In literature, vitrified pellets obtained by lithium-borate fusion are recommended to reduce matrix effects.

The following oxides were determined: SiO_2, Al_2O_3, CaO, MgO, total Fe_2O_3, Na_2O, K_2O, TiO_2, MnO, P_2O_5. The high values of MgO and Fe_2O_3 are characteristic of serpentinites, and the variations of SiO_2, Al_2O_3 and CaO may reflect hydrothermal alteration processes, carbonation or the presence of secondary phases (talc, chlorite, calcite).

XRF spectrometry can be affected by spectral interferences and matrix effects, especially in rocks with high Fe and Mg content. The RIGAKU SUPERMINI spectrometer allows advanced ZAF corrections, but results can be influenced by residual moisture, porosity, and uneven pellet preparation.

4.2 ICP-OES determinations

The ICP-OES analyses were performed using the PerkinElmer system (Optima 2100), equipped with an echelle polychromator (λ = 163-782 nm), segmented SCD detectors and 40 MHz solid-state RF generator, adjustable between 750 and 1500 W. The vertical dual-view plasma allows radial and axial measurements, depending on the sample matrix.

Mineral or residual samples (~0.5-1 g) were completely digested in a microwave system using acid mixtures (HCl + HNO_3 or HCl + HF, as appropriate). The resulting solutions were filtered and diluted to 50-100 mL with ultrapure water and acidified (2-5% HNO_3). Plasma introduction was performed by pneumatic nebulization with a GemTips (cross-flow) or OneNeb (flow-blurring) nebulizer at a rate of 0.8-1.0 mL/min.

Calibration was performed using certified multi-element standards (Merck, SCP Science). Quality control included checks with secondary standards and reanalyzing samples every 10 positions. The Hg lamp was used for automated optical alignment on the 253.652 nm line.

Radial and axial modes were used, depending on concentration and matrix. RF power was maintained at 1400 W. Plasma gas (argon, 99.999 %) was supplied at a flow rate of 8-10 L/min. Syngistix™ for ICP software allowed signal monitoring, drift evaluation and automatic interpretation of the results.

The detection limits for the metals of interest (e.g. Fe, Ni, Cr, Co, Mn, Cu, Zn) were in the range of 0.1-1.0 µg/L, depending on the matrix and wavelength selected. Internal precision (RSD) was better than 2 % for all elements at concentrations > 10 µg/L. Background correction and internal standard (e.g. Sc, Y or Rh) were applied to compensate for nebulization and matrix variations. Magnesium (Mg) was also analyzed, with a detection limit of approximately 0.2-0.3 µg/L and an RSD < 1.5 % precision in homogeneous samples with concentrations > 5 µg/L. Iron (Fe), essential in the characterization of ultrabasic samples, was determined with increased sensitivity in the axial mode, with a detection limit of approximately 0.5 µg/L and a precision of up to 1 % for concentrations > 10 µg/L.

4.3 Complementary determination of H_2O and CO_2 in serpentinite samples

The complete determination of the chemical composition of serpentinite cannot be achieved by X-ray fluorescence spectrometry (XRF) alone, as this method does not allow the quantification of volatile compounds such as structurally bound water (H_2O) or carbon dioxide (CO_2). These volatile constituents are crucial in assessing the degree of serpentinization, in petrogenetic studies, and in estimating geological carbon sequestration capacity. In this context, complementary methods such as loss-on-ignition (LOI), gravimetric analysis, differential thermogravimetric analysis (TGA/DTG), and Fourier Transform Infrared Spectrometry (FTIR) are necessary.

4.3.1 Loss on Ignition (LOI)

The LOI (Loss on Ignition) method is widely used for the global determination of the content of volatile compounds in geological samples, in particular H_2O and CO_2. Samples dried at 105 °C are weighed and then calcined in steps:

- 550 °C: mass loss is attributed to the removal of weakly or structurally bound H_2O (including OH- from serpentinized minerals);
- 950-1000 °C: the additional loss indicates the release of CO_2 from carbonate minerals (calcite, dolomite, magnesite), if present.

This method is relatively simple, robust and economical, but it does not accurately distinguish between H_2O and CO_2 contributions without careful thermal separation or further analysis.

5 Experimental results

The chemical composition of the 10 serpentinite samples was analyzed using two complementary methods: X-ray fluorescence spectrometry (XRF) and inductively coupled plasma optical emission spectrometry (ICP-OES). Each method provided distinct insights into the oxide content, allowing both validation of the results and highlighting possible interferences or analytical limits.

The XRF method was used to determine the total content of major oxides (SiO_2, MgO, Fe_2O_3, Al_2O_3, CaO), but also minor oxides such as Cr_2O_3, NiO, Co_2O_3 or ZnO. The equipment used, a RIGAKU SUPERMINI spectrometer, allowed direct analysis on pressed powders without acid digestion, leading to a full compositional picture. The XRF values thus reflect the total content of elements present, including resistant phases such as spinels or magnetite. The results obtained are summarized in Table 1.

Table 1. Results obtained by the XRF method

Component	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
SiO_2	30.6346	31.6994	32.5750	37.1061	35.5835
Al_2O_3	1.5757	1.4549	2.6565	1.6212	0.8671
CaO	0.6338	6.6731	4.5117	1.1184	1.0949
MgO	34.4199	29.6674	32.3137	34.9387	36.2016
Na_2O	0.0000	0.0000	0.0000	0.0000	0.0000
K_2O	0.1461	0.1252	0.0888	0.1439	0.0517
TiO_2	0.0000	0.0000	0.0484	0.0000	0.0000
SO_3	0.3803	0.0354	0.2256	0.0544	0.0679
Fe_2O_3	18.1343	10.3226	13.1519	10.4036	12.8030
MnO	0.3380	0.2349	0.2953	0.1899	0.1501
Cl	0.1778	0.0197	0.0638	0.0279	0.0393
$P_{(2)}O_5$	0.0212	0.0000	0.0295	0.0150	0.0149
SrO	0.0000	0.0983	0.0000	0.0000	0.0000
BaO	0.0000	0.0000	0.0000	0.0000	0.0000

Component	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
CuO	0.0474	0.0385	0.0774	0.0000	0.0000
PbO	0.0000	0.0000	0.0000	0.0000	0.0000
ZnO	0.0000	0.0224	0.0000	0.0000	0.0000
NiO	0.5167	0.4121	0.5513	0.5930	0.6587
Co_2O_3	0.0503	0.0296	0.0000	0.0000	0.0311
Cr_2O_3	0.7271	0.4121	0.4425	0.3468	0.4371
As_2O_3	0.0000	0.0129	0.0000	0.0000	0.0000
PC	11.9696	18.7194	12.9012	13.3034	11.7034
SiO_2	35.4499	30.0952	34.8346	40.1367	38.4711
Al_2O_3	1.0868	0.5560	0.8096	0.4228	2.5736
CaO	1.2679	1.1052	1.8520	0.0836	0.5129
MgO	35.7086	36.0462	34.9228	33.8041	34.5798
Na_2O	0.0000	0.0000	0.0000	0.0000	0.0000
K_2O	0.0546	0.0884	0.0935	0.0650	0.0712
TiO_2	0.0000	0.0000	0.0631	0.0000	0.0000
SO_3	0.0743	0.2057	0.1067	0.0650	0.0779
Fe_2O_3	10.9541	15.3026	14.1102	13.2005	10.1705
MnO	0.1673	0.4914	0.2346	0.2810	0.3255
Cl	0.0311	0.0609	0.1402	0.0655	0.0830
P_2O_5	0.0270	0.0150	0.0205	0.0200	0.0329
SrO	0.0223	0.0000	0.0000	0.0000	0.0000
BaO	0.0000	0.0000	0.0000	0.0000	0.0000
CuO	0.0000	0.0000	0.0200	0.0278	0.0790
PbO	0.0000	0.0969	0.0000	0.0000	0.0000
ZnO	0.0186	0.0372	0.0142	0.0000	0.0000
NiO	0.5227	0.7218	0.6367	0.7474	0.7871
Co_2O_3	0.0000	0.0390	0.0000	0.0000	0.0546
Cr_2O_3	0.3536	0.1811	0.3087	0.2881	0.4599
As_2O_3	0.0000	0.0000	0.0000	0.0000	0.0000
PC	13.7473	14.9854	11.8110	10.8072	11.5607

The results of the ICP-OES determinations are summarized in Table 2:

Table 2. Results obtained by the ICP-OES method

	Component	
Sample	MgO	Fe_2O_3
Sample 1	32.7087	12.1276
Sample 2	27.5605	2.1990

Sample 3	31.9716	7.3890
Sample 4	32.9002	5.1271
Sample 5	32.1332	7.4581
Sample 6	32.4726	5.4386
Sample 7	33.5165	9.1507
Sample 8	32.5809	8.0190
Sample 9	31.9594	7.8273
Sample 10	33.6514	5.2005

The MgO content varied predictably between 29.6% and 36.2%, which is characteristic for highly serpentinized rocks. In comparison, values obtained by ICP-OES were slightly underestimated, with differences of up to 6%, which is partly attributable to the incomplete dissolution of refractory minerals during acid digestion. The same trend was observed for Fe_2O_3, with differences of about 1-2% between the two methods. This phenomenon is common in geochemical studies on serpentinite, where XRF captures the entire iron contribution, whereas ICP-OES depends on the solubility of minerals in acid.

In terms of SiO_2, the results are between 35% and 41%, reflecting a stable composition and a complete transformation of olivine and pyroxenes to serpentine. The values of Al_2O_3 and CaO_3 were relatively constant, but some samples exhibited localized variations, which may indicate the presence of secondary phases, such as chlorite or calcite.

Trace oxides (NiO, Cr_2O_3, Co_2O_3) were present in all samples, with concentrations confirming the ultrabasic origin of the protolith. Similarly, the presence of ZnO and PbO in some samples could be correlated with late hydrothermal contamination or metallic sulfide inclusions.

A peculiarity of the data set is the signaling of significant levels of Ag_2O and Rh_2O_3 by the XRF method, with concentrations between 500-2000 ppm for silver and about 3000 ppm for rhodium. These values raise suspicions of possible spectral interferences, especially in the absence of confirmation by ICP-OES. In the literature, such results may occur due to the overlap of silver emission lines with transition elements, or may be the result of Compton scattering enhanced by the basic composition of the mineral matrix. Validation of these data requires further investigation with techniques such as SEM-EDS or ICP-MS to rule out analytical artifacts. Some examples of the occurrence of blatantly erroneous results for some elements are summarized in Table 3:

Table 3. Erroneous results obtained by the XRF method

Sample	Component	
	Ag_2O	Rh_2O_3
Sample 1	0.0000	0.0000
Sample 2	0.0000	0.0000
Sample 3	0.0549	0.0000
Sample 4	0.0595	0.0000
Sample 5	0.1987	0.0000
Sample 6	0.0709	0.2915
Sample 7	0.0000	0.0000
Sample 8	0.0000	0.0000

Sample 9	0.0000	0.0000
Sample 10	0.1539	0.0000

Comparative analysis of the two methods highlighted the advantages and limitations of each. XRF provides a total picture, including insoluble forms, but is sensitive to matrix effects and may overestimate the concentrations of some elements in trace. On the other hand, ICP-OES is more accurate for soluble oxides and gives reproducible results for major and minor dissolvable elements, but underestimates refractive components.

The differences observed between samples in MgO and Fe_2O_3 reflect not only the internal mineralogical variation but also the degree of serpentinization homogeneity. Samples with higher MgO and lower Fe_2O_3 suggest a dominant presence of lizardite, while those with higher iron contents may contain higher proportions of chlorite or magnetite. These observations are important for the petrogenetic interpretation of ultrabasic sequences and may contribute to the identification of zones of economic interest for transition-metal deposits.

The results of the H_2O and CO_2 content determinations are summarized in Table 4:

Table 4. H_2O and CO_2content of serpentinite samples

Sample	Component	
	CO_2	H_2O
Sample 1	1.4642	10.5054
Sample 2	0.0000	18.7194
Sample 3	0.0000	12.9012
Sample 4	0.0000	13.3034
Sample 5	0.0000	11.7034
Sample 6	0.0000	13.7473
Sample 7	0.0000	14.9854
Sample 8	1.0359	10.7751
Sample 9	1.8058	9.0014
Sample 10	0.3946	11.1660

6 Interpretation of results and discussion

The results obtained from analyzing the 10 serpentinite samples reveal notable differences in magnesium (Mg) and iron (Fe) concentrations, depending on the analytical method employed. In this study, determinations for most oxides were performed using X-ray fluorescence spectrometry (XRF). At the same time, values for magnesium and iron were also validated by inductively coupled plasma optical emission spectrometry (ICP-OES).

By XRF, MgO contents ranged from 29.6% to 36.2%, while Fe_2O_3 ranged from 15.4% to 21.1%. These values are in agreement with the literature for serpentinites of ophiolitic origin, with a mineralogy rich in lizardite and clinohrysotile. In contrast, the values determined by ICP-OES for the same elements were in all cases lower. For Mg, the differences were significant, in some cases up to 5-6%, and for Fe, between 1-2%, which emphasizes a systematic underestimation in the ICP-OES method when applied to serpentinized matrices.

The chemical mechanism of each method can explain this discrepancy. ICP-OES requires complete acid digestion of the sample, and in ultrabasic rocks, rich in refractory phases such as magnetite, chromite or spinels, complete solubilization is not always possible. Thus, the insoluble fraction of Fe and Mg present in these oxides is not quantified, leading to lower than real values. XRF, by analyzing the whole sample (including insoluble components), more faithfully reflects the total content.

The differences between the two methods are relevant not only analytically but also in petrogenetic interpretation. In the context of serpentinite studies, where the Mg/Fe ratio is indicative of the degree of alteration and the identification of the predominant serpentine type, underestimating iron or magnesium may alter the conclusions regarding the metamorphic processes involved. For example, a sample with an artificially overestimated Mg/Fe ratio could be misinterpreted as being less altered or having a composition closer to that of olivine. However, this effect may be strictly analytical.

Another important aspect is to assess the correlation between the two data sets. Although the ICP-OES values for Mg and Fe were consistently lower, the relative distribution of the samples was similar to that obtained by XRF. This suggests that, although the absolute values differ, the methods converge in terms of differentiation between samples. In this sense, ICP-OES can be used to confirm trends but not for absolute quantification without a solubility correction.

These differences must be taken into account in any study using geochemical data from serpentinites, particularly when results from different methods are compared. The methodological recommendation is that, in such contexts, XRF should be used as the main method for total estimation and ICP-OES as a control method, with the insoluble fraction taken into account.

In conclusion, the comparative analysis of the results for magnesium and iron demonstrates the need for an integrated approach in the study of serpentinites. The values obtained by XRF are closer to the actual total content of the sample, while ICP-OES provides useful but incomplete information on the soluble fraction. The choice of method should take into account the geological context, the type of minerals expected, and the desired level of accuracy of interpretation.

Comparison between ICP-OES and XRF methods for the determination of iron in ferrous serpentinite

Ferrous serpentinite contains significant amounts of iron oxides and silicates (e.g. magnetite, hematite, ferromagnetizing olivine), which are difficult to dissolve completely in ordinary acid solutions. This affects the correct determination of iron by liquid analytical methods (e.g. ICP-OES) [5]. Some examples from the literature are given in Table 5:

Table 5. Examples from the literature of the differences in iron contents determined by XRF and ICP-OES methods

Sample	Method	Total Fe (%)	Remarks
Serpentinite Balkans	XRF	7.85	Melt pellet analysis; total iron detected
	ICP-OES	6.10	Partial dissolution with HNO_3 and HCl - Fe underestimated
Serpentinite California	XRF	8.30	High presence of magnetite; total value
	ICP-OES	6.50	No HF attack - incomplete dissolution of oxides
Serpentinite Norway	XRF	7.40	Value close to mineralogically estimated total iron
	ICP-OES	5.90	Partial attack - missing recovery from olivine ferromagnesian olivine

The data in the table confirm that the XRF method gives values closer to the true total iron content. In contrast, ICP-OES underestimates the iron concentration if sample dissolution is not complete. The differences are frequently between 1-2% absolute Fe, which is significant in the geochemical interpretation of serpentinite [13].

The determination of silver (Ag) by X-ray fluorescence (XRF) in serpentinite samples can be affected by multiple spectral and matrix interferences. Since silver is a rare element in ultrabasic rocks, its detection in high concentrations (>500 ppm) requires a rigorous analysis of the sources of error [11]. In case of occurrence of implausible results for silver content, the following causes may be present:

- Spectral interferences (line overlaps): the Lα line of silver (~2.98 keV) may overlap with the emission lines of other heavy elements, such as:
  - Cd Lα = 3.13 keV
  - Sn Lα = 3.44 keV
  - In Lα = 3.29 keV

These overlaps can lead to Ag misreporting if interfering elements occur in the matrix [13].

- 2.2.2 Matrix effects: Serpentinite has a matrix rich in MgO, FeO and SiO_2, which influences X-ray absorption and emission:
  - - Fe can partially absorb the Ag signal
  - - Mg-Fe matrix reduces the accuracy of background corrections
  - - Standard empirical corrections may fail in such unusual compositions.

Verification and control measures are employed to address these issues:

- Verification of samples with suspect contents by alternative methods (e.g., ICP-MS, SEM-EDS);
- Use of melts and not only pressed pellets to reduce matrix effects;
- Correlation of Ag values with sample mineralogy and geological localization;
- Application of specific matrix corrections and verification against certified standards [11].

The high Ag contents reported by XRF in serpentinite may be the result of spectral interferences, inadequate matrix corrections or contamination. Confirmation by other methods and mineralogical and geological evaluation of the samples is essential to validate the result [11].

Rhodium (Rh) is a very rare element in nature and occurs in extremely low concentrations in ultrabasic rocks. Detection of high concentrations (>3000 ppm) of Rh in serpentinite analyzed by XRF is very unusual and requires careful evaluation of possible analytical and geological interferences. In case of the occurrence of unverifiable results for rhodium content, the following causes may be present:

- Spectral interferences: the Kα line of Rh (~20.2 keV) may suffer interferences with other heavy metals or be influenced by secondary reflections. L-lines from elements such as Mo, Ru, Pd and Zr can interfere with the Rh signal if present in the matrix.
- Matrix effects: The serpentinite matrix, rich in MgO, FeO, and silicates, affects X-ray absorption and emission:
  - High Fe can affect Rh excitation;
  - The unusual composition leads to biased results in the absence of melting or specific calibrations [11].
- Background signals and contamination:
  - Inhomogeneous powders may contain metallic inclusions or refractory oxides that affect spectra.

Rhodium occurs naturally only in concentrations on the order of ppb (0.001 ppm) in normal serpentinites. Values of 3000 ppm are improbable and indicate either a serious analytical error or major contamination. In areas with platiniferous mineralization, Rh can reach a maximum of a few ppm [12].

For the edification of these aspects, verification and control measures are challenged:

- Confirmation by ICP-MS or electron microprobe (EPMA);

- Verification of suspect samples by SEM-EDS;
- Use of calibrated Rh-calibrated ultrabasic rock melts and standards;
- Assess geologic location and exclude samples from anthropogenic or contaminated sources.

Values of 3000 ppm Rh in serpentinite are highly suspect. In the absence of documented noble mineralization, these are most likely the result of severe XRF interference or sample contamination. It is essential to verify the results by complementary methods and mineralogical analysis [12].

Conclusions

The mineralogical and geochemical study of the serpentinite samples shows a composition dominated by lizardite and antigorite minerals, locally accompanied by accessory phases such as magnetite and carbonate minerals (magnesite, calcite). X-ray fluorescence spectrometry (XRF) analyses indicate a significant content of magnesium oxides ($MgO > 35\%$) and silicon ($SiO_2 > 40\%$), consistent with the ultrabasic nature of these rocks. The low Al_2O_3, CaO, K_2O and TiO_2 contents reflect an advanced degree of hydrothermal alteration and an initial feldspar-poor composition.

Loss on ignition (LOI) gravimetric determinations yield significant mass loss values (>12%), primarily due to structural water (H_2O) bound within the serpentine network and, to a variable extent, carbon dioxide (CO_2) from secondary carbonate mineralization. The integration of the analytical methods used - XRF, LOI - provides a coherent and complementary picture of the chemical and mineralogical composition of the samples studied. This approach allows not only the identification of the main mineral phases but also the quantification of the volatile components, which are essential in assessing the degree of hydrothermal alteration and the geochemical potential of these rocks.

In the current context of geological carbon sequestration studies, the analyzed serpentinite proves to be a valuable candidate due to its ability to incorporate CO_2 in stable form through mineral carbonation reactions. Thus, the integrated characterization performed in this work provides a robust analytical framework for further investigation of the applicability of serpentinite in geoengineering and environmental technologies.

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