



# Origins of ore-forming fluids in the Mežica carbonate-hosted Pb-Zn deposit inferred from sphalerite halogen systematics

## Izvor rudotvornih fluidov v Pb-Zn rudišču Mežica določen na podlagi halogenske sistematike sfalerita

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*Ključne besede:* sfalerit, halogeni, geokemija, izvor fluidov, Mežica, Slovenija

### Abstract

Halogen (Cl-Br-I) systematics in sphalerite from the Pb-Zn deposit of Mežica provide new insights into the origin and evolution of ore-forming fluids. The data confirm and refine previous interpretations based on stable isotope analyses and sphalerite trace-element compositions, indicating that the fluids were derived from evaporated seawater and subsequently modified by basinal brines. Two principal fluid types are identified: a Br-poor fluid consistent with evaporatively concentrated seawater, and a Br- and I-enriched fluid representing a basinal brine modified through interaction with organic matter. Particularly notable are Br-rich samples characterized by exceptionally high Br/Cl ratios coupled with pronounced iodine enrichment. These values significantly exceed the typical range observed in MVT-type deposits and constitute a key geochemical hallmark of the Mežica mineralizing system. Stratigraphic and regional geological constraints indicate that mineralization occurred from the Late Triassic to the Early Jurassic. Restricted lagoonal and shallow-marine environments facilitated repeated seawater evaporation and the formation of dense brines, which infiltrated deeply into the subsurface. Subsequent basin deepening following the Triassic-Jurassic transition likely curtailed further brine generation. Organic matter played a pivotal role in the system, contributing both reduced sulfur and a significant proportion of halogen elements. The evolution of the mineralizing system was governed by the interplay between fluid mixing and fluid-rock interaction, ultimately producing the distinctive halogen signature observed in Mežica sphalerite.

### Izveček

Sistematika halogenov (Cl-Br-I) v sfaleritu iz Pb-Zn rudišča Mežica prinaša nova spoznanja o izvoru in evoluciji rudotvornih raztopin. Pridobljeni podatki potrjujejo in nadgrajujejo predhodne interpretacije, utemeljene na analizah stabilnih izotopov in elementne sestave sfalerita, ter kažejo na izvor raztopin iz evaporirane morske vode z naknadno modifikacijo pod vplivom bazenskih slanici. Identificirana sta bila dva glavna tipa fluidov: z bromom osiromašen fluid, ki ustreza evaporativno koncentrirani morski vodi, ter fluid, obogaten z bromom in jodom, ki predstavlja z organsko snovjo preoblikovano bazensko slanico. Posebej izstopajo vzorci, bogati z Br, za katere so značilna izjemno visoka razmerja Br/Cl ter izrazita obogatitev z jodom, kar bistveno presega običajen razpon halogenskih razmerij v rudiščih tipa MVT in predstavlja ključno geokemijsko značilnost mežiškega rudotvornega sistema. Stratigrafski in regionalno-geološki podatki kažejo, da je orudenje potekalo v obdobju od poznega triasa do zgodnje jure. Restriktivna lagunska in plitvomorska okolja so omogočala ponavljajoče se izhlapevanje morske vode in nastanek gostih slanici, ki so pronicale globoko v podzemlje, medtem ko je kasnejše poglobljanje sedimentnih okolij po triasno-jurski meji verjetno omejilo njihovo nadaljnje nastajanje. Organska snov je imela v sistemu pomembno vlogo, saj je prispevala tako reducirano žveplo kot tudi pomemben delež halogenih elementov. Evolucijo rudotvornega sistema je nadzorovalo prepletanje mešanja fluidov in interakcij med kamnino in rudotvorno raztopino, kar je privedlo do značilnega halogenskega podpisa sfalerita iz Mežice.

## Introduction

Halogens are essential to the chemistry of crustal fluids and ore-forming systems because they strongly affect metal solubility, complex formation, and fluid salinity (e.g., Rosset, 1975; Walter et al., 2016; Frenzel et al., 2020; Han et al., 2022; Kendrick, 2024). Within this group, fluorine (F) and chlorine (Cl) are by far the most abundant halogens in the continental crust, while bromine (Br) and iodine (I) are present only in smaller amounts (Yardley, 2005; Kendrick, 2024). Mass-balance calculations indicate that most fluorine is stored in solid Earth reservoirs, primarily within the crust and mantle (Han et al., 2022). This reflects its moderately incompatible behavior combined with relatively low mobility at Earth's surface, leading to its retention within crustal rocks (e.g., Kendrick, 2024). From a mineralogical perspective, this is further supported by the stability of common fluorine-bearing minerals such as fluorite and apatite. In contrast, Cl, Br, and I are strongly incompatible and highly soluble, commonly occurring in readily dissolved phases such as salts. These properties allow them to remain mobile in surface and near surface environments, making them highly reactive and deeply involved in a wide range of geochemical processes, which in turn leads to their widespread distribution among crustal rocks, the oceans, and other near surface reservoirs (Han et al., 2022; Kendrick, 2024). Halogen contents and their ratios are particularly informative. The relative abundances of Cl and Br can be used to distinguish between seawater-derived fluids, evaporite dissolution, and magmatic or metamorphic contributions (Markl & Bucher, 1998; Svensen et al., 2008; Dolejš & Zajacz, 2018; Hammerli & Rubenach, 2018; Kendrick et al., 2011). However, it should be noted that halogen systematics are not always uniquely diagnostic of fluid sources, as similar signatures may arise from different reservoirs and can be significantly modified by processes such as evaporation, fluid-rock interaction, and fluid mixing (e.g., González-Esvertit et al., 2024). Iodine is particularly sensitive to interactions with organic-rich sedimentary rocks and hydrocarbons. As a result, elevated I/Cl ratios in ore minerals can indicate contributions from basinal fluids that have interacted with mature shales or oil-gas systems (e.g., Fusswinkel et al., 2022; Scharrer et al., 2023). The Br/I ratio further helps to evaluate the origin of bromine by distinguishing between signatures produced by evaporative concentration and those derived from interaction with organic matter (e.g., Collins, 1969; Flores et al., 2008; Kendrick et al., 2011).

The region spanning northern Italy, Slovenia, and southern Austria forms an economically important metallogenic province, hosting more than one hundred carbonate-hosted Pb-Zn deposits collectively referred to as Alpine-type deposits (e.g., Drovenik et al., 1980; Melcher et al., 2023; Summino et al., 2023; Giorno et al., 2025). Among these, the Mežica Pb-Zn deposit, hosted in Middle to Upper Triassic platform carbonates within the Northern Karawanke/Drau Range units of the Eastern Alps, represents one of the most significant (Melcher et al., 2023). The formation of these deposits is characterized by the involvement of Cl-rich basinal brines, which acted as highly efficient metal-transporting agents (Leach et al., 2010). Their elevated salinity enhances the leaching of metals from the basement rocks, while chloride complexation stabilizes these metals in solution, enabling long distance fluid migration (e.g., Kesler et al., 1996; Leach et al., 2010; Emsbo et al., 2016; Sangster, 2017). In addition to chlorine, evolving brines may also incorporate other halogens, particularly bromine and iodine, during deep circulation and interaction with sedimentary and organic-rich lithologies (e.g., Kendrick et al., 2002, 2005, 2011). The resulting halogen signatures provide valuable tracers of fluid origin, migration pathways, and fluid-rock interaction processes.

Despite extensive research on the mineralogy, fluid inclusions, and stable isotope systematics of the Mežica Pb-Zn deposit (e.g., Drovenik et al., 1980; Spangenberg & Herlec, 2006; Herlec et al., 2010; Melcher et al., 2023), there is still no information on the halogen chemistry of the main ore and gangue minerals, including sphalerite. This is an important gap because halogen concentrations and ratios in ore minerals can provide sensitive records of the composition and evolution of mineralizing fluids, especially in systems where fluid mixing is thought to have occurred (e.g., Kendrick et al., 2011; Frenzel et al., 2020). Previous studies, based on stable isotopes and sphalerite trace-element data, suggest that mixing between Middle to Late Triassic seawater and evaporite-derived basinal brines played a major role in the mineralization process (e.g., Drovenik et al., 1980; Spangenberg & Herlec, 2006; Herlec et al., 2010; Melcher et al., 2023). However, direct geochemical evidence for this process has so far been limited. By analyzing the halogen content of sphalerite, this study adds a new, independent tracer of fluid sources and mixing processes, offering a more detailed understanding of how fluids evolved during ore deposition in the Mežica district.

## Geological context

From a structural perspective, the study area is situated within the Eastern Alps, specifically in the North Karavanke subunit (Placer, 2008). The present-day geological architecture of the Eastern Alps consists of an imbricated stack of nappe systems, which are subdivided into the Lower, Middle, and Upper Austroalpine units based on their position relative to the high-pressure eclogite belt (e.g., Schmid et al., 2004; Vrabec et al., 2012; Janák et

al., 2015). Regionally, the North Karavanke unit corresponds to the Drauzug-Gurktal nappe system, an integral component of the Upper Austroalpine (Hass et al., 2020). The Drauzug-Gurktal system comprises Paleozoic basement rocks overlain by a Permo-Mesozoic sedimentary cover. These units are disconformably overlain by Oligo-Miocene rocks of the Pannonian Basin System (e.g., Placer et al., 2008; Ivančič et al., 2024, 2025)

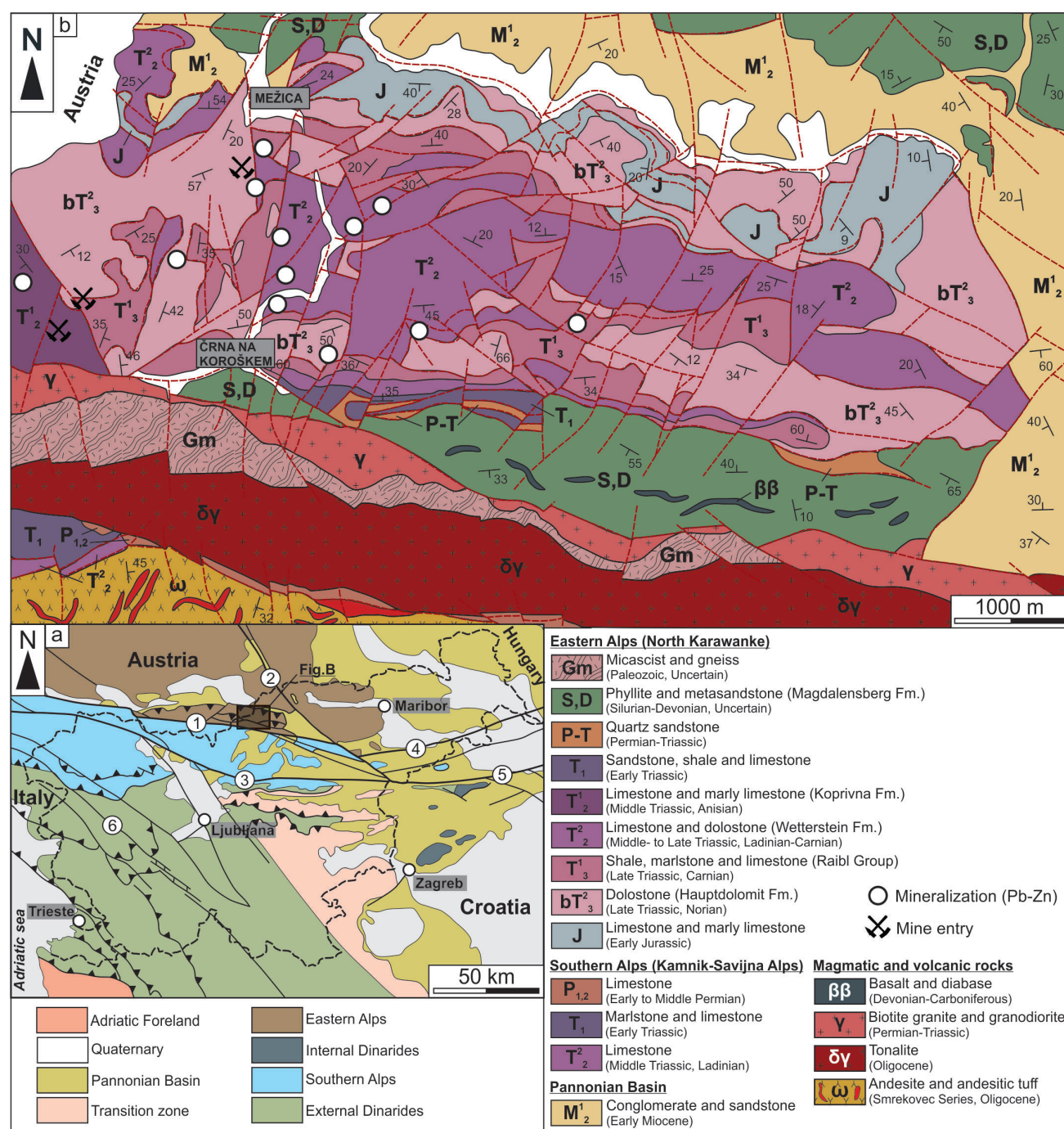


Fig. 1. Geology of the Mežica mine area. Figure (a) shows the location of the study area within its regional geological context (modified after Placer, 2008), while Figure (b) presents a geological map highlighting the lithological units surrounding the Mežica mine. Key: (1) Periadriatic Fault, (2) Lavanttal Fault, (3) Sava Fault, (4) Ljutomer Fault, (5) Donat Fault, (6) Idrija Fault. Map adapted and modified from Mioč & Žnidarčič (1983).

The basement unit consists of low-grade metasedimentary rocks, including micaschists of uncertain age, as well as rocks of the Silurian-Devonian Magdalensberg Formation (Mioč & Žnidarčič, 1983). Separated by unconformity, these basement units' transition upward into the Permo-Mesozoic cover sequence. The Permo-Mesozoic rock sequence of the Drauzug-Gurktal nappe cover begins with Permo-Triassic (Werfen Fm.) strata composed of continental sedimentary rocks, which were deposited onto the basement units of Silurian-Devonian Magdalensberg Series (Mioč & Žnidarčič, 1983; Dozet & Buser, 2009). Anisian rocks crop out west of Mežica in the Topla Valley and consist of dark grey, bedded limestone interlayered with dolostone, collectively known as the Koprivna Formation, which attains a total stratigraphic thickness of approximately 300 m (Mioč & Žnidarčič, 1983; Dozet & Buser, 2009). Anisian beds are overlain by approximately 1000 m thick Wetterstein Formation, composed of Ladinian to Early Carnian platform carbonates (Dozet & Buser, 2009). The Wetterstein Formation comprises platformal shallow-marine deposits characterized by interlayered limestone and dolostone, locally containing stromatolitic and oncoidal facies with typical Lofer cyclic development (Štrucl, 1984; Dozet & Buser, 2009). These features indicate deposition in a shallow lagoonal, subtidal setting with periodic emersion and the formation of paleokarst surfaces. The upper 600 m of the Wetterstein Formation is mineralized with lead and zinc (Drovenik et al., 1980; Štrucl, 1984; Herlec et al., 2010; Melcher et al., 2023). Wetterstein Formation is overlain by Julian and Tuvanian rocks of the Raibl Group. The Raibl Group records alternating carbonate and clastic sedimentation driven by sea-level fluctuations in a marginal-marine setting during the Carnian (e.g., Jurkovšek, 1978; Bechstädt & Schweizer, 1991; Jurkovšek et al., 2002; Kolar-Jurkovšek & Jurkovšek, 2009). Carbonate intervals reflect restricted tidal, lagoonal, and locally evaporitic environments, whereas clastic intervals represent inner- to outer-shelf sedimentation (Bechstädt & Schweizer, 1991). Notably, regressions are characterized by carbonate production, while transgressions favor clastic influx, producing three 50–100 m thick depositional cycles, locally named Raibl shale horizons. Lithotypes include shale, oolitic and oncoidal limestones (Jurkovšek et al., 2002; Krainer et al., 2011), formed through a combination of deltaic input, platform redistribution, and sea-level controlled sedimentation. The Hauptdolomit, which overlies the Raibl Group (Mioč & Žnidarčič, 1983; Cerny,

1989), represents a shallow-water, restricted carbonate platform dominated by tidal-flat, lagoonal, and barrier-shoal environments (e.g., Fruth & Scherreiks, 1982; Mioč & Žnidarčič, 1983; Fruth & Scherreiks, 1984). Regionally, several environmentally controlled facies units have been recognized, with inter- to infratidal carbonates locally exceeding 1000 m in thickness. Geochemical patterns support facies differentiation and indicate early diagenetic dolomitization superimposed on original tidal-flat and lagoonal deposits. Overlying the Hauptdolomit, the Kössen Formation records a mixed carbonate-siliciclastic succession deposited on a shallow peritidal shelf along the Western Tethyan margin in the Late Triassic (Cerny, 1989; Della Porta et al., 2023; Herlec et al., 2010). It is characterized by peritidal cyclothems composed of calci-mudstone, stromatolitic laminites, and occasional coral boundstones, reflecting repeated transitions between intertidal flats, restricted lagoons, and shallow subtidal environments (Della Porta et al., 2023). Early diagenetic features, such as dissolution cavities, meniscus cements, and microbial crusts, further indicate intermittent subaerial exposure and consistently very shallow-marine conditions (Turnšek et al., 1999; Della Porta et al., 2023). The Kössen Formation is conformably overlain by Early Jurassic red and brown massive limestones and intraformational breccias (Ramovš & Rebek, 1970; Buser & Dozet, 2009).

## Materials and methods

### Materials and sample preparation

Sphalerite samples used in this study were acquired from Moring orebody of the Mežica mine. The analyses were performed on sphalerite concentrates prepared by crushing the ore samples, followed by manual gravitational separation using panning. The resulting mineral concentrates were air-dried and subsequently packaged for analysis by instrumental neutron activation analysis (INAA).

### Instrumental neutron activation analysis (INAA)

One-gram samples were sealed in poly vials and irradiated at a thermal neutron flux of  $7 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  using a computer-controlled rabbit system, which transported the vials directly to the reactor core and subsequently returned them to the laboratory fume hood for processing. After irradiation, the samples were allowed to decay for an appropriate interval to minimize contributions from aluminum and other very short-lived radionuclides. They were then counted sequentially for

the nuclides of interest (Cl, I, Br). Measured activities were corrected for decay and quantified using a calibrated standard curve. Each analytical batch included two standards. Detection limits for the analyzed elements are provided in Table 1. The detailed analytical procedure is described in Hoffman (1992). All analyses were carried out at Activation Laboratories, Ontario, Canada.

Table 1. Detection limits for Br, Cl, and I determined by instrumental neutron activation analysis (INAA).

| Element | Detection limit         |
|---------|-------------------------|
| Br      | 5.0 mg kg <sup>-1</sup> |
| Cl      | 100 mg kg <sup>-1</sup> |
| I       | 0.5 mg kg <sup>-1</sup> |

## Results

### Sphalerite petrography

The zinc ore investigated in this study was collected from the Moring ore body of the Mežica mine (Fig. 2). The sample represents a mineralized

breccia in which sphalerite occurs in textural associations indicative of both clast replacement (Fig. 2c–d, f) and open-space infilling (Fig. 2e–g). Replacement sphalerite is fine-grained and disseminated within host-rock clasts, and is commonly associated with minor carbonate. In contrast, open-space infill sphalerite forms as successive breccia cements. Along clast margins, it develops as dark orange to brown subhedral crystals with locally preserved crystal terminations (Fig. 2e, f). Toward the interior, this sphalerite grades into massive, lighter orange, texturally homogeneous cavity-filling aggregates. The occurrence of angular features and locally coarser grains, texturally comparable to those observed along clast margins, may reflect complete replacement of earlier clasts; however, this interpretation remains equivocal due to the absence of preserved carbonate relics (Fig. 2g). Secondary fracture porosity is subsequently infilled by vein carbonates and late-stage zinc minerals, predominantly smithsonite. Under long-wave ultraviolet irradiation ( $\lambda = 365$  nm), all investigated sphalerite exhibits photoluminescence expressed in varying orange hues (Fig. 2a, b).

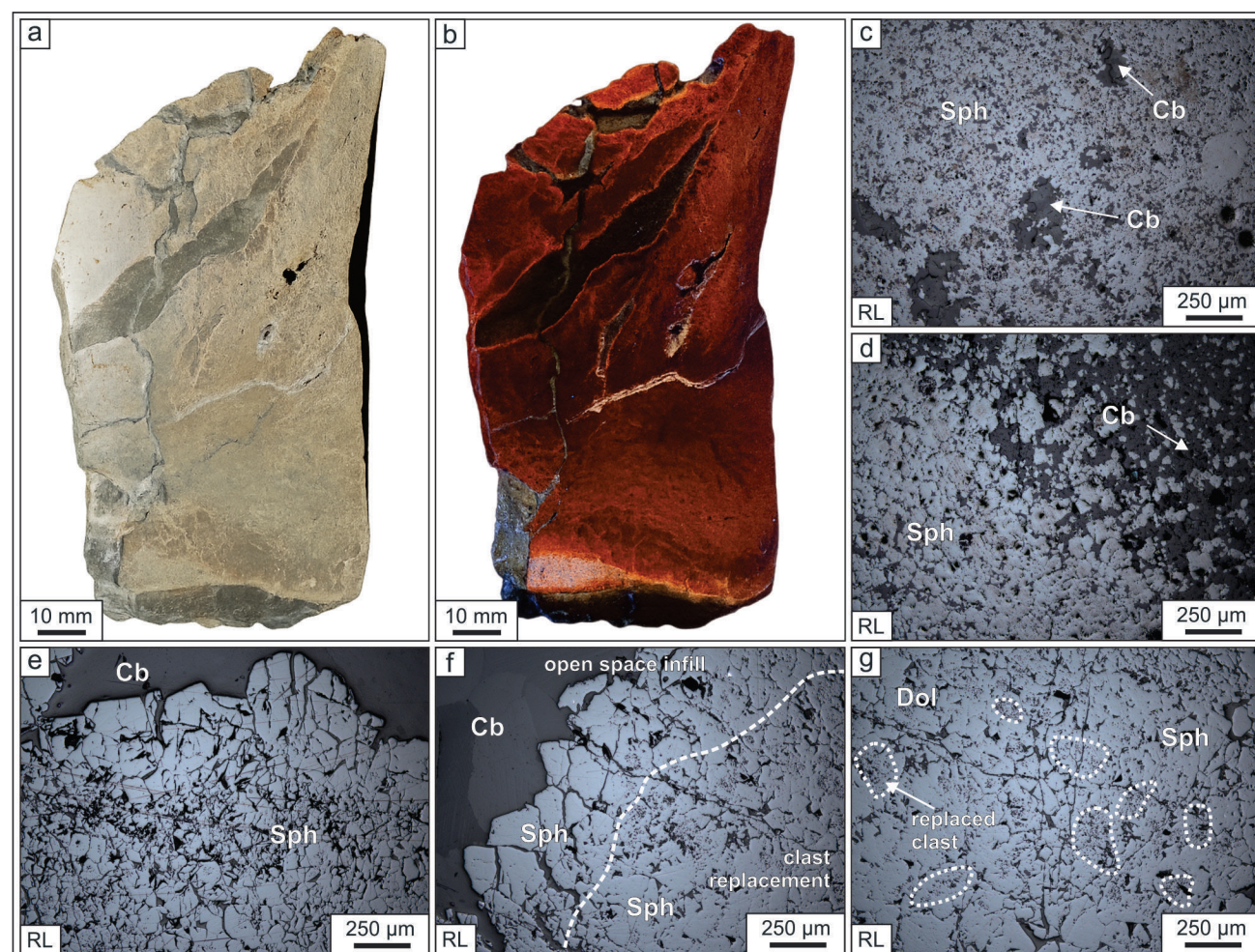


Fig. 2. Hand-sized specimen and photomicrographs illustrating the principal microtextural features of the analyzed sphalerite.

## Halogen geochemistry of Mežica sphalerite

A total of five sphalerite mineral concentrate samples were analyzed by INAA, and their halogen concentrations are summarized in Table 2. Sphalerite contains measurable amounts of all analyzed halogens, although abundances vary by up to an order of magnitude among samples. Halogen concentrations define two compositionally distinct types, with the samples classified as either Br-rich or Br-poor based on their halogen signatures. Br-rich samples (ME-H-1 to ME-H-3) contain elevated bromine concentrations of 17–26 mg kg<sup>-1</sup>, accompanied by chlorine values of 500–600 mg kg<sup>-1</sup> and iodine contents of 2.4–5.5 mg kg<sup>-1</sup>. In contrast, Br-poor samples (ME-H-4 and ME-H-5) exhibit markedly lower bromine concentrations (BDL–7.0 mg kg<sup>-1</sup>) but consistently higher chlorine levels (700 mg kg<sup>-1</sup>) and comparatively low iodine contents (≈1.02 mg kg<sup>-1</sup>).

## Discussion

### Halogen ratios as fluid provenance indicators

Halogen ratios, particularly Br/Cl, I/Cl, and Br/I, are powerful geochemical tracers for constraining the origin and evolution of crustal and hydrothermal fluids (e.g. Kendrick et al., 2011; Burisch et al., 2016; Frenzel et al., 2020; Scharer et al., 2023). The rationale behind their use stems from the distinct chemical behaviors of Cl, Br, and I during evaporation, halite crystallization, and organic-matter interaction. Bromine and iodine are strongly incompatible with evaporites during seawater evaporation, leading to progressive enrichment of Br and I in residual bittern brines (Zherebtsova & Volkova, 1966; Holser, 1979; Kendrick et al., 2011). Thus, elevated Br/Cl ratios typically reflect brines formed by evaporation of seawater beyond halite saturation (McCaffrey et al., 1987; Hanor, 1994; Kendrick et al., 2005; Sun et al., 2019), whereas lower Br/Cl values indicate brines derived from halite dissolution or reflect seawater infiltration (Br/Cl=1.54×10<sup>-3</sup> (molar); e.g., Kendrick et al., 2011). In contrast, iodine exhibits an even lower compatibility in evaporite minerals but a strong affinity for organic matter,

making I/Cl ratios sensitive indicator of fluid interaction with organic-rich sediments or diagenetic pore waters (Kennedy & Elderfield, 1987; Worden, 1996; Kendrick et al., 2011; Fusswinkel et al., 2022; Scharer et al., 2023). The Br/I ratio offers a useful indicator of the relative influence of evaporative and organic sources. This is because biological processes preferentially concentrate iodine over bromine, producing relatively low organic Br/I ratios (<10; e.g., Collins, 1969; Flores et al., 2008) compared to the very high ratio of seawater (≈1900; Kendrick et al., 2011).

Halogen ratios in Mežica sphalerite define two compositional groups (Table 2 and Fig. 3), namely a Br-rich type and a Br-poor type. These groups form two clearly distinguishable groups in Br/Cl, I/Cl and Br/I space. The Br-rich sphalerite displays exceptionally high Br/Cl ratios (1.5–2.3×10<sup>-2</sup>; average 1.8 × 10<sup>-2</sup>), more than an order of magnitude above seawater. Such values indicate fluids that evolved well beyond halite saturation, where continued removal of chlorine during halite precipitation produced strong enrichment in bromine (Zherebtsova & Volkova, 1966; McCaffrey et al., 1986; Walter et al., 1990; Hanor, 1994; Sun et al., 2019). These samples also show elevated I/Cl ratios (1.3–3.1×10<sup>-3</sup>; average: 1.9 × 10<sup>-3</sup>) that cannot be generated by simple seawater evaporation because iodine does not increase to this extent along an evaporative trajectory. The high I/Cl ratios therefore require a significant input of iodine from organic-rich lithologies or diagenetic pore waters (Biester et al., 2004; Kendrick et al., 2011; Fusswinkel et al., 2022). The resulting intermediate Br/I ratios, which fall between about 10 and 17 (average: 10.98), are far lower than seawater values (≈1900) yet higher than those of typical organic endmembers which are usually below 10 (e.g., Collins, 1969; Flores et al., 2008). This pattern is consistent with mixing between a highly evaporated, seawater-derived brine and a halogen-enriched fluid (I and Br) produced through interaction with buried organic matter, diagenetic pore waters, and/or hydrocarbons (Zherebtsova & Volkova, 1966; Nissenbaum, 1977; McCaffrey et al., 1986; Birkle et al., 2009). However, the magni-

| Sample | Type    | Br [mg kg <sup>-1</sup> ] | Cl [mg kg <sup>-1</sup> ] | I [mg kg <sup>-1</sup> ] |
|--------|---------|---------------------------|---------------------------|--------------------------|
| ME-H-1 | Br-rich | 21                        | 600                       | 3.1                      |
| ME-H-2 | Br-rich | 26                        | 500                       | 2.4                      |
| ME-H-3 | Br-rich | 17                        | 500                       | 5.5                      |
| ME-H-4 | Cl-poor | BDL                       | 700                       | 1.03                     |
| ME-H-5 | Cl-poor | 7                         | 700                       | 1.02                     |

Table 2. Concentrations of halogens (Cl, Br, I) in sphalerite from the Mežica deposit determined by instrumental neutron activation analysis. Values are reported in mg kg<sup>-1</sup>. BDL – value below detection limit.

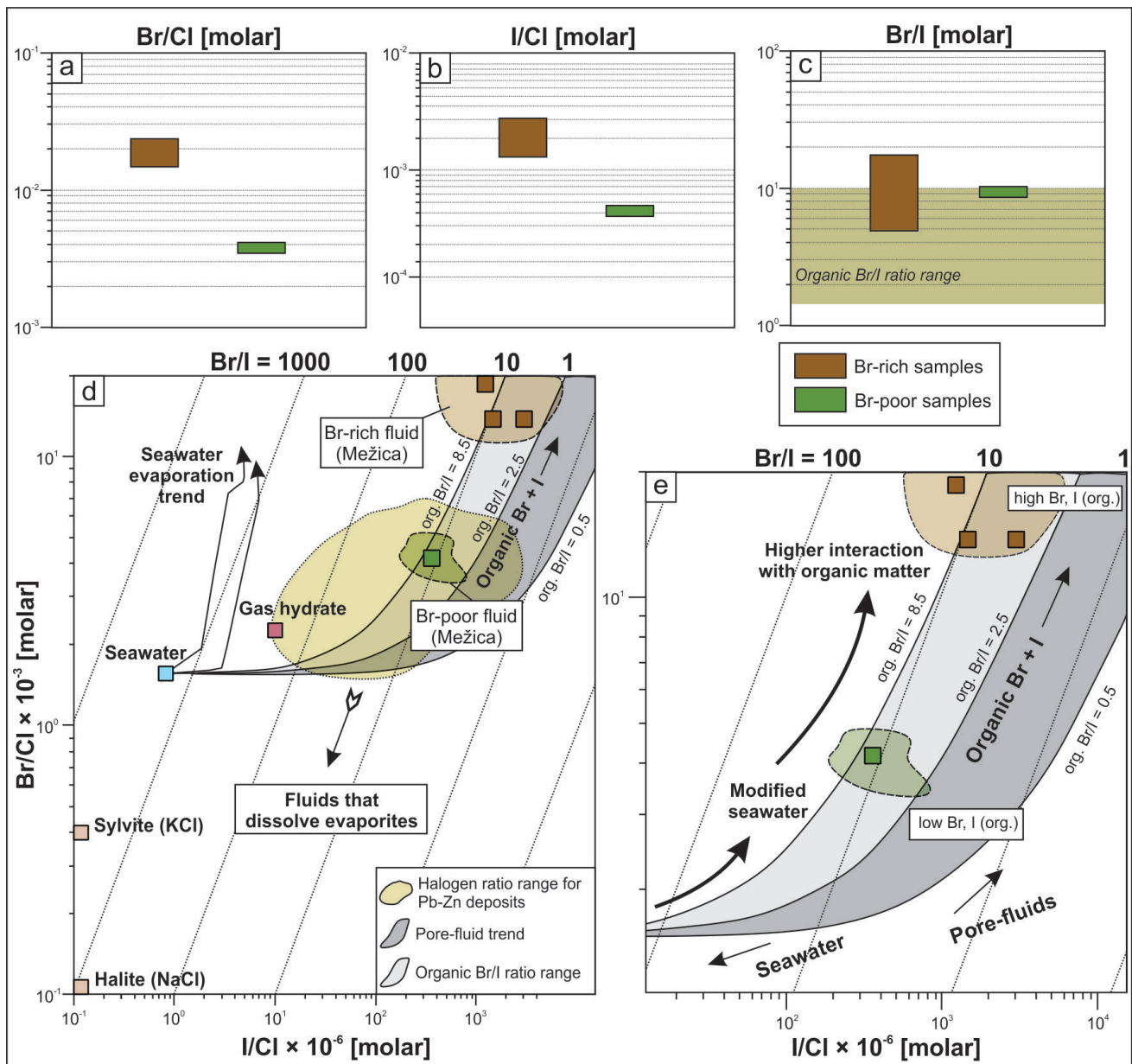


Fig. 3. Plots showing ranges of molar Br/Cl (a), I/Cl (b), and Br/I (c) ratios of Br-rich and Br-poor sphalerite from the Mežica mine. The shaded field marks the characteristic range of organic Br/I ratios (Collins, 1969; Biester et al., 2004; Flores et al., 2008; Kendrick et al., 2011). Panel (d) presents Br/Cl vs. I/Cl halogen systematics for Mežica sphalerite, compared with fields for global Pb-Zn deposits. Panel (e) highlights the Mežica samples trending from seawater toward modified and organic-influenced pore fluids. The framework for figures (d) and (e) is adapted from Kendrick et al. (2011) using data from Zhrebtsova & Volkova (1966), Bentor (1969), Carpenter and Miller (1969), Collins (1969), Hitchon et al. (1971), Böhlke & Irwin (1992), Ferguson et al. (1993), Kendrick et al. (2002, 2005), Popov (2003), Bottomley et al. (2005), Fehn & Snyder (2005), and Fu & Zhan (2009).

tude of enrichment suggests a more complex scenario, involving interaction among, and progressive overprinting by, multiple fluid sources rather than simple binary mixing (e.g., González-Esvertit et al., 2025).

Br-poor samples display lower Br/Cl values ( $4.4 \times 10^{-3}$ ) than the Br-rich group, yet the ratios remain well above seawater ( $1.54 \times 10^{-3}$ ) and clearly above the threshold expected for halite dissolution (approximately  $5.0\text{--}6.0 \times 10^{-4}$ ). Such values cannot be generated through halite dissolution and instead point to a fluid that preserves a modified marine signature, consistent with limited evapo-

ration or interaction with Br-bearing fluids or organic matter (Fig. 3d–e). Their I/Cl ratios ( $4.0 \times 10^{-4}$  to  $4.1 \times 10^{-4}$ ; average:  $4.0 \times 10^{-4}$ ) are much lower than those of the Br-rich samples but still two orders of magnitude higher than seawater, which rules out involvement of halite dissolution fluids because these contain only trace amounts of iodine (e.g., Holser, 1979; Worden, 1996). Although the relatively low I/Cl ratios might at first imply a more seawater dominated fluid, the Br/I ratio of 10.90 fall fully within the range expected for fluids influenced by organic matter, which typically show values below 10 (e.g., Collins, 1969;

Biester et al., 2004; Kendrick et al., 2011). This suggests that also the Br-poor fluid component experienced interaction with organic-rich sediments and/or Br- and I-enriched diagenetic fluids, likely akin to those contributing to the Br-rich endmember. Accordingly, the Br-poor samples are best interpreted as representing a moderately evolved, seawater-derived fluid that underwent only limited Br enrichment via fluid mixing, without necessitating significant gypsum dissolution or extensive evaporative concentration.

The halogen compositions of the Br-poor samples overlap with those of global basinal brines associated with similar Pb-Zn mineralizations (Fig. 3d), which typically show modest Br-enrichment together with variable contributions from organic sources (Fig. 3d). In contrast, the Br-rich samples are anomalous because they display both extreme Br/Cl ratios and substantial iodine enrichment, placing them outside the compositional fields of typical MVT systems and basinal brines (Kendrick et al., 2005, 2011; Liu et al., 2017). Such signatures can develop when basinal brines interact with organic-rich sediments or oilfield fluids, which release organically bound bromine and iodine (Birkle et al., 2009; Kendrick et al., 2011). The high I/Cl ratios in the Br-rich samples, which exceed predicted values for evaporative bittern brines by three orders of magnitude (Zherebtsova & Volkova, 1966), provide strong evidence that the elevated halogen contents in this fluid were derived primarily from organic matter rather than from evaporative concentration alone (Zherebtsova & Volkova, 1966; Nissenbaun, 1977; McCaffrey et al., 1986; Kendrick et al., 2011). These observations suggest that Mežica sphalerite formed from seawater-derived fluids that experienced variable evaporative concentration and fluid-rock interaction. This interpretation aligns with previous studies, which attribute mineralization to mixing between Middle to Late Triassic seawater and regional basinal brines (e.g., Drovenik et al., 1980; Spangenberg & Herlec, 2006; Herlec et al., 2010; Melcher et al., 2023). Pb-Zn mineralization is further inferred to have occurred in the presence of hydrocarbons, preserved as pyrobitumen accumulations between ore sulfides and as coatings on gangue hydrothermal carbonates (e.g., Spangenberg & Herlec, 2006).

### Implications for Mežica deposit formation

The halogen compositions of sphalerite from the Mežica district indicate mineralization from chemically evolved basinal brines ultimately derived from evaporated seawater, with significant

variability reflecting complex fluid evolution. The Br-Cl-I systematics can be explained either by progressive modification of a single evaporative parent brine along distinct fluid-rock interaction pathways, or alternatively by mixing between compositionally distinct fluid endmembers. In the latter scenario, one fluid corresponds to a seawater-derived brine with a strong evaporative signature, whereas the other represents a Br- and I-enriched fluid that underwent extensive interaction with organic matter, diagenetic pore waters, and/or hydrocarbons prior to mineralization. Such mixing could also have acted as a trigger for sphalerite precipitation (e.g., Leach et al., 2010). Within a single-fluid framework, the observed variability may reflect differential interaction with organic-rich platform carbonates and shales of the Raibl Group, as well as with evaporitic units in the underlying Late Paleozoic succession (e.g., Bojar et al., 2016; Šoster et al., 2025a), which likely contributed halogens and metals to the evolving fluid. However, the presence of compositionally distinct halogen signatures, together with regional evidence for fluid mixing in MVT systems, suggests that interaction and mixing between multiple fluid reservoirs was the most plausible and likely dominant mechanism, whereas derivation from a single evolving fluid appears less likely (e.g., Leach et al., 2010).

Across the Alpine district, the timing of mineralization has been constrained through Rb-Sr dating of sphalerite from the Bleiberg deposit (Melcher et al. 2010; Henjes Kunst 2014; Melcher et al. 2023) and U-Pb dating of syn-mineralization carbonates from the Gorno deposit (Giorno et al. 2022; Summino et al. 2023; Giorno et al. 2025). These datasets collectively indicate a Late Triassic to Early Jurassic age for ore formation. Although radiometric ages in the region include an older Carnian cluster, the older timing cannot apply to Mežica because the Carnian formations of the Raibl Group inside the mine are themselves mineralized, as demonstrated by Štrucl (1960, 1961, 1970), Cerny (1989) and Herlec et al. (2010). This shows that mineralization postdates Carnian period. In the absence of direct geochronology for Mežica, the younger Late Triassic to Early Jurassic age cluster is the only geologically consistent timeframe for mineralization.

The stratigraphic sequence above the mineralized levels of the Wetterstein Formation provides a depositional framework that strongly supports the origin and circulation of dense evaporated seawater-derived brines. The Raibl Group (Carnian) records alternating restricted lagoonal carbonates,

tidal flat deposits, and organic bearing shales that reflect reduced water exchange and elevated salinity during the Carnian (Bechstadt & Schweizer, 1991; Krainer et al., 2011), conditions well suited for evaporative concentration of seawater (e.g., Warren, 2016). These semi-restricted conditions continue into the Main Dolomite (Norian), a thick and widespread tidal flat to lagoonal carbonate platform interpreted as a setting where prolonged reflux of dense marine brines occurred (Ramovš & Rebek, 1970). The overlying Kössen Formation (Rhaetian) maintains this pattern and contains peritidal cycles, and stromatolitic laminites, all of which indicate shallow, periodically restricted marine environments where repeated partial evaporation was likely. After the Triassic-Jurassic boundary, intensified tectonic activity and the onset of rifting produced rapid subsidence and a shift into deeper marine conditions (e.g., Berra et al., 2009; Froitzheim & Manatschal, 1996; Chevalier et al., 2003; Rožič et al., 2017; Gale & Rožič, 2024). These deeper marine conditions are incompatible with continued formation of dense evaporative brines.

Previous studies have shown that organic matter played a major role in the sulfur budget of the Topla-Mežica system and actively interacted with the ore-forming fluid (e.g., Spangenberg & Herlec, 2006; Herlec et al., 2010). The shift in  $\delta^{34}\text{S}$  values recorded in sphalerite is explained by mixing between a regionally derived  $\text{H}_2\text{S}$  source produced by thermochemical sulfate reduction and locally derived sulfur generated through bacteria-mediated sulfate reduction of organic matter, supplemented by  $\text{H}_2\text{S}$  released from diagenetic pyrite and organosulfur compounds (Spangenberg & Herlec, 2006; Herlec et al., 2010; Palinkaš et al., 2013).

Building on the established role of organic matter in controlling sulfur systematics, the halogen data presented here further suggest that organic-fluid interaction also influenced the halogen budget, underscoring a broader geochemical role of organic matter in the system. Chlorine is primarily associated with evaporative concentration of seawater, whereas elevated Br and I concentrations likely reflect subsequent modification of the fluid through interaction with organic-bearing lithologies and/or mixing with halogen-enriched

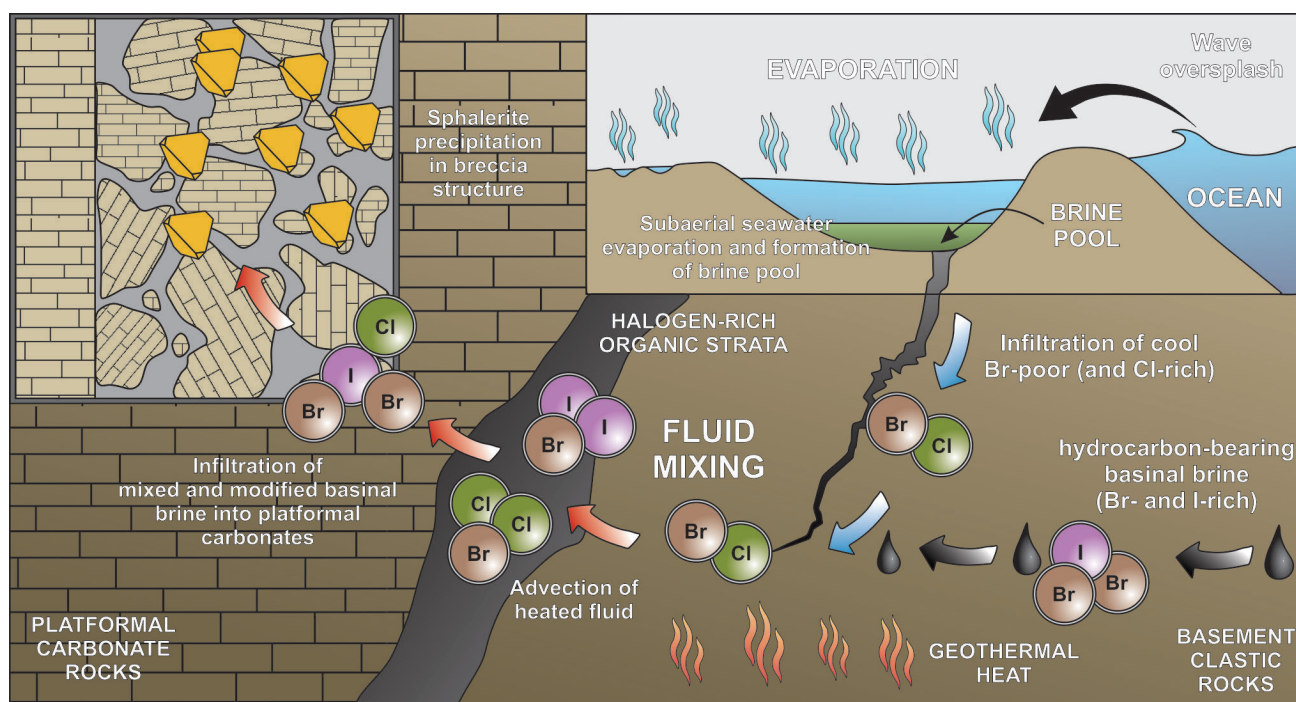


Fig. 4. Conceptual model of brine evolution controlling the halogen signature of sphalerite from the Mežica deposit. Subaerial evaporation of seawater produced highly concentrated saline brines, which subsequently refluxed into the subsurface along available structural pathways, most likely exploiting pre-existing normal faults. At depth, these dense brines interacted with geothermally heated rocks, reaching temperatures of approximately  $\approx 150^\circ\text{C}$ . This heating promoted buoyancy-driven flow and upward migration through the surrounding formations. During deep circulation, these fluids encountered compositionally distinct regional basal brines that had extensively interacted with buried organic matter and hydrocarbons and carried dissolved organic components enriched in Br and I. Mixing between these fluids likely resulted in the observed anomalous halogen ratios of the ore-forming brine. As the fluids ascended, they further interacted with organic-rich stratigraphic units, including shales and platform carbonates, where thermal degradation of organic matter and hydrocarbons promoted the release of organically bound halogens, possibly causing additional Br and I enrichment. The chemically modified brines were ultimately emplaced into platform carbonate rocks, where sphalerite precipitated within breccia bodies and vein systems, preserving the characteristic halogen signature observed in the ore.

fluids. In this context, the Br- and I-enriched signatures are most plausibly explained by interaction with organic-rich units, including shales and platform carbonates of the Raibl Group, as well as externally derived hydrocarbon phases, augmented by contributions from deeper regional basinal fluids. Thermal conditions of approximately 150 °C (Melcher et al., 2023) are compatible with fluid circulation at moderate burial depths within basinal settings and would have facilitated the breakdown of halogen-, metal-, and sulfur-bearing organic compounds, releasing these elements into the fluid (e.g., Saxby, 1973; Surdam & MacGowan, 1987; Qin et al., 2018; Sheik et al., 2020; Šoster et al., 2025b). Rather than a single progressive fluid evolution, the data are therefore more plausibly explained by mixing between compositionally distinct fluids, including a Cl-dominated (Br-poor), evaporated seawater-derived brine and a Br- and I-enriched fluid modified through extensive organic matter interaction. Such mixing, potentially coupled with fluid-rock interaction and fluid mixing, likely played a key role in generating the observed halogen variability and may have contributed to sphalerite precipitation within breccia zones and vein systems in the Mežica system.

### Conclusions

Halogen ratios in sphalerite from the Mežica district define two compositional endmembers, a Br-rich and a Br-poor type, reflecting mixing between an evaporated seawater-derived brine and a compositionally distinct regional basinal brine. The evaporated seawater component is characterized by a Br-poor signature acquired during subaerial evaporation, whereas the Br- and I-enriched endmember reflects a fluid that underwent extensive interaction with organic matter, diagenetic pore waters, and hydrocarbon phases. Both fluid types display halogen systematics incompatible with simple halite dissolution, confirming an origin ultimately linked to evaporated seawater and subsequent modification and fluid mixing. Regional geochronological constraints from Alpine-type carbonate-hosted Pb-Zn deposits indicate that mineralization occurred during the Late Triassic to Early Jurassic. At Mežica, the presence of mineralization within Carnian units of the Raibl Group demonstrates that ore formation post-dates their deposition, thereby excluding older age clusters. In the absence of direct geochronological constraints, the Late Triassic-Early Jurassic interval represents the most geologically consistent timing for mineralization. The stratigraphic architecture of the host rock succession provides

a robust framework for the generation and circulation of mineralizing fluids. Restricted lagoonal and tidal flat environments documented in the Raibl Group, Main Dolomite, and Kössen Formation indicate conditions favorable for repeated evaporative concentration of seawater during the Late Triassic, promoting the formation and reflux of dense brines into the subsurface. Following the Triassic-Jurassic transition, tectonically driven subsidence and basin deepening likely curtailed such conditions, effectively terminating large-scale evaporative brine production. Organic matter played a fundamental role in the Mežica mineralizing system. In addition to contributing reduced sulfur, as demonstrated by previous isotopic studies, it also exerted a significant control on the halogen budget. Elevated Br and I concentrations are best explained by interaction between regional basinal fluids and organic-rich lithologies, including shales and platform carbonates of the Raibl Group, as well as externally derived hydrocarbon phases. Thermal conditions of  $\approx 150$  °C, would have facilitated the breakdown of halogen-bearing organic compounds, releasing Br and I into the fluid. The halogen data indicate that fluid mixing between an evaporated seawater-derived brine and a Br- and I-enriched regional basinal brine, coupled with fluid-rock interaction, was the dominant process controlling the chemical evolution of the mineralizing system. This interplay generated the characteristic halogen signatures preserved in Mežica sphalerite that caused the ore precipitation in Mežica ore-forming system.

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