

Origin of the Jadar Volcano-Sedimentary Li-B Deposit, Serbia

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Abstract

The Jadar deposit (Serbia) is a unique end member of the volcano-sedimentary Li deposit class, where the main ore mineral is jadarite ($\text{LiNaSiB}_3\text{O}_7(\text{OH})$), to date only recorded at the Jadar locality. We provide the first account of the features of the Jadar deposit based on the study of drill hole material, complemented by petrographic analysis, whole-rock, and isotopic geochemistry. The Li-B mineralization is hosted by sediments interlayered with tuffs that were deposited in a fault-bounded lacustrine basin. Mineralization processes initially involved alteration of volcanic glass through near-neutral and heated meteoric fluids, which resulted in the formation of hectorite. Lithium clays were later overprinted by higher-pH brines, which underwent significant evaporation, combined with conditions of Na^+ and $\text{SiO}_{2(\text{aq})}$ saturation, resulting in formation of siliceous gels that were the precursors to jadarite formation and extensive zeolitization of the intrabasinal sediments. Formation of jadarite occurred in two stages: (1) early diagenesis accompanied by zeolitization and precipitation of primary dolomite, which resulted in the sediment-hosted Li mineralization, (2) late remobilization of $\text{Li}(\text{B-Na})$ -saturated fluids, leading to formation of epigenetic jadarite-albite infills of fractured rocks. Isotopic geochemistry combined with mineral chemistry proxies indicate that early mineralizing processes were largely dominated by diagenetic fluids that experienced a thermal influence from the coeval cooling of the Miocene S-type granite member of the nearby Cer Mountain Complex. Late thermal maturation of organic matter then resulted in acidic fluids that dissolved the early ore assemblage and led to formation of late diagenetic lithiophosphate and low-Na borates.

Introduction

The Jadar deposit (Serbia) ranks among the top 10 lithium deposits globally, holding 85.4 million short tons (Mt) of indicated resources at 1.76% Li_2O and 16.1% B_2O_3 , with an additional 58.1 Mt of inferred resources at 1.87% Li_2O and 12% B_2O_3 (Rio Tinto, 2022). The Jadar deposit is a unique end member of the emerging volcano-sedimentary Li deposit group on account of its unique ore mineralogy (Putzolu et al., in press), namely the occurrence of the hydrous borosilicate mineral jadarite ($\text{LiNaSiB}_3\text{O}_7(\text{OH})$), a new Li species yet to be observed in other deposits (Stanley et al., 2007). Volcano-sedimentary (VS) Li deposits occur in lacustrine sediments rich in fragmental volcanic rocks deposited in endorheic basins (i.e., restricted extensional basins or volcanic calderas) associated with felsic magmatic provinces (Putzolu et al., in press). More conventional VS deposits, such as those in the northwestern and southern borders of the Basin and Range province (US and Mexico), are classified as clay type and contain Li in trioctahedral smectite clays with a chemical composition ranging from Li-bearing Mg smectite (i.e., saponite and/or stevensite) toward F-bearing hectorite compositions ($\text{Na}_{0.6}(\text{Mg,Li})\text{Si}_4\text{O}_{10}(\text{F,OH})$) (Putzolu et al., in press). The most widely accepted genetic model for Li smectites involves neoformation

processes under high-pH conditions generated by dissolution of felsic volcanic glass-rich rock types and enhanced evaporation (Castor and Henry, 2020; Benson et al., 2023). In a small number of clay-type VS deposits Li smectites are observed in association with Mg-F illite, with a stoichiometry similar to tainiolite ($\text{KMg}_2\text{LiSi}_4\text{O}_{10}(\text{OH,F})_2$), which, according to the recent model of Benson et al. (2023), can be formed through dissolution-reprecipitation processes triggered by high K^+ , Li^+ , and F^- hydrothermal fluids promoting illitization of the parental Li smectite. Several VS Li deposits contain significant volumes of borates (e.g., Na and Ca borates) and borosilicates (i.e., searlesite, $\text{NaBSi}_2\text{O}_5(\text{OH})_2$), and to date this mineralization type represents the main global source of boron (U.S. Geological Survey, 2024). Typical examples of mixed clay/borate-type VS systems are the Bigadiç (Turkey) and Rhyolite Ridge (US) deposits (Helvacı and Palmer, 2017; Reynolds and Chafetz, 2020; Kadir et al., 2023). Despite this close association of Li clays and borate resources, these VS deposits are characterized by a mineralogical and geochemical decoupling between Li and B across the orebodies. The geologic features of Jadar deposit do not conform with this paradigm, since, in most of the mineralized sections of the deposit, Li and B are found together in jadarite. It is interesting to note that the discovery of Jadar and jadarite in 2004 was the result of an exploration program targeted on B exploration in the Miocene VS basins of Serbia, which are considered to be similar targets to

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the Turkish borates (Rio Tinto, pers. commun., 2021). In this paper, we present the first geologic account for the origin of the Jadar deposit. To constrain the features of this new mineralization type, we present petrographic and lithogeochemical data from representative drill holes that characterize the ore facies and Li-B distribution, as well as results from a program of O-H-C-Sr isotope geochemistry that constrain the nature of mineralizing fluids and permit assessment of the role of diagenetic vs. higher-temperature processes during the basin-wide Li-B ore-forming events.

Regional Geology

The Jadar deposit is located in the Western Balkans Li-B metallogenic zone of the Dinarides belt (Fig. 1), a region demonstrated to have high potential for VS-style Li-B mineralizations (Borojević Šošćarić and Brenko, 2022). The Western Balkans Li-B metallogenic zone developed subparallel to the Sava-Vardar zone, a SE-trending geologic feature that marks the suture between the African and Eurasia plates (Schmid et al., 2008, 2020). The Sava-Vardar zone stretches across the Balkan region toward Western Turkey and becomes covered by Neogene sediments of the Pannonian basin northward

(Schmid et al., 2008). High volumes of intermediate to felsic plutonic and volcanic rocks were emplaced within the Sava-Vardar zone during the postcollisional evolution of the Dinarides-Hellenide orogen, including Oligocene metaluminous I-type granitoids, Miocene peraluminous S-type granitoids, and effusive to pyroclastic rocks (Koroneos et al., 2011; Löwe et al., 2021). The Oligocene granitoids were emplaced following a stage of postcollisional transpression within the Dinarides belt, whereas during the Miocene, S-type granites were emplaced during extension and associated opening of the Pannonian basin (e.g., Cvetković et al., 2002, and references therein). The opening of the Pannonian basin tectonically marks a shift to crustal thinning and hyperextension followed by the local exhumation of metamorphic core complexes (Koroneos et al., 2011; Löwe et al., 2021; Borojević Šošćarić and Brenko, 2022). Paleogeography of western Dinarides changes significantly during the Oligocene to Miocene. During the Oligocene stage, the area was characterized by marine sedimentation influenced by a tectonically trapped inland sea (i.e., Paratethys), which during the Oligocene-Miocene transition was subjected to uplift and hence to a lowering of the water table level (Marović et al., 2007; Balling et al.,

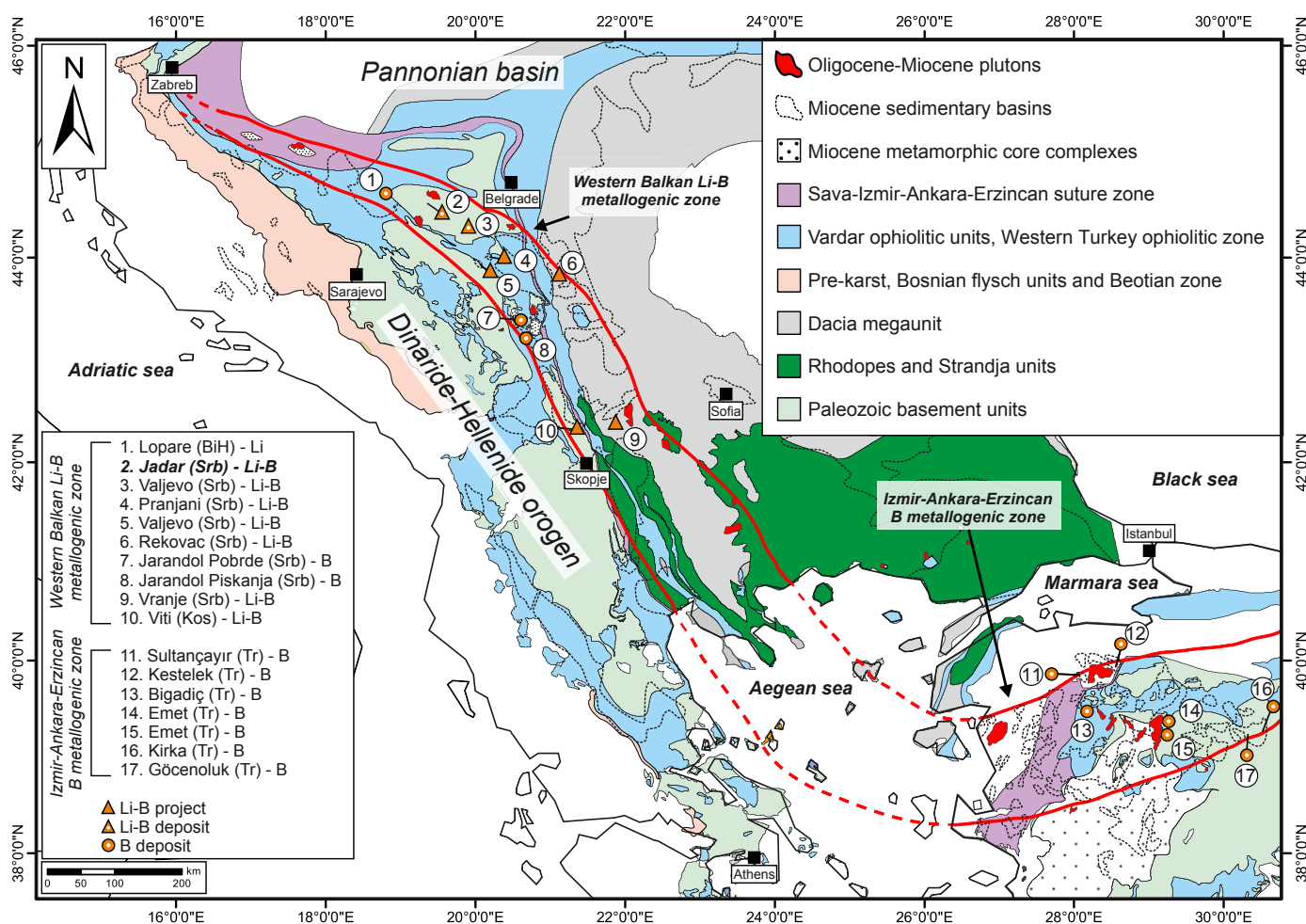


Fig. 1. Regional geologic map showing the location of Li-B volcano-sedimentary deposits in the western Balkans and Izmir-Ankara-Erzincan metallogenic zones (modified from Borojević Šošćarić and Brenko, 2022). Abbreviations: BiH = Bosnia and Herzegovina, Kos = Kosovo, Srb = Serbia, Tr = Turkey.

2021). This led to the development of high-salinity brackish lakes throughout the Miocene forming the Western Balkan Lake system (Obradović and Vasić, 2007; Palcu et al., 2021). The development of lacustrine basins was contemporaneous to crustal thinning, as shown by the close association between the lake systems and the Miocene Prosara-Motajica-Cer and Studenica-Kopaonik metamorphic core complexes in western and central Serbia, respectively (Borojević Šoštarić and Brenko, 2022, and references therein). The extensional tectonic regime triggered the formation of fault-controlled basins (i.e., grabens and semigrabens) that experienced input of reworked volcanoclastic/plutonic material and developed hydrologically closed lacustrine environments.

In addition to Jadar, other Serbian VS systems include the Valjevo, Pranjani, Rekovac, Jarandol-Piskanja, and Prajani basins, which show high potential for boron mineralization in the form of Na and Ca borates and borosilicates (i.e., searlesite) but, until now, no jadarite has been documented. Lithium in these smaller basins ranges from geochemically anomalous to grade level, and is associated with Li-bearing clay-rich units within the sedimentary sequences (Borojević Šoštarić and Brenko, 2022, and references therein). In most of these basins the lacustrine cycle was governed by conditions of permanent stratification of the water column aiding anoxia and high organic matter preservation (Obradović et al., 1997). As a result, prior to becoming potential targets for Li and B exploration, lacustrine lakes from western Serbia were mostly explored because of their oil shale potential (Čokorilo et al., 2009).

Local Geology

Jadar sits in a SE-trending valley that covers an area of 3×2.5 km, a few kilometers south of the Cer Mountain Granitoid Complex (Fig. 2A). The orebody is hosted by unexposed Lower to Middle Miocene volcano-sedimentary units that were intercepted through drilling at depths from 100 to 720 m below surface. This Miocene sequence lies unconformably on basement rocks of the Jadar-Kopaonik thrust sheet, which is a composite nappe derived from the most distal portions of the Adria passive margin (Schmid et al., 2008). Basement rocks in the study area are mostly exposed to the south of Jadar valley and occur also at depth below the Jadar deposit itself (Fig. 2A, B). The Jadar-Kopaonik thrust sheet comprises unmetamorphosed to low-grade metamorphic Palaeozoic clastic sediments (e.g., Sudar and Kovacs, 2006; Schefer et al., 2010; Löwe et al., 2023) that include Middle Devonian to upper Carboniferous turbidites, which are transgressively overlain by Permian to Upper Jurassic limestones (Filipović et al., 2003; Löwe et al., 2021). This succession is overlain by the Late Jurassic ophiolitic mélange and ophiolites emplaced during the obduction of the Western Vardar Ocean (Dimitrijević, 1997; Schmid et al., 2008; Stojadinović et al., 2013). Late Cretaceous (Senonian) flysch unconformably overlies the Jadar-Kopaonik thrust sheet (Schmid et al., 2008), which is in turn overthrust onto the Drina-Ivanjica composite nappe (Fig. 2B) (Schmid et al., 2020).

Basement rocks are intruded by the Cer Mountain Granitoid Complex (Fig. 2A, B), which is a composite intrusion formed during the two phases of felsic magmatism mentioned previously. The older Oligocene granitoids include I-type monzonitic to

monzodioritic rocks containing quartz, plagioclase, K-feldspar, biotite, hornblende, and accessory titanite and ilmenite and show oldest emplacement ages of 32.21 ± 0.3 Ma (U-Pb on zircons; Stojadinović et al., 2017) and cooling ages of 25.4 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$ on amphibole; Löwe et al., 2021). The younger Miocene intrusive rocks include S-type two-mica granite dominated by quartz, muscovite, biotite, K-feldspar, and plagioclase. Previous studies (i.e., Stojadinović et al., 2013; Löwe et al., 2021) reported cooling/exhumation ages of the Miocene granitoids at around 20 to 15 and 16.66 ± 0.25 Ma ($^{40}\text{K}/^{40}\text{Ar}$ and $^{40}\text{Ar}/^{39}\text{Ar}$ on mica). Granitic facies from Cer Mountain have maximum Li concentrations of about 400 ppm, and they host no economic Li mineralizations (Borojević Šoštarić and Brenko, 2022). However, granitoids from Cer Mountain show a strong peraluminous character and anomalous large-ion lithophile element (i.e., LILE, such as Rb) concentrations (Borojević Šoštarić and Brenko, 2022), which is a feature consistent with a fertile geochemical footprint as described for rare metal granite systems (e.g., Romer and Pichavant, 2020). Furthermore, metasomatized to hydrothermal facies have been observed in the upper cupola sections of the Miocene S-type granite, as well as in the southernmost part of the laccolith. These units include muscovitized and greisen-altered facies with anomalous Li, Sn, Be, Nb, Ta, Bi, and U, spodumene pegmatites, and tourmaline-rich aplitic dikes (Lazić et al., 2009; Huska et al., 2014; Borojević Šoštarić and Brenko, 2022).

The Jadar fault-block basin developed during Miocene regional-scale extension, which in the study area resulted in the reactivation of thrust faults as low-angle detachments (e.g., Lesnica fault, Fig. 2A, B). Extension in the Jadar area was accompanied by denudation and isostatic uplift of continental crust that occurred around 18 to 17 Ma and was likely contemporaneous with the Miocene S-type magmatism (Löwe et al., 2021). Following the emplacement of the S-type granitoids and Cer Mt. metamorphic core complex exhumation, the study area was subjected to a high heat flow, with temperature above 150°C until around 14 Ma (Löwe et al., 2021, and references therein). Miocene sedimentation in the Jadar basin was partially coeval with the MCC exhumation and with cooling of the Miocene the S-type granitoids (Koroneos et al., 2011; Stojadinović et al., 2013; Löwe et al., 2021). The sedimentary cycle started in Eggenburgian (around 20.8–18.3 Ma) with basal siliciclastic sediments and evolved toward a more lacustrine environment until the beginning of Badenian (around 16 Ma), when the lacustrine cycle ceased through marine transgression (Andjelković, 1986; Obradović and Vasić, 2007). Key geologic features of the Jadar basin have been first described by Obradović et al. (1997) and later revised as a result of Rio Tinto exploration activities. From bottom to the top, four major lithological groupings are recognized (Fig. 3):

1. Basement rocks of the Jadar-Kopaonik nappe: These at depth in the basin include metamorphosed Cretaceous limestones, sandstones, and locally conglomerates.
2. Lacustrine units: These have thickness up to 500 m in the center of the system, whereas they pinch out onto the pre-Miocene country rocks in the southwest flank of the basin. Intrabasinal lake sediments include siltstones and marls with high contents of kerogen and dolomite, whereas the marginal and upper lacustrine units consist of more

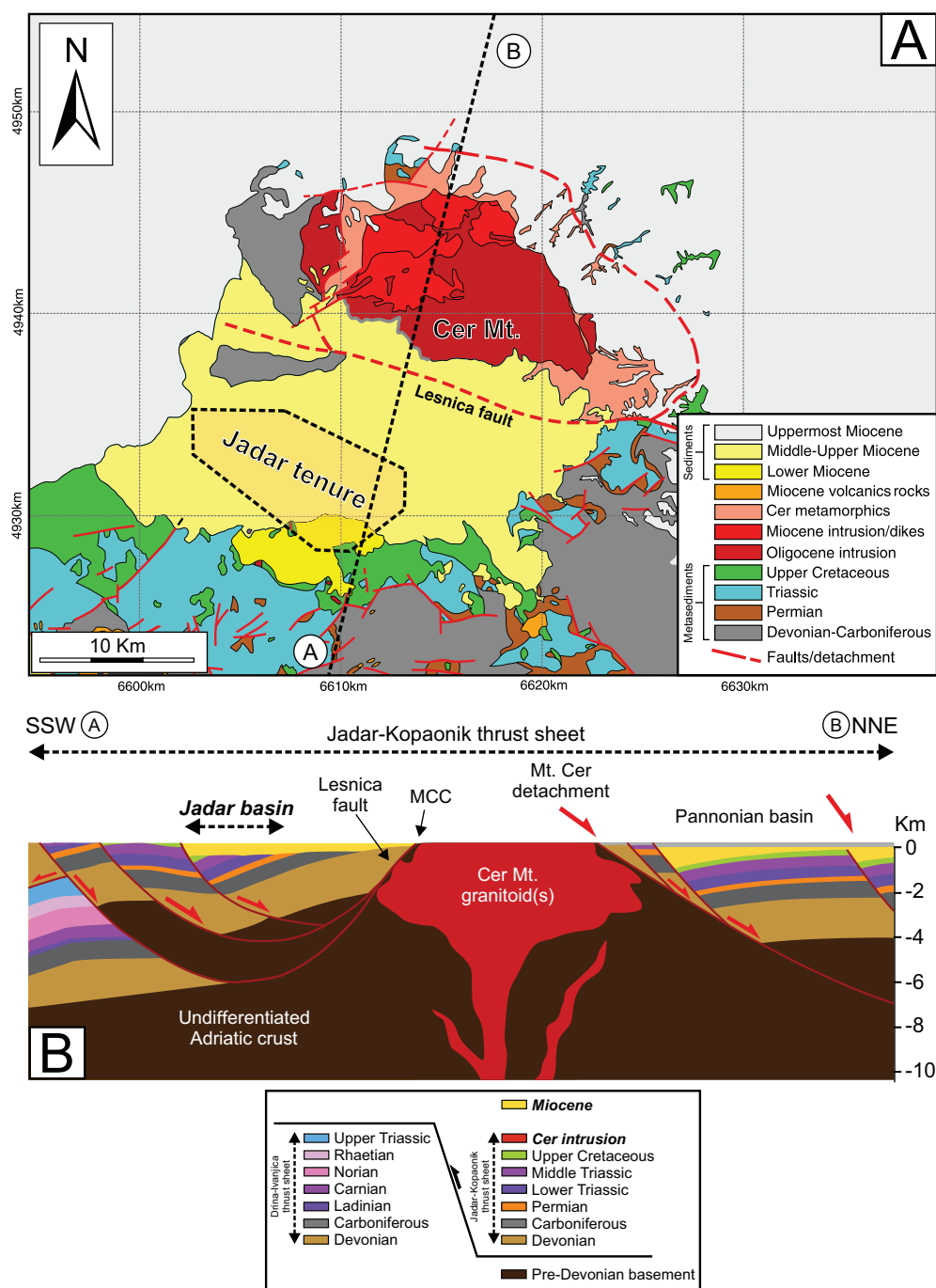


Fig. 2. (A) Geologic map of the study area showing the location of the Jadar tenure (modified from Stojadinovic et al., 2017). (B) Balanced cross section highlighting the structural relationship between the Miocene Jadar basin, the pre-Miocene Jadar-Kopaonik and Drina-Ivanjica nappes, and the Cer Mountain laccolith (modified from Löwe et al., 2021). The cross-section trace is shown in Figure 2A. Abbreviation: MCC = Cer Mountain Metamorphic Core Complex.

clay-dominated siltstones. Lacustrine units are the main host of the jadarite ore that includes upper, middle, and lower jadarite zones with thickness ranging from 1 to 15, 1 to 20, and 1 to 50 m, respectively (Fig. 3). Furthermore, borate mineralization consists of Na borate (NaBo) lenses and breccias in the lower jadarite zone and of Ca(Na) borate (CaNaBo) horizons in the uppermost section of the lacustrine sequence (Fig. 3).

3. Transition zone: This has a maximum thickness of 35 m and consists of layered calcite-gypsum sediments that cap the Li-B ore system on a basin scale.
4. Marine unit: This has a maximum thickness of 350 m in central part of the Jadar basin and is the latest infill of the system marking the end of the lacustrine cycle.

At several depths throughout the basin, lacustrine units are interlayered with tuffs and breccias. Tuffs form 1- to 2-m-

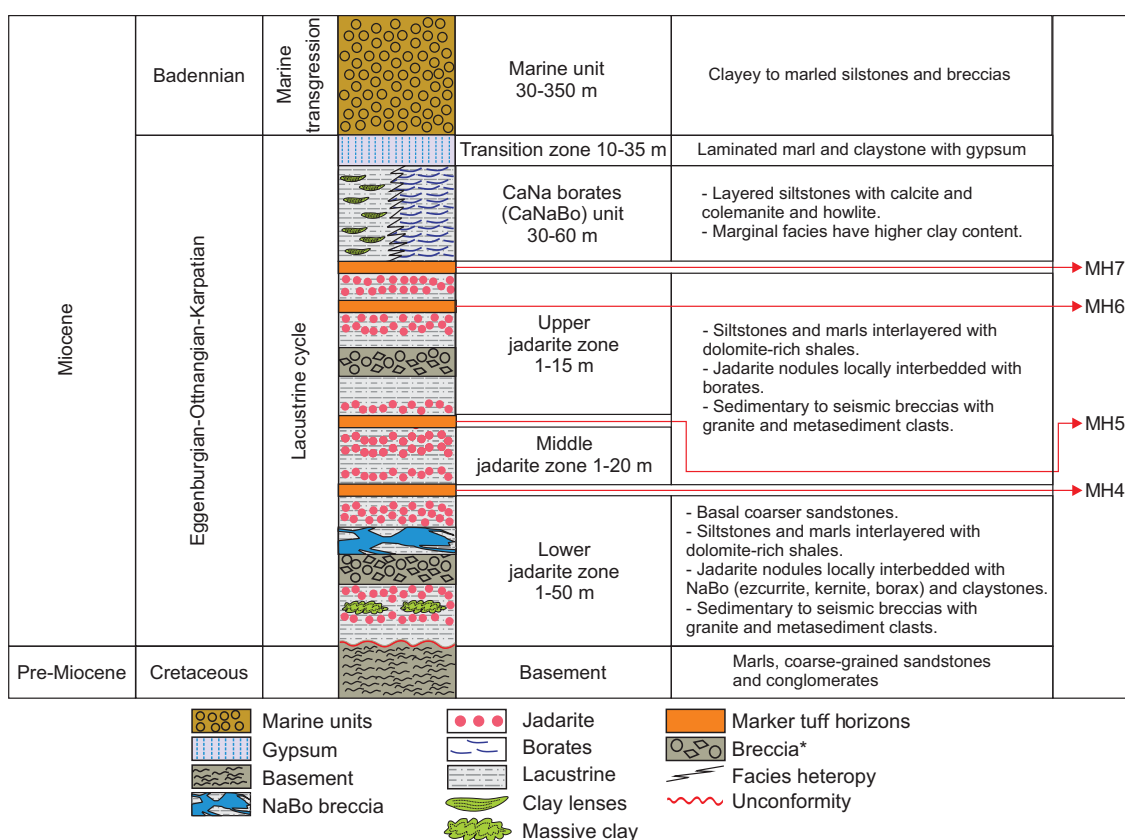


Fig. 3. Stratigraphy of the Jadar basin showing the location of main mineralized intervals (modified after Obradović et al., 1997; Rio Tinto, 2022). Abbreviations: MH4 to MH7 = marker tuff horizons. Notes: * = includes sedimentary and seismic breccia units.

thick fine-grained beds and have been recognized on a basin scale and have been used as marker horizons (i.e., from oldest to youngest: MH4, MH5, MH6, and MH7; Fig. 3). Brecciated units vary as follows: sedimentary breccias containing metasedimentary and granite clasts; to seismic breccias, which are associated with lacustrine units affected by synsedimentary deformation.

Materials and Analytical Methods

The mineralization has been studied in drill holes, selected to represent the range of facies variation through the system, from the marginal to more intrabasinal/lake center settings. Whole-rock geochemistry is based on exploration data produced in the 2012 to 2019 period by Rio Tinto (Rio Sava Exploration) and includes analyses performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). Bulk-rock mineralogy, petrography, and paragenesis of the mineralization were determined on a suite of legacy samples collected from drill holes in 2011. Mineralogy has been determined using X-ray diffraction (XRD) of bulk-rock powders, clay aggregates, and of area of interest on thin sections and blocks (in situ XRD analysis), and by means of Fourier transform infrared spectroscopy (FTIR). The textural relationships and the paragenetic evolution of the mineralization, as well as the mineral chemistry of selected phases, were studied through scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS), automated SEM mineralogy, followed

up by detailed transmission electron microscopy (TEM). The relationship between the Li-B mineralization and the organic fraction has been determined by a combination of ultraviolet (UV) and white-light reflected microscopy, whereas FTIR was used to classify organic matter. The features of mineralizing fluids in the system have been determined using Sr, O, H, and C isotope geochemistry on jadarite, Li clays, and dolomite mineral separates.

Details of the analytical procedures and sample locations are reported in Appendices 1 and 2, respectively.

Drill Hole Observations

Lacustrine units

Intrabasinal facies are the main host of the jadarite mineralization and dominate the investigated profiles at the center of the basin, as well as in the lowermost sections of the most marginal drill hole. This facies includes massive to finely laminated shales, variable in their content of dolomitic beds, with the jadarite mineralization occurring either as stratabound nodules associated with dolomite and secondary quartz layers (Fig. 4A, B) or as slightly discordant clusters of nodules associated with synsedimentary load casts and flame structures (Fig. 4C). Intrabasinal lacustrine sections show a vertical evolution of jadarite textures; this includes lowermost domains with nodular jadarite that evolves upward to jadarite in the form of locally folded layers (i.e., enterolithic jadarite) that displace the surrounding sediments (Fig. 4D, E). In the

lower lacustrine sequence, jadarite is hosted in a blackish and dolomite-poor fine-grained sediment. Here, jadarite forms clustered nodules and locally spherulites rimmed by secondary quartz (Fig. 4F) and develops zoned textures with denser whiter cores surrounded by sparser and darker rims containing fine-grained Fe sulphide inclusions (Fig. 4G). Massive

clay-rich horizons are often found within the intrabasinal facies and are crosscut by the dolomite-bearing sediments and by later jadarite veins (Fig. 4H, I). Lacustrine units in the uppermost and marginal facies of the basin have reduced jadarite and dolomite contents compared to the intrabasinal facies, and comprise laminated siltstones with clay-altered and

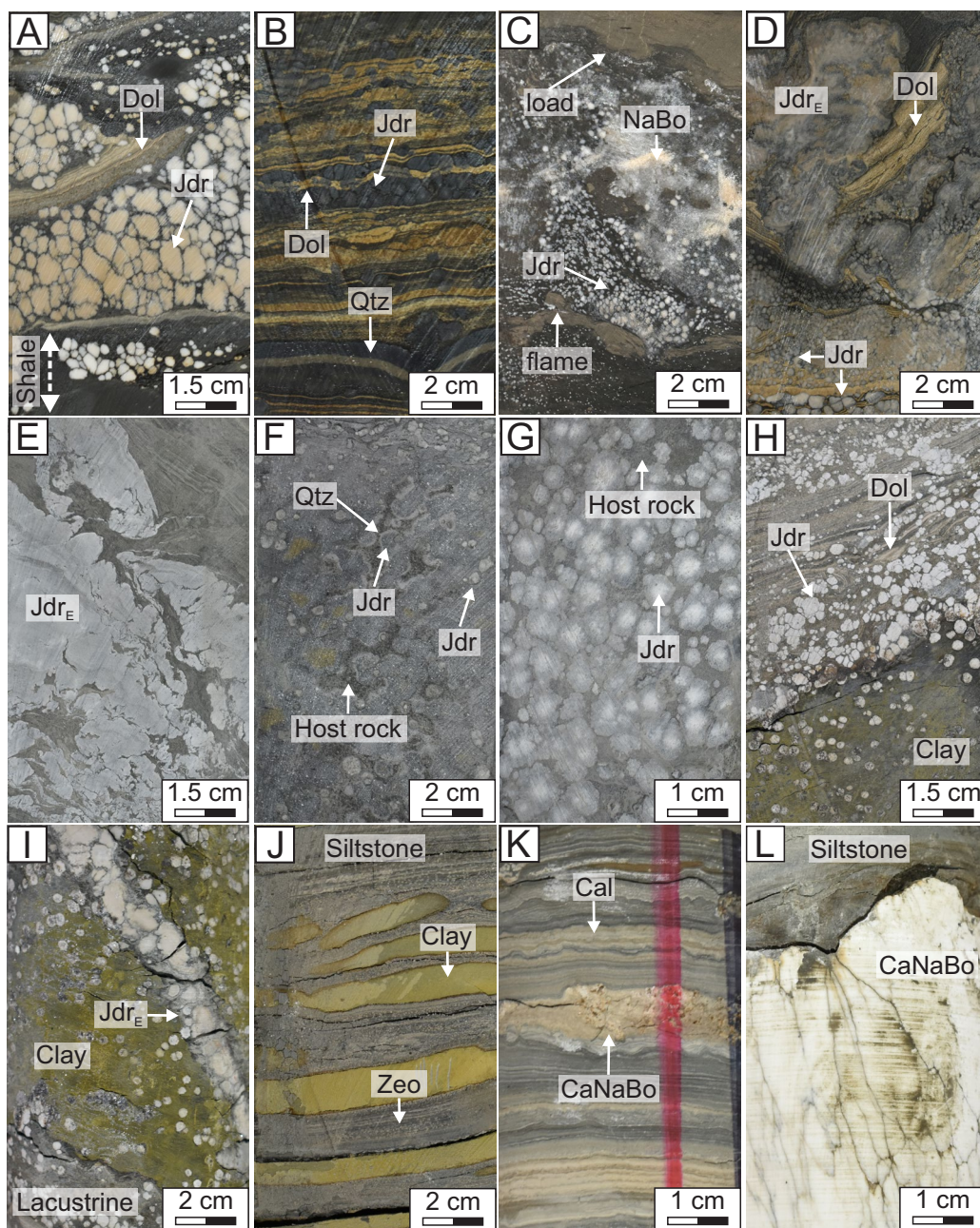


Fig. 4. Mineralization styles occurring in the lacustrine facies (A-I intrabasinal facies, J-L marginal facies). (A) Nodular jadarite in a massive shale. (B) Nodular jadarite in layered shale interbedded with dolomite and secondary quartz beds. (C) Clusters of jadarite nodules associated with sediment loading and flame structures. (D) Nodular jadarite coalescing to form enterolithic jadarite (Jdr_E). (E) Enterolithic jadarite (Jdr_E) displacing hosting sediments. (F) Spherulitic jadarite rimmed by secondary quartz. (G) Zoned spherulitic jadarite. (H) Dolomite- and jadarite-rich lacustrine unit crosscutting massive clay layer. (I) Jadarite enterolithic vein crosscutting clay horizon. (J) Clay- and zeolite-altered tuff lenses in a siltstone. (K) Stratiform borates (colemanite) in a calcite-rich sediment. (L) Vertically elongated borate (howlite) in a siltstone. Please note that pictures are oriented along the sedimentary polarity. Abbreviations: CaNaBo = Ca and Na borate, Dol = dolomite, Jdr = jadarite, NaBo = Na borate, Qtz = quartz, Zeo = zeolite.

zeolitized tuff lenses (Fig. 4J). In this facies, Ca(Na) borates are common and either form whitish beds interlayered with calcite (Fig. 4K) or subvertically elongated nodules (Fig. 4L).

Tuff horizons

Tuff layers have been observed at several levels in the sedimentary sequence and are present as four key stratigraphic marker horizons labeled by Rio Tinto geologists (i.e., MH4, MH5, MH6, and MH7). These units consist of fine-grained layers between 1 and 2 m thick, which locally show evidence of reworking (Fig. 5A). Primary features of tuff are largely obliterated by alteration, with fine-grained mica (biotite > muscovite) representing the prevailing relict primary phase

(Fig. 5A). Tuff-like horizons are also observed as centimeter-scale thick layers interbedded within the lacustrine units (Fig. 5B). These beds are strongly altered to secondary minerals such as spherulitic zeolites, borates, and jadarite (Fig. 5B, C). Jadarite in tuffs is either hosted in stockwork veins in association with searlesite (Fig. 5C) or forms clusters of nodules that locally coalesce at the boundary between the tuffs and the hosting sediments (Fig. 5D).

Breccia units

Higher energy of sedimentation episodes marked the local disruption of lacustrine facies and the development of thick brecciated units. These units have been documented through-

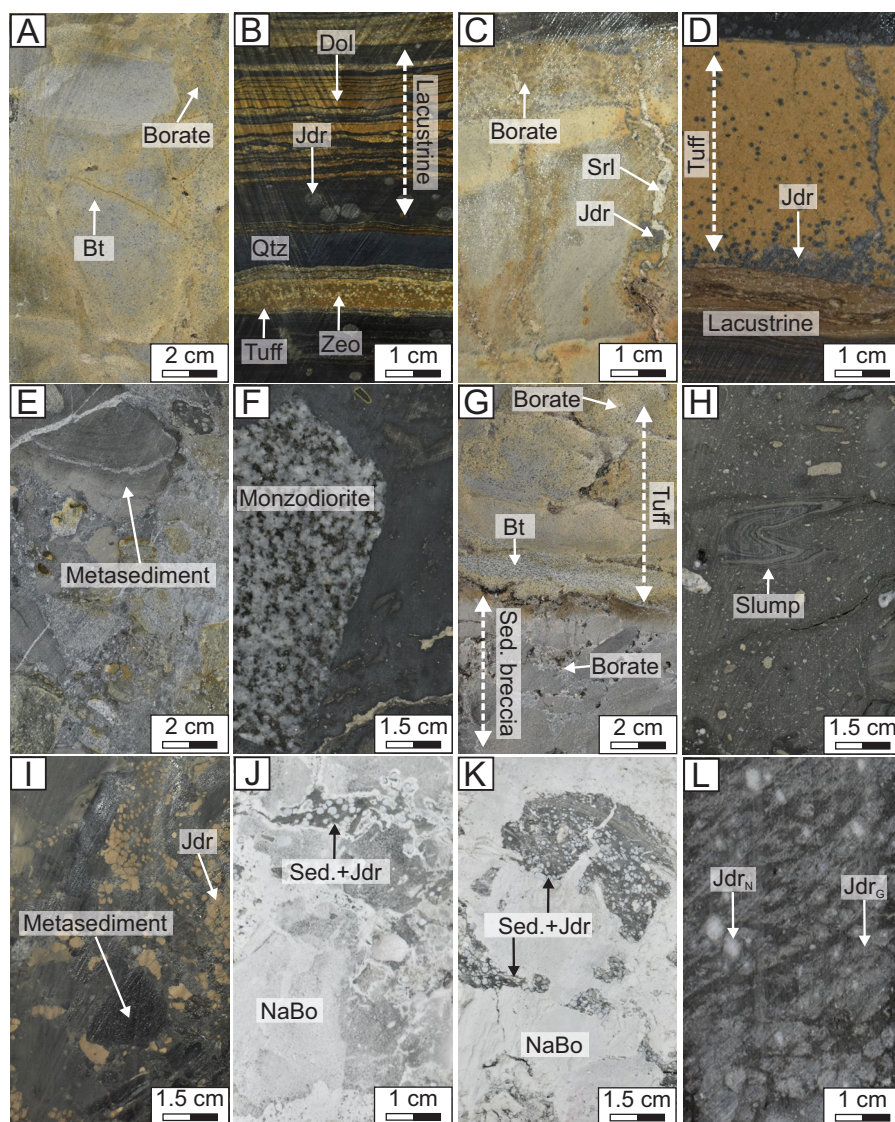


Fig. 5. Features of intrabasinal tuff horizons (A-D) and of reworked/brecciated units (E-L). (A) Reworked mica-bearing tuff horizon. (B) Zeolitized tuff layer interbedded with mineralized lacustrine sediments. (C) Tuff horizon containing spherulitic borates and jadarite + searlesite veins. (D) Nodular jadarite clusters in a tuff. (E, F) Sedimentary breccia containing metasedimentary and granitoid clasts. (G) Reworked tuff on top of a sedimentary breccia containing spherulitic to intraclast borates. (H) Seismic breccia showing soft-sedimentary deformation features. (I) Breccia units with jadarite mineralization within the matrix. (J, K) NaBo breccia unit (ezcurrite and kernite in Fig. 5J and borax in Fig. 5K) enveloping relict sedimentary clasts. (L) Fine-grained ghost jadarite (Jdr_G) associated with NaBo breccia. Please note that pictures are oriented along the sedimentary polarity. Abbreviations: Bt = biotite, Dol = dolomite, Jdr = jadarite, Jdr_N = nodular jadarite, NaBo = Na borate, Qtz = quartz, Srl = searlesite, Zeo = zeolite.

out the system, with marginal sections of the basin showing higher volumes of exotic nonlacustrine material. Reworked units include breccias with metasedimentary and granite clasts (Fig. 5E, F) and are locally associated with reworked tuff layers (Fig. 5G). Brecciation locally involved lacustrine units, leading to the soft-sediment deformation of varved layers, suggesting active seismic shaking and liquefaction of the unconsolidated sedimentary package (seismic breccia-like, Fig. 5H). Reworked units locally contain borates and jadarite present as late intraclast cements or in the matrix of breccias (Fig. 5I). Breccias are also presented at depth within the lower jadarite zone, where the sedimentary layering is disrupted by the emplacement of Na borates (hereafter “NaBo breccia”) (Fig. 5J, K). In association with the NaBo breccia zones, Li-B mineralization consists of a fine-grained and dark jadarite (so-

called “ghost jadarite”) locally associated with nodular jadarite (Fig. 5L).

Lithogeochemistry

Lithium and boron in mineralized drill cores from both intrabasinal and marginal facies show a broadly positive correlation, which indicates the presence of a single dominant host phase (jadarite) for both Li and B (Fig. 6A). However, a portion of the data is less well correlated and points to a more complex mineralogical department of both Li and B based on the difference between the measured Li and B grades and the theoretical geochemistry expected if all Li and B were hosted in jadarite. Based on contrasting Li vs. B endowment, distinctive lithogeochemical domains have been defined (Fig. 6A):

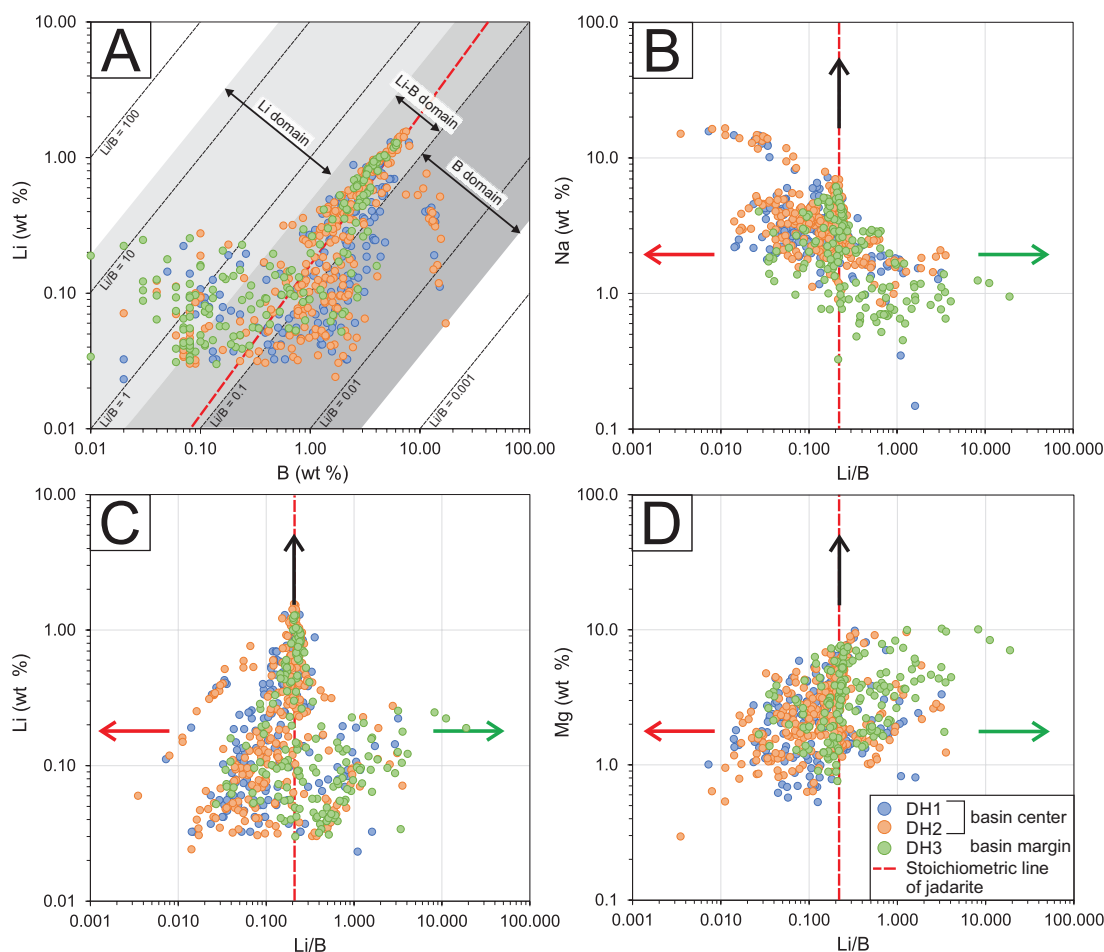


Fig. 6. Lithogeochemical data from the basin center (DH1 and DH2) and the marginal facies (DH3) of intercepts exceeding the 300-ppm Li cutoff: (A) Li (wt %) vs. B (wt %) plot highlighting the presence of main lithogeochemical domains according to variable Li/B ratios. Partial correlation between lithogeochemical data and the jadarite stoichiometry line (red dashed line) defines the domains where jadarite accounts for the measured Li and B grades, whereas lithogeochemical data displacement from the calculated stoichiometric line defines domains where the observed Li and B grades are controlled by additional ore phases. (B) Negative correlation between the Na (wt %) vs. Li/B ratio indicating that Na borate facies accounts for the high B and low Li lithogeochemical domains. (C, D) Relationship between the Li/B ratio and the Li (wt %) and MgO (wt %) contents. Subpopulation of data showing positive correlations indicate the presence of Mg(Li) clays in the low to intermediate Li-grade domains, whereas the subpopulations of data characterized by vertical trends are due to the presence of jadarite in the Li-B domain. Notes: Green arrows indicate expected trends of lithium excess over boron if compared to the jadarite stoichiometry; red arrows indicate expected trends of boron excess over lithium if compared to the jadarite stoichiometry; black arrows indicate the expected trends of lithium and boron endowment resulting from the presence of jadarite. Tabular geochemical data are reported in Appendix 3.

1. Li-B domain: This shows the highest Li grades up to ~1.5 wt % Li, has B contents up to ~7.5 wt % B, and has a Li/B ratio ~0.5 to 0.1. Its overall geochemistry follows the ideal jadarite line. This domain represents the main Li-B ore observed in the sediment-hosted facies (Fig. 4A).
2. B domain: This reflects higher B contents (up to ~17 wt % B), and lower Li (up to ~0.7 wt % Li) and a lower Li/B ratio (<0.1). Here, an excess of B over Li is observed as compared to the jadarite stoichiometry. Increased B endowment compared to Li is correlated with increasing bulk Na concentrations (Fig. 6B). The B domain includes two distinct populations of data with variable Li/B ratios and Na concentrations (Fig. 6B). A subset of data has the highest Na (up to ~16 wt % Na) and the lowest Li/B ratio (down to ~0.003) and shows the most pronounced displacement from the jadarite stoichiometric line. This group of data corresponds to the NaBo breccia detected in the lower lacustrine sequences of the intrabasinal facies (e.g., Fig. 5J). Another subpopulation within the B domain has lower Na content (up to ~5 wt % Na) and relatively higher Li/B ratio (~0.01–0.1) and is less offset from the jadarite line. This subdomain includes lacustrine to altered tuff facies where the CaNaBo mineralization occurs within intermediate Li grade intercepts (e.g., Figs. 4K, 5A, respectively).
3. Li domain: This shows intermediate Li grades (up to ~0.3 wt % Li); it contains negligible B and yields the highest Li/B ratios (~0.5–20) (Fig. 6A). In this domain, the Li/B ratio is correlated with bulk-rock concentrations of Li and Mg (Fig. 6C, D, respectively). This domain is observed both in the intrabasinal and in the marginal zones of the system, yet the marginal sections display a higher number of intercepts with anomalously high Li/B ratios. This domain includes massive clay layers interbedded with jadarite-rich zones and clay-altered tuff lenses (Fig. 4I, J, respectively).

The downhole litho-geochemistry of representative profiles of the intrabasinal and marginal zones of the Jadar deposit is shown in Figure 7A and B (see App. 3, Table A1 for tabular data). The intrabasinal profile displays a higher thickness of the lacustrine section and shows a typical NaBo breccia within the lower Li-B ore zone. Key features of the marginal

profile include the occurrence of several lacustrine-hosted borate-bearing horizons, the notable absence of a jadarite zone in the upper sequence, which here includes lacustrine sediments interbedded with claystone units. In the intrabasinal profile (Fig. 7A), Li and B are well correlated in most of mineralized samples and show the higher grades in the lower and middle jadarite zones. High Li-B grades in the middle jadarite zone are also observed in non-lacustrine rock types, such as sedimentary breccias (Fig. 5I). High-grade samples have Li/B and Na/B ratios in line with those of stoichiometric jadarite, whereas negative excursions of the Li/B ratio are common in the lower lacustrine zone where the NaBo breccia disrupts the jadarite-bearing sediments (Fig. 5J). Intercepts with high Li/B ratio are occasionally found within the middle Li-B zone and also in the uppermost section of the lacustrine basin. Intercepts with high Li/B ratios show peak values of the Mg/Ca ratio. The Li/B-Mg/Ca correlation is not observed for the high Li/B ratio facies in the upper lake sequence, where anomalous Li/B values match with peaks in the Na/B ratio. The marginal profile (Fig. 7B) shows a similar correlation of Li and B grades in the jadarite-rich ore zones, yet the ore grades in this portion of the system are lower than in the basin center. Samples with an Li/B ratio higher than theoretical jadarite are common throughout the profile and are increasingly more abundant in the upper lacustrine zone where only minor jadarite is present. These intercepts show high Mg/Ca and Na/B ratios, likely due to the presence of magnesian clays and zeolite-altered tuff horizons and sediments (Fig. 4J).

Ore Mineralogy, Facies, and Paragenesis

A summary of the unconventional Li and B mineral species observed in the Jadar deposit is given in Table 1.

Sediment-hosted mineralization

The Li-B ore in this facies is associated with shales containing beds of micritic dolomite (dolomicrite) interlayered with zeolitized laminae and mica-rich layers (Fig. 8A). Here, jadarite forms clusters of stratabound nodules and locally develops both enterolithic veins (Fig. 8B) and vertically elongated nod-

Table 1. Summary of Li and B Minerals Observed in the Jadar Volcano-Sedimentary Deposit

Mineral	Stoichiometry	Group	Li (wt %)	B (wt %)	Occurrence style
Jadarite	$\text{LiNaSiB}_3\text{O}_7(\text{OH})$	Borosilicate	3.3–3.4	14.60	Occurs as nodules and enterolithic veins in the sediment-hosted ore, as glass shard replacement in tuffs and as epigenetic replacement in breccias
Searlesite	$\text{NaBSi}_2\text{O}_5(\text{OH})_2$	Borosilicate	-	5.30	Occurs as late infill of jadarite veins, as well as spherulites in tuffs
Hectorite	$\text{Na}_{0.3}(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	Smectite	0.5–0.7	-	Occurs as displacive nodules and glass shard replacement in tuffs
Lithiophosphate	Li_3PO_4	Phosphate	17.2–18	-	Forms a late replacement of the early diagenetic Li(B) ore
Kernite	$\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \times 3\text{H}_2\text{O}$	Borate	-	15.80	Occurs as crystalline cement of brecciated units, mostly in the lower jadarite zone
Ezcurrite	$\text{Na}_4\text{B}_{10}\text{O}_{17} \times 7\text{H}_2\text{O}$	Borate	-	18–18.4	Occurs as crystalline cement of brecciated units, mostly in the lower jadarite zone
Ulexite	$\text{NaCaB}_5\text{O}_6(\text{OH})_6 \times 5\text{H}_2\text{O}$	Borate	-	13.38	Occurs as crystalline cement of brecciated units, mostly in the lower jadarite zone
Probertite	$\text{NaCaB}_5\text{O}_7(\text{OH})_4 \times 3\text{H}_2\text{O}$	Borate	-	15.4–15.6	Forms a late replacement of searlesite
Howlite	$\text{Ca}_2\text{B}_5\text{SiO}_9(\text{OH})_5$	Borate	-	13.83	Occurs as vertically elongated crystals in the upper borate zone
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \times 5\text{H}_2\text{O}$	Borate	-	15.70	Occurs in laminated sediments in the upper borate zone
Sassolite	H_3BO_3	Borate	-	17.76	Forms a late replacement of the early diagenetic Li(B) ore

Please note that reported Li and B concentrations reflect nominal stoichiometric values (source: handbookofmineralogy.org); dashes indicate data is absent

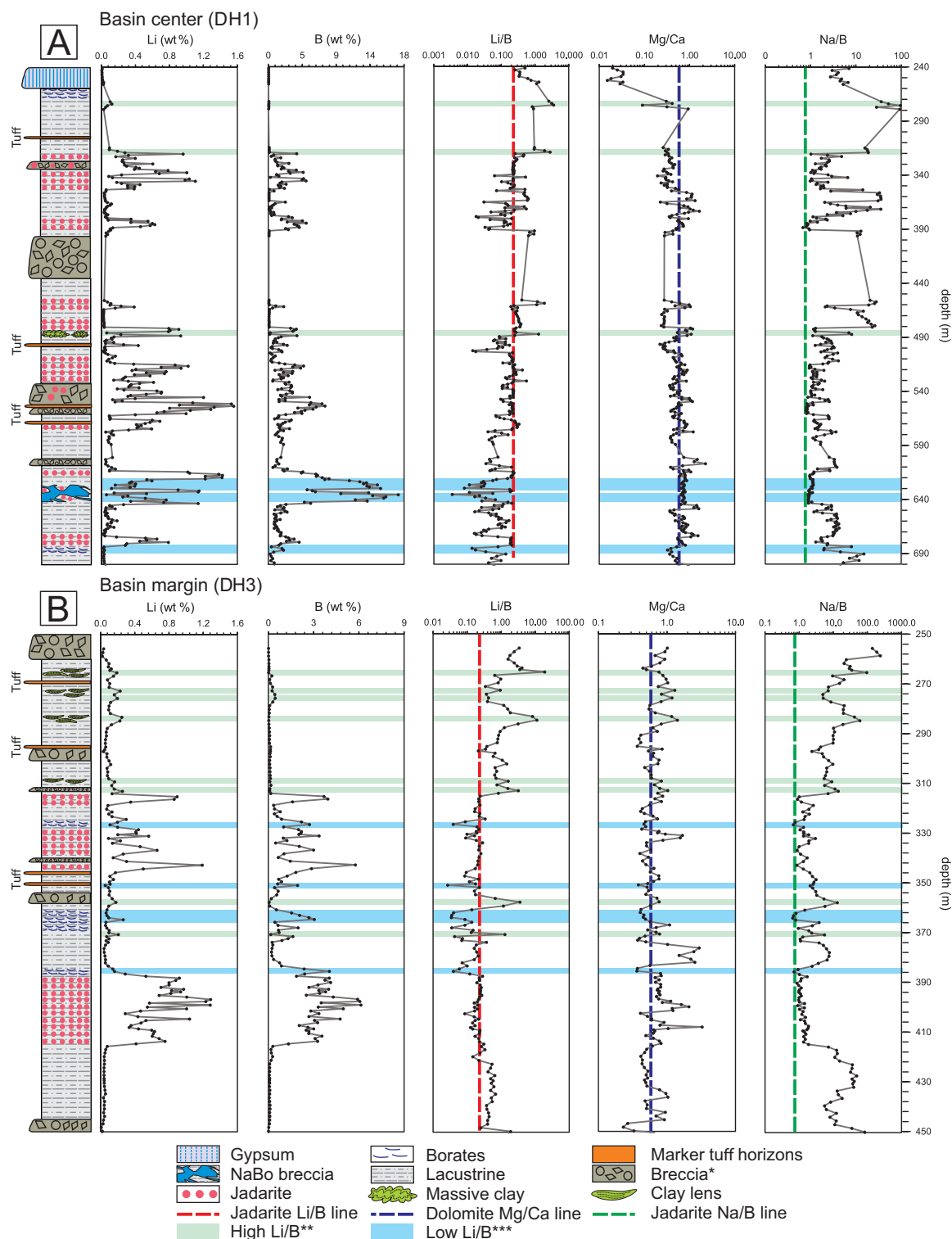


Fig. 7. Lithogeochemical logs of Li and B grades (wt %), as well as Li/B, Mg/Ca, and Na/B ratios for representative profiles of the intrabasinal (A) and marginal (B) sections of the Jadar basin. Notes: ° = includes sedimentary and seismic breccia units; ** = Li/B ratios higher than jadarite stoichiometry; *** = Li/B ratios lower than jadarite stoichiometry.

ules that grew within the dolomite beds (Fig. 8C). Jadarite in shales is often enveloped by Na zeolites (natrolite and/or analcime, Fig. 8A, B) and occurs in sedimentary beds that also contain fine-grained muscovite and zeolites (Fig. 8C).

Shales are locally disrupted by beds rich of volcanogenic material such as fine-grained muscovite that can host searlesite and jadarite (Fig. 8D). Mica-rich domains within the lacustrine facies are also locally interbedded with other authigenic

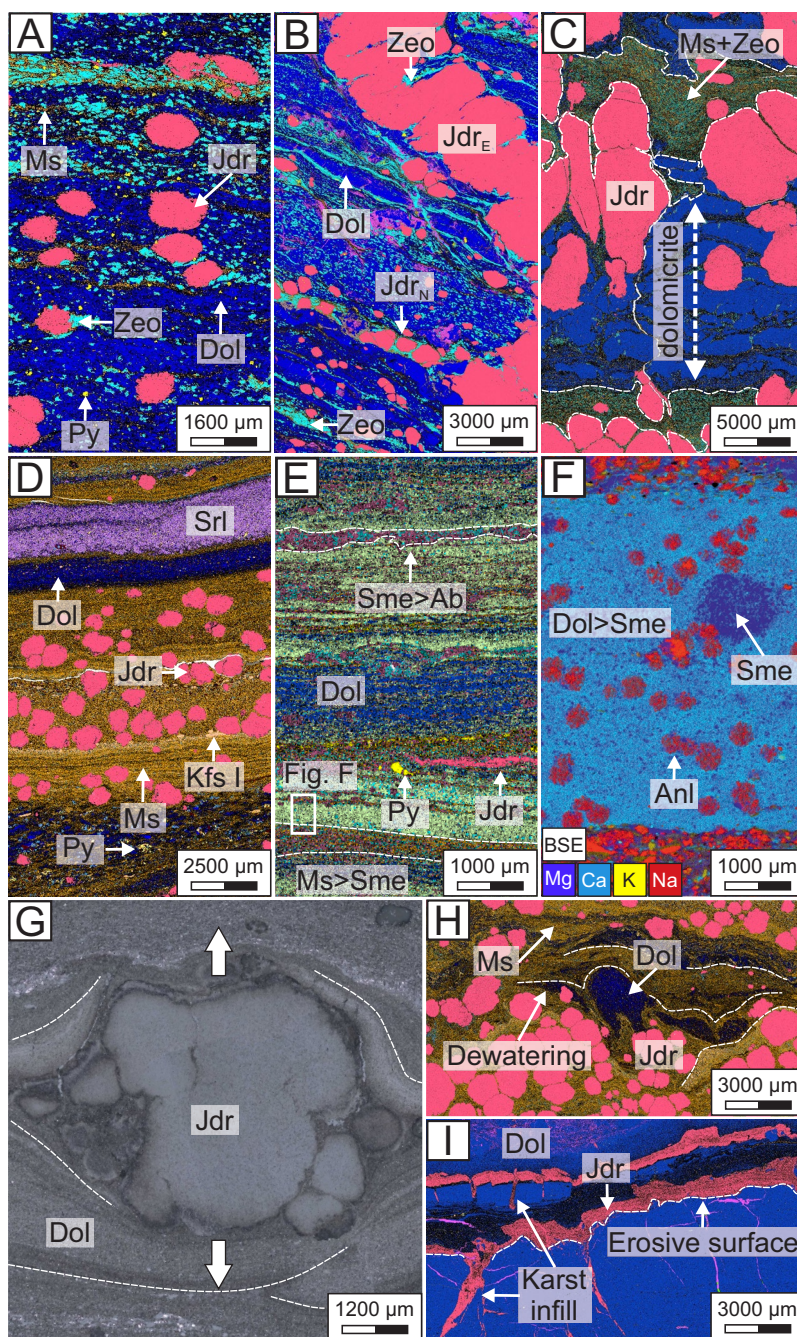


Fig. 8. Mineralogy and textures of the sediment-hosted Li-B mineralization. (A) Dolomite-rich shale with interstitial to laminar Na zeolites and stratabound nodular jadarite. (B) Nodular jadarite (Jdr_N) associated with enterolithic-type jadarite (Jdr_E). (C) Jadarite associated with zeolite + muscovite layers interbedded with dolomite. (D) Mica-rich beds facies interlayered with the sediment-hosted ore. (E) Mica-rich facies overprinted by secondary silicates including smectite, albite, and zeolite. (F) Analcime and dolomite replacing a smectite bed. (G, H) Nodular jadarite triggering soft-sediment deformation of the hosting dolomite and mica. (I) Jadarite concretions filling karstic to erosional cracks within dolomite. Notes: A to E and H to I = automated scanning electron microscopy mineral phase map; F = backscattered electron-energy dispersive spectrometry (BSE-EDS) overlaid elemental map; G = reflected-light photomicrograph. Abbreviations: Ab = albite, Anl = analcime, Dol = dolomite, Jdr = jadarite, Kfs = K-feldspar, Ms = muscovite, Py = pyrite, Sme = undifferentiated smectite, Srl = searlesite, Zeo = undifferentiated Na zeolite.

minerals including albite and smectite, with the latter being replaced by spherulitic Na zeolites (analcime) and dolomite (Fig. 8E, F).

The jadarite formation in the sedimentary units is accompanied by soft-sediment displacement of the surrounding car-

bonates (i.e., displacive growth mechanism, Fig. 8G), as well as by loading and dewatering structures of the mica host (Fig. 8H). Furthermore, jadarite locally penetrates karst fractures and erosive surfaces developed onto the dolomite-rich intervals (Fig. 8I).

Tuff-hosted mineralization

Mineralization styles in tuffs are subdivided into either clay or borate/borosilicate dominated. According to XRD analysis of fine-fraction material separated from the tuffs (App. 4, Figs. A1–A4), Li clays are characterized by a basal reflection (i.e., *d00l*) at 13 Å that decouples into two *d00l* centered at 13 and 17 Å after ethylene glycol solvation, and additionally by a *d060* peak at 1.52 Å. These features indicate that Li clays include a mixed layer phase dominated by smectite with minor vermiculite, and that the smectite component belongs to an Mg-rich trioctahedral end member (Moore and Reynolds, 1989). Further analysis by heat treatment, ethylene glycol saturation, and Cs solvation indicates that the Mg smectite component corresponds to hectorite, rather than saponite and/or stevensite (Christidis and Koutsopoulou, 2013). To evaluate the mineral chemistry of clays, separates were analyzed for Li by inductively coupled plasma-optical emission spectrometry (ICP-OES), whereas other major oxides and fluorine were measured by in situ SEM-EDS (App. 4, Table A1). Lithium contents of clays are around 0.85 wt % Li₂O, which are slightly lower than hectorite-like clays free of any mixed-layer phase as those measured in the Thacker Pass and Hector deposits (Morissette, 2012; Benson et al., 2023, and references therein). Other major and minor elements detected in the Jadar Li clays include Mg (~22–26 wt % MgO) and F (~1–2 wt % F). Combining the XRD and chemical features, Li clays in the Jadar deposit can be classified as F-bearing hectorite inter-layered with a minor nonswelling component (vermiculite). For the sake of simplicity, hereafter we will refer to this Li-rich clay as “hectorite.”

Three textural types of hectorite have been observed in the tuff units: (1) pseudomorphs after shard-like morphologies; this hectorite generation is replaced by Na zeolites (analcime) and enveloped by a secondary K-feldspar groundmass (Fig. 9A); (2) clay clusters that fill voids within the altered host tuff (Fig. 9B); and (3) nodules rimmed by fine-grained dolomite aggregates (Fig. 9C). Analysis by TEM further defined the nanoscale paragenetic relationship between hectorite and related dolomite. Dolomite has variable morphologies from pan-shaped grains (Dol I) to recrystallized rhombohedra (Dol II) that appear to lack any diagnostic microbial or precursor carbonate texture and occur as a replacement of hectorite packages (Fig. 9D). Borate/borosilicate-mineralized tuffs are mostly enriched in jadarite and searlesite, which both form nodular to spherulitic clusters and veinlets (Fig. 10A). This mineralized facies contains abundant relict biotite and secondary albite; the latter likely formed after alteration of primary feldspar grains (Fig. 10B). Tuffs are characterized by ubiquitous and extensive potassic alteration, which led to the formation of secondary K-feldspar late in the mineralizing process, occurring within the fine-grained groundmass (Figs. 9A–C, 10A, B). Tuff horizons locally show the most intense and texturally destructive alteration process and are characterized by secondary K-feldspar with vuggy to ghost morphologies (Fig. 10C–E). Ghost textures show blocky boundaries that locally contain relict grains of primary feldspars (Fig. 10C, D) and cusped to bubble-walled morphologies (Fig. 10E).

Breccia-hosted mineralization

Jadarite in volcanoclastic breccias shows textures and paragenesis that contrast with those of nodular to enterolithic jadarite from the sediment-hosted ore. Here, jadarite occurs as fine-grained epigenetic aggregates (hereafter “ghost jadarite”) that replace the host-rock (Fig. 11A). Ghost jadarite displays zebra-like banded texture consisting of alternating layers of jadarite and of pyrite, albite II, and chlorite. (Fig. 11B). The host rock of this breccia type is dominated by relict magmatic minerals, including K-feldspar I, albite I, and mica (biotite and muscovite). The coarser relict primary phases include feldspars, which are present as rounded to subangular clasts largely affected by albitization and zeolitization (analcime) (Fig. 11A). Ghost jadarite is also locally observed in breccia developed from lacustrine units, where it is mostly found as fine-grained concretions that developed within highly fractured cataclastic zones (Fig. 11C).

Jadarite paragenesis and relationship between Li-B mineralization and zeolitization

To summarize, multiple processes have produced a range of jadarite types, which occur in different mineralogical assemblages and show variable paragenetic relationships. Jadarite in altered tuffs occurs as grains with bubble-bordered boundaries, where entire bubble morphologies were locally preserved (Fig. 12A, B). Jadarite is also paragenetically associated with opal-A (see App. 5, Figs. A1–A3 for FTIR characterization) in the form of late rims growing onto the surfaces of nodules (Fig. 12C). Mineralized veins show a recurring mineralizing zoning that consists in early jadarite, followed by searlesite forming at the final stage of the open space filling process (Fig. 12D).

A close paragenetic relationship exists between Li ore deposition (as jadarite and hectorite) and zeolitization. Zeolites in the sediment-hosted mineralization overgrow the surface of both jadarite nodules and enteroliths, and form stratabound lenses interlayered with dolomite beds (Fig. 13A, B). Zeolites locally show discordant relationships with the sedimentary layering, expressed as development of natrolite + analcime + jadarite veins, in which zeolites form tabular aggregates intergrown with dolomite (Fig. 13C, D). In the clay-altered tuff horizons, zeolitization occurred shortly after Li enrichment, resulting in the formation of analcime replacements of hectorite (Fig. 13E). Ghost jadarite from the breccia units also displays a close relationship with zeolitization—here, analcime replaces relict primary feldspars and forms veinlets along the boundaries of ghost jadarite aggregates (Fig. 13F). This Na zeolite type also records a further episode of sodic alteration, leading to an extensive albitization of earlier analcime (Fig. 13G). The detected analcime types show variable mineral chemistries; specifically, analcime pseudomorphs after shards have a high Si/Al ratio, whereas vein-hosted analcime type in breccias have a lower Si/Al ratio (App. 6., Fig. A1, Table A1).

Late-mineralizing processes

Mineralization in the Jadar deposit locally shows evidence of alteration of the early borosilicate assemblage (i.e., jadarite and searlesite) and of a redistribution of Li and B into secondary phases. Locally, jadarite nodules from the sediment-host-

ed mineralization have irregular and corroded surfaces, likely developed as a result of later dissolution processes (Fig. 14A). Altered jadarite nodules are associated with a later borate-phosphate assemblage (Fig. 14A, B) that according to in situ XRD includes the minerals sassolite (H_3BO_3) and lithiophosphate (Li_3PO_4) (App. 7, Figs. A1-A4 and A5-A8, respectively). Lithiophosphate either occurs as tabular grains associated with sassolite (Fig. 14B) or as infill of open spaces within the carbonate sediments (Fig. 14C). Lacustrine sediments with evidence of Li-B remobilization also show abundant authigenic apatite occurring as needle-shaped aggregates (Fig. 14D, E). Alteration of early borosilicates also controlled the formation of late CaNaBo (i.e., probertite— $\text{NaCaB}_5\text{O}_7(\text{OH})_4 \times 3(\text{H}_2\text{O})$) lenses (Fig. 14D) and CaNaBo replacive fronts that form via the breakdown of searlesite nodules (Fig. 14F).

Relationship with organics

We have observed a close relationship between the Li-B ore and organic matter in the sediment-hosted mineralization. Organic matter can be broadly classified as either syngenetic or epigenetic. Syngenetic organics include vitrinite fragments, fusinite, amorphous organic matter, and alginite (App. 8, Figs. A1-A4). Amorphous organic matter and alginite form small layers (~20–50 μm in length) and developed conformably with the lacustrine sediments. The epigenetic organic fraction is mostly dominated by bitumen, which form micro- to macroscale pods and veins discordant to sedimentary layering (App. 8, Figs. A5-A7). The FTIR mapping of a bitumen vein (Fig. 15) has shown that epigenetic organics are dominated by transmission bands at 3,400, 1,620, and 876 cm^{-1} . The 3,400- cm^{-1} band usually ascribed either to O-H or to the N-H

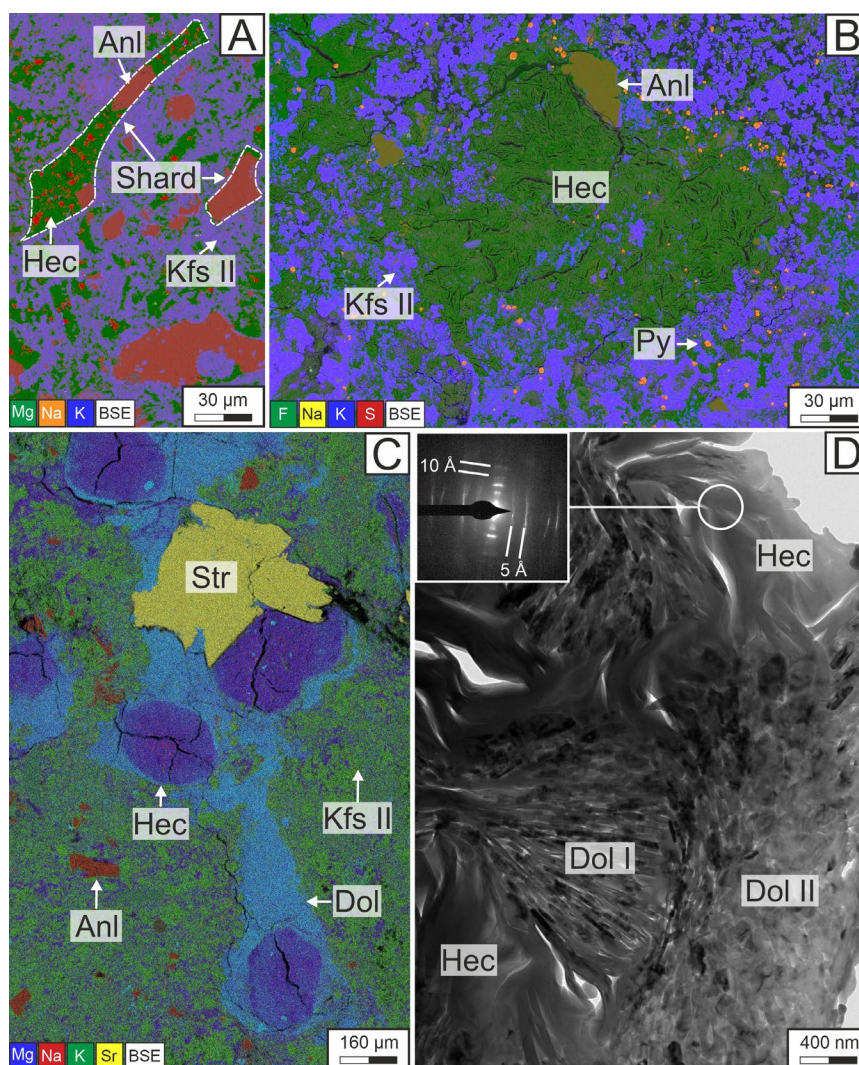


Fig. 9. Mineralogy and textures of the clay-altered tuff units. (A) Hectorite-analcime intergrowth forming pseudomorphs after shards. (B) Authigenic hectorite filling voids within secondary K-feldspars. (C) Nodular-type hectorite rimmed by fine-grained dolomite. (D) Nanoscale association between clays and carbonate, showing primary dolomite needles (Dol I) and rhombohedra (Dol II) developed through pseudomorphic alteration of hectorite. The inset displays selected area electron diffraction (SAED) on clay packages. Here, the 10-Å reflection is a proxy of smectite-group clays that are subjected to structural collapse under the effect of the transmission electron microscopy (TEM) vacuum. Notes: A to C = backscattered electron-energy dispersive spectrometry (BSE-EDS) overlaid elemental maps; D = TEM textural images with inset indicating location and result of the selected area electron diffraction (SAED). Abbreviations: Anl = analcime, Dol = dolomite, Hec = hectorite, Kfs = K-feldspar, Py = pyrite, Str = strontianite.

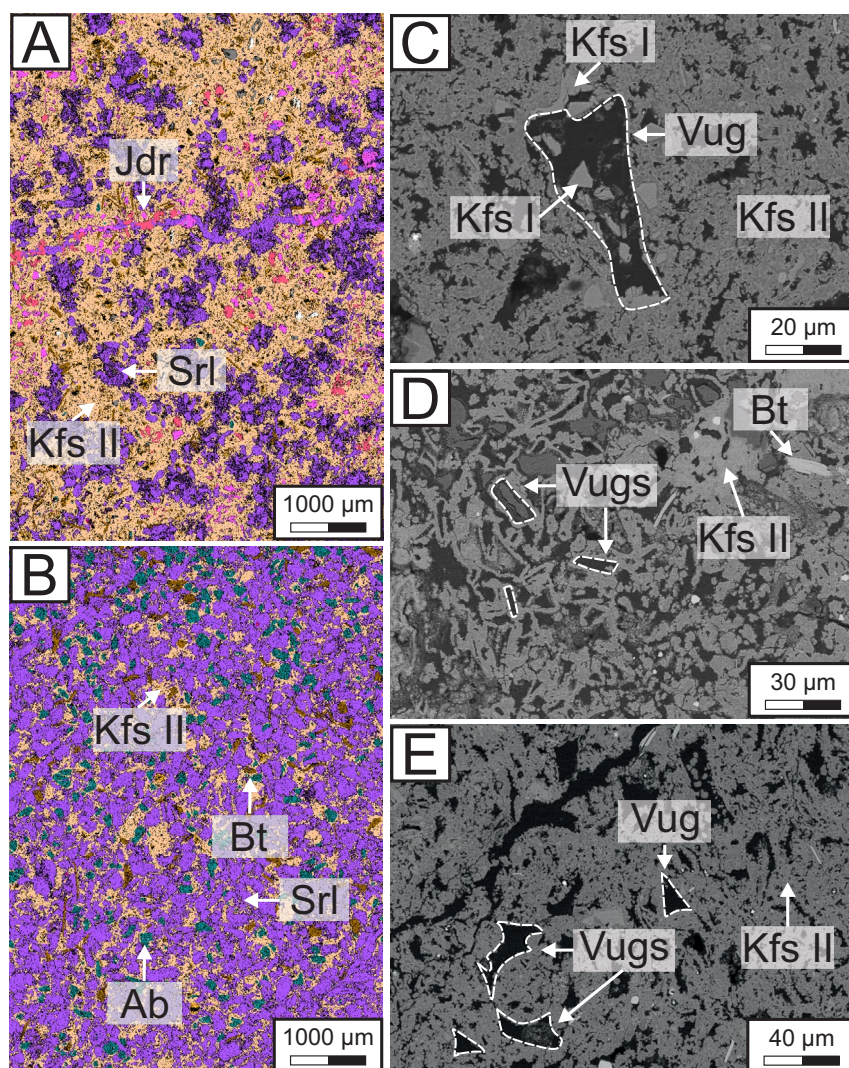


Fig. 10. Mineralogy and textures of the borate/borosilicate-rich and barren tuff horizons (A-B and C-E, respectively). (A) Nodular to vein-hosted searlesite + jadarite mineralization in a tuff horizon. (B) Late authigenic K-feldspar enveloping searlesite and primary biotite grains. (C, D) Blocky vugs locally containing relict primary feldspar grains. (E) Cuspsate to bubble-walled vugs. Notes: A and B = automated scanning electron microscopy mineral phase maps; C to E = backscattered electron (BSE) photomicrographs. Abbreviations: Ab = albite, Bt = biotite, Jdr = jadarite, Kfs = K-feldspar, Srl = searlesite.

stretching vibration, whereas the asymmetric bands at 1,620 and 876 cm^{-1} are due to the stretch of the C=C and O-H bonds in aromatic compounds. No bands in the range of aliphatic compounds ($\sim 2,700\text{--}3,000\text{ cm}^{-1}$) have been observed. Other features of the FTIR footprint of the investigated area include broad bands between 1,000 and 1,150 cm^{-1} that are due to the stretching vibration of the Al-O-Si bond of aluminosilicates in the mineral matrix.

Isotopic Geochemistry

Isotopic analyses of dolomite, jadarite, and hectorite are reported in Appendix 9 (Tables A1-A3). Dolomite from the sediment-hosted mineralization shows slightly negative $\delta^{13}\text{C}$ values spanning within a narrow range (i.e., -3.6 to -0.8‰ $\delta^{13}\text{C}_{\text{V-PDB}}$; V-PDB = Vienna-Pee Dee Belemnite). The oxygen composition shows the most significant fluctuation, with values between 26.8 and 28.5 ‰ $\delta^{18}\text{O}_{\text{V-SMOW}}$ (V-SMOW = Vienna-standard mean ocean water). Dolomite from Jadar plots away

from the field of late diagenetic dolomites formed via burial diagenesis and has a C-O footprint like carbonates from shallow saline environments such as playa lakes (Fig. 16A). The observed isotopic variation of dolomite is largely controlled by fluctuations of the $\delta^{18}\text{O}$, with a subordinate contribution of a $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ covariation (Fig. 16B).

The oxygen and hydrogen composition of jadarite plots subparallel to the kaolinite-smectite lines in the $\delta^{18}\text{O}$ - δD projection, with values between 24.4 to 28.6 ‰ $\delta^{18}\text{O}_{\text{V-SMOW}}$ and -27 to -16‰ $\delta\text{D}_{\text{V-SMOW}}$ (Fig. 16C). The oxygen and hydrogen isotope composition of hectorite varies between 6.7 to 7.9 ‰ $\delta^{18}\text{O}_{\text{V-SMOW}}$ and -113 to -103‰ $\delta\text{D}_{\text{V-SMOW}}$ (Fig. 16C).

The Sr isotope signature of both jadarite and hectorite is homogeneous, with values between 0.7128 and 0.7130 $^{87}\text{Sr}/^{86}\text{Sr}$ for jadarite and values of 0.7126 $^{87}\text{Sr}/^{86}\text{Sr}$ for hectorite, whereas the measured isotopic ratios of dolomite are slightly lower and range between 0.7115 and 0.7121 $^{87}\text{Sr}/^{86}\text{Sr}$ (App. 9, Table A3).

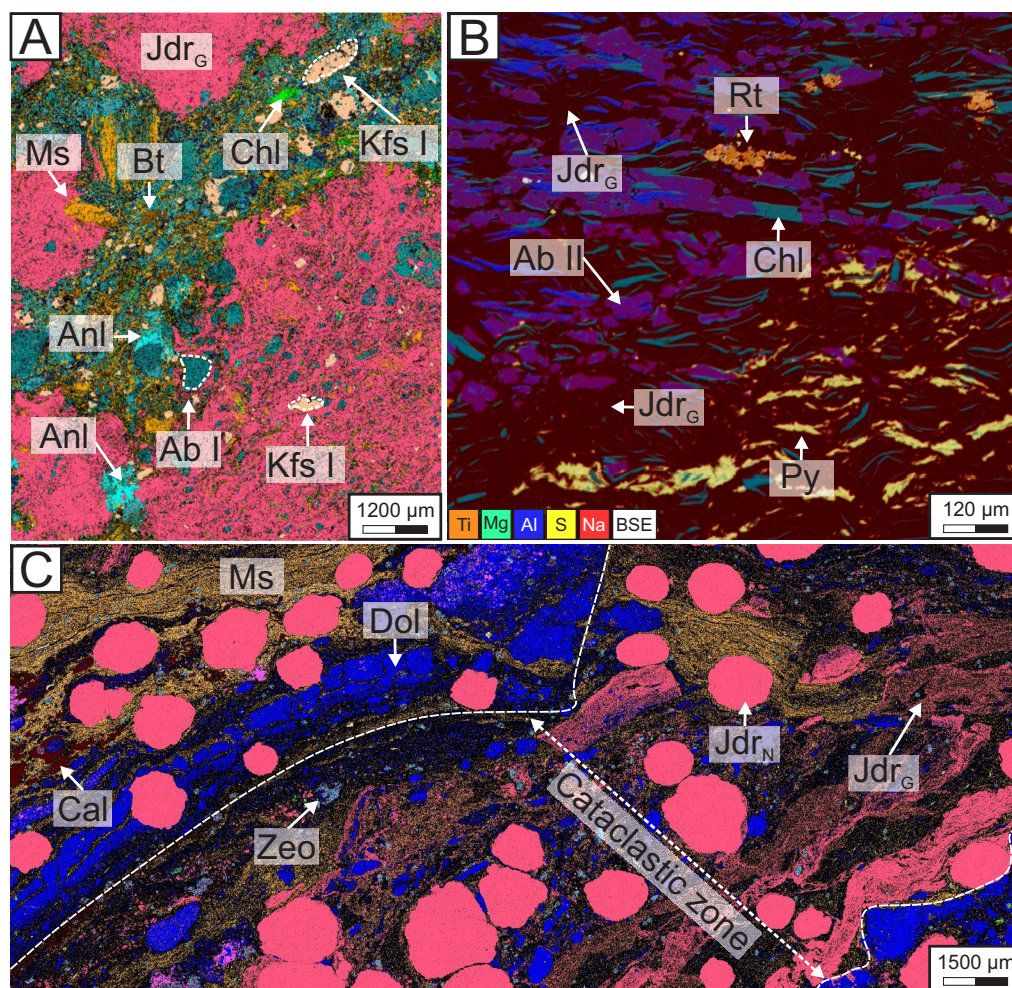


Fig. 11. Mineralogy and textures of ghost jadarite (Jdr_G) in brecciated units. (A) Ghost jadarite filling voids between reworked primary magmatic minerals (i.e., altered feldspar grains, as well as muscovite and biotite). (B) Ghost jadarite associated with pyrite and authigenic silicates including albite and chlorite. (C) Brecciated lacustrine unit with ghost jadarite superimposing the nodular jadarite (Jdr_N) in lacustrine sediments. Notes: A and C = automated scanning electron microscopy mineral phase maps, B = backscattered electron-energy dispersive spectrometry (BSE-EDS) overlaid chemical map. Abbreviations: Ab = albite, Anl = analcime, Bt = biotite, Cal = calcite, Chl = chlorite, Dol = dolomite, Jdr = jadarite, Kfs = K-feldspar, Ms = muscovite, Py = pyrite, Rt = rutile, Zeo = undifferentiated zeolite.

Discussion

Genesis of the jadarite-type VS Li-B deposit

Existing models for the Li enrichment in VS deposits are mostly based on the diagenetic to higher-temperature alteration of intrabasinal Li-bearing igneous rocks (Putzolu et al., in press). Some authors have explained the genesis of Li clays through the closed hydrologic system diagenesis (CHSD) of volcanic glass-rich volcanoclastic units (Castor and Henry, 2020). During CHSD, Li smectites crystallize under near-neutral pH from the aging of amorphous gels (palagonite-like)—these having formed as an early product of the hydrolysis of volcanic glass. As this process develops, the $(Na^+ + K^+)/H^+$ ratio and SiO_2 activity increase in residual pore waters, raising the pH of the system. Increasing pH suppresses smectite formation and favors the formation of Na zeolites and secondary K-feldspars (Hall, 1998; Langella et al., 2001). Another model links the genesis of Li clays to direct precipitation from lake waters with high activities of Li^+ , Mg^{2+} , and F^- and under a condition of

silica saturation (Benson et al., 2023). Both models fit with Li deposition environments where dissolution of volcanic-glass-rich rock types, as well as high evaporation in closed hydrologic settings, leads to high pH conditions.

The Jadar basin experienced several stages of input of igneous material of both volcanoclastic and plutonic origin, leading to the deposition of mechanically reworked units ranging from tuffaceous to granite detritus in the form of conglomerate, breccias, and debris flow (Fig. 5A, F, G), as well as in situ tuffs that likely were deposited through ash falls (Fig. 5D). Reworked granitoid units are unmineralized and only display propylitic alteration that potentially predates deposition in the Jadar basin. Volcanoclastic horizons display ore-grade-level Li-B contents and contain both jadarite and hectorite that locally form cusped to bubble-walled morphologies (Figs. 9A, 12A, B), which suggest that a portion of the Li-B ore formed through the in situ replacement of vesiculated and fragmental material rich in volcanic glass shards. The observed paragenesis of Li-B ore and alteration assemblage indicates that the

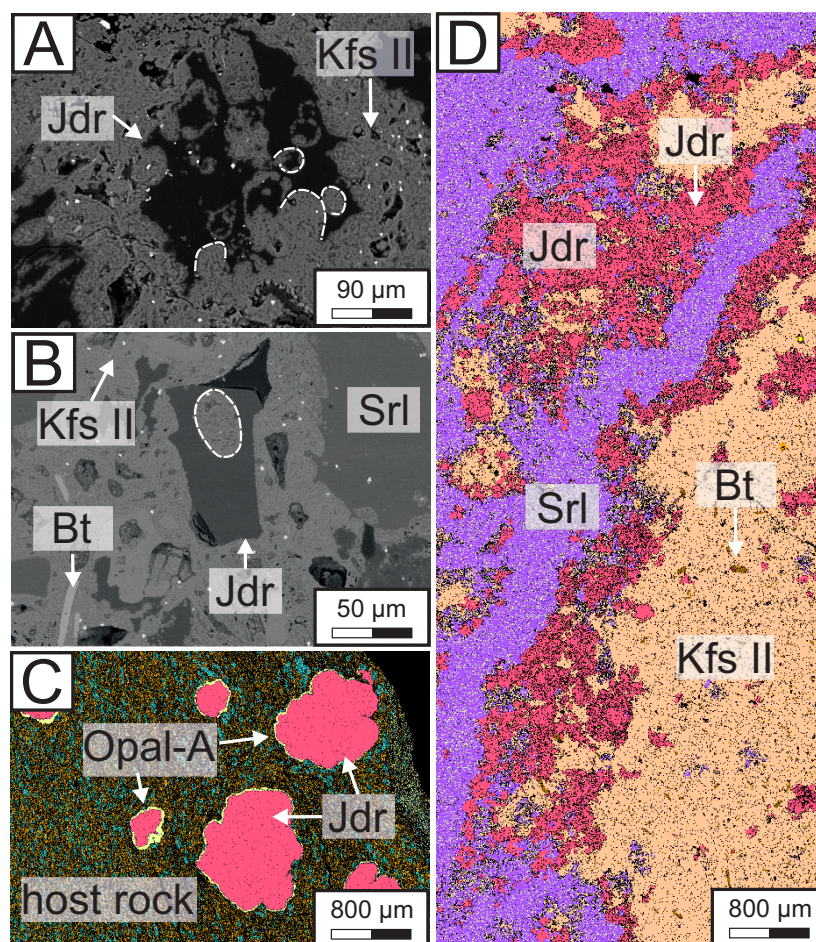


Fig. 12. Summary of paragenetic pathways for jadarite formation. (A, B) Jadarite grains from altered tuff units with bubble-bordered boundaries (white dashed lines). (C) Nodular jadarite rimmed by opal-A. (D) Mineralized vein with a jadarite to searlesite precipitation sequence. Notes: A and B = backscattered electron (BSE) photomicrographs; C and D = automated scanning electron microscopy mineral phase maps. Abbreviations: Bt = biotite, Jdr = jadarite, Kfs = K-feldspar, Srl = searlesite.

deposition of hectorite and jadarite is followed by extensive zeolitization and K-feldspar authigenesis (Figs. 8A, B, 9A, 10). This mineralizing sequence indicates that CHSD can partially explain the formation of jadarite-type mineralization. However, in the Jadar basin, the bulk of Li is fixed in jadarite from sediments displaying lake center facies characterized by high dolomite and kerogen contents and finely laminated sedimentary layering (Figs. 4B, 8A; App. 8, Figs. A1-A4). Hectorite-rich units, which account for only a subordinate volume of the Li resources, are observed mostly in the marginal facies, and they are locally interlayered with the jadarite zones. The apparent suppression of hectorite formation, followed by extensive dolomitization and zeolitization, is arguably the key diversion of the paragenetic pathway of the Jadar deposit compared to clay-type VS Li deposits. The later development of the jadarite (dolomite + zeolite) facies as a distinctive overprint of the hectorite-rich units is supported by the presence of sharp lithological contacts and crosscutting relationships between the Li clay altered tuffs and the jadarite-bearing lacustrine sediments (Fig. 4H, I). This observation is also in agreement with nanoscale paragenetic study, which shows that dolomite formed as a product of the breakdown of hectorite (Fig. 9D). This is also supported by

the slightly negative $\delta^{13}\text{C}$ values recorded for dolomite (Fig. 16A, B), indicating minimal input of organic carbon from the decay of organic matter that favored a genetic pathway from a mineral precursor (Warren, 2000). Breakdown of Mg clays (i.e., saponite and stevensite) during alteration of volcanoclastic units is observed in modern high-pH lakes in volcanic terranes (e.g., Lake Magadi, Kenya) and is associated with the development of alkali-rich siliceous gels and Mg^{2+} -saturated pore waters (e.g., Eugster and Jones, 1968; Renaut et al., 2021). As the early formed Mg clays in the Jadar deposit contained high Li, their alteration to form dolomite contributed significantly to Li^+ remobilization and silica saturation needed for later mineralizing processes. Then, textural evidence points to the aging and diagenetic maturation of metastable and poorly crystalline silica gels that aided the formation of some of the observed jadarite types: nodular jadarite, which forms coalescing clusters of nodules locally displaying wavy morphologies inherited from the plastic movements of the colloid/gel precursor (Fig. 5D), and jadarite in the form of spherulitic aggregates (Fig. 4F), which in diagenetic to low-temperature hydrothermal systems record the formation of poorly crystalline and metastable silica polymorphs, such as opal-A, consistent with an origin from silica gels (e.g., Wil-

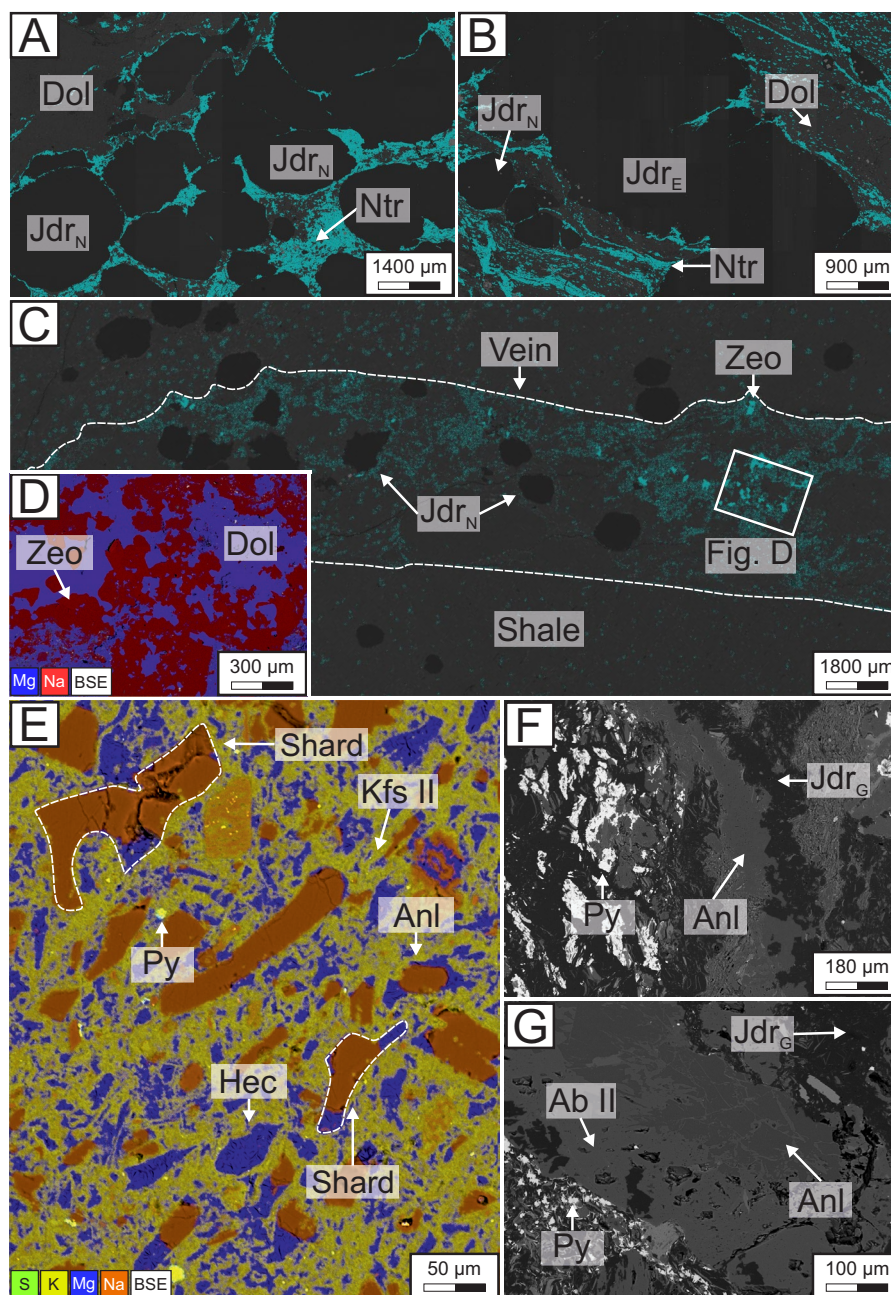


Fig. 13. Paragenetic relationship between the Na zeolite types and formation of jadarite and hectorite. (A, B) Distribution of Na zeolites and relationship with nodular and enterolithic jadarite (Jdr_N and Jdr_E , respectively) in the sediment-hosted mineralization. (C, D) Distribution of Na zeolites in jadarite-rich veins. (E) Paragenetic relationship between analcime and hectorite in the mineralized tuff horizons. (F) Close-up view showing an analcime veinlet coeval with ghost jadarite (Jdr_G). (G) Late albite overprinting analcime in the ghost jadarite-rich brecciated facies. Notes: A to C = automated scanning electron microscopy zeolite distribution maps overlain with backscattered electron (BSE) images; D and E = BSE images overlain with energy dispersive spectrometry (EDS) elemental maps; F and G = BSE images. Abbreviations: Ab = albite, Anl = analcime, Dol = dolomite, Hec = hectorite, Jdr = jadarite, Kfs = K-feldspar, Ntr = natrolite, Py = pyrite, Zeo = undifferentiated Na zeolite.

liams and Crerar, 1985; Jorge et al., 2005; Renaut et al., 2021; Renaut and Owen, 2023). This paragenesis confirms an early mineralizing episode of CHSD where the alteration of volcanic glass formed a hectorite mineralization associated with Na zeolites and secondary K-feldspar. This alteration stage is similar to mineralizing processes previously described in clay-type VS Li deposits (Castor and Henry, 2020).

However, the later hectorite breakdown and formation of jadarite from a siliceous gel is the unique process observed at Jadar that distinguishes it from other more conventional clay-type VS deposits. This additional mineralizing stage can be explained by an integrated CHSD plus chemical divides model (Hardie and Eugster, 1970; Tosca and Tutolo, 2023, and references therein). The chemical divides model explains

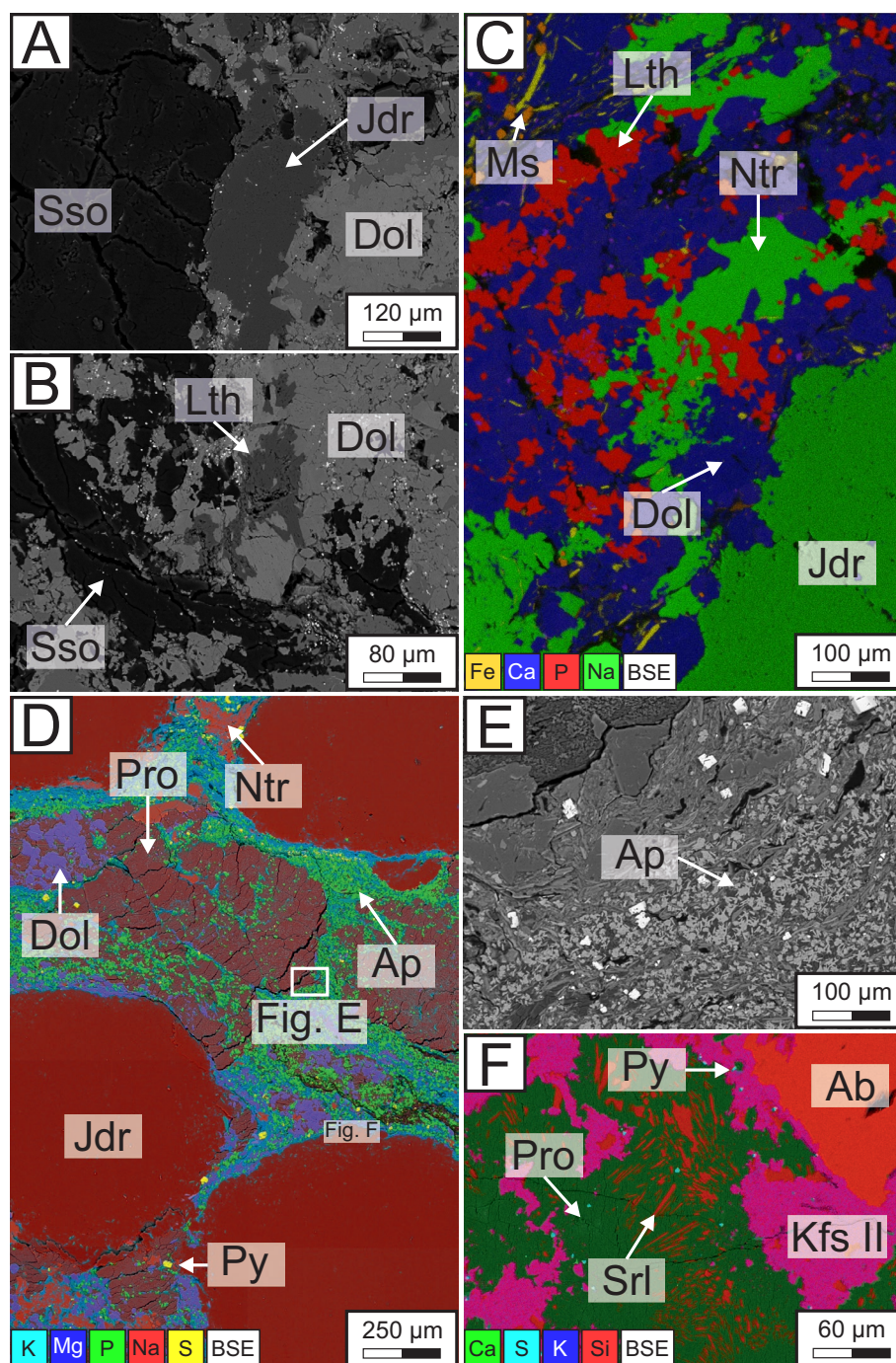


Fig. 14. Mineralogy and textures of late minerals in the sediment- and tuff-hosted ores. (A, B) Partially altered jadarite grains associated with late sassolite and lithiophosphate. (C) Late lithiophosphate filling open spaces. (D, E) Late apatite filling intergranular spaces in lake sediments. (F) Late CaNaBo (probernite) enclosing relict searlesite. Notes: A, B, and E = back-scattered electron (BSE) photomicrographs; C, D, and F = BSE-energy dispersive spectrometry (EDS) overlaid chemical maps. Abbreviations: Ab = albite, Ap = apatite, Dol = dolomite, Jdr = jadarite, Kfs = K-feldspar, Lth = lithiophosphate, Ms = muscovite, Ntr = natrolite, Pro = probernite, Py = pyrite, Srl = searlesite, Sso = sassolite.

the evolution of closed alkaline lakes with waters/fluids endowed of a range of elements sourced from the alteration of volcanoclastics and/or geothermal springs. Water removal by strong evaporation is the main trigger of the hydrogeochemical changes to the lake waters, which then will precipitate minerals in order of increasing solubility (Hardie and Eug-

ster, 1970; Eugster and Hardie, 1978; Tosca and Tutolo, 2023, and references therein). Removal of specific components by mineral precipitation is the main controlling factor to the resulting chemistry of the residual brines and/or fluids, exerting a first-order control on the mineralogy of later evaporitic phases. The mineralogical features of the Jadar basin indicate

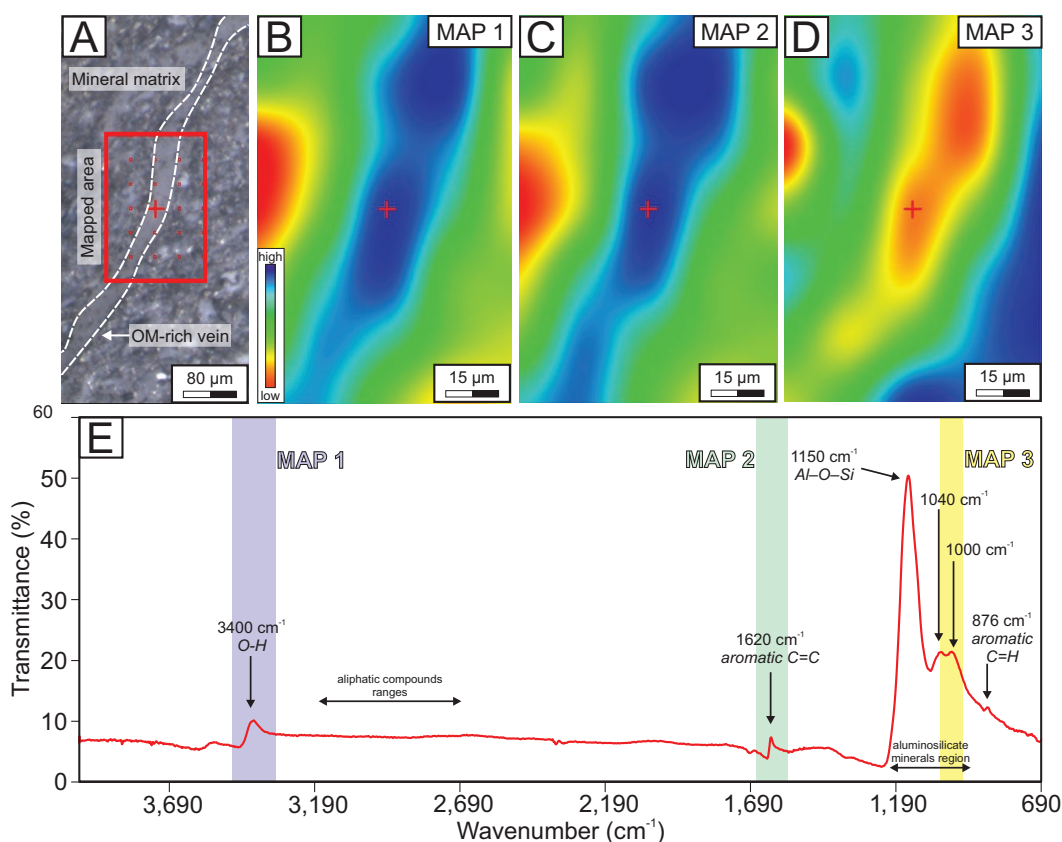


Fig. 15. Fourier transform infrared spectroscopy (FTIR) results on epigenetic bitumen. (A) Camera view of late bitumen vein crosscutting lake sediments. Red square shows the analyzed area. (B-D) Extracted FTIR intensity maps of selected wavenumber (cm⁻¹) regions. (E) FTIR transmittance spectrum of analyzed area displayed in Figure 15A. Abbreviations: OM = organic matter.

that the solute composition of system was dominated by Na⁺, Li⁺, Mg²⁺, B³⁺, Al³⁺, SiO_{2(aq)}, K⁺, HCO₃⁻, and CO₃²⁻ and, based on the absence of halite, the system was low in Cl⁻. Dolomite is the earliest neoformed mineral in the sediment-hosted Li-B mineralization (Fig. 17A, B), and jadarite nucleation and zeolitization occurred shortly afterward, as indicated by the displacive growth features that jadarite produced in the surrounding dolomitic sediments (Fig. 8A, B, G). Therefore, the early saturation of the system in the dolomite component was key to removal of Mg²⁺-Ca²⁺-HCO₃⁻-CO₃²⁻, thereby saturating the residual fluids in Na⁺, Li⁺, Mg²⁺, B³⁺, Al³⁺, and SiO_{2(aq)}, which were enriched in the mother gel that precipitated jadarite (Fig. 17B). The chemical divide approach can also explain the observed evolution of mineral phases in equilibrium with jadarite. Formation of jadarite is coeval with opal-A, Na zeolites, and searlesite (Figs. 8, 12). These phases occur as rims on jadarite, and thus likely formed as by-products from elemental excess (i.e., Si⁴⁺ > Li⁺ + Na⁺ + B³⁺, Si⁴⁺ + Al³⁺ + Na⁺ > Li⁺ + B³⁺, Si⁴⁺ + Na⁺ + B³⁺ > Li⁺ + Na⁺, respectively) of the chemistry of the mother gel when compared to jadarite stoichiometry (Fig. 17B-D). Late potassic alteration, which led to the formation of authigenic K-feldspar, commonly occurs at the end of this paragenetic pathway, demonstrating that residual fluid batches are now spent of Li⁺, Na⁺, and B³⁺ and then become K⁺ saturated (Figs. 10, 17B-D). Evidence of intense silica stripping and remobilization from the host-rock mass are provided in the tuffs that show the most developed

and texturally destructive alteration facies. In these horizons, secondary K-feldspars have developed a vuggy texture with ghost morphologies of both phenocrysts and volcanic glass shards (Fig. 10C-E). This indicates that the mineralizing process effectively mobilized silica from the primary components of the host rock, leaving behind a K-feldspar residuum—a process that likely required fluids with pH values above the field of stability of quartz and/or amorphous silica compounds (i.e., pH > 9; Kehew, 2000).

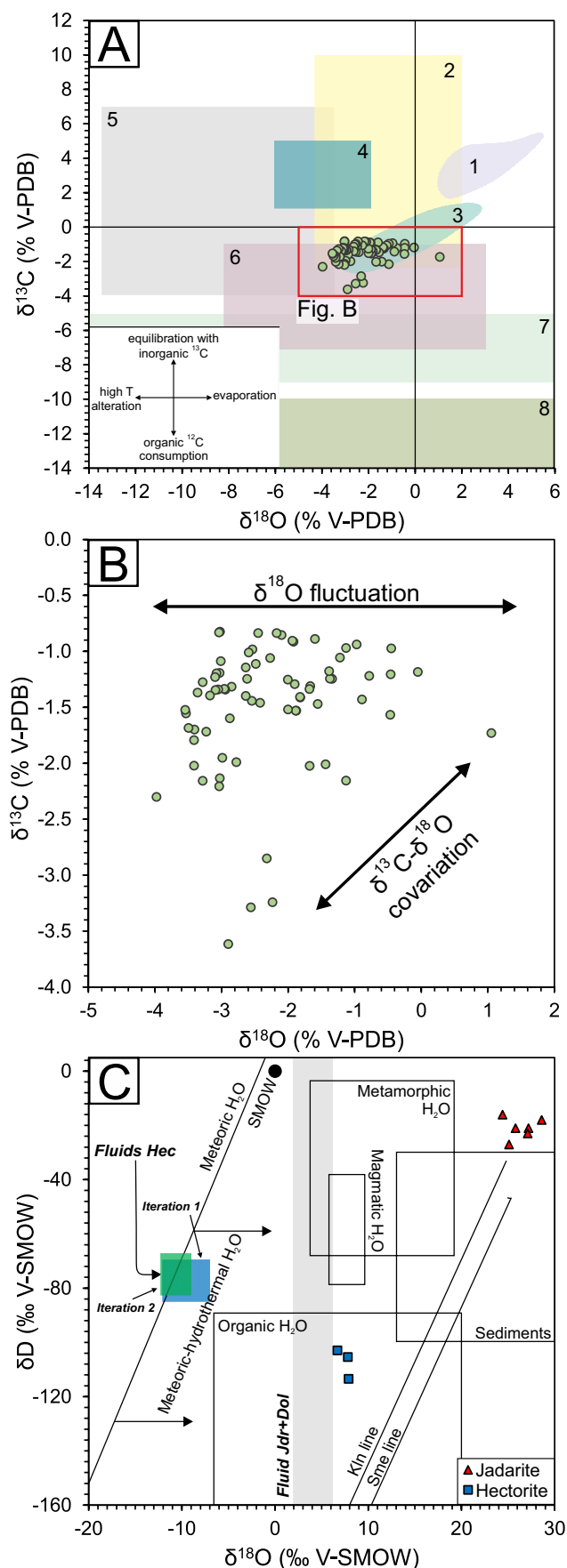
Even though the observed mineralizing processes reflect alkaline conditions, the latest stages of mineral deposition record a pH retrogression toward near-neutral to slightly acidic pH levels. Early borosilicates, such as jadarite and searlesite, show dissolution and replacement features reflective of interaction with a later fluid component. Dissolution of the early borosilicate phases formed a sassolite + lithiophosphate assemblage after jadarite (Fig. 14A, B), and probertite after searlesite (Fig. 14F). Sassolite is a common solid phase found in fluid inclusions of metasomatic granitic facies (i.e., greisen) formed from fluxes of acidic fluids (Legros et al., 2022). Furthermore, in lake environments that contain tephra units, low pH fluids remobilize PO₄³⁻ ions from magmatic apatite to form late diagenetic phosphates (e.g., Liesegang and Wuttke, 2022), which are paragenetically comparable to the authigenic apatite II and lithiophosphate observed at Jadar. This suggests that the stability of this assemblage in the Jadar deposit required a late decrease in pH. Maturation of the organics mat-

ter is the most likely agent of pH change in the Jadar deposit. Maturation of primary kerogen (macerals and alginite) led to the formation of late bitumen veins that contain highly mature aromatic organic components (Fig. 15; App. 8, Fig. A5-A7). Organic maturation and a consequent pH decrease was likely aided by the burial of the basin through later sedimentation and by the enhanced heat flow provided during contemporaneous cooling of the Miocene rocks of the Cer Mountain, and likely yielded organic ligands including carbonic acids. The maturation of organic matter and acid release under reducing conditions is an important feature since it has led to the breakdown of primary $\pm$ Li-bearing borosilicate phases and causes the Li-B redistribution and mineralogical-geochemical decoupling in later phases.

Nature of Li-B mineralizing fluids and ore-forming environment

Stable and radiogenic isotopes have been used to further constrain the mineralizing history of the system. The $\delta^{18}\text{O}$ composition of dolomite and jadarite have been used to calculate isotopic equilibrium curves to assess both the composition and the temperature of the fluid in equilibrium with the jadarite-bearing assemblage (Fig. 18A). This approach is based on evidence of equilibrium between mineral pairs and calculations from established mineral-fluid fractionation equations. Textural observations support that jadarite formed contemporaneously to shortly after dolomite (e.g., Fig. 8A, G), and whereas well-established mineral-fluid fractionation equations exist for dolomite, no equation exists for jadarite or similar Na borosilicates. However, evidence presented here (Fig. 13) and in previous studies support that the formation of Na borosilicates as jadarite and searlesite is paragenetically related with the formation of Na zeolites (e.g., Hay and Moiola, 1963; Hay et al., 1991). Accordingly, the oxygen equilibrium curves of jadarite have been calculated using the analcime fractionation equation. Following this approach, the fluid in equilibrium with the jadarite-dolomite assemblage yields formation temperatures between 60° and 95°C, and a heavy oxygen isotope signature ranging between 3 and 5‰ $\delta^{18}\text{O}_{\text{V-SMOW}}$ (Fig. 18A). The obtained isotopic composition of the jadarite-forming fluid is displaced from the meteoric water line and is similar to modern evaporated alkaline brines from the Searles Lake, western United States (Figs. 16C, 18A).

Fig. 16. (A) Carbon and oxygen isotope compositions of dolomite from the Jadar basin (sediment-hosted mineralization). Colored fields in panel A display the expected isotopic composition of dolomite formed in various geologic environments: 1 = Lake Natron, Magadi, Bogoria (Hillaire-Marcel and Casanova, 1987); 2 = sabkha dolomite (Geske et al., 2015); 3 = Lake Turkana (Halfman et al., 1989); 4 = burial dolomite (Nelson and Smith, 1996); 5 = hydrothermal dolomite (Geske et al., 2015); 6 = playa and lake dolomite (Riechelmann et al., 2020); 7 = CO_2 degassed from magma (Gerlach and Taylor, 1990); 8 = organically derived carbon (Longstaffe, 1989). (B) Close-up view on C-O data of dolomite showing the main vectors (i.e., $\delta^{18}\text{O}$ fluctuation and $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ covariance) accounting for the observed isotopic footprint. (C) δD - $\delta^{18}\text{O}$ plot showing the isotopic composition of jadarite and hectorite. Blue and green fields display the isotopic composition of the calculated fluids in equilibrium with hectorite (iterations 1 and 2, respectively), whereas the vertical gray field indicates the oxygen composition of the fluid in equilibrium with the jadarite-dolomite assemblage. Abbreviations: Dol = dolomite, Hec = hectorite, high-T = high-temperature, Jdr = jadarite, Kln = kaolinite, Sme = smectite V-PDB = Vienna-PeeDee Belemnite, V-SMOW = Vienna-standard mean ocean water.



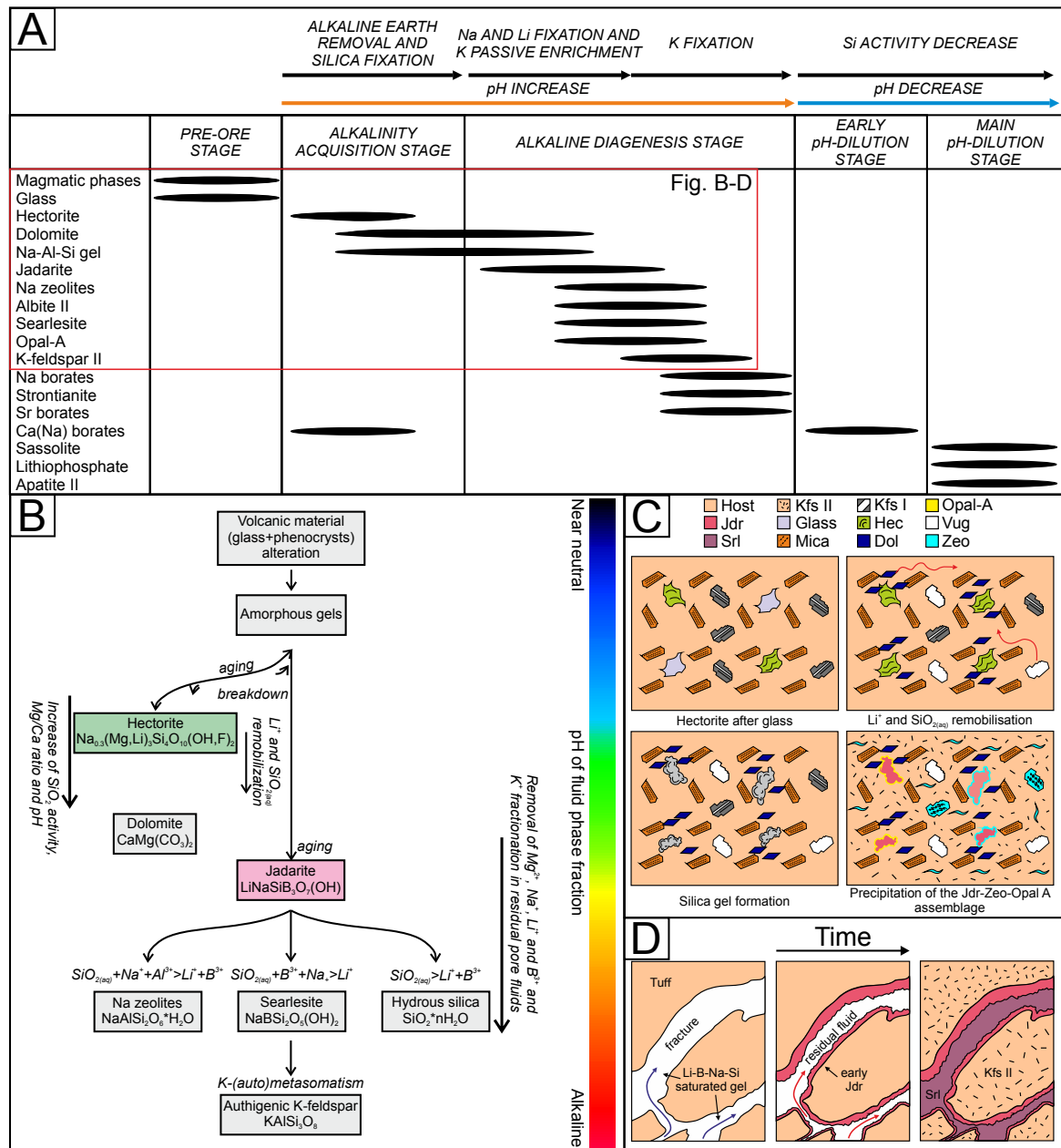


Fig. 17. (A) Mineral paragenesis in the Jadar deposit. Red box indicates the paragenetic processes that are highlighted in panels B to D. (B) Mineralogical and hydrogeochemical evolution in the Jadar deposit based upon the integration of the closed hydrologic system diagenesis and geochemical divides models. (C, D) Sketches displaying the diagenetic pathways that led to the formation of the jadarite + dolomite + zeolite + opal-A and jadarite + searlesite assemblages, respectively. Abbreviations: Dol = dolomite, Jdr = jadarite, Hec = hectorite, Kfs = K-feldspar, Srl = searlesite, Zeo = zeolite.

The calculated oxygen isotope equilibrium curve of hectorite does not intercept the dolomite + jadarite equilibrium (Fig. 18A). Fluids and temperature in equilibrium with hectorite have been modeled as follows: iteration 1, which considers the temperature obtained from the jadarite-dolomite equilibrium to assess the $\delta^{18}\text{O}$ and δD composition of the hectorite-forming fluid, and iteration 2, which considers previously published isotopic values of fluids in equilibrium with Li clays from similar mineral systems (i.e., Kırka volcano-sedimentary deposit, Turkey; Yücel-Öztürk, 2023) to back calculate the resulting temperature of the hectorite-forming

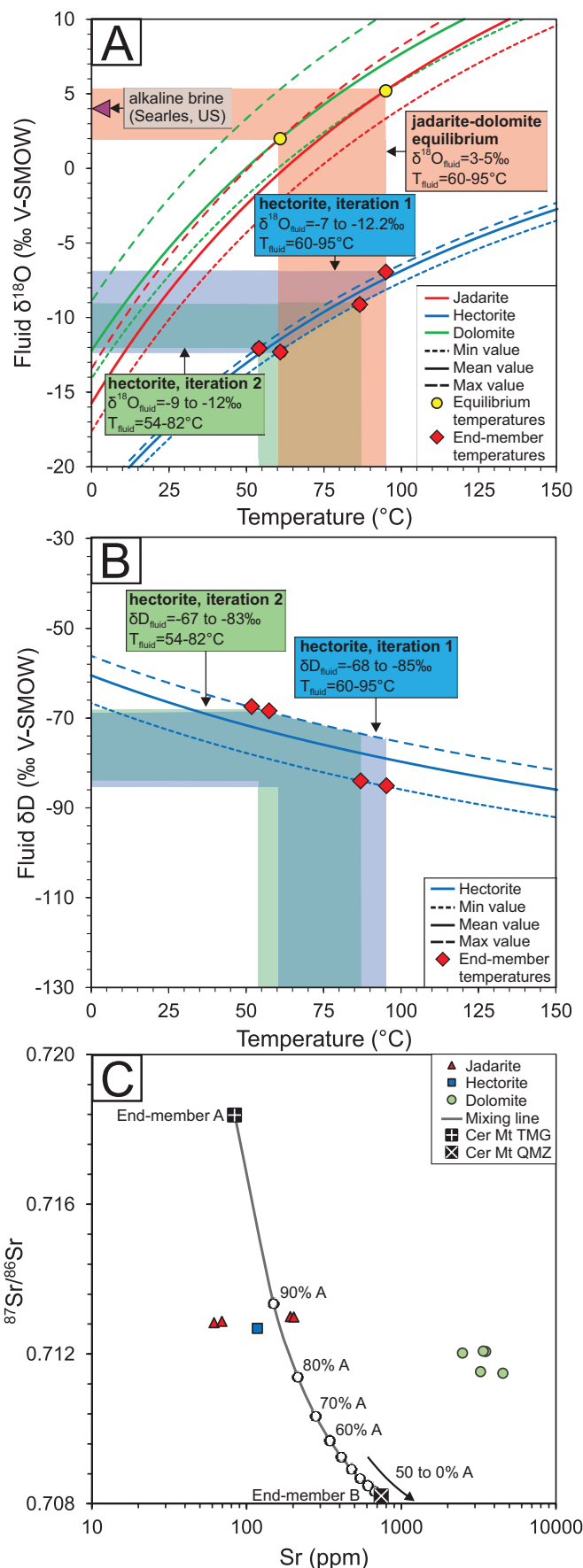
fluid. The above iterations result in consistent isotopic compositions and temperatures for the hectorite-forming fluids, with values of -12.2 to -7‰ $\delta^{18}\text{O}$ and -85 to -68‰ δD for iteration 1; -12 to -9‰ $\delta^{18}\text{O}$ and -83 to -67‰ δD for iteration 2 (Fig. 18A, B). The obtained fluids plot along the meteoric water line and are displaced toward higher $\delta^{18}\text{O}$, likely due to their heating under a geothermal regime (Fig. 16C). Fluid modeling carried out using an iteration based on the $\delta^{18}\text{O}_{\text{fluid}}$ as the independent variable (i.e., iteration 2) yielded a range of temperature values of 54° to 82°C , which are close to the those obtained for the jadarite-dolomite equilibrium

(Fig. 18A). The measured Sr isotope compositions of jadarite, hectorite, and dolomite compositions form a narrow range, indicating a homogeneous source. Modeling using a binary mixing source has been carried out by considering the isotopic and geochemical compositions of Miocene S-type granites (end member A) and the Oligocene metaluminous I-type granites (end member B) from Cer Mountain. The modeling indicates that the compositions of jadarite and hectorite fit with a 9:1 mixing between end members A and B, whereas the hosting dolomite has a slightly less radiogenic footprint that can be explained with an 8:2 mixing between the above two components (Fig. 18C).

This modeling shows that hectorite formed from a relatively unevaporated and heated meteoric water, whereas the jadarite- and dolomite-forming fluid match well with the features of evaporated brines occurring in alkaline lakes. However, the fluid temperature and the Sr isotope mixing models indicate that neither temperature gradient nor a shift of the fluid source(s) are feasible explanations for the observed evolution of fluids. However, the dolomite shows C-O isotope trajectories that are mostly controlled by the fractionation of ^{18}O and by a minor $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ covariance (Fig. 16A, B). This indicates that the precipitation of dolomite, and of jadarite, in the lake center facies was likely driven by intense evaporation in a hydrologically closed portion of the basin, which had hydrological and morphological conditions resembling those of modern shallow playa lakes (Warren, 2000; Yuan et al., 2022).

This is supported by the presence of soft-sediment deformation textures and erosive features (Fig. 8H, I), indicating that diagenesis took place shortly after deposition in a shallow lake environment that was subjected to episodes of lowstanding of the water table and of drought. Therefore, strong evaporation appears as the most likely process that drove the system from the hectorite- to the jadarite-forming stage. Evaporative concentration of meteoric water has also been observed in other VS Li deposits, and it generally ascribed to optimal architecture of the hosting basin, which allows minimal fluids outflow,

Fig. 18. Fluid and source modeling based on the H-O-Sr isotopes. (A) Oxygen isotope equilibrium curves showing the ranges of $\delta^{18}\text{O}$ and temperature values of the fluid in equilibrium with the jadarite-dolomite assemblage and with hectorite. Fractionation equations used for the modeling of jadarite, dolomite, and hectorite are from Karlsson and Clayton (1990), Chacko and Deines (2008), and Savin and Lee (1988), respectively. The $\delta^{18}\text{O}$ -temperature values of the jadarite-dolomite assemblage have been obtained by means of the mineral pair approach, whereas the features of possible fluids in equilibrium with hectorite have been assessed through the temperature of the jadarite-dolomite assemblage (iteration 1) and the $\delta^{18}\text{O}$ values of fluids assessed for Turkish volcano-sedimentary deposits (iteration 2) (Yücel-Öztürk, 2023). The $\delta^{18}\text{O}$ composition of modern alkaline brines from the Searles Lake (US) is added for comparison (Hay et al., 1991). (B) Hydrogen isotope equilibrium curves showing the ranges of δD and temperature values of the fluid in equilibrium with hectorite. The features of possible fluids in equilibrium with hectorite have been assessed through the temperature of the jadarite-dolomite assemblage (iteration 1) and the δD values of fluids assessed for Turkish volcano-sedimentary deposits (iteration 2) (Yücel-Öztürk, 2023). Fractionation equations used for the modeling of hectorite is from Yeh (1980). (C) Two-component mixing modeling of the $^{87}\text{Sr}/^{86}\text{Sr}$ and absolute Sr composition of jadarite, hectorite and dolomite. End-member compositions used for the modeling are the Oligocene and Miocene granitoids from Cer Mountain. (Koroneos et al., 2011). Abbreviations: QMZ = quartz monzodiorite to monzodiorite, TMG = two-mica granite, V-SMOW = Vienna-standard mean ocean water.



as well to a dry climate (Putzolu et al., in press). In the specific case of western Balkans, tectonic uplift during the Oligocene-Miocene transition aided the formation of fault-bounded basins (Marović et al., 2007; Balling et al., 2021). However, arid climate has been documented only from the late Badenian (around 13.4 Ma) (Utescher et al., 2007), which postdates the end of the lacustrine cycle in the Jadar basin (Obradović and Vasić, 2007). Lacustrine sedimentation in the Jadar basin (Eggenburgian to Karpatian) is contemporaneous with climatic conditions governed by high temperature and moderate precipitation rates (i.e., Miocene Climate Optimum), therefore, a climatic effect only cannot account for high evaporation needed to generate an isotopically heavy brine. Isotopic modeling indicates that the jadarite-dolomite equilibrium is characterized by temperatures up to about 100°C, thus pointing out that a high heat flow existed at the time of the Li-B ore deposition. The presence of a higher-temperature and perhaps deeply sourced component is supported by the ore remobilization features observed in brecciated units. These facies are generally found at depth in the basin (lower jadarite zone) and include the NaBo ore, as well as the ghost jadarite. Here, the Li-B ore postdates the lacustrine sedimentation and is structurally controlled, including subparallel to perpendicular sets of fractures and within cataclastic zones (Figs. 5J, K, 11) that were likely formed via hydrofracturing. Zeolites (i.e., analcime) occurring in the above facies show textural and chemical features that contrast with those observed in the sediment- and tuff-hosted ores. Analcime here occur as tabular crystals often appearing in veins (Figs. 11A, 13C, D, F) with an absence of textural features supporting diagenesis of volcanoclastic rocks as a genetic process for origin of the brecciated units (i.e., as spherulites and/or pseudomorph after shards). This crosscutting analcime type is also characterized by much lower Si/Al ratios than those measured for Na zeolites formed through diagenesis of volcanic glass (App. 6, Fig. A1). Specifically, the composition of vein-type analcime is displaced toward the chemical field of zeolites that formed at higher temperatures and in the presence of Na(Al³⁺)-saturated fluids rather than from the lower-temperature diagenesis of volcanoclastic rocks (Luhr and Kyser, 1989).

Based on the paragenetic features and the isotopic modeling, we propose the following model (Fig. 19):

1. Mineralization in the Jadar basin initially developed in a system of heated meteoric fluids, which drove alteration of intrabasinal tuffs and led to the formation of a hectorite-dominated Li ore.
2. Prolonged periods of evaporation, occurring within a closed hydrological regime and driven by a high-heat flow, promoted the increase of pH of pore waters, leading to hectorite alteration and the formation of Li-B-saturated and isotopically heavy siliceous gels that were the precursor to the jadarite formation.
3. Spatial decoupling of the hectorite + CaNaBo vs. jadarite + NaBo ore zones, documented on a basin scale, was controlled by the paleohydrology of the basin and shows a zonal division: at the basin margin, the hectorite + CaNaBo zone represents a section of the basin where the episodic recharge of meteoric water resulted a more near-neutral diagenetic environment; in the core of the basin, the jadarite + NaBo mineralized facies developed in a more hydrologically closed environment, where heavier and hyperalkaline fluids migrated to form a brine pool system.
4. The cooling of the intrusive Miocene granitoids (i.e., two-mica granite) increased the heat flow in the basin and likely enhanced ore redistribution via the onset of geothermal activity.

Although Sr isotopes indicate that the Li(B) mineralization has a footprint likely inherited from the nearby Cer Mountain complex, some key questions still remain:

1. Are intrabasinal tuffs the extrusive expression of the Miocene S-type granitic stage of Cer Mountain?
2. Can the initial ore Li-B endowment of Cer Mountain explain the volumes of Li-B mineralization in the Jadar basin?
3. To what extent are Li and B sourced from alteration of intrabasinal volcanoclastic rocks vs. external input via higher-temperature fluids?
4. If present, what are the mineralogical expressions of the magmatic-hydrothermal Li-B mineralization in the Cer Mountain intrusive and extrusive units?

The Jadar Li-B deposit compared to other volcano-sedimentary systems

Mineralogical and geochemical features observed at Jadar suggest that it represents an end member of the emergent volcano-sedimentary (VS) Li(B) deposit class. Other VS systems have been classified as clay and mixed clay/borate-types (Putzolu et al., in press). Representative examples of clay-type Li ores are the McDermitt caldera, Clayton Valley, and Hector deposits (western US, Morissette, 2012; Benson et al., 2017, 2023; Castor and Henry, 2020; Coffey et al., 2021; Putzolu et al., 2023), whereas typical mixed clay/borate-type ores are Rhyolite Ridge (western US) and deposits from Turkey (e.g., Kırka and Bigadiç, Helvacı and Palmer, 2017; Reynolds and Chafetz, 2020; Kadir et al., 2023; Yücel-Öztürk, 2023). The Turkish deposits show many features in common with the Jadar basin, especially Li clay formation linked to alteration of intrabasinal ignimbrites (Kadir et al., 2023). However, where present, zeolitization in these deposits marks a stage of Na⁺ fractionation and pH rise of pore waters that suppresses the Li fixation in clays. This process has been described for the clay-type VS mineralization in the Oregon limb of the McDermitt caldera (i.e., McDermitt deposit) and results in a spatial decoupling between analcime-altered rock types and Mg(Li) clay units (Putzolu et al., 2023). These features have only been observed in the marginal facies of the Jadar deposit, where hectorite in altered tuffs is overprinted by later analcime. However, mineralizing processes in the lake center facies of the Jadar deposit are in strong contrast with such features. At Jadar, the Li-B mineralization in the form of jadarite occurs in lithofacies that show an extensive sodic alteration including secondary albite and Na zeolites (i.e., analcime and natrolite). These features imply that hyperalkalinity and suppression of hectorite formation was the main trigger for the Li-B fixation in the lake center facies. As discussed previously, the hectorite breakdown and formation of primary dolomite are key features aiding this process. Therefore, dolomite plays a role as a pH buffer, which is in line with observations made

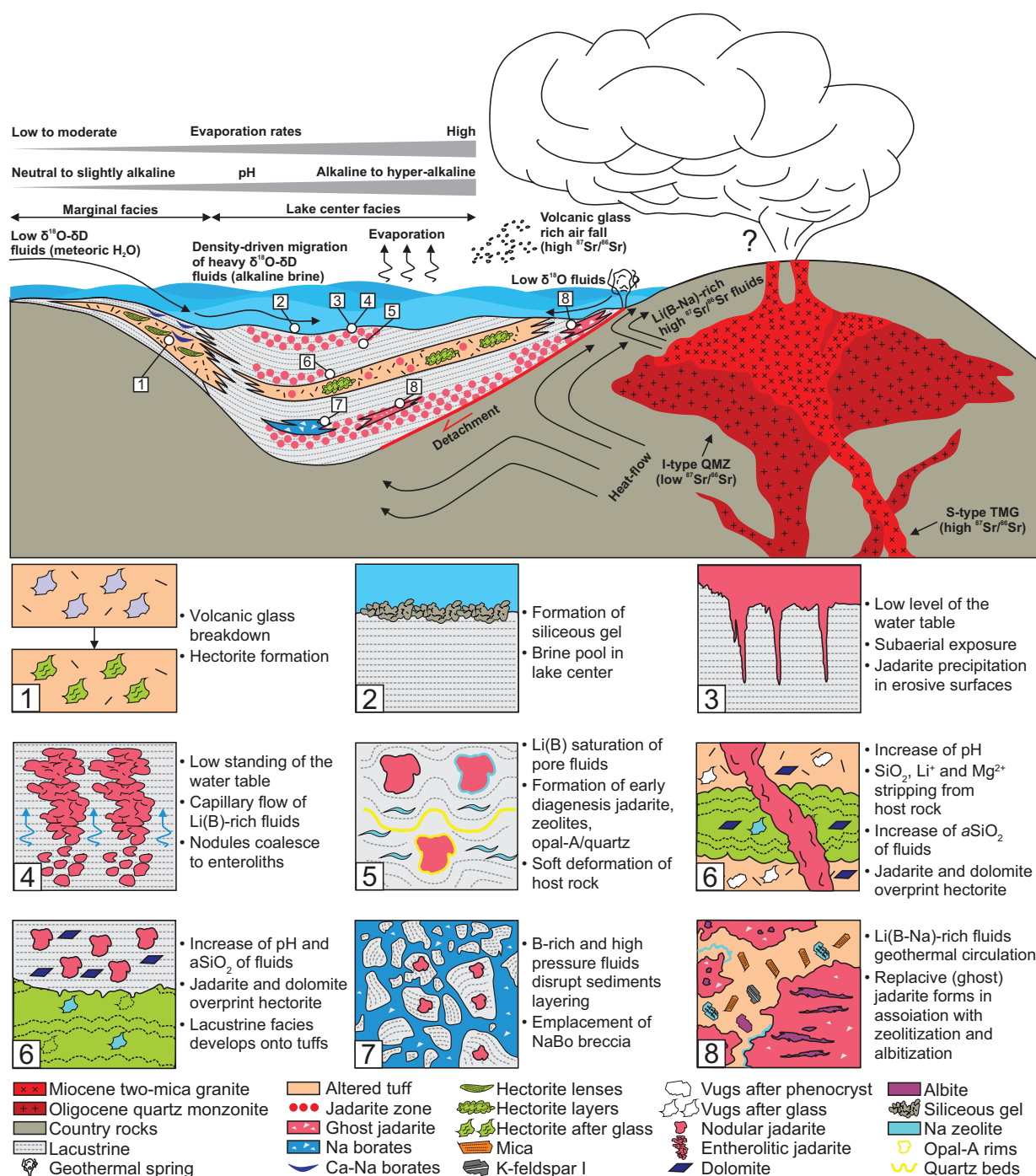


Fig. 19. Simplified model of early diagenetic to geothermal processes accounting for the formation of the hectorite and jadarite ore types (see subsection "Nature of Li-B mineralizing fluids and ore-forming environment" in the Discussion for details). Abbreviations: QMZ = quartz monzodiorite to monzodiorite, TMG = two-mica granite.

in other alkaline lakes, where it has been documented that alteration of Mg clays to form Mg(Ca) carbonates allows a pH rise of the system by increasing the Mg^{2+}/Ca^{2+} ratio of pore waters. The reactivity of the volcanogenic host rock was likely another controlling factor for the onset of hyperalkaline conditions. Clay-type mineralization, as in the McDermitt caldera, overlies rhyolite units that contain abundant volcanic glass and primary feldspars (Henry et al., 2017). The early

stage of alteration of this igneous assemblage type is dominated by albitization of primary K-feldspar and by formation of Ca(Na) zeolites and high-SiO₂ zeolites (e.g., clinoptilolite and/or heulandite) as products of glass alteration (Putzolu et al., 2023, in press). These alteration processes result in a fractionation of Na⁺ and SiO₂ in early formed hydrous silicates, which eventually consumes alkalinity and hampers the formation of high-pH residual pore waters with a high silica activ-

ity. At Jadar, volcanogenic units comprise muscovite-biotite volcanoclastic rocks, with only a minor feldspar component. Micaceous rocks are stable under high pH (Lamarca-Irisarri et al., 2019), which results in low fluid-rock interaction and thus promotes the Na⁺ and SiO₂ enrichment in the fluid fraction and the alkali and silica saturation of pore waters that is key to form the jadarite-zeolite-albite assemblage.

Considering that VS deposits form in extreme and ephemeral settings characterized by high pH and closed hydrologic conditions, these systems are easily subjected to epigenetic modifications resulting from changes of the pressure-temperature-composition (P-T-x) of the surrounding geologic environment. Epigenetic processes can potentially play a role in remobilizing the ore, and thus in controlling the evolution of the Li-B deportment through time during the aging of the system. A key example of this process is the Thacker Pass deposit in the Nevada limb of the McDermitt caldera, where alteration of early Mg(Li) clays led to the formation of tainiolite-like illite and to a twofold upgrade of the whole-rock Li grade (Benson et al., 2023). According to the latest model, this process occurred during the caldera resurgence stage through the circulation of hot (200°–300°C) hydrothermal fluids saturated in K⁺, Li⁺, and F⁻ (Benson et al., 2023). Illitization of Li smectites has not been observed in the Jadar deposit, where hectorite is interlayered with vermiculite (App. 4, Figs. A1-A4). Vermiculite is a common species in alkaline-saline lakes (Darragi and Tardy, 1987; Meunier, 2005); therefore, rather than recording a postformation process, vermiculitization likely occurred during the early stage of diagenesis in a lacustrine environment. The absence of illitization in the Jadar deposit could arise from several reasons: even though isotopic modeling points to diagenetic processes occurred under a geothermal regime, the obtained temperatures are well below those required for the illitization of smectite; the Jadar deposit is hosted by fault-bounded basin, which contrasts with caldera-hosted systems, as it is unlikely to develop hydrothermal circulation through volcanic resurgence processes; the formation of Li illite requires a significant F⁻ flux, likely from an external source such as hydrothermal fluids and/or a vapor phase exsolved from an underplating cooling ignimbrite (Ingraffia et al., 2020; Benson et al., 2023). In the Jadar deposit, high F is only present in the hectorite-altered units. However, there is no evidence of a further F addition to the system, as secondary fluorite has not been observed. Nonetheless, postformation processes in the Jadar deposit included the breakdown of the early Li-B assemblage (jadarite + searlesite) and the formation of epigenetic borates (sassolite and proberite) and lithiophosphate. As discussed above, this process produces a late Li vs. B decoupling and was likely aided by a pH retrogression of the system caused by acid released through transformation of kerogen to bitumen. Facilitating the decay of kerogen to form bitumen requires that the basin undergoes stages of organic bloom followed by anoxia to allow preservation of carbonaceous matter, which then needs to experience a significant heat flow to reach the oil generation window. Although this organic maturation is likely to be specific to buried basins like Jadar, sassolite has also been documented in the late diagenetic assemblages of the Kramer borate deposit (western US, Smith et al., 1958), suggesting that postformation processes are common in VS settings.

Conclusions

The Jadar deposit is a unique example of a Li-B volcano-sedimentary mineralization where the high-grade mineral-phase jadarite accounts for most of the measured Li resources. In this paper we have presented the first geologic description of the Jadar deposit, defining a genetic model for this novel type of Li mineralization. The origin of the Jadar deposit follows three distinctive ore-forming stages:

1. Mineralization initially involved alteration of volcanic glass-rich volcanoclastic rocks and formation of hectorite-like clays in the marginal facies of the basin and locally in the more intrabasin sections of the system. This stage marks episodes of alteration under near-neutral pH through hot unevaporated meteoric fluids and resulted in an Li-bearing assemblage with characteristics similar to more conventional clay-type VS ores.
2. Increasing evaporation of lake waters, likely enhanced by the high heat flow at the time of diagenesis, resulted in a rise of the pH and in the onset of hyperalkaline conditions more focused toward the center of the basin. The transition of the system from a near-neutral to an hyperalkaline regime was pivotal to remobilize Li and silica from the hectorite units and to form heavy brine-like fluids. This process is the main diversion of the Jadar system from other typical VS deposits and resulted in the formation of the jadarite-dolomite-zeolite assemblage in the intrabasin lake facies. Core observations, as well as isotopic and petrographic evidence, support that ore-forming processes occurred in a geothermal regime likely generated by the cooling of the Miocene S-type granite members of the nearby Cer Mountain complex.
3. The Jadar deposit also exhibits features that indicate the initial Li-B ore was subjected to a late remobilization via reequilibration with low-pH fluids originating from the maturation of kerogen and to the oil generation. This late process led to the formation of late diagenetic ore phases as low-Na borates (i.e., sassolite) and lithiophosphate.

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