

Research Paper

Potassium and sulfur isotope geochemistry of jarosite in sulfur-rich sediments in Victoria, Australia

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ABSTRACT

Jarosite is a critical K-bearing indicator mineral of acidic and oxidizing sulfate-rich environments. While S isotope geochemistry of jarosite has been extensively studied, K isotopes remain largely unexplored despite their potential to trace alkali dynamics, mineral formation processes, and fluid-mineral interactions. This study presents a systematic investigation of K and S isotopes in morphologically diverse jarosite samples from two coastal sites in Victoria, Australia: Fossil Beach (FB) and Southside Beach (SB). The jarosite samples exhibit a wide range of $\delta^{41}\text{K}$ values, from -1.70‰ to $+1.14\text{‰}$. A positive correlation ($R^2 = 0.42$) exists between $\text{K}/(\text{K} + \text{Na})$ ratios and $\delta^{41}\text{K}$ values. This trend, where K-rich jarosite is enriched in ^{41}K , contradicts equilibrium fractionation theories and suggests Rayleigh-type fractionation during progressive precipitation. Sulfur isotopes show distinct site variations: FB samples display highly positive $\delta^{34}\text{S}$ values ($+15.47\text{‰}$ to $+40.30\text{‰}$) that are consistent with closed-system sulfate reduction in a sulfate-limited reservoir with no external sulfate input, while SB samples range from -5.54‰ to $+23.39\text{‰}$ and lack extreme positive enrichments, consistent with a marine-buffered system oxidation and marine sulfate influx. Integrating the K and S isotope data from this study with previously published Fe isotope data thus distinguishes between the environment (recorded by S) and mineral formation mechanism (recorded by K and Fe), enabling a holistic reconstruction of jarosite formation pathways. This work showcases the use of K, Fe, and S isotopes as tracers for reaction pathways in acid-sulfate systems, with significant implications for both interpreting weathering intensity in terrestrial environments and understanding jarosite formation in analogous Martian settings.

1. Introduction

Jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$, a member of the alunite supergroup of sulfate minerals, is a critical mineralogical indicator of acidic, oxidizing, and sulfate-rich environments (Alpers et al., 1989; Bigham and Nordstrom, 2000; Das et al., 1996; Dill, 2001). Its trigonal crystal structure (space group $R\bar{3}m$) follows the general formula $\text{DG}_3(\text{TX}_4)_2(\text{X})_6$, wherein the D site (12-coordinated) accommodates monovalent cations, most notably K^+ and Na^+ , that form a continuous solid solution with the isostructural end-member natrojarosite (Basciano and Peterson, 2007, 2008; Bayliss et al., 2010; Spratt et al., 2013; Stoffregen et al., 2000; Welch et al., 2007). The composition of this D site, quantified by the $\text{K}/(\text{K} + \text{Na})$ ratios, exerts primary control on the mineral stability, solubility, and lattice parameters (Welch et al., 2007), thereby encoding critical information about the precipitating fluid chemistry and

crystallization conditions. Recently, a monoclinic polymorph (space group $\text{C}2/m$), characterized by an ordered distribution of iron-site vacancies and a lower symmetry, has been identified in synthetic and natural natrojarosite samples (Grey et al., 2011; Grey et al., 2013; Scarlett et al., 2010; Whitworth et al., 2023), suggesting that jarosite may also record structural state transitions relevant to its diagenetic history. The discovery of jarosite in significant quantities on Mars, interpreted as evidence for past aqueous, acidic environments, has further underscored the importance of deciphering its formation and preservation pathways (Aubrey et al., 2006; Farrand et al., 2009; Langevin et al., 2005).

The sulfur ($\delta^{34}\text{S}$) and iron ($\delta^{56}\text{Fe}$) isotope geochemistry of jarosite has been utilized to constrain redox processes and formation mechanisms in acid-sulfate environments (Bian et al., 2015; Dauphas et al., 2017; Lin et al., 2014; Paris et al., 2013). However, these proxies

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primarily track the behavior of the sulfate and ferric iron ions, respectively, and do not directly interrogate the alkali dynamics at the D site. Potassium isotopes ($\delta^{41}\text{K}$) represent a largely unexplored yet structurally specific tracer for jarosite systems. Potassium occupies a unique structural position within the jarosite–natrojarosite solid solution $[\text{K}_{1-x}\text{Na}_x\text{Fe}(\text{SO}_4)_2(\text{OH})_6]$, where variable K/Na ratios can directly reflect fluid composition and crystallization conditions. Because K^+ and Na^+ exhibit distinct ionic radii and bonding environments within the D site, K isotope fractionation could potentially be sensitive to the structural state (e.g., trigonal vs. monoclinic symmetry) and the rate of precipitation, factors that are not resolvable by S or Fe isotopes alone. Recent advances in K isotope analysis have revealed significant fractionation during silicate weathering, hydrothermal alteration, and fluid–mineral interactions (e.g., Cao et al., 2026; Hu et al., 2020; Li et al., 2019a; Ramos et al., 2020; Teng et al., 2020; Wang et al., 2020a; Wang et al., 2021; Zheng et al., 2022), suggesting $\delta^{41}\text{K}$ could provide novel constraints on alkali sources, crystallization kinetics, and post–formational fluid–mineral interactions in jarosite. In low-temperature aqueous systems, lighter K isotopes preferentially enter the solid phase while heavier isotopes remain in the fluid (Wang et al., 2021). While recent work on alunite, representing the Al-endmember, has provided the first constraints on K isotope fractionation in the alunite supergroup (Li et al., 2026; Li et al., 2019b). Jarosite is the Fe-endmember, and the substitution of Fe^{3+} for Al^{3+} in the octahedral site may modify the D-site bonding environment and K isotope fractionation. No experimental or theoretical constraints exist for K isotope fractionation between jarosite and aqueous fluids, and the relationship between K isotope fractionation and alkali substitution in the jarosite–natrojarosite solid solution remains unexplored. Furthermore, K isotopes have not been integrated with Fe and S isotopes in jarosite to reconstruct formation pathways.

The sulfur-rich coastal sediments of Victoria, Australia, provide an exceptional natural laboratory to investigate these questions. At Fossil Beach and Southside Beach, jarosite occurs in diverse morphologies (beds, veins, coatings, nodules, pebbles, and boulders) within oxidized zones of sulfide-bearing outcrops (see photos in Whitworth et al., 2020b). Whitworth et al. (2020b) demonstrated that these samples span a continuous K–Na solid solution and reported a positive correlation between $\text{K}/(\text{K} + \text{Na})$ and $\delta^{56}\text{Fe}$, suggesting preferential partitioning of heavy Fe isotopes into K-rich jarosite. Here, we present a systematic investigation of K and S isotopes, integrated with Fe isotopes in morphologically diverse jarosite samples from these sites. This work aims to: 1) investigate the controls on K isotope fractionation, particularly the role of alkali substitution and crystallization kinetics, 2) assess the covariation among K, Fe, and S isotopes, and 3) explore whether $\delta^{41}\text{K}$ signatures can distinguish diagenetic pathways and structural states. Furthermore, by characterizing the isotopic behavior of jarosite

in this well-constrained terrestrial analogue, this work develops a framework applicable to interpreting jarosite in extraterrestrial environments, particularly the ancient acid-sulfate systems inferred on Mars.

2. Geological background and sample description

The samples investigated in this study are the same as those reported in Whitworth et al. (2020b), and detailed site descriptions, outcrop morphology, and sampling procedures can be found therein. In brief, jarosite samples were collected from two coastal localities (Fossil Beach and Southside Beach) along the Victoria coastline, Australia (Fig. 1). At Fossil Beach (FB), the Gellibrand Marl, deposited during a marine transgression in the Miocene, comprises a fossiliferous, calcareous clayey silt horizon with hard limestone concretions overlain by a non-calcareous, poorly fossiliferous, and leached clayey silt horizon. At Southside Beach (SB), the Anglesea Formation and Addiscot Formation consist of carbonaceous, pyritic clayey siltstones and fine sandstones, with interbedded silty claystones. The Anglesea Formation and Addiscot Formation form subdivisions of the Demon's Bluff Group, which is a marginal marine siliciclastic and volcanic group deposited during the Eocene to Oligocene (Holdgate et al., 2001; Holdgate and Gallagher, 2003). The presence of pyritic precursor minerals in both stratigraphic successions provides the requisite reduced sulfur and Fe reservoir for subsequent oxidation and acid–sulfate alteration for jarosite formation. A total of 12 jarosite samples were collected from Fossil Beach and 37 from Southside Beach (Table S1), encompassing diverse morphological occurrences, and featuring a spectrum of diagenetic conditions.

Jarosite at both localities occurs in a remarkable diversity of morphologies (see photos in Whitworth et al., 2020b). In cliff outcrops and at the bottom of the cliffs within the intertidal zone, jarosite occurs as pebbles (4 to 64 mm), cobbles (64 to 256 mm), and boulders (>256 mm). Within the cliff exposures, jarosite is present as autochthonous beds (1 to 6 cm in thickness) and veins (0.2 to 1 cm in thickness) that precipitated along sedimentary fabrics and fracture networks, whereas surficial manifestations include coatings (<0.1 to 1 cm in thickness) and nodules (0.5 to 6 cm). The mineralogical assemblages (XRD), elemental compositions (ICP–MS), and iron isotope data (MC–ICP–MS) of these samples were previously reported by Whitworth et al. (2020b).

Briefly, the major minerals include jarosite and quartz, with accessory halite, gypsum, kaolinite, illite, alunite, goethite, and pyrite. Literature lattice parameters of jarosite ($a = 7.288\text{--}7.328 \text{ \AA}$; $c = 16.626\text{--}17.093 \text{ \AA}$) serve as qualitative indicators of D site (K, Na) and G site (Fe) occupancies, reflecting the systematic structural response to ionic substitution within the jarosite supergroup (Basciano and Peterson, 2007, 2008). Elemental data indicate that the jarosite samples span a continuous K–Na solid solution. Although most samples are

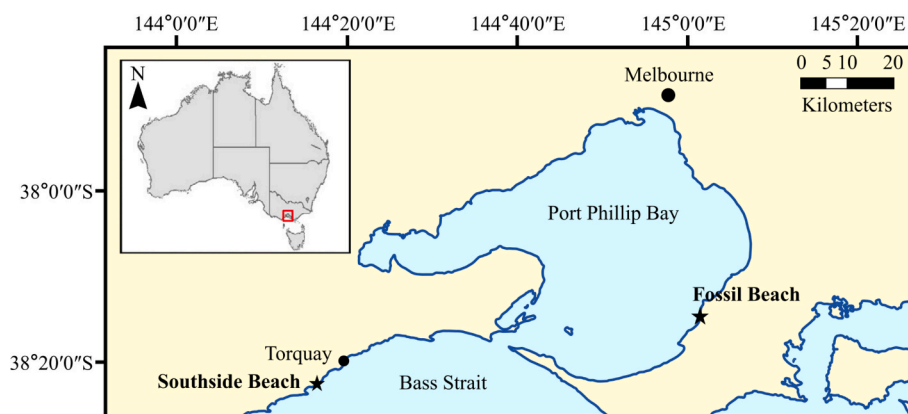


Fig. 1. Simplified map with the location of Fossil Beach and Southside Beach in Victoria, Australia. The red box on the insert shows where these sites are located relative to the rest of Australia. Simplified from Whitworth et al. (2020b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Na-enriched relative to K, with a mean $K/(K + Na)$ ratio of 0.28 at FB and 0.22 at SB, seven SB and two FB samples exhibit K-dominant compositions. The modal $(K + Na):Fe$ ratios of pure jarosite approximate the stoichiometric 1:3 proportion, whereas deviations in mixed samples reflect the presence of ancillary Fe- or Na-bearing minerals such as iron oxyhydroxide or halite. Iron isotope compositions ($\delta^{56}Fe$) range from -1.91 to $+0.10\text{‰}$ for FB samples and from -1.56 to $+1.24\text{‰}$ for SB samples (Whitworth et al., 2020b). On average, morphotypes exhibit a progression from isotopically light nodules (-0.36‰), coatings (-0.34‰), veins (-0.29‰) to heavier boulders (-0.01‰) and pebbles (0.29‰). Notably, boulder samples display the largest $\delta^{56}Fe$ spread from -1.91 to $+1.24\text{‰}$ (Fig. 2a).

The associated sediment samples (six from FB and eleven from SB) were also collected to characterize the protolith reservoir from which K, Fe, and S were mobilized during oxidative weathering. These sediments comprise quartz, kaolinite, and illite as predominant minerals, with minor pyrite, halite, gypsum, calcite and smectite-group clays (Whitworth et al., 2020b). Their $\delta^{56}Fe$ values range from -0.54 to $+0.56\text{‰}$ at FB and from -0.27 to $+1.30\text{‰}$ at SB (Whitworth et al., 2020b), overlapping with the isotopic range of the jarosite samples.

3. Analytical methods

3.1. K isotope analysis

Jarosite was isolated from matrix material under a binocular microscope using tweezers, picks, and brushes (Whitworth et al., 2020b). The isolated jarosite samples were dissolved in 0.5 mL of 1.0 M HNO_3 and 0.05 M HF for chemical purification using ion-exchange chromatography. The separation procedure followed the two-stage ion exchange protocol that has been described in Li et al. (2016). One milliliter (mL) of 100–200 mesh BioRad® AG50W- $\times 12$ resin and 0.4 mL of 100–200 mesh BioRad® AG50W- $\times 8$ resin were used to separate K from matrix elements for the first and second stages, respectively. The recovery of K was $>99\%$ through the two-stage column chemistry, and the total procedural blank was 21.4–29.0 ng ($n = 2$, done along with the samples). Sample loads were $> 20 \mu g$.

The K isotope ratios were measured using a Nu 1700 Sapphire multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) housed at the State Key Laboratory of Critical Earth Material Cycling and Mineral Deposits, School of Earth Sciences and Engineering, Nanjing University. The instrument was operated under

low-energy mode (An et al., 2022), which routinely results in an internal precision (two relative standard error [RSE]) of $^{41}K/^{39}K$ ratio better than $\pm 0.04\text{‰}$. All K isotope ratios were measured using a standard-sample-standard bracketing routine. The K concentration of the samples typically matched the bracketing standard, with concentration matching between samples and bracketing standard better than $\pm 5\%$ at 200 ppb. Each isotopic analysis consisted of 40 cycles of 5 s integration time. The long-term external reproducibility of K isotope analysis is better than $\pm 0.07\text{‰}$ (2 standard deviations) in $^{41}K/^{39}K$, based on repeat analyses of multiple NIST SRM 3141a against in-house A-K, as well as purified USGS rock standards. All the samples in this study were tested at least three times (An et al., 2022).

Potassium isotope compositions are reported using the standard per mil (‰) notation of $\delta^{41}K$ for a $^{41}K/^{39}K$ ratio, where

$$\delta^{41}K = \left[\left(\frac{^{41}K/^{39}K}{^{41}K/^{39}K}_{\text{standard}} \right) - 1 \right] \times 1000 \quad (1)$$

During the study, USGS rock standards AGV-2 and seawater were treated as unknown samples to validate the accuracy of the total chemical and mass spectrometry procedures. The K isotope compositions of measured standards ($\delta^{41}K_{AGV-2} = -0.42 \pm 0.02\text{‰}$, $\delta^{41}K_{\text{seawater}} = 0.14 \pm 0.07\text{‰}$, 2SD) are consistent with the literature values within uncertainties.

3.2. S isotope analysis

Purification of S was achieved using 1 mL of 100–200 mesh BioRad® AG50W $\times 12$ resin. The samples were dissolved and loaded into the column in 1 M HCl, then collected using 5 mL deionized water (18.2 M Ω /cm), with S recovery of $>99\%$, and the total procedural blank was 120 ng ($n = 1$, done along with the samples). Sample loads were $> 50 \mu g$. The collected solution was acidified with HNO_3 to make a 2% HNO_3 matrix.

Sulfur isotope ratios were measured using a Neptune Plus MC-ICP-MS (Thermo Scientific, Bremen, Germany) at Nanjing University, China, following the method of Yang et al. (2019). In brief, to eliminate isobaric interferences from oxygen species, such as $^{16}O_2^+$, the signals of S isotopes were acquired in high mass resolution mode, specifically on the interference-free plateau. The S isotopic ratios were determined using the Standard-Sample Bracketing (SSB) method. Sulfur isotope compositions are reported using the standard per mil (‰) notation of $\delta^{34}S$ for a $^{34}S/^{32}S$ ratio, where

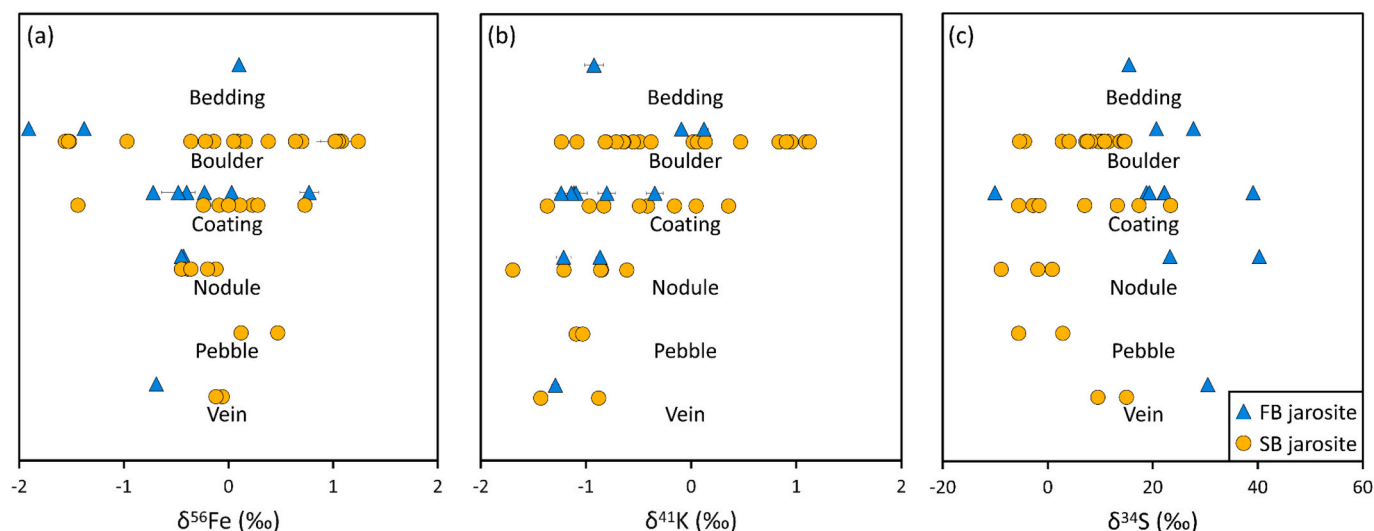


Fig. 2. Comparison of the (a) $\delta^{56}Fe$, (b) $\delta^{41}K$, and (c) $\delta^{34}S$ values of the different jarosite morphologies at both sites. Fossil Beach and Southside Beach are shown as triangles and circles, respectively. Error bars (reflecting 2SD values) are smaller than the symbols employed for most samples. Iron isotope data from Whitworth et al. (2020b).

$$\delta^{34}\text{S} = \left[\left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{\text{sample}} / \left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right)_{\text{standard}} - 1 \right] \times 1000 + \delta^{34}\text{S}_{\text{VCDT}} \quad (2)$$

Ammonium sulfate at the same S concentration was used as the working standard. The $\delta^{34}\text{S}_{\text{VCDT}}$ is the $\delta^{34}\text{S}$ value for the working standard on the scale of VCDT, which was determined in previous works ($-6.78 \pm 0.07\text{‰}$, Lin et al., 2014). Long-term analysis of the $\delta^{34}\text{S}_{\text{VCDT}}$ value of another in-house ammonium sulfate standard (AS) yielded a value of $-6.73 \pm 0.09\text{‰}$ (2SD), representing the long-term external reproducibility of the MC-ICP-MS analytical method for S isotopes.

4. Results

4.1. K isotope results

The jarosite samples exhibit a large range of $\delta^{41}\text{K}$ values that substantially exceeds those of the associated sediments. Overall, $\delta^{41}\text{K}$ of FB jarosite ranges from -1.29‰ to $+0.13\text{‰}$ ($n = 11$, mean = $-0.90 \pm 0.43\text{‰}$, 1σ), whereas SB samples span a significantly larger range from -1.70‰ to $+1.14\text{‰}$ ($n = 36$, mean = $-0.40 \pm 0.75\text{‰}$, 1σ). In contrast, the sedimentary protoliths from both sites display a restricted $\delta^{41}\text{K}$ range of -1.00‰ to -0.05‰ ($n = 16$, mean = $-0.50 \pm 0.24\text{‰}$, 1σ), suggesting that the observed isotopic variability in jarosite is primarily generated by mineral-specific fractionation processes rather than inherited from the source reservoir.

Systematic differences in $\delta^{41}\text{K}$ are observed among morphotypes (Fig. 2b). The more isotopically homogeneous and ^{41}K -depleted signatures are recorded by space-restricted precipitation forms of jarosite: pebble samples range from -1.09‰ to -1.03‰ ($n = 2$, mean = $-1.06 \pm 0.04\text{‰}$, 1σ), nodules from -1.70‰ to -0.61‰ ($n = 7$, mean = $-1.04 \pm 0.36\text{‰}$, 1σ), and veins from -1.43‰ to -0.88‰ ($n = 3$, mean = $-1.20 \pm 0.29\text{‰}$, 1σ). Coating samples show a wide range of $\delta^{41}\text{K}$ values (-1.37‰ to $+0.36\text{‰}$, $n = 14$, mean = $-0.68 \pm 0.53\text{‰}$, 1σ), with FB coatings exclusively negative (-1.23‰ to -0.34‰). Boulder samples display the largest isotopic spread (-1.23‰ to $+1.14\text{‰}$; $n = 21$, mean = $-0.08 \pm 0.75\text{‰}$, 1σ) and represent the sole reservoir of positive $\delta^{41}\text{K}$

at FB, with one SB boulder attaining the heaviest K isotope composition measured in this study ($+1.14\text{‰}$).

The K/(K + Na) ratios (D-site composition) of jarosite samples further distinguish the two localities. SB jarosite exhibits a broad K/(K + Na) ratio range (0.04 to 0.63), whereas FB jarosite is comparatively Na-dominated and chemically homogeneous (K/(K + Na) = 0.04 to 0.36). Across the entire dataset, $\delta^{41}\text{K}$ values covary positively with K/(K + Na) ratios ($R^2 = 0.42$). This correlation is moderate within the FB sample set ($R^2 = 0.52$, Fig. 3b) and similarly evident in the SB sample set ($R^2 = 0.49$, Fig. 3a).

4.2. S isotope results

The sulfur isotope compositions ($\delta^{34}\text{S}$) exhibit distinct variations between the two studied sites (Fig. 4). At Fossil Beach, $\delta^{34}\text{S}$ values are predominantly positive, ranging from $+15.5\text{‰}$ to $+40.3\text{‰}$, with only one outlier at -10.1‰ . $\delta^{34}\text{S}$ values of two sediment samples from FB are $+47.22\text{‰}$ and $+11.03\text{‰}$, respectively. In contrast, the $\delta^{34}\text{S}$ values of jarosite from SB range from -5.5‰ to $+23.4\text{‰}$, notably lacking the extreme positive values (e.g., $> +30\text{‰}$) observed at Fossil Beach, with samples clustering near the $\delta^{34}\text{S}$ value of modern seawater ($\sim +20.99\text{‰}$, Rees et al., 1978).

5. Discussion

5.1. Sulfur isotope constraints on sulfate sources and redox environments

Sulfur isotope compositions of jarosite from Fossil Beach and Southside Beach provide key constraints on the initial depositional environments and redox conditions under which precursor sulfide minerals formed. Although the equilibrium S isotope fractionation factor between jarosite and aqueous sulfate has not been experimentally determined, the $\delta^{34}\text{S}$ values of jarosite are widely interpreted to closely approximate the isotopic composition of the dissolved sulfate from which the mineral precipitated (Rye and Alpers, 1997; Seal et al., 2000), due to the negligible S isotope fractionation associated with Fe^{2+}

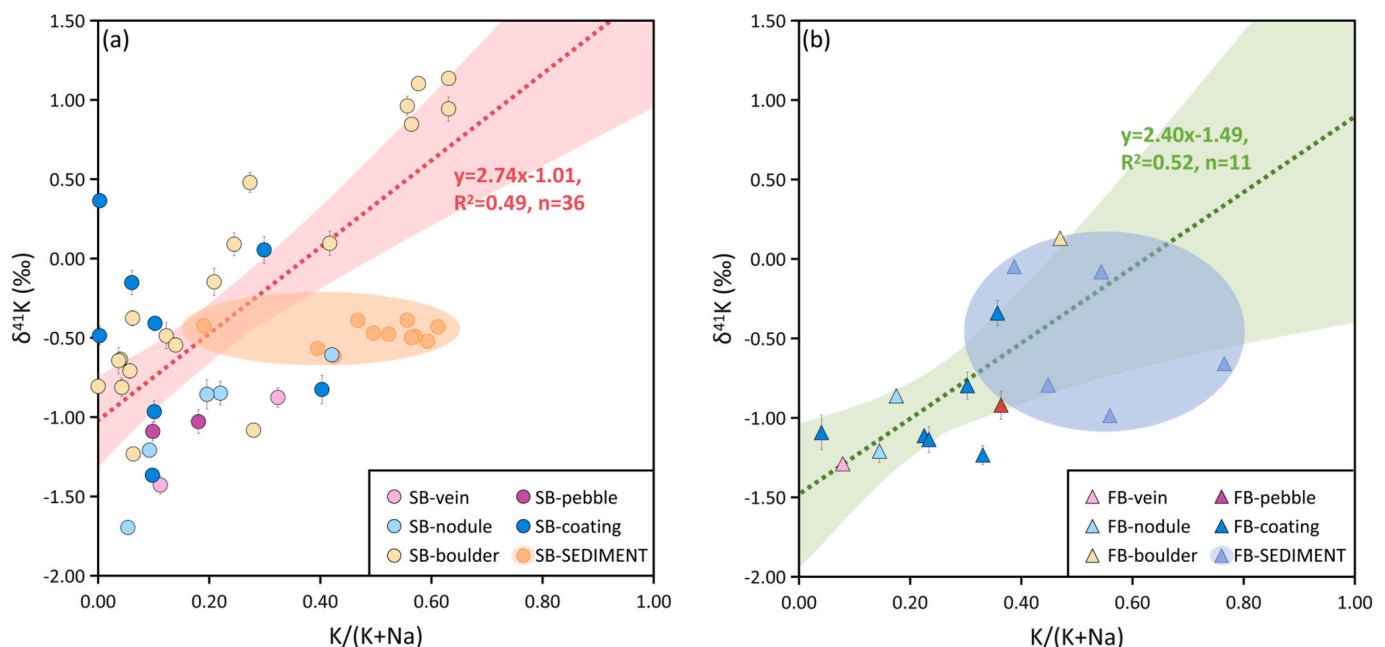


Fig. 3. (a) Plot of the alkali ratio (K/(K + Na)) against $\delta^{41}\text{K}$ for the Southside Beach jarosite and sediment samples. (b) Plot of the alkali ratio (K/(K + Na)) against $\delta^{41}\text{K}$ for the Fossil Beach jarosite and sediment samples. The red dotted line in (a) and the green dotted line in (b) represent the linear regressions for Southside Beach and Fossil Beach jarosite samples, respectively, with shaded areas showing 95% confidence bands. Sediment samples are plotted for comparison but were not included in the regressions. In the regression equations, $x = \text{K}/(\text{K} + \text{Na})$ and $y = \delta^{41}\text{K}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

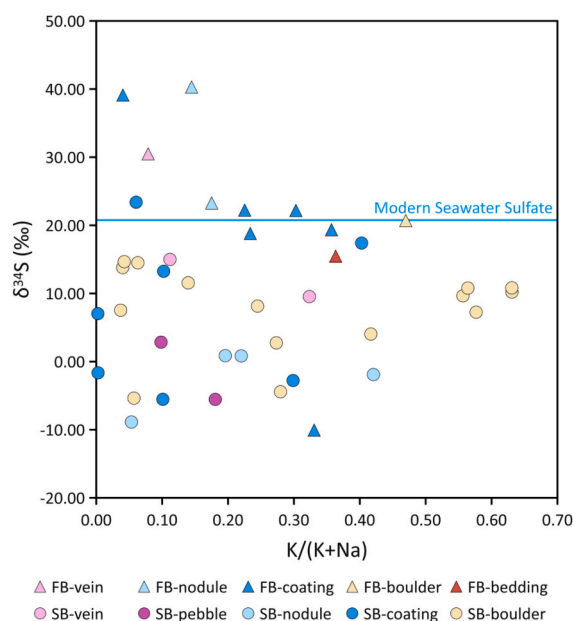


Fig. 4. The $\delta^{34}\text{S}$ against the alkali ratio ($\text{K}/(\text{K} + \text{Na})$) for Southside Beach and Fossil Beach jarosite samples. The blue line represents the $\delta^{34}\text{S}$ value of modern seawater sulfate ($\sim +20.99\text{‰}$; Rees et al., 1978). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

oxidation and subsequent jarosite crystallization under acidic conditions. As reviewed by Seal (2006), the oxidative weathering of sulfide minerals to sulfate is a quantitative, unidirectional process that produces no resolvable sulfur isotope fractionation, and the precipitation of sulfate minerals from such fluids likewise does not significantly alter the $\delta^{34}\text{S}$ signature. This interpretation is further supported by experimental synthesis of alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$, a member of the alunite supergroup to which jarosite also belongs. Precipitation of alunite from supersaturated $\text{Al}_2(\text{SO}_4)_3$ solutions at low temperatures (20°C to 50°C) produced a $\Delta^{34}\text{S}$ fractionation of $+0.84 \pm 0.34\text{‰}$, slightly favoring the incorporation of ^{34}S into the mineral (Prietz and Mayer, 2005). Consequently, the large $\delta^{34}\text{S}$ variation observed in this study (from -5.5‰ to $+40.3\text{‰}$) cannot be produced during sulfide weathering and oxidation. Therefore, the $\delta^{34}\text{S}$ signatures of jarosite should primarily reflect the isotopic composition of sulfate in the depositional or early diagenetic fluids, rather than fractionation during jarosite precipitation.

At Fossil Beach, jarosite $\delta^{34}\text{S}$ values range predominantly from $+15.47\text{‰}$ to $+40.30\text{‰}$, with a single sample at -10.06‰ , which is the only one that contains detectable pyrite (Whitworth et al., 2020b). Sediment sample JS-FB-8B exhibits an exceptionally high $\delta^{34}\text{S}$ value of $+47.22\text{‰}$, confirming the existence of a localized sulfate reservoir strongly enriched in ^{34}S . Such extreme enrichment may originate from a sulfate-limited reservoir with no external sulfate input during early diagenesis (Johnston, 2011; Rees et al., 1978), which may involve abiotic pathways, thermochemical reduction, or microbial activity (e.g., released fluid of microbial sulfate reduction). According to the Rayleigh distillation model for bacterial sulfate reduction (BSR) presented by Seal (2006), the preferential reduction of $^{32}\text{S}\text{SO}_4^{2-}$ by sulfate-reducing bacteria progressively enriches the residual sulfur reservoir in ^{34}S . Under a sulfate-limited reservoir with no external sulfate input, this residual sulfate is subsequently reduced to sulfide and incorporated into sedimentary pyrite. As a result, early diagenetic pyrite exhibits a wide range of $\delta^{34}\text{S}$ values, from ^{32}S -enriched compositions formed during early reduction to ^{34}S -enriched compositions formed from the later, highly evolved sulfate reservoir (as recorded by the $+47.22\text{‰}$ sediment sample). The oxidation sequence, from pyrite to sulfate to jarosite, proceeds after the post-depositional environmental shift (e.g., tectonic uplift,

sea-level regression, etc.) from reducing to oxidizing conditions has occurred. Subsequent oxidative weathering of these isotopically distinct pyrite populations transfers their sulfide $\delta^{34}\text{S}$ signatures to sulfate with negligible isotopic fractionation (Seal, 2006; Seal et al., 2000). The resulting sulfate, derived from oxidation of either ^{32}S -rich or ^{34}S -rich pyrite, then serves as the sulfur source for jarosite precipitation. The wide range of jarosite $\delta^{34}\text{S}$ values at FB is most parsimoniously explained by the superposition of two isotopically contrasting pyrite-derived sulfate endmembers, although we acknowledge that this interpretation is not unique.

At Southside Beach, jarosite $\delta^{34}\text{S}$ values range from -5.54‰ to $+23.39\text{‰}$, a notably narrower and less extreme distribution than observed at Fossil Beach. A substantial proportion of the data clusters near the $\delta^{34}\text{S}$ value of modern seawater sulfate ($\sim +20.99\text{‰}$; Rees et al., 1978), while several samples exhibit negative values extending to -5.54‰ . The absence of strongly positive $\delta^{34}\text{S}$ values indicates that SB lacked the highly ^{34}S -enriched sediment that characterizes FB. The restricted range and proximity to seawater composition are consistent with a marine-buffered system where sulfate availability was sustained by marine influx, although alternative explanations (e.g., tidal flushing, groundwater exchange, or sea spray) cannot be ruled out (Torres et al., 2018). Independent mineralogical evidence from the same sample suite supports marine influence at SB. Halite is present as an accessory mineral, and the predominance of natrojarosite over K-jarosite is consistent with formation from seawater with a high Na/K ratio (Whitworth et al., 2020b). Additionally, a redox transition from a lower pyritic horizon to an upper oxidized horizon is observed, consistent with fluctuating marine sulfate supply. The negative $\delta^{34}\text{S}$ values at SB are consistent with sulfate derived from oxidation of sedimentary pyrite. Parnell et al. (2010) reported a similar case from the Houghton impact structure, where supergene sulfate minerals (including jarosite) with strongly negative $\delta^{34}\text{S}$ values (down to -37‰) were interpreted to have formed by oxidation of pyrite that had itself been produced by microbial sulfate reduction. This terrestrial analogue supports our conclusion that the low $\delta^{34}\text{S}$ jarosite at SB preserves a direct record of pyrite oxidation without significant isotopic overprint.

The $\delta^{34}\text{S}$ ranges of jarosite from FB and SB partially overlap, and that BSR-derived isotopic heterogeneity is the common source for both sites. However, the key differences lie in the distribution patterns rather than the mere existence of overlap. At FB, the presence of extreme positive values (up to $+40.3\text{‰}$) and the direct observation of a ^{34}S enriched sediment (JS-FB-8B, $+47.22\text{‰}$) indicate that sulfate-limited reservoir with no external sulfate input was the dominant process, and subsequent oxidation quantitatively transferred this isotopic signature to jarosite without significant mixing. In contrast, SB samples lack any values exceeding $+24\text{‰}$ and exhibit a substantial fraction (approximately 25% of samples) clustering near the seawater sulfate composition, consistent with marine-buffered system. The negative $\delta^{34}\text{S}$ values at SB reflect localized oxidation of ^{32}S enriched pyrite. Thus, while BSR generated the initial isotopic heterogeneity at both sites, the post-depositional redox regime determined whether extreme isotopic compositions were preserved or homogenized.

We emphasize that the marine-buffered system versus sulfate-limited reservoir with no external sulfate input framework proposed here should be regarded as a working hypothesis rather than a uniquely determined environmental history. The available S isotope data are insufficient to exclude other possibilities, such as variable contributions from multiple pyrite populations, non-steady-state sulfate reduction, or post-depositional isotopic overprinting. Additional petrographic, microtextural, or multiple-sulfur-isotope studies would be required to test this hypothesis further.

5.2. Potassium isotope fractionation during jarosite precipitation

The $\delta^{41}\text{K}$ systematics of SB and FB morphotypes likely reflect controls of crystallization kinetics and fluid chemistry on K isotope

fractionation. Both SB and FB samples exhibit positive correlations between $K/(K + Na)$ and $\delta^{41}K$ values ($R^2 = 0.49$ and 0.52 , respectively; Fig. 3a, b), demonstrating a connection between alkali substitution and isotopic partitioning. The scatter in the data likely reflects the superposition of multiple processes and the complexities are further explored in Section 5.5.

Experimental measurements of Na–K partitioning between jarosite and aqueous sulfate solutions at 150–250 °C yield distribution coefficients $K_D = (X_{Na}/X_K)_{jarosite}/(m_{Na+}/m_{K+})_{fluid}$ ranging from 0.0075 to 0.045 (Stoffregen, 1993). Applying the highest $K/(K + Na)$ ratio observed in this study (0.63), the equilibrium fluid at 150 °C would require a minimum Na/K molar ratio of ~ 78 . At the lower ambient temperatures of this coastal site, the preferential incorporation of K^+ into jarosite is even larger (Stoffregen, 1993), such that the precipitating fluids must have had Na/K ratios significantly greater than the conservative estimate (i.e., >78). Thus, all jarosite samples in this study, regardless of their $K/(K + Na)$ ratios, precipitated from fluids with very large Na/K ratios, although the exact values remain uncertain. For comparison, seawater has a Na/K ratio of 46. Geochemical modeling using Geochemist's Workbench (with background ion concentrations referenced to seawater composition) shows that at Na/K ratios of 46 and 78, K^+ accounts for 97.981% and 97.974% of total dissolved K species (Table S2), respectively, which are virtually identical. Under these conditions, the bonding environment of dissolved K^+ in the fluid phase should have remained invariant across all precipitation events. Therefore, the observed trend cannot be explained by fluid compositional effects, assuming a uniform aqueous speciation condition for aqueous K^+ .

The crystallographic site of K in jarosite is the next factor to be considered. According to equilibrium isotope fractionation theory, heavier isotopes preferentially partition into mineral lattice sites with stronger, shorter bonds (Schauble, 2004). In the jarosite structure, the larger K^+ (1.64 Å) occupying D-sites should weaken K–O bonds relative to smaller Na^+ (1.39 Å; Shannon, 1976), resulting in significantly longer average K–O bond lengths (e.g., ~ 2.876 Å in K-jarosite) compared to Na–O bonds (e.g., ~ 2.807 Å in natrojarosite; Basciano and Peterson, 2008). The K–Na jarosite system forms a continuous solid solution,

with D–O bond lengths varying linearly with $K/(K + Na)$ ratio across the entire compositional range (Basciano and Peterson, 2008). In the K-rich jarosite solid-solution, the longer and weaker K–O bonds result in weaker average D–O bonding. This leads to a greater contrast in the bonding environment between the solid and aqueous K^+ compared to that in the Na-rich jarosite solid-solution. For K isotopes, although no direct experimental constraint exists for jarosite specifically, experimental studies on alunite have revealed a significant enrichment of heavy K isotopes (^{41}K) in the mineral phase during precipitation from hydrothermal fluids (Li et al., 2026). Furthermore, first-principles calculations by Li et al. (2019a, 2019b) predicted positive equilibrium K isotope fractionation between alunite and aqueous K^+ . Therefore, if K isotope fractionation was controlled by equilibrium partitioning, Na-rich jarosite, with its shorter and stronger D–O bonds, would preferentially incorporate ^{41}K to a greater extent than K-rich jarosite. Consequently, K-rich compositions would exhibit lower $\delta^{41}K$ values relative to Na-rich compositions under equilibrium control, which is opposite to our observed positive correlation. However, the positive correlation between $K/(K + Na)$ and $\delta^{41}K$ values in both sample sets (Fig. 3) contradicts the theoretical prediction based on equilibrium isotope fractionation. Therefore, closed-system batch equilibrium partitioning did not dominate K isotope fractionation during rapid jarosite precipitation in these coastal acid-sulfate systems.

5.3. K and Fe isotopes versus $K/(K + Na)$ ratios in jarosite

5.3.1. K–Fe isotope trends and controls during jarosite precipitation

As shown in Fig. 5, $\delta^{41}K$ and $\delta^{56}Fe$ exhibit a positive correlation ($R^2 = 0.33$) across the Southside Beach samples, with higher $K/(K + Na)$ ratios corresponding to higher δ values of both isotope systems. This positive correlation contradicts equilibrium fractionation predictions (Basciano and Peterson, 2008; Schauble, 2004), which would expect divergent trends: substitution of larger K^+ for Na^+ in the D-site elongates the (K,Na)–O bonds, weakening their bond strength, while simultaneously shortening Fe–O bonds and strengthening Fe–O interactions (Basciano and Peterson, 2008), thus driving $\delta^{41}K$ and $\delta^{56}Fe$ in opposite directions. Instead, the positive correlation can be understood

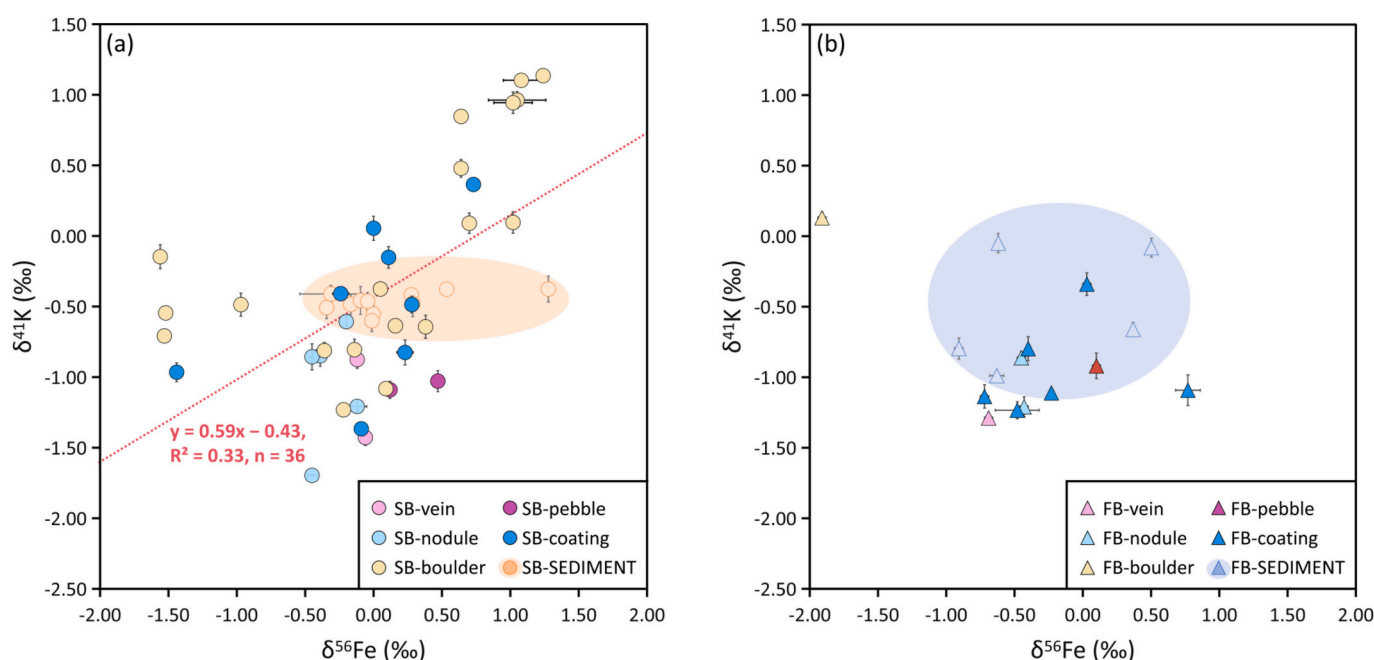


Fig. 5. (a) Plot of $\delta^{56}Fe$ against $\delta^{41}K$ for the Southside Beach jarosite and sediment samples. Error bars represent 2SD (some are smaller than the symbol size). The red dashed line in (a) represents the linear regression for Southside Beach jarosite samples ($R^2 = 0.33$, $p < 0.001$, $n = 36$). No significant correlation was found for Fossil Beach jarosite samples ($R^2 = 0.03$, $p = 0.60$, $n = 11$). In the regression equation, $x = \delta^{56}Fe$ and $y = \delta^{41}K$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

by considering the precipitation sequence driven by the different thermodynamic stabilities of K- and Na-jarosite.

Experimental studies demonstrate that K-jarosite precipitates preferentially over natrojarosite from solutions containing both cations. Dutrizac (1983) showed preferential K incorporation even at low K/Na ratios, Stoffregen (1993) demonstrated that K-jarosite requires substantially lower H_2SO_4 activities than natrojarosite, and we acknowledge that natural fluid variations may modulate the actual sequence. The early-formed phase would have a longer time in contact with the solution and undergo more isotope exchange before being isolated and accumulating heavier isotopes (^{41}K and ^{56}Fe) through continued fluid–mineral exchange. Experimental evidence from Whitworth et al. (2020a) demonstrates that during jarosite recrystallization in the presence of aqueous Fe(II), jarosite becomes isotopically heavier (enriched in ^{56}Fe) as lighter isotopes are partitioned into the fluid, with an equilibrium fractionation factor $\Delta^{56}\text{Fe}_{\text{jarosite–fluid}} = +2.26\text{‰}$ at 22 °C. For K isotopes, as discussed in Section 5.2, experimental and theoretical evidence from alunite indicates positive K isotope fractionation between the mineral phase and aqueous K^+ (Li et al., 2026). In a Rayleigh-type process, the early-formed K-rich jarosite is progressively removed from the fluid system upon precipitation, isolating it from further exchange. The residual fluid thus becomes progressively depleted in K and in heavy isotopes. Consequently, later-formed Na-rich jarosite precipitates from this evolved fluid and incorporates lighter isotopes, generating a positive correlation between $\text{K}/(\text{K} + \text{Na})$ and both $\delta^{41}\text{K}$ and $\delta^{56}\text{Fe}$.

Whitworth et al. (2020a) reported that the equilibrium Fe isotope fractionation between endmember K-jarosite and natrojarosite is negligible ($\Delta^{56}\text{Fe} \approx +0.07\text{‰}$). This observation rules out equilibrium compositional effects as the primary driver of the large $\delta^{56}\text{Fe}$ range ($> 3\text{‰}$) observed in natural jarosite samples. Instead, given the large equilibrium fractionation between jarosite and aqueous Fe^{2+} ($\Delta^{56}\text{Fe}_{\text{jarosite–fluid}} = +2.26\text{‰}$; Whitworth et al., 2020a), the observed range can be readily explained by Rayleigh fractionation during progressive precipitation from a finite fluid reservoir, without invoking repeated dissolution–reprecipitation cycles. The largest isotopic spread in boulder samples is consistent with prolonged reworking in the intertidal zone, as supported by mineralogical evidence that sample JS-SB-34C and JS-SB-35B contain intermingled goethite and are cemented with quartz, indicating post-formational modification (Whitworth et al., 2020b). Whitworth et al. (2020b) proposed that the large $\delta^{56}\text{Fe}$ variations in jarosite could originate from three potential sources: (1) variable $\delta^{56}\text{Fe}$ values of the precursor sulfides, (2) thermodynamic differences between Na- and K-bearing jarosite, and (3) open-system Rayleigh distillation, where K-rich jarosite precipitates first and the residual fluid (and subsequently precipitated Na-rich jarosite) becomes progressively lighter. In this study, the Fe isotope composition of the sediments shows a relatively wide range (-0.54‰ to $+1.30\text{‰}$), whereas the K isotope composition of the sediments is much more restricted (Fig. 5). Therefore, using K isotopes as a proxy can suppress the influence of precursor heterogeneity (factor 1) and better isolate the effects of solid–solution composition and crystallization pathways (factors 2 and 3). However, the experimental determination of K isotope fractionation between jarosite and aqueous fluids is lacking at present. Future experimental work is needed to quantify the relative contributions of these three factors to the coupled Fe–K isotope signatures observed in natural jarosite samples.

5.3.2. Rayleigh modeling of the covariation of $\delta^{41}\text{K}$ and $\delta^{56}\text{Fe}$

To quantitatively explain the observed trend of $\delta^{41}\text{K}$ and $\delta^{56}\text{Fe}$, we performed a Rayleigh fractionation model. The model assumes progressive precipitation of jarosite from a finite fluid reservoir, with initial $\delta^{41}\text{K}_{\text{fluid}} = -0.5\text{‰}$ and $\delta^{56}\text{Fe}_{\text{fluid}} = -0.5\text{‰}$, based on the mean composition of local unaltered sediments. The Fe isotope fractionation factor $\Delta^{56}\text{Fe}_{\text{jarosite–fluid}} = +2.26\text{‰}$ is taken from experimental data (Whitworth et al., 2020a). For K isotopes, we explored $\Delta^{41}\text{K}_{\text{jarosite–fluid}}$ values of 0.0,

+2.0, and +4.0‰. These values are guided by the best available evidence from alunite, as no experimental or theoretical constraint currently exists specifically for jarosite. Specifically, experimental work by Li et al. (2026) on alunite precipitation, although not fully equilibrated, yielded the highest observed fractionations of approximately +0.30‰ to +0.40‰, which we adopt as a lower-end reference. Although the alunite experiments of Li et al. (2026) were conducted at hydrothermal temperatures (98–400 °C), they yielded positive $\Delta^{41}\text{K}$ values. Because the K isotope fractionation factor of alunite is predicted to increase at lower temperatures (Li et al., 2019a, 2019b), these experimental values represent a conservative lower limit for $\Delta^{41}\text{K}$ in low-temperature jarosite. Meanwhile, first-principles calculations by Li et al. (2019a, 2019b) predict significantly larger positive fractionations at ambient temperatures, up to +3.24‰. We thus adopted a broad 0 to +4‰ range for $\Delta^{41}\text{K}_{\text{jarosite–fluid}}$, acknowledging its approximate nature and using the model only as a semi-quantitative framework. Based on the measured $(\text{K} + \text{Na})/\text{Fe}$ ratios of the sediments (ranging from 0.01 to 10.30; Whitworth et al., 2020b), we set $\text{K}/\text{Fe} = 0.30, 0.45$, and 0.60 in our model to capture a representative range of conditions. Additional modeling with initial $\delta^{56}\text{Fe}_{\text{fluid}}$ values of -1.0‰ and 0.0‰ is provided in Fig. S1.

As shown in Fig. 6a and b, Rayleigh fractionation produces a progressive decrease in both $\delta^{41}\text{K}$ and $\delta^{56}\text{Fe}$ of the instantaneous solid and residual fluid with increasing $X_{\text{Fe–jarosite}}$ (the fraction of dissolved Fe precipitated as jarosite). In contrast, closed-system batch equilibrium fractionation (dashed lines) yields only minor isotopic shifts. Fig. 6c and d provide direct tests against the measured data. Under closed-system batch equilibrium fractionation (Fig. 6c), all model curves are restricted to a narrow domain with $\delta^{56}\text{Fe} > -0.5\text{‰}$ and $\delta^{41}\text{K} > -0.5\text{‰}$, regardless of the chosen $\Delta^{41}\text{K}$ or K/Fe ratio. This theoretical field fails to capture the majority of our samples, especially those with $\delta^{56}\text{Fe} < -1.0\text{‰}$ and $\delta^{41}\text{K} < -1.0\text{‰}$. In contrast, Rayleigh fractionation (Fig. 6d) produces model curves that extend smoothly toward low $\delta^{56}\text{Fe}$ and low $\delta^{41}\text{K}$, encompassing the observed data range.

It is important to note that the model does not aim to reproduce every single data point, as natural samples are inevitably affected by additional complexities such as variable initial fluid composition, mixing with seawater, or multiple dissolution–reprecipitation cycles. Some positive $\delta^{41}\text{K}$ values may record later overprinting by a higher $\delta^{41}\text{K}$ fluid (e.g., seawater incursion, $\delta^{41}\text{K}_{\text{seawater}} \approx +0.14\text{‰}$, Wang et al., 2020a, 2020b) or repeated cycles of partial dissolution and reprecipitation that can reverse the fractionation direction. We also acknowledge that the Rayleigh model is non-unique, as the exact $\Delta^{41}\text{K}_{\text{jarosite–fluid}}$ values remain experimentally unconstrained for jarosite; the model should therefore be viewed as a semi-quantitative illustration rather than definitive proof, and future experimental calibration is urgently needed. Nonetheless, the key observation that batch equilibrium fractionation cannot reproduce the full range of measured data provides strong support for the dominance of Rayleigh fractionation during jarosite formation in these coastal acid–sulfate systems.

5.4. Structural controls on the scatter of K isotope data

The crystal–chemical properties of jarosite are governed by the D-site, whose composition primarily influences the *c* cell parameter (Basciano and Peterson, 2007, 2008; Stoffregen et al., 2000). The Victorian jarosite samples exhibit a positive correlation between $\delta^{41}\text{K}$ and *c* cell parameter (Fig. 7d), consistent with the positive correlation between $\delta^{41}\text{K}$ and $\text{K}/(\text{K} + \text{Na})$ ratios (Fig. 7b). This co-variation reflects the progressive precipitation sequence inherent to the Rayleigh model, wherein both parameters are controlled by the extent of fluid evolution.

Notably, samples with monoclinic *C2/m* symmetry (JS-SB-35 A, –35B, –35E, and –35F; Whitworth et al., 2023) fall within the lower range of *c* cell parameters yet exhibit a significant scatter in $\delta^{41}\text{K}$ values (Fig. 7d). The *C2/m* structure results from ordered iron-site vacancies,

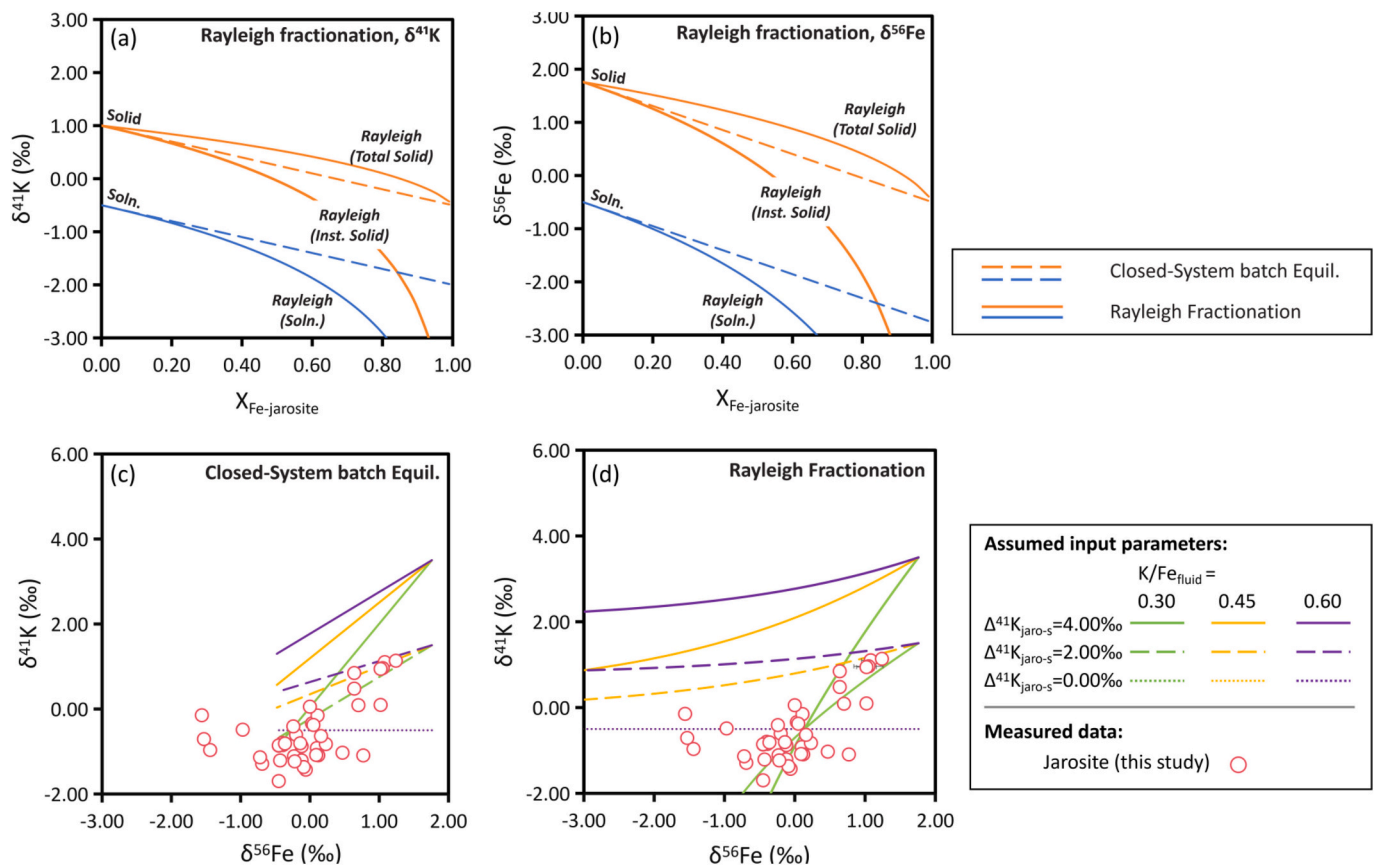


Fig. 6. Theoretical modeling of K and Fe isotope fractionation during progressive jarosite precipitation from an acidic sulfate fluid, compared with measured data from Victorian coastal sediments. (a) $\delta^{41}\text{K}$ evolution as a function of precipitated Fe fraction ($X_{\text{Fe-jarosite}}$) with initial $\delta^{56}\text{Fe}_{\text{fluid}}$ value of -0.5‰ . (b) $\delta^{56}\text{Fe}$ evolution as $X_{\text{Fe-jarosite}}$ with initial $\delta^{56}\text{Fe}_{\text{fluid}}$ value of -0.5‰ . (c) $\delta^{41}\text{K}$ vs. $\delta^{56}\text{Fe}$ under closed-system batch equilibrium. (d) $\delta^{41}\text{K}$ vs. $\delta^{56}\text{Fe}$ under Rayleigh fractionation. The colored lines show model sensitivity ranges obtained by varying assumed input parameters, including K/Fe ratios in the fluid (0.30, 0.45, 0.60) and the K isotope fractionation factor $\Delta^{41}\text{K}_{\text{jaro-s}}$ (0.00, 2.00, 4.00‰). Error bars for the measured samples are smaller than the symbol size and are thus not visible. The $\Delta^{41}\text{K}_{\text{jaro-s}} = 0.00\text{‰}$ trend lines overlap in panels (c) and (d).

which lower the symmetry from rhombohedral $R\bar{3}m$ to monoclinic $C2/m$ (Grey et al., 2011; Scarlett et al., 2010). This structural transition modifies the stacking of crystal layers and alters the geometric configuration around the D-site (Basciano and Peterson, 2007). Critically, the effect of K/Na substitution on the average D—O bond length differs between the two symmetries. In the rhombohedral $R\bar{3}m$ structure, the difference between the average K—O bond length ($\sim 2.876 \text{ \AA}$ in K-jarosite) and the average Na—O bond length ($\sim 2.807 \text{ \AA}$ in natrojarosite) is $\sim 0.070 \text{ \AA}$ (Basciano and Peterson, 2008). In contrast, for the monoclinic $C2/m$ structure, the average K—O bond length at 293 K is $2.904 \text{ \AA}$ (Grey et al., 2013), while the average Na—O bond length at 300 K is $2.859 \text{ \AA}$ (Grey et al., 2011). Notably, the Na—O bond length at 65 K is $2.853 \text{ \AA}$ (Grey et al., 2011), differing by only $0.006 \text{ \AA}$ from the 300 K value, indicating that thermal expansion between 293 K and 300 K is negligible. Thus, the K—O versus Na—O bond length difference in the $C2/m$ structure is $\sim 0.045 \text{ \AA}$, significantly smaller than the $\sim 0.070 \text{ \AA}$ observed in the rhombohedral structure. The reduced sensitivity of the D-site bond length to alkali substitution in the $C2/m$ structure implies that the local coordination environment around K^+ is less variable with changing K/(K + Na) ratios compared to the $R\bar{3}m$ structure, which may affect the K isotope behavior, although the jarosite formation in these coastal acid-sulfate systems was dominated by non-equilibrium isotope fractionation.

A break in the $\delta^{41}\text{K}$ - c relationship is observed at $c \approx 16.70 \text{ \AA}$. The low- c group ($n = 18$) shows no significant correlation ($R^2 = 0.03$, $p = 0.50$), while the high- c group ($n = 13$) exhibits a significant positive correlation ($R^2 = 0.78$, $p < 0.001$). The slopes differ significantly ($p <$

0.05). All $C2/m$ samples fall in the low- c group, suggesting that formation-time $C2/m$ may explain the scatter, although transformation to $R\bar{3}m$ cannot be excluded. Therefore, the scatter may reflect the combined influence of two superimposed processes. The extent of fluid evolution during progressive precipitation (e.g., the Rayleigh fractionation mentioned in Section 5.3.2) drives the overall positive correlation between $\delta^{41}\text{K}$ and K/(K + Na). At the same time, the structural state of the mineral ($R\bar{3}m$ vs. $C2/m$) modulates the local coordination environment around the D-site. In the $C2/m$ structure, the reduced sensitivity of D—O bond length to K/Na substitution implies that local bonding distortions around K^+ are less directly tied to bulk composition, allowing structural effects to emerge as an additional source of $\delta^{41}\text{K}$ variability, which can explain the scatter in the $\delta^{41}\text{K}$ - c relationship.

Importantly, the $C2/m$ phase is metastable and tends to transform to the $R\bar{3}m$ structure over extended timescales or through shorter thermal events (Grey et al., 2011; Grey et al., 2013; Whitworth et al., 2023), so the final structure does not necessarily record the formation-time structure. Therefore, we cannot fully distinguish whether a sample formed as $R\bar{3}m$ or $C2/m$; the $C2/m$ samples simply highlight one possible mechanism for scatter. However, in contrast to Fe isotopes, which reveal no correlation with the a cell parameter and appear insensitive to crystallographic variations (Fig. 7c), the $\delta^{41}\text{K}$ captures additional complexity with the c cell parameter. The K/(K + Na) ratio quantifies the bulk chemical composition of the D-site and serves as a necessary constraint (Fig. 7b) but cannot reveal the considerable scatter of $\delta^{41}\text{K}$ in Fig. 7d. Thus, the $\delta^{41}\text{K}$ scatter still may capture a transitional structural state that is not resolvable by bulk composition or cell parameters alone.

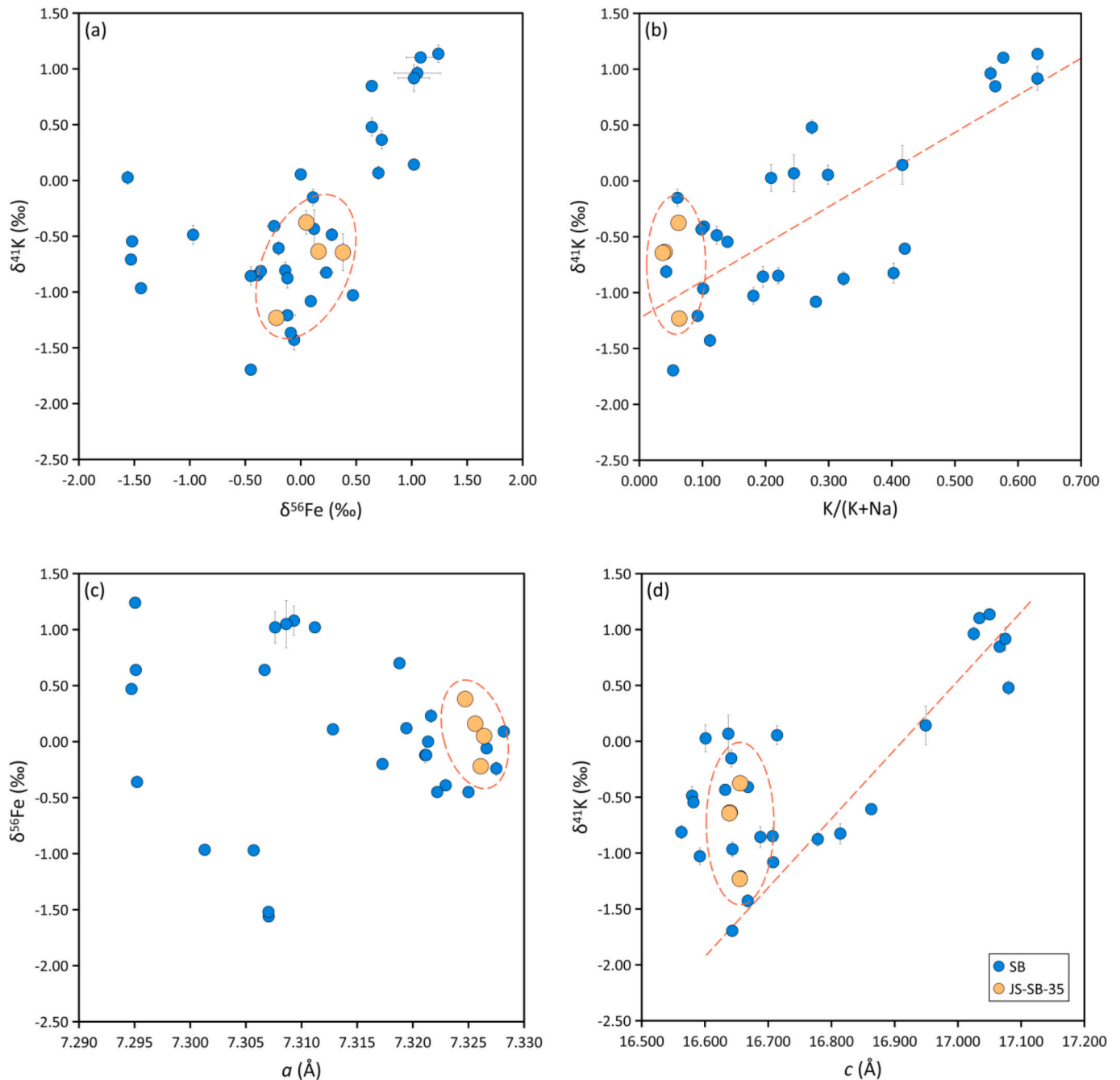


Fig. 7. Plots of isotopic, elemental and structure parameters for Southside Beach jarosite samples, with samples of Js-SB-35 highlighted in light red: (a) $\delta^{41}\text{K}$ and $\delta^{56}\text{Fe}$; (b) $\delta^{41}\text{K}$ and $\text{K}/(\text{K} + \text{Na})$; (c) $\delta^{56}\text{Fe}$ and a cell parameter; (d) $\delta^{41}\text{K}$ and c cell parameter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

It integrates both crystallization pathway and structural information, offering a more complete record of the jarosite formation.

5.5. Multi-stage formation pathway of jarosite

Building on the sulfur isotope constraints, the integrated K–Fe–S isotope data, together with morphological observations and Rayleigh fractionation modeling (Section 5.3.2), allow reconstruction of the formation history for jarosite in the Victorian coastal sediments. This evolution links each step to specific isotopic fingerprints and accounts for the distinct isotopic signatures of different jarosite morphologies (Fig. 8).

The process initiates with early diagenetic formation of sedimentary

pyrite. Sulfate reduction, such as bacterial sulfate reduction, converts seawater sulfate ($\delta^{34}\text{S} \approx +20.99\text{‰}$) to H_2S , generating early pyrite with strongly negative $\delta^{34}\text{S}$ (locally below -20‰), as well as complementary ^{34}S enrichment in late-stage pyrites (e.g., JS-FB-8B with $\delta^{34}\text{S} = +47.22\text{‰}$). Subsequent pyrite oxidation produces Fe^{2+} and sulfate; Fe^{2+} rapidly oxidizes to Fe^{3+} , and hydrolysis releases H^+ , creating acidic conditions. Sulfur isotopes show no fractionation during oxidation (Seal et al., 2000), so sulfate $\delta^{34}\text{S}$ reflects the precursor pyrite. Meanwhile, ^{54}Fe enters solution preferentially, leaving Fe^{3+} slightly enriched in ^{56}Fe . At the same time, dissolution of K-bearing silicates releases K^+ into the fluid. Seawater may mix with the acidic fluid, supplying marine sulfate and high Na^+/K^+ ($\text{Na}/\text{K} \approx 46$). This mixing raises pH and shifts the fluid from K-rich to Na-dominated. Such a seawater influence is

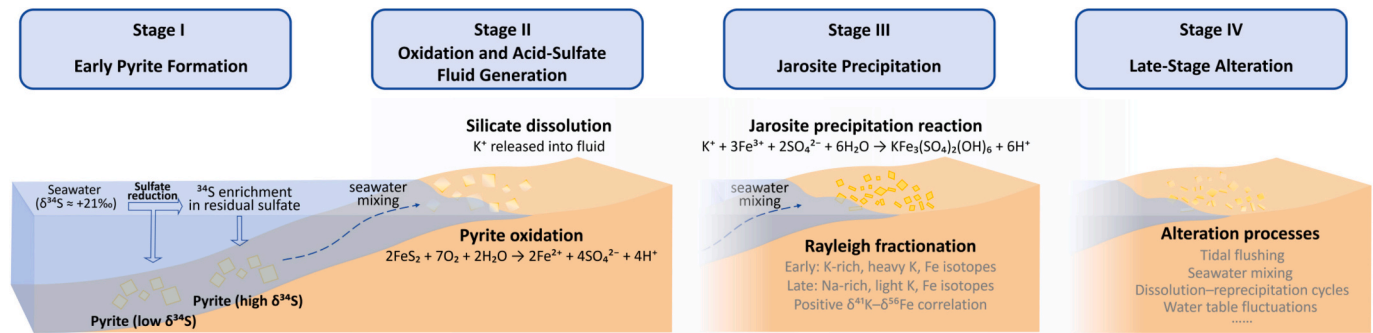


Fig. 8. Conceptual diagram illustrating the multi-stage formation pathway of jarosite in the Victorian coastal sediments, integrated with the observed K-Fe-S isotope systematics. Sulfate reduction, pyrite oxidation, jarosite precipitation, and Rayleigh fractionation are consistent with observations or experimental constraints from this study or previous work. Seawater mixing, silicate dissolution, and late-stage alteration are inferred or hypothesized processes.

recorded at both sites by jarosite samples with $\delta^{34}\text{S}$ values near seawater composition, though such samples are rare at Fossil Beach.

Jarosite precipitation initiates when oxidative weathering generates sufficient acidity and oxidizing potential, and when the accumulated activities of K^+ , Fe^{3+} , and SO_4^{2-} in the pore fluid cross the thermodynamic stability threshold. Thermodynamic phase diagrams (Fig. 9a–b, generated using the Geochemist's Workbench, see Table S2 for details) demonstrate that the accumulation of ionic activities significantly expands the stability field of jarosite, mitigating its requirement for highly

acidic and oxidizing conditions. Local fluid chemistry and elemental stoichiometry further control the evolution of mineral phases (Fig. 9c–f, plotted using MATLAB code; see Test S1 for details). In a closed system simulating the weathering of pyrite ($\text{Fe:S} = 1:2$), competition occurs between goethite and jarosite at $\text{pH} = 1.5$ (Fig. 9c). As the activities of K^+ and SO_4^{2-} increase and cross the phase boundary, the iron phase transitions from goethite to jarosite. Conversely, if the system receives an input of external sulfur (e.g., $\text{Fe:S} = 1:4$, Fig. 9d), the excess sulfur facilitates the formation of stable aqueous iron–sulfate complexes. This suppresses the stability field of goethite and forces the jarosite precipitation boundary to shift toward higher K^+ activities. However, the impact of external sulfur on phase equilibrium is significantly diminished under relatively less acidic conditions. As illustrated in Fig. 9e–f, when the pH increases to 2.0, the relationship between goethite and jarosite is similar regardless of the addition of external sulfur. In this study, the paragenetic assemblage of jarosite and goethite is distinctly observed in samples JS-SB-34C and JS-SB-35B. This mineral assemblage explicitly shows that the mineralizing fluids were either situated in a relatively less acidic environment, or that the input of external sulfur into the microenvironment was limited.

Because K-jarosite is thermodynamically more stable than Na-jarosite, early-formed jarosite is K-rich. This initial precipitate preferentially incorporates heavier isotopes of both K and Fe, resulting in high $\delta^{41}\text{K}$ and high $\delta^{56}\text{Fe}$. As precipitation proceeds, the fluid becomes progressively depleted in K^+ and in heavy isotopes. Consequently, later-formed jarosite becomes increasingly Na-rich and isotopically light (low $\delta^{41}\text{K}$, low $\delta^{56}\text{Fe}$). As demonstrated in Section 5.3.2, Rayleigh fractionation amplifies the initial isotopic differences and produces the observed positive correlation between $\delta^{41}\text{K}$ and $\delta^{56}\text{Fe}$. It is also possible that late-stage processes, such as fluctuating water tables or repeated seawater flushing, may have caused partial dissolution and reprecipitation of some samples, potentially overprinting their original isotopic signatures, although direct evidence for such resetting is not available in this study.

5.6. Implications for planetary studies

The correlation between $\delta^{41}\text{K}$ and $\text{K}/(\text{K} + \text{Na})$ ratios established in this study provides a reference framework for interpreting jarosite formation in Martian environments. On Mars, where jarosite similarly forms from acidic, oxidizing fluids (Madden et al., 2004), K isotopes may offer a quantitative tool to distinguish between different fluid sources and precipitation pathways.

It is important to recognize that K isotope signatures in jarosite record information at two levels. The primary control on $\delta^{41}\text{K}$ variations documented in this study is Rayleigh fractionation during progressive precipitation, which produces the observed positive correlation between $\delta^{41}\text{K}$ and $\text{K}/(\text{K} + \text{Na})$. At present, this Rayleigh model remains semi-quantitative, as the K isotope fractionation factor between jarosite and

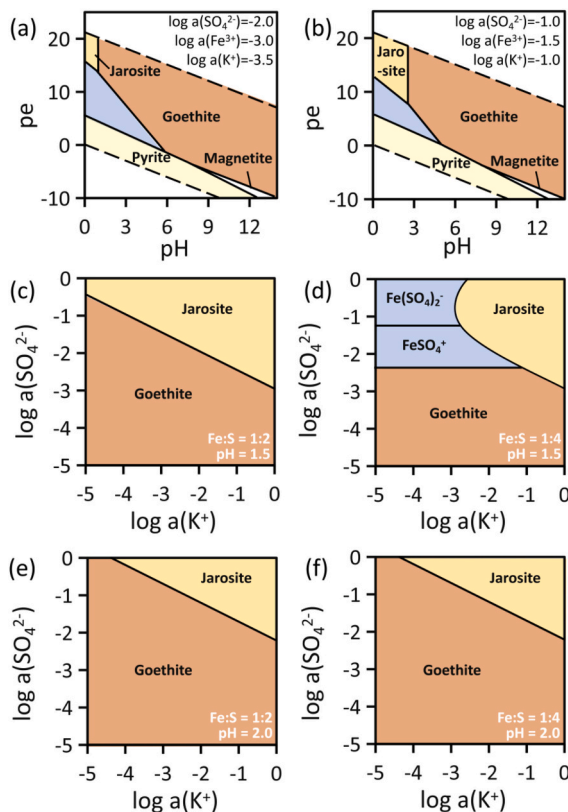


Fig. 9. Thermodynamic phase diagrams for jarosite and associated Fe phases. (a–b) pe – pH diagrams illustrating the expansion of the jarosite stability field with increasing ionic activities of K^+ , Fe^{3+} , and SO_4^{2-} ; the unmarked blue area is dissolved species (e.g., FeSO_4^+ and $\text{Fe}(\text{SO}_4)_2^-$). These diagrams were constructed using the Geochemist's Workbench with the thermo.tdat thermodynamic database. (c–f) Plots of $\log a(\text{K}^+)$ versus $\log a(\text{SO}_4^{2-})$ at Fe:S ratios of 1:2 (c, e) and 1:4 (d, f), under $\text{pH} = 1.5$ (c–d) and $\text{pH} = 2.0$ (e–f), with pe values of 18.0. These diagrams were constructed using MATLAB, with the code provided in Text S1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fluid has yet to be experimentally determined. The initial $\delta^{41}\text{K}$ of the precipitating fluid is itself a function of the fluid source, which ultimately derives from the composition of the protolith undergoing alteration. With future experimental calibration of the jarosite–fluid fractionation factor, this framework could be applied more rigorously to infer initial fluid $\delta^{41}\text{K}$ from measured jarosite compositions, thereby providing constraints on fluid provenance and the environmental conditions of jarosite formation.

Remote sensing studies detected jarosite solid solutions across diverse terrains on Mars (Bishop et al., 2013; Farrand et al., 2009; Ling et al., 2016), yet ambiguities persist regarding their genetic contexts, whether derived from volcanic hydrothermal fluids, evaporating brines, or sulfide oxidation fronts. The relationship between $\delta^{41}\text{K}$ and $\text{K}/(\text{K} + \text{Na})$ ratios established here serves as a quantitative tool for future missions. For instance, if the Rayleigh fractionation effect can be quantitatively accounted for, which currently awaits experimental calibration of the K isotope fractionation factor, jarosite with high $\text{K}/(\text{K} + \text{Na})$ and heavy $\delta^{41}\text{K}$ could in principle be used to infer a K-enriched fluid source, potentially from subsurface hydrothermal systems or evaporatively concentrated solutions. Conversely, low $\text{K}/(\text{K} + \text{Na})$ and light $\delta^{41}\text{K}$ values would reflect either later-stage precipitation from the same evolving fluid or a distinct fluid source, emphasizing the need for experimental constraints to resolve such ambiguities. This distinction is vital for interpreting settings like Mawrth Vallis, for example, where competing hypotheses invoke either volcanic ash alteration or groundwater upwelling (Farrand et al., 2009; Michalski and Niles, 2010).

Thus, jarosite in this study demonstrates that potassium isotopes are more than passive tracers but dynamic recorders of fluid–mineral interactions, recording both the crystallization pathway (via Rayleigh fractionation) and, when properly deconvolved, the isotopic composition of the parental fluid, which in turn reflects fluid source and environmental conditions. Applying this knowledge to Mars refines our capacity to discern the chemistry, kinetics, and history of aqueous activities that shaped its surface.

6. Conclusions

This integrated K–Fe–S isotope study of jarosite from the coastal sediments of Victoria, Australia, provides a quantitative framework for understanding the formation processes of this mineral in coastal acid–sulfate environments. Sulfur isotopes are consistent with two distinct redox regimes: sulfate-limited reservoir with no external sulfate input at Fossil Beach versus marine-buffered pyrite oxidation at Southside Beach. Iron isotopes preserve primary redox fingerprints from sulfide oxidation, with $\delta^{56}\text{Fe}$ ranging from -1.91‰ to $+1.24\text{‰}$. Potassium isotopes track fluid–mineral interaction and crystallization history, exhibiting a wide $\delta^{41}\text{K}$ range from -1.70‰ to $+1.14\text{‰}$ and a positive correlation with $\text{K}/(\text{K} + \text{Na})$ ratios. This positive correlation contradicts equilibrium fractionation theory, which would predict K-rich jarosite to be relatively enriched in light ^{39}K compared to Na-rich jarosite. Rayleigh fractionation modeling semi-quantitatively reproduces the observed co-variation between $\delta^{41}\text{K}$ and $\delta^{56}\text{Fe}$, demonstrating that closed-system batch equilibrium fractionation may not dominate the isotopic signatures. Furthermore, $\delta^{41}\text{K}$ is sensitive to the structural phase transition from R3m to C2/m symmetry, capturing local coordination changes around the D-site that are not revealed by chemical composition or cell parameters alone. Collectively, these findings establish potassium isotopes as a powerful tracer of crystallization kinetics, fluid evolution, and structural response in acid–sulfate systems, with potential applicability to interpreting jarosite formation in both terrestrial and Martian environments.

CRediT authorship contribution statement

Yuqi Li: Writing – review & editing, Writing – original draft,

Visualization, Methodology, Investigation, Data curation. Andrew J. Friedrich: Writing – review & editing, Validation, Resources. Tao Yang: Writing – review & editing, Resources, Methodology, Investigation. Anne J. Whitworth: Writing – review & editing, Validation, Resources. Weiqiang Li: Writing – review & editing, Writing – original draft, Validation, Supervision, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

The supplementary figures (Fig. S1–S3) include sensitivity tests of the Rayleigh and equilibrium fractionation models under varying initial fluid $\delta^{56}\text{Fe}$ values (Fig. S1), as well as cross-plots of $\delta^{34}\text{S}$ versus $\delta^{56}\text{Fe}$ (Fig. S2) and $\delta^{34}\text{S}$ versus $\delta^{41}\text{K}$ (Fig. S3) for all jarosite and sediment samples. Supplementary Table S1 compiles the complete isotopic, elemental, and morphological data for all samples, while Supplementary Table S2 provides the Geochemist's Workbench geochemical speciation results for seawater-like basis. The MATLAB code used to generate the thermodynamic phase diagrams in Fig. 9 is supplied as Supplementary Text S1. The regression equations, confidence intervals, *p*-values, and sample numbers for the main correlations are supplied as Supplementary Text S2.

Data availability

The data supporting the findings of this study are available through Mendeley Data at: <https://doi.org/10.17632/j4fzs25psc.1>.

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