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Krypton-81 dating constrains timing of deep groundwater flow activation

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Key points

- Meteoric waters at up to 3 km in basinal aquifers are <1.1 Ma.
- Recent rapid denudation of the Colorado Plateau enabled deep circulation of meteoric water and flushing of connate brines.
- Krypton-81 dating can illuminate the timescales and extent of meteoric circulation in response to geologic and/or climatic forcings.

Abstract

Krypton-81 dating provides new insights into the timing, mechanisms, and extent of meteoric flushing versus retention of saline fluids in the subsurface in response to changes in geologic and/or climatic forcings over 50 ka to 1.2 Ma year timescales. Remnant Paleozoic seawater-derived brines (2-2.5 km depth) associated with evaporites in the Paradox Basin, Colorado Plateau, are beyond the ^{81}Kr dating range (>1.2 Ma) and have likely been preserved due to negative fluid buoyancy and low permeability. ^{81}Kr dating of formation waters above the evaporites indicates topographically-driven meteoric recharge (0.03-0.8 Ma) and salt dissolution since the Late Pleistocene. Formation waters below the evaporites, in basal aquifers, contain relatively young meteoric water components (0.4-1.1 Ma based on ^{81}Kr) that partially flushed remnant brines and dissolved evaporites. We demonstrate that recent, rapid denudation of the Colorado Plateau (<4-10 Ma) activated deep, basinal-scale flow systems as recorded in ^{81}Kr groundwater age distributions.

Plain language summary

Landscape changes over geological time alter hydraulic gradients and the presence or absence of near-surface confining units, which drive the evolution of subsurface flow systems. However, our understanding of the time required for groundwater flow systems to respond to geological processes, such as shifts in topography, stratigraphy, and permeability structures, is still limited. This study uses krypton-81 dating to constrain the age of meteoric waters in the Paradox Basin in the Colorado Plateau and constrain the timing of groundwater recharge into basinal aquifers. We discovered that rapid, widespread erosion and incision in the Colorado Plateau in the last 10 Ma activated deep meteoric circulation, partially flushing connate brines from aquifers above and below thick, evaporite confining units, and dissolving salt. krypton-81 dating may provide insights into timescales and drivers of subsurface fluid flow and connectivity with the near-surface in other environments.

1. Introduction

Constraining the dynamic interface between circulating meteoric waters and deeper more stagnant saline fluids is important for groundwater supplies (Kang and Jackson, 2016; Ferguson, McIntosh, Perrone et al., 2018), mineral resources

(Sanford, 1994; Garven, 1995), energy extraction and storage (Garven, 1989; Spangler et al., 1996; Zheng et al., 2012), isolation of anthropogenic waste products (Cherry et al., 2014; Sturchio et al., 2014; Ferguson, McIntosh, Perrone et al., 2018), and subsurface microbial life (Warr et al., 2018; Lollar et al., 2019). Circulating meteoric waters, present in the upper few kilometers of the Earth's crust (McIntosh and Ferguson, 2021), transport an appreciable mass of fluids and solutes on timescales of tens of years to ka to Ma (Castro et al., 1998; Lehmann et al., 2003; Zhou et al., 2005; Schlegel et al., 2011; Aggarwal et al., 2015; Gerber et al., 2017; Jasechko et al., 2017). Remnant Paleozoic age (>250 Ma) seawater is present at depth and in the interior of sedimentary basins often associated with evaporite deposits (Carpenter, 1978; Hanor, 1994; Lehmann et al., 2003; Ma et al., 2009; Kharaka and Hanor, 2014), while even older saline fluids (>1 Ga) are trapped within isolated fracture systems in crystalline basement rocks (Holland et al. 2013; Warr et al., 2018).

The depth of meteoric circulation and interface with more stagnant saline fluids has evolved over geologic time in response to changes in topography, stratigraphy, and permeability (Bethke and Marshak, 1990; Lazear et al., 2013; Yager et al., 2017; Ferguson, McIntosh, Grasby et al., 2018; Chaudhary et al., 2019). For example, past orogenic events drove ore-forming brines (e.g., Wisconsin and Illinois basins; Bethke and Marshak, 1990) and hydrocarbons to distal margins of basins (e.g., Western Canada Sedimentary Basin; Garven, 1989). Pleistocene continental glaciation enhanced the depth of meteoric circulation by increasing hydraulic heads at the ground surface (Person et al., 2007). Low permeability layers can impede meteoric infiltration, reduce flow rates, and control response times of flow systems to changes in driving forces (Neuzil, 1986; Tóth, 1999) and their removal can increase circulation rates. Basinal brines can be brought close to the surface by denudation (Yager et al., 2017). High-relief landscapes of sedimentary basins in western North America were shaped by erosion and incision along rivers during the Laramide Orogeny (e.g., Permian Basin; Chaudhary et al., 2019; Grand Mesa; Aslan et al., 2019) or during the Neogene period (e.g., denudation of Colorado Plateau; Lazear et al., 2013). This erosion and incision would have increased hydraulic gradients, breached or removed aquitards, while denudation would have brought deeper strata closer to the surface.

The depth of circulation of meteoric waters is a function of the hydraulic head (e.g., topography or glaciation) available to drive regional groundwater flow and the tendency for saline fluids at depth to stagnate due to negative buoyancy (Ferguson, McIntosh, Grasby et al., 2018; McIntosh and Ferguson, 2021). The driving force ratio (DFR) compares these two forces (Bachu, 1995; Ferguson, McIntosh, Grasby et al., 2018). If a basin has a DFR greater than 1, trapping of high-density residual brines would be expected. Conversely, if a basin has a DFR less than 1, residual brines may be flushed by regional groundwater flow (Ferguson, McIntosh, Grasby et al., 2018). Most sedimentary basins containing paleo-seawater have DFR >1, for example in the Permian, Illinois, Appalachian, and Michigan basins (Ferguson, McIntosh, Grasby et al., 2018).

Interestingly, the Paradox Basin in the Colorado Plateau has a low DFR (<1; Ferguson, McIntosh, Grasby et al., 2018) based on relatively high modern relief, suggesting that saline fluids within the basin should have been flushed by topographically-driven regional groundwater flow. Yet, evaporated paleo-seawater (EPS) is present at depth within extensive Pennsylvanian marine evaporite confining units and, to a lesser extent, in the over- and under-lying aquifer systems (Kim et al., in press). We hypothesize that recent denudation of the Colorado Plateau and deep incision of the Colorado River (<4-10 Ma) created high topographic gradients that led to partial flushing of remnant saline fluids (e.g., EPS), while EPS is retained within evaporite confining units due to their low permeability and relatively short timescales of flushing. To test this hypothesis, we applied ^{81}Kr dating to provide constraints on the timescales and extent of meteoric water circulation vs. retention of connate brines in the Paradox Basin.

^{81}Kr is derived solely from atmospheric sources produced by cosmic rays with negligible subsurface production (Collon et al., 2004; Sturchio et al., 2014), unlike more traditional tracers, such as ^{4}He or ^{36}Cl (Ballentine and Burnard, 2002; Phillips, 2000), and can date groundwater from ~40 ka to 1.2 Ma (half-life 229,000 years; Loosli and Oeschger, 1969) beyond the range of radiocarbon. Recent advances in Atom Trap Trace Analysis (ATTA) (Jiang et al., 2012 & 2020; Lu et al., 2014) which has reduced sample size alongside the development of gas extraction devices for field sampling (Yokochi, 2016; Jiang et al., 2020) have enabled the application of ^{81}Kr as an age tracer of subsurface flow systems (Aggarwal et al., 2015; Matsumoto et al., 2018 & 2020; Ram et al., 2021). ^{85}Kr (10.7-year half-life), which is present in the modern atmosphere, has been used as a monitor for modern air contamination (Sturchio et al., 2014; Yokochi et al., 2019).

Most ^{81}Kr studies to date have been in confined fresh to brackish water aquifer systems (Lehmann et al., 2003; Sturchio et al., 2004; Matsumoto et al., 2018; Yechieli et al., 2019; Yokochi et al., 2019). Sturchio et al. (2014) applied ^{81}Kr to the dating of saline meteoric groundwater (~130 and ~330 ka) in carbonates overlying evaporites at the Waste Isolation Pilot Plant, New Mexico. In the Baltic Artesian Basin, ^{81}Kr dating of groundwater from the basal, saline aquifer system identified three distinct fluid components (300 ka to >1.2 Ma) with Pleistocene glaciation suppressing the interface between meteoric water and basinal brines (Gerber et al., 2017). These past studies have focused on using ^{81}Kr to examine changes in groundwater systems due to shifts in climate during the Pleistocene Epoch. Here, we measure ^{81}Kr in fresh to saline fluids to investigate the effects of geological processes, such as denudation and incision, on activation of deep meteoric flow systems. In addition, we combine ^{81}Kr ages with geochemical results to estimate the age distribution of meteoric water components of the basinal fluids.

1. **Study Site**

The Paradox Basin, in the Colorado Plateau, is a foreland basin (Barbeau,

2003) located in Utah and Colorado, USA (Fig. 1a), underlain by Precambrian basement rocks (Bremkamp and Harr, 1988). The basal sedimentary units are comprised of Cambrian, Devonian (e.g., McCracken Sandstone (Ss) member of Elbert Formation (Fm)), and Mississippian (e.g., Leadville Limestone (Ls)) formations deposited in marine environments (Fig. 1c). During the Pennsylvanian, marine evaporites were cyclically deposited with interbedded black shales, comprising the Paradox Fm (up to 2.5 km thick) (Fig. 1c; Hite et al., 1984). Examples of members of Paradox Fm are the Ismay-Desert Creek carbonate and Cane Creek shale. Overlying the Paradox Fm evaporites, the Pennsylvanian Honaker Trail Fm contains eolian and fluvial beds. Thick deposition of Permian (e.g., Cutler Fm), Jurassic (e.g., Navajo Ss), Cretaceous (e.g., Burro Canyon Fm), and Tertiary sediments, from erosion of Precambrian rocks in the Uncompahgre Uplift, led to plastic flow of the evaporites and formation of salt anticlines and associated faults along the northeastern side of the basin (Fig. 1b). Intrusion of laccoliths such as the Abajo and La Sal mountains occurred during the Tertiary (28 Ma; Nuccio and Condon, 1996). The Mancos Shale was deposited in the Western Interior Cretaceous seaway within the upper hydrostratigraphic unit as a regional confining unit.

Relatively recently, rapid denudation of the Colorado Plateau and deep incision of the Colorado River within $<$4-6 Ma (Murray et al., 2019) or $<$10 Ma (Lazear et al., 2013) created steep topographic gradients (Lazear et al., 2013) and likely led to widespread paleofluid flow events (Garcia et al., 2018; Bailey et al.,2021). The maximum net eroded sediment thickness, derived from subtraction of the modern topographic surface from the paleosurface, is about 1-3 km within the past 10 Ma across the Paradox Basin (Lazear et al., 2013). For example, the Leadville Ls would have reached a depth of ~5000 m during maximum burial (Nuccio and Condon, 1996), compared to only ~2000 m today. Since the denudation of Colorado Plateau, most of the Mancos Shale has been eroded within the Paradox Basin, except in the Book Cliffs area and southwestern Colorado (Molenaar, 1981).

The Paradox and Lower Honaker Trail formations form a regional confining unit (middle hydrostratigraphic unit) that separates aquifer systems in the upper and lower hydrostratigraphic units (Fig. 1c; Hanshaw and Hill, 1969; Thackston et al., 1981). Beneath the Paradox Fm, the Mississippian

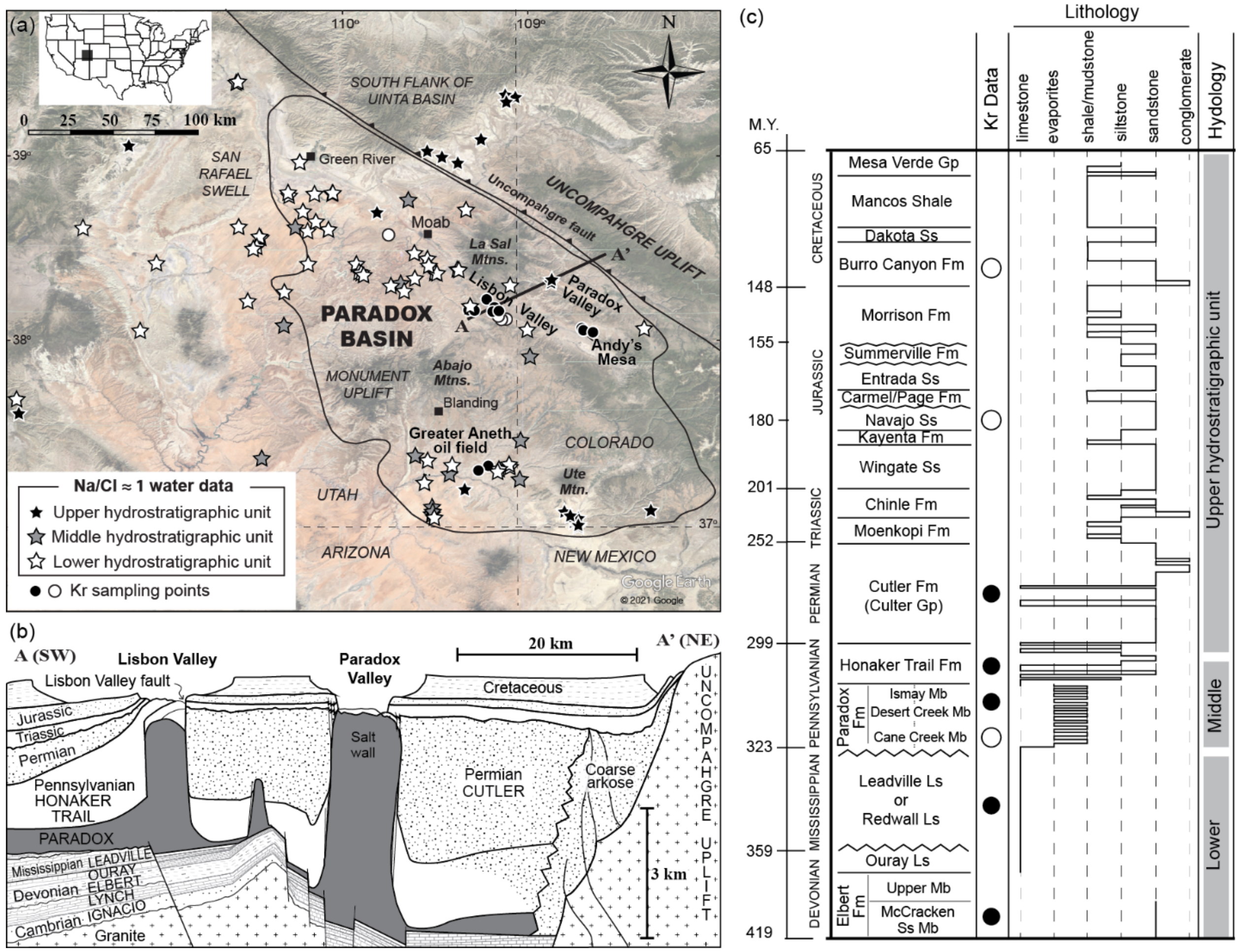

Figure 1. (a) Location of the Paradox Basin and spatial distribution of dissolution of evaporite (Na/Cl ~1). (b) Schematic cross section of A-A' in (a) across the Paradox Basin, modified from Baars (1966), Stevenson and Baars (1986), and King et al. (2014). (c) Stratigraphic column with sample formation, lithology, and hydrostratigraphic unit (Hanshaw and Hill, 1969). For the Kr sampling points of (a) and Kr data column of (c), open circles indicate extracted gas samples from groundwater, while closed circles indicate produced gas samples from gas producing wells.

through Devonian formations comprise a single, lower hydrostratigraphic unit, or basal aquifer system, with regional groundwater flow towards the southwest and with local recharge around laccoliths or along the margins of the salt anticlines. In the upper hydrostratigraphic unit above the Paradox Fm, groundwater flow is mainly controlled by local topography with recharge around salt anticlines, uplifts, and mountains.

1. **Methods**

To constrain the ^{81}Kr ages of formation waters, a total of 13 dissolved and produced gas samples were collected for krypton isotopes in 2018 and 2020 from near surface (<500 m depth) to basal geologic formations (up to 2.7 km depth). The location and geologic formation of samples are displayed in Figure 1a & 1c and Table S1. Nine gas samples were collected directly from oil and gas producing wells. Three gas samples were extracted from fresh to brackish groundwater monitoring wells and one gas sample was extracted from a lithium exploration well completed in the Cane Creek member of the Paradox Fm. One modern air sample was collected to measure ^{85}Kr in the atmosphere, so that possible contamination with modern air in the samples can be quantified and corrected. A gas extraction device was connected between a wellhead and a gas cylinder and used to evacuate aluminum gas tanks and collect gas samples to prevent air contamination during sampling. In case of groundwater wells, a hydrophobic membrane was used to extract dissolved gas from water and convey the extracted gas to evacuated tanks. ^{81}Kr samples were analyzed by Atom Trap Trace Analysis (ATTA) in the Hefei National Laboratory at the University of Science and Technology of China (Jiang et al., 2012 & 2020). ^{81}Kr results were paired with previously published hydrochemical data (Kim et al., in press), from corresponding water samples from the same wells (where available) or the same fields where the gas samples were collected (Table S2). The hydrochemical data were used to calculate the extent of meteoric recharge, salt dissolution, and mixing with remnant EPS-derived brines. Only ^{81}Kr data for the Permian Cutler Fm from the Andy's Mesa field were compared with available water data from a different field (Greater Aneth oil field; Spangler et al., 1996). ^{85}Kr was also analyzed in the Hefei National Laboratory to identify and correct for air contamination during sampling (Jiang et al., 2012).

Hydrochemical data, including Na/Cl, Cl/Br, and water stable isotopes were compiled from previously published sources (Mayhew and Heylmun, 1965; Hanshaw and Hill, 1969; Blondes et al., 2018; Kim et al., in press) to calculate the extent of meteoric recharge, salt dissolution, and mixing with remnant EPS-derived brines.

The DFR was used to evaluate the mobility (e.g., flushing or retention) of saline fluids in the Paradox Basin over geologic time. The DFR is calculated by comparing the force due to pressure and topographic differences to drive regional groundwater flow to the force due to negative buoyancy acting on saline fluids (Ferguson, McIntosh, Grasby et al., 2018; McIntosh and Ferguson, 2021):

$$DFR = \left(\frac{\rho}{\rho_0}\right)\frac{|\nabla E|}{|\nabla H_0|_h}$$

1. **Widespread Meteoric Circulation**

Formation waters with molar Na/Cl ~1 across the Paradox Basin, in upper and lower hydrostratigraphic units, indicate widespread influx of meteoric waters and dissolution of halite associated with the Paradox Fm evaporites (Fig. 1a). High molar Cl/Br of formation waters, found at shallow depth (15 m) above salt anticlines ("salt anticline brine") and beneath the evaporites (e.g., Leadville Ls brine), also indicate dissolution of the evaporites by meteoric circulation (Fig. 2b).

In addition to the salt dissolution-derived brines, EPS within the Paradox Fm, represented by a brine sample from the Cane Creek member ("Cane Creek brine"), is another major source of salinity in the formation waters of the Paradox Basin and has a distinct geochemical and isotopic signature with low Na/Br (28) and Cl/Br (156) molar ratios relative to modern seawater (565 and 659, respectively) and the highest $^{18}O_{water}$ and D_{water} values (Table S2; Kim et al., in press). Water stable isotope values (

Fig. 2b-c; Table S2) show the variable amount of mixing between meteoric water recharge and remnant EPS for each formation water.

The salt anticline brines and Burro Canyon Fm brackish groundwater have low D_{water} values and are consistent with Holocene to Pleistocene recharge (Noyes et al., 2021) with almost 100% meteoric water, while deep basinal brines (Honaker Trail Fm brine, Desert Creek brine, Leadville Ls brine, and McCracken Ss brine) consist of varied proportions of meteoric water and EPS (Fig. 2b-c). For example, the Leadville Ls brine contains ~74 % meteoric water and ~26 % EPS based on D values. This is somewhat consistent with PHREEQC inverse mixing model results using major ion chemistry indicating 96 % meteoric water and 4 % EPS in the Leadville Ls brine sample (Kim et al., in press). Both results are in qualitative agreement with the high proportion of meteoric waters in the lower hydrostratigraphic unit, dilution of connate saline fluids, and regeneration of salinity via salt dissolution.

1. **Meteoric Flushing vs. Retention of Evaporated Paleo-Seawater-Derived Brine**

Shallow salt anticline brines (<~8 ka) and fresh to brackish shallow groundwater (3 ka to 36 ka) from the Cretaceous Burro Canyon Fm and Jurassic Navajo Ss are relatively young (based on ^{14}C; Noyes et al., 2021) compared to deep brines (>530 ka), indicating meteoric circulation and salt dissolution since at least the Late Pleistocene (Fig. 2a). The ^{81}Kr age of groundwater in the Navajo Ss aquifer is 15-34 ka, consistent with ^{14}C age results. In the deeper brines, the ^{81}Kr age of formation waters in the Cutler and Honaker Trail formations and Desert Creek member of the Paradox Fm are ~890 ka, 530-754 ka, and 600 ka - 1.2 Ma with detectable ^{81}Kr, respectively, suggesting that the meteoric components of fluids in the upper hydrostratigraphic unit are younger than 1.2 Ma.

The Cane Creek brine from the Paradox Fm evaporite has too much uncertainty to correct for

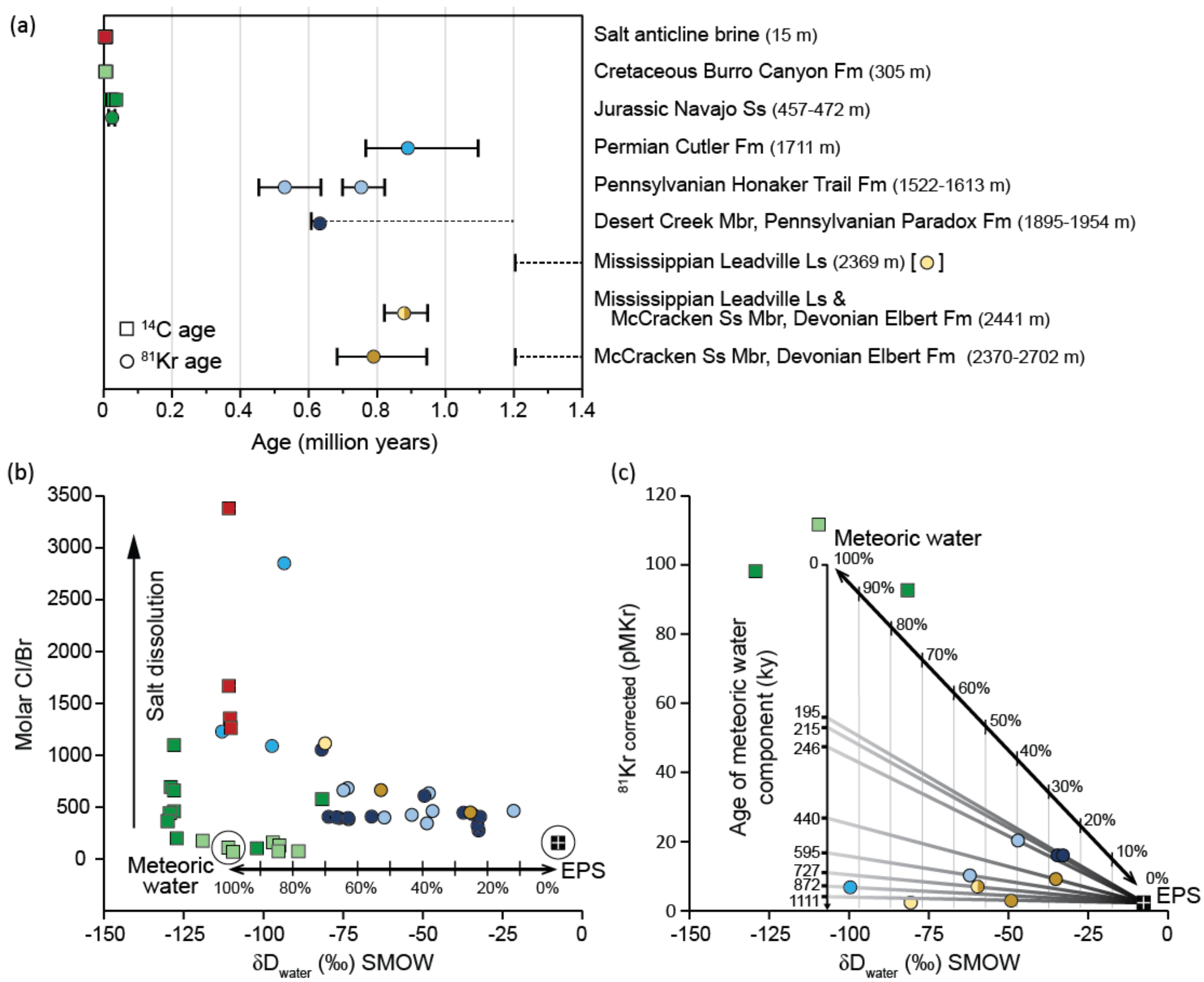

Figure 2. (a) ^{81}Kr data from this study and ^{14}C data from previous studies (Noyes et al., 2021; US Bureau of Reclamation, unpublished data) of different geologic formations. The sample depth is shown in parentheses next to the formation name. (b) D_{water} values of formation waters showing a binary mixing relationship between meteoric water and evaporated paleo-seawater (EPS) components. High Cl/Br of formation waters indicates salt dissolution by influx of meteoric water. (c) Corrected ^{81}Kr abundance of fluids versus corresponding D_{water} values of formation waters. The estimated ^{81}Kr age of the meteoric water component of formation waters was calculated using D_{water} values. Abbreviations used: Mbr – Member; Fm – Formation; Ls – Limestone; Ss – Sandstone.

^{81}Kr (Table S2). Given the chemical and isotopic signatures indicative of Paleozoic EPS (i.e. Cl:Br « 659, Na:Cl « 0.85, ^{18}O ~5‰), the Cane Creek brine is likely the oldest, beyond the ^{81}Kr dating limit (>1.2 Ma, Fig. 2a), and has the same ^{81}Kr as the underlying oldest formation water with <2.5 pMKr in the lower hydrostratigraphic unit. The low permeability of the Paradox Fm evaporites, which even impeded vertical He diffusion (Tyne et al., in review), likely enabled retention of these paleofluids and prevented influx of meteoric waters (Gloyna and Reynolds, 1961; Neuzil, 1986).

Formation waters in the lower hydrostratigraphic unit contain variable ^{81}Kr from <2.5 to 9.1 pMKr (Table S2). The ^{81}Kr ages of the formation waters with detectable ^{81}Kr range from 790 to 878 ka, which is younger than the overlying EPS (Fig. 2a). This indicates the presence of meteoric waters in the basal aquifers, which is consistent with Cl/Br and D_{water} results of Leadville Ls brine (Fig. 2b), and relatively recent circulation of meteoric water. The ^{81}Kr ages of the formation waters beyond the ^{81}Kr dating limit suggest the presence of residual EPS in the basal aquifers due to preservation, dispersive processes or as the result of diffusion from the overlying Paradox Fm. We hypothesize that relatively young meteoric water diluted the EPS-derived brines and dissolved halite resulting in salt dissolution-derived brines. Further evidence of meteoric water flushing beneath the Paradox Fm is observed in the atmosphere-derived noble gas ratios and lower than predicted ^{4}He concentrations (Tyne et al., in review).

1. **Timing of meteoric water recharge into formation above/below Paradox Fm**

A simple binary mixing model using the measured ^{81}Kr and D_{water} of formation waters was constructed to calculate the estimated age of meteoric water components of each formation water and better constrain the timing of meteoric recharge (Fig. 2c). The binary mixing model accounts for the proportion of ^{81}Kr abundances between two endmembers: 1) meteoric water with different ^{81}Kr (age) for each formation water and 2) EPS with consistent low ^{81}Kr abundance. The proportion of the two endmembers for each formation water was based on D_{water} values of fluids (Fig. 2b). D_{water} was used in this study rather than $^{18}O_{water}$, as more samples were included in a mixing space consisting of the two endmembers with D_{water} and other parameters (Cl/Br or ^{81}Kr). The D_{water} value of the initial meteoric water endmember was assumed to be the average of the fresh-brackish groundwater samples (PW-8, PW-11, and PW-12; -106.8 ‰), which had an average ^{81}Kr abundance of ~100 pMKr indicating meteoric water in contact with the atmosphere. The saline fluid endmember was represented by EPS with assumed ^{81}Kr value (2.5 pMKr) from the underlying oldest formation waters (Leadville Ls brine) in the basin and measured D_{water} (-7.57 ‰) values from the Cane Creek brine.

In the Lisbon Valley area in the northeastern parts of the basin (Fig. 1a), formation waters in the Honaker Trail Fm consist of 40-55 % meteoric water with an ^{81}Kr age of 250-600 ka and 45-60 % EPS (Fig. 2c). Formation waters in the Leadville Ls and McCracken Ss are composed of 28-52 % meteoric water with an ^{81}Kr age of 440 ka - 1.1 Ma and 48-72 % EPS. The lower hydrostratigraphic unit shows an older and wider range of meteoric components than the upper hydrostratigraphic unit, indicating deep circulation of meteoric water into the basal aquifer system in the Lisbon Valley area was activated as early as ~1.1 Ma.

Formation waters in the Cutler Fm in the Andy's Mesa field in the northeastern parts of the basin (Fig. 1a) contain a large component (93 %) of older (870 ka) meteoric water, compared to the meteoric water component of formation waters in the underlying Honaker Trail Fm from the Lisbon Valley (Fig. 2c). It is possible that meteoric water circulation was activated earlier in the Cutler Fm with limited fracture connectivity between formations (Anna et al., 2014). However, because the D values used for the Cutler Fm came from a different field (Greater Aneth oil field; Spangler et al., 1996) than the ^{81}Kr data, the percent meteoric water may have been over- or under-estimated.

In the Greater Aneth oil field located along the southwestern margin of the Paradox Basin (Fig. 1a), meteoric water components for formation waters in the Desert Creek member of the Paradox Fm are lower in proportion (28 %) and relatively young (250-600 ka), compared to over- and under-lying formations in other parts of the basin (Fig. 2c). The differences in the extent and timing of meteoric recharge may be explained by differences in the local permeability structure, depth, and topography. The Paradox Fm in the Greater Aneth oil field contains fewer evaporites deposited in the carbonate shelf and is located at relatively shallow depths (1.8 km; Spangler et al., 1996), which may have enabled influx of meteoric water into the Paradox Fm.

1. **The evolution of meteoric circulation**

In order to constrain the evolution of meteoric circulation over geologic time, it is necessary to understand the past topography and burial history including denudation and incision events. Prior to widespread erosion of the Mancos Shale and overlying units, underlying formation waters were deeply buried. The basin before 10 Ma (Fig. 3a) was covered by an addition ~1300 m of sediments (Nuccio and Condon, 1996). Furthermore, considering the incision rate of 126 m/Ma (Darling et al., 2012), the elevation of the regional discharge was also 1260 m higher (Fig. 3a) compared to the modern topography (Fig. 3b). The saline fluids (e.g., EPS) may have been expelled very slowly (red arrow in Fig. 3a) due to compaction (Bethke and Marshak, 1990), compared to the shallow regional flow system (blue arrow in Fig. 3a). Because of a higher ratio of the structural gradient of the groundwater flow system (E) to equivalent freshwater head gradient (h) before 10 Ma, DFR values for deeper formations were likely much higher than 1 (Fig. 3c), indicating the retention of most of saline fluids. Furthermore, brine densities before meteoric influx were likely higher than they are today, resulting in even stronger tendency to retain with higher DFR values before 10 Ma.

Following widespread erosion of Mancos Shale and other units from 10 Ma and incision of rivers (Fig. 3b), the modern water table with elevations as high as

2500 masl near the La Sal Mountains and regional discharge areas of ~1100 masl along the Colorado and San Juan rivers shows DFR <1, indicating active circulation of meteoric water throughout the basin (Fig. 3c). The deep meteoric circulation would have flushed residual saline fluids in aquifers above and below the evaporite (Fig. 3b). Internal drains within the basin (e.g., Dolores River in the Paradox Valley or Salt Creek in the Sinbad Valley) would

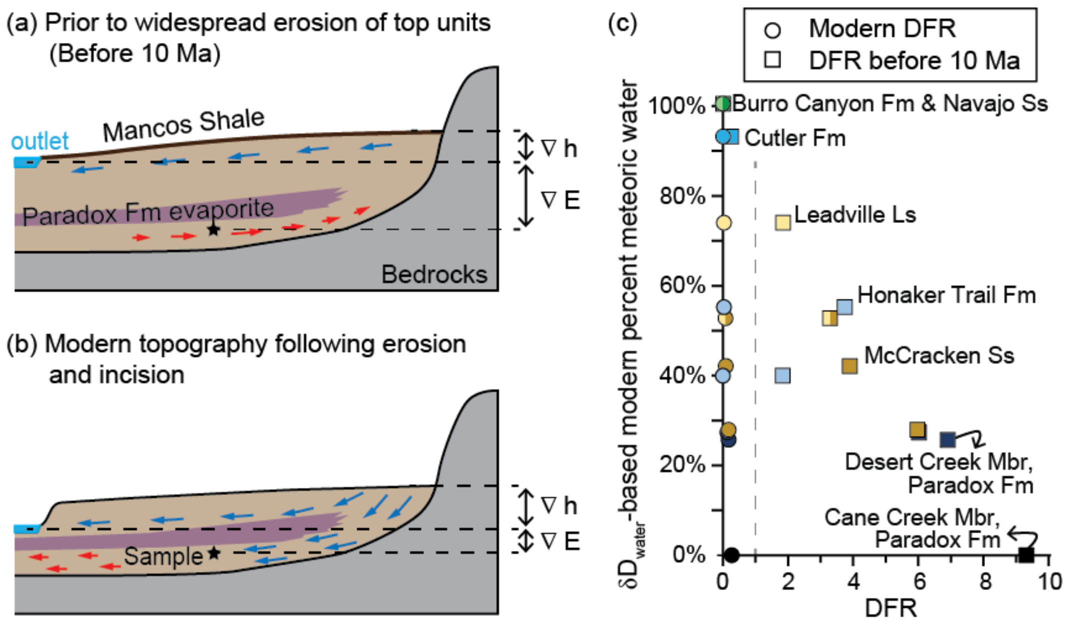

Figure 3. Schematic diagrams (a-b) of evolution of meteoric circulation in response to changes in the equivalent freshwater head gradient (∇h) and topographical gradient (∇E) of an aquifer by erosion and incision over geologic time, prior to denudation of the Colorado Plateau (a) and following erosion of the Mancos Shale and incision of river outlets (b). Blue arrows represent fresh groundwater flow, while red arrows represent saline fluid migration. Length of arrows represent magnitude of flow. (c) Comparison of DFR values for each formation based on before 10 Ma and modern topography. The color of the symbol is identical to Figure 2.

show higher DFR values due to their higher elevation than regional discharge areas, yet their sufficient high head gradients from the La Sal mountains still enable circulation of meteoric water below the Paradox Fm. The rate and depth of circulation of meteoric water would have increased as incision of the Colorado Plateau created lower elevation discharge points over time. The lack of waters beyond the ^{81}Kr ages with meteoric components suggests that although incision of the Colorado Plateau began 4 -10 Ma (Lazear et al., 2013; Murray et al., 2019), there was insufficient incision to activate regional groundwater flow in the deeper parts of the Paradox Basin until ~1 Ma.

Changes in topography, stratigraphy, and permeability structures due to denudation would have increased hydraulic gradients, removed low permeability layers, or brought deeper strata closer to the surface, which enhance the extent and rate of meteoric circulation and deeper interface with stagnant saline fluids. Increases in meteoric circulation depth has also been observed in other sedimentary basins in the southwestern US, such as the Permian (Engle et al., 2016; Chaudhary et al., 2019), Uinta (Zhang et al., 2009) and San Juan (Scott et al., 1994) basins, that have been affected by denudation. The role of landscape evolution over the last few million-years on the timing and extent of recent deep meteoric circulation (<1.2 Ma) through subsurface flow systems could be further tested by ^{81}Kr dating of basinal fluids.

1. **Conclusions**

This study showed that ^{81}Kr is an effective tool to illuminate the timescales and extent of meteoric flushing vs. retention of brines in sedimentary basins. The application of ^{81}Kr combined with D_{water} to examine the meteoric component of saline fluids in the Paradox Basin revealed deep meteoric circulation ~390 ka to 1.1 Ma. Rapid denudation enhanced topographic gradients and altered the permeability structure (i.e., erosion of shale confining units) enabling deep circulation of meteoric water and partial flushing of basal aquifers, while evaporated paleo-seawater (>1.2 Ma) is still retained within the evaporite confining unit.

Past applications of ^{81}Kr have focused on how climate shifts during the Pleistocene have affected groundwater flow systems (Lehmann et al., 2003; Sturchio et al., 2014). Our results demonstrate that ^{81}Kr can be used to provide insights into the evolution of groundwater flow systems due to geological processes operating on times scales of up to ~1 Ma. The shift from a static to dynamic view of geology that this helps to facilitate is necessary as we seek to understand how groundwater flow systems have changed over geologic time and what effects this may have on geochemical cycles and subsurface life, and energy extraction, storage, and waste isolation.

Data Availability Statement

Kr data archiving is underway. The Kr data will be stored and publicly available on Hydroshare (at: http://www.hydroshare.org/resource/d2a724a994b34fa388 0ca21562912788). Na/Br, Cl/Br, TDS, $^{18}O_{water}$, and D_{water} data are available through Mayhew and Heylmun (1965), Hanshaw and Hill (1969), Spangler et al. (1996), Blondes et al. (2018), and Kim et al. (in press). ^{14}C data are available through Noyes et al. (2021) and unpublished data from US Bureau of Reclamation.

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