Formation and Stability of Heterogeneous Organo–Ionic Surface Layers on Geological Carbonates

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ABSTRACT: Many geological processes from oil recovery to underground CO₂ storage are affected by natural molecules adsorbed on rock surfaces. Yet, geochemical models tend to overlook their formation and stability, let alone existence. With a suite of analytical techniques, we address this “missing-link” and describe fundamental mechanisms for (i) the deposition of surface-active molecules in complex brines and oils on underground minerals and (ii) the desorption of heterogeneous sorbents and its dependence on aqueous composition. First, we show that organic and inorganic constituents of both formation water and crude oil form an organo–ionic surface layer on calcite. Primary modifiers are revealed as aqueous and nonaqueous polyaromatic molecules with polar and metal-binding functional groups and solubility characteristics of asphaltenes. Formed via π-stacking and ionic and hydrogen bonding interactions, the heterogeneous organo–ionic layer establishes a physical barrier between the mineral and ambient atmosphere/fluid, impacting the dissolution and wettability of rocks. Second, we investigate desorption of the organo–ionic layer in various brines under flow and static conditions. With chromatographic and spectroscopic methods (including Raman and sum-frequency generation), we show that the release of adsorbed material from carbonate surfaces encompasses key coupled reactions: (i) dissolution of “brine-soluble” asphaltenes, leading to relative interfacial enrichment of bulky “brine-insoluble” asphaltenes, (ii) nanoscale orientational changes of surface asphaltene assemblies, carbonate ions, and water molecules at the brine–rock interface, and (iii) dissolution and surface reconstruction of the carbonate mineral. Through these reactions, the “low-salinity effect” is uncovered as a two-stage desorption process: the initial release or selective extraction of “water-soluble” sorbents and subsequent delamination of residual “water-insoluble” asphaltenes from the dissolving mineral surface. Illuminating the surface reactions of geological minerals, we conclude that surface passivation by heterogeneous organo–ionic matter is not only ubiquitous in nature but also a key regulator of the interfacial chemistry, reactivity and wettability of underground rocks.

INTRODUCTION

Adsorption of organic matter on natural minerals is ubiquitous. As a barrier between the mineral and ambient atmosphere or fluid, sorbent molecules affect all geochemical phenomena from rock weathering and land management to the sustenance and survival of life. Therefore, the composition, assembly, and stability of natural sorbents on mineral surfaces are crucial factors even for anthropogenic endeavors from oil and gas recovery to underground CO₂ storage.

While carbonate formations hold a majority of the world’s crude oil (CRO), the extraction of oil from underground rocks is a big challenge. A key problem is the limited understanding of how minerals interact with complex underground fluids: brines and oils. Though it is generally accepted that oil displacement from “oil-wet” rock surfaces is difficult, the fundamental nature of fluid–mineral interfaces remains overlooked, even in standard workflows of reservoir development. Reactions of minerals with brines and oils, during both natural diagenesis and reservoir engineering, are not often investigated with the same rigor as the composition and structure of host rocks. Consequently, chemical reactions and dynamic equilibria across fluid–fluid and fluid–mineral interfaces, which underlay key transitions between “oil-wet” and “water-wet” surface states, remain to an important extent unclear. (Throughout this work, we will use the term “wettability” in its physicochemical sense; i.e., it is equivalent to local contact angles. Additional aspects such as pore geometry, fluid distribution, and hysteresis form essential

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aspects of wettability in its petroleum engineering sense refer to a larger length scale and are not addressed in this work.)

Addressing the initial (i.e., prerecovery) surface chemistry of minerals within oil reservoirs, physical models often consider rock surfaces as initially pristine and in contact with a highly saline (connate or formation) water film. As the oil migrates upward from the source rock and makes contact with the reservoir rock, certain oil components adsorb onto the mineral surface, resulting in wettability changes toward (more) oil-wet. Here direct adsorption of oil molecules occurs if the net forces (resulting from electrostatic, van der Waals, and hydration effect) between the oil—water and water—mineral interfaces are sufficiently attractive to squeeze out the water film (Figure 1a). This model has also been extended to explain how low-salinity brines improve oil recovery during water-flooding (Figure 1b), viz., by increasing repulsive electrostatic forces between oil—brine and brine—mineral interfaces and increasing thickness of the water film (i.e., electric double-layer expansion). However, new evidence suggests that certain key elements, intrinsic to all oil reservoirs, are routinely being underestimated: (i) the actual chemical nature and interfacial properties of mineral-bound organic matter and (ii) the solubility of oil components in brines.

Crude oils exhibit remarkable physicochemical complexity, with the number of distilled organic components greatly exceeding 100 000 as well as the dynamic (re)assembly of chemical constituents into emulsions, (nano)aggregates and particles. From this chemical haystack, certain molecules bind to mineral surfaces and form "organic layers," possibly leading to alterations in the geochemical properties of carbonates such as dissolution rates and wettability. However, mechanistic studies of organic molecules, undergoing surface deposition and desorption in carbonate rocks, are limited and those uncovering the chemical identity of primary sorbents report mixed observations.

To explain wettability changes in brine- and oil-laden carbonate rocks, the dissolution rates and surface potential of the pristine (uncontaminated) mineral are often utilized. Such approaches involve two main assumptions: (i) brines undergo instantaneous equilibration with the dissolving mineral, and (ii) the mineral-bound organic matter is physically and chemically indistinguishable from the bulk oil. However, the validity of these assumptions appears questionable.

First, carbonate minerals undergo dissolution even under alkaline conditions. Published rates of calcite dissolution at pH 9 are between 10−9 and 10−10 mol/(cm2 s). Considering the molar mass of calcite (100.09 g/mol), these rates correspond to about 10−1 to 10−2 μg/(cm2 s). While seemingly small, the rates correspond to dissolution of about 9−86 mg of the carbonate mineral over 1 cm2 in a single day under continuous flow. Thus, substantial mineral dissolution can occur over the time scales of reservoir development and production, which are on the order of decades. Kinetics of carbonate dissolution is also affected by surface deposits of oil and its long-chain fatty acid and polycyclic aromatic hydrocarbons. Recent studies even show that non-equilibrium fluids, under flow, substantially alter the surface potential and reactivity of minerals. Thus, the displacement of oil in reservoir rocks and the out-of-equilibrium conditions innate to this soluble mineral appear closely connected.

Second, rock-bound organic matter is often reported as enriched in polar groups and polyaromatic hydrocarbons, compositionally distinct from the bulk oil. In this respect, reservoir oil is also spatially categorized as free, adsorbed, or inclusion oil. While the free oil is localized toward the center of the rock pores, the adsorbed oil is bound to rock surfaces and the inclusion oil is trapped in voids within the mineral structure. Compositional differences between these oil types can elucidate the interfacial chemistry of reservoir rocks. Yet multiple components such as fatty acids, asphaltenes, resins, and naphthenic acids are suggested as "surface-active", portraying a lack of consensus on the composition of adsorbed oil.

A small but nontrivial fraction of CRO is water-soluble, dissolving into complex brines (formation and high-salinity injection water), simple brines and distilled water. Some of these water-soluble oil components can bind to mineral surfaces, altering mineral wettability. Thus, oil—brine phase transfer reactions appear crucial in setting initial reservoir conditions and subsequent oil recovery process. Yet computational and laboratory studies tend to utilize purely inorganic compositions of formation water and injection brines.

Figure 1. Literature mechanisms for wettability alterations of reservoir rocks on (a) initial oil contact and (b) subsequent brine exposure. (a) Adhesion of organic molecules (black) via the oil—brine interface to carbonate surfaces upon contact. Here a “stable” brine film (blue) can prevent physical contact between the oil and mineral surfaces. Adapted with permission from ref 27. Copyright 1986 Society of Petroleum Engineers (SPE). (b) Low-salinity flooding is proposed to alter surface charges at the oil—brine and brine-mineral interfaces. This in turn increases repulsion between the two interfaces and increased thickness of the brine film (right, black arrows). Calcium and (bi)carbonate ions are released into the brine upon carbonate dissolution (dashed lines). Adapted with permission from ref 13. Copyright 2017 Elsevier. (c) Open questions on the roles of surface-active molecules including their (1) dissolution from crude oil into formation/connate water and injection brines (red), (2) interactions with ion solutes (green dots), (3) deposition on rock surfaces either via the brine film (red) or directly from oil contact (black), and (4) dissolution or mobilization of rock-bound molecules during oil recovery.
With growing evidence of key roles of rock-bound and aqueous organic solutes in oil reservoirs, their mechanistic functions in improved oil recovery (IOR) require attention (Figure 1c). For low-salinity waterflooding of carbonate reservoirs alone, a multitude of microscopic mechanisms are proposed such as mineral dissolution,\textsuperscript{49,50} double-layer expansion,\textsuperscript{51} and also salinity-related changes to the mineral–brine and oil–brine surface charges\textsuperscript{52,53} and adhesion interactions.\textsuperscript{54} However, regardless of the IOR mechanism, the chemical nature of the organo–mineral interface and its impact on the dissolution, surface potential, oil adhesion, and wettability alterations of mineral surfaces remain unresolved (Figure 1c). This lack in the fundamental understanding of IOR can only be addressed with in-depth analytical investigations of the interfacial chemistry of minerals in reservoir-pertinent oil and brine compositions.

Our study aims to address two questions: which surface-active components of underground brines and oils modify carbonate surfaces, and how, and what is the mechanistic relevance of the mineral-bound surface layer in low-salinity waterflooding? Thereby, we aim to establish a conceptual framework for both the initial deposition of sorbents from complex brines and oils on underground rocks and the subsequent stability of the adsorbed layer upon contact with various brines.

Though chemical and structural analyses of carbonate reservoir rocks have provided key physicochemical insights, these rocks represent the final state which arises by their interactions with underground brines and CROs over millions of years. To illuminate mechanisms that underlay this final state, we adopt a laboratory approach that starts with the pristine calcite material, systematically reacting it with complex brines and CRO at 95 °C. By illuminating microscopic details of mineralogical reactions, with initially formation water and then CRO, we aim to establish a conceptual picture of the formation, composition, and stability of geologically pertinent organo–carbonate interfaces.

To conclusively establish any reservoir-pertinent mechanism in the laboratory, well-defined and reproducible methods mimicking the reservoir complexity are needed. Here we apply an established two-step “artificial diagenesis” or “aging” method.\textsuperscript{26} Initial equilibration of formation water (FW) and CRO at elevated temperature leads to an exchange of molecules between the two fluids. Subsequently equilibrating calcite crystals in these fluids establishes a surface adlayer, rendering a more oil-wet mineral surface. Using this aging protocol, we will investigate the formation, composition, and stability of the carbonate-bound surface layer, also observed in reservoir core samples.\textsuperscript{21,20,23}

At first, we investigate the surface modifications of reservoir rocks in formation water and CRO using multiple analytical techniques such as total organic carbon (TOC) analyses, Raman spectroscopy, solubility testing, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and potentiometric titrations. With this comprehensive approach, we establish the primary chemical fingerprint of surface-active molecules from complex brine and oil and their depositional mechanisms and layer organizations on the carbonate surface.

And, second, simulating waterflooding conditions, we perform chromatography of packed beds of oil-aged calcite under the flow of various brines, and analyze effluents with UV–visible absorbance spectroscopy and pH measurements as well as proton nuclear magnetic resonance (H\textsuperscript{1} NMR) spectroscopy. Microscopic changes at the brine–carbonate interface are studied with in situ confocal Raman microscopy (CRM), ex situ scanning electron microscopy (SEM), and sum-frequency generation (SFG) spectroscopy. With these complementary analytical methods, we characterize key microscale reactions and structural changes that elucidate the desorption of rock-attached heterogeneous sorbent layers under low-salinity conditions.

In all, this study presents a body of evidence that addresses the formation, composition, and stability of organo–ionic layers on carbonate surfaces. We provide a new conceptual picture for the interfacial interactions of heterogeneous and geologically pertinent surface-active species with mineral surfaces.

### MATERIALS AND METHODS

**Preparation of Fluid and Mineral Specimens.** Mineral samples were freshly cleaved Iceland spar (Ward’s Science) and calcite powder (≥99.0%, powder, ACS reagent, Sigma-Aldrich). Dead crude oil from a carbonate reservoir was used. Results of chemical analysis of the CRO, conducted by Saybolt Nederland B.V., are summarized in Supporting Information Table S1. Brines (see Table 1 for the compositions) were prepared by dissolving reagent grade chemicals (calcium chloride, magnesium chloride, magnesium sulfate, sodium bicarbonate, and sodium chloride from Sigma-Aldrich) into deionized water, rendering a more oil-wet mineral surface.

**Table 1. Composition and Geochemical Analysis of Synthetic Brines: Formation Water (FW)/Ultrahigh-Salinity Water (UHSW), High-Salinity Water (HSW), and Low-Salinity Water (LSW)**

|               | FW/UHSW | HSW  | LSW  |
|---------------|---------|------|------|
| **Cations (ppm)** |         |      |      |
| Na\textsuperscript{+} | 59491   | 18345| 1834 |
| Ca\textsuperscript{2+} | 19040   | 650  | 65   |
| Mg\textsuperscript{2+} | 2439    | 2117 | 212  |
| **Anions (ppm)** |         |      |      |
| Cl\textsuperscript{−} | 350     | 4290 | 430  |
| SO\textsuperscript{4−} | 132060  | 35534| 3553 |
| HCO\textsuperscript{3−} | 354     | 696  | 69   |
| **TDS** | 213734  | 57670| 5767 |
| **pH** | 6.8     | 7.2  | 7.5  |

Established procedures were used to (i) generate reservoir-pertinent compositions of FW and CRO and (ii) modify carbonate surfaces with these equilibrated brines and oils.\textsuperscript{26} In brief, equal volumes of FW and CRO (125 mL each) were equilibrated in the presence of (brine-immersed) calcite at 95 °C for 2 days. On cooling to room temperature (RT), the equilibrated brine (eqFW) and oil (eqCRO) phases were separated and used within 2 weeks. To modify calcite surfaces, freshly cleaved Iceland spar crystals were aged in a sequential manner at 95 °C, first in eqFW for 16 h and then in eqCRO for 7 days. Preceding surface characterization, the eqFW-aged crystals were briefly rinsed with deionized (DI) water to eliminate any evaporative salt deposition and the oil-aged crystals were cleaned in toluene to remove oil residues. Calcite powder was aged in this manner.

**Solution State Analytics.** Total organic carbon contents were quantified using a carbon analyzer (Shimadzu TOC-L) using the
combustion catalytic oxidation method. For instrument calibration, commercial aqueous solutions for both organic and inorganic carbon (Nacalai Tesque Inc.), corresponding to concentration ranges of 0–10 mg/L potassium hydrogen phthalate and 0–100 mg/L sodium carbonate, were used. Brine batches were diluted with DI water (1:100, v/v), achieving salt contents within the permissible limit for TOC analyses. Absorbance spectra were acquired using a Tecan infinite M200 pro plate reader. 1H NMR (Bruker Avance 400 MHz, 128 scan accumulations) spectroscopy was used to characterize mineral-binding hydrocarbons using benzene-d6 as a deuterated solvent.

To investigate the complexation of Ca2+ ions, a HI-931 automated potentiometric system (Hanna Instruments) equipped with a Ca2+ ion selective electrode (HI-4104) was used. A calcium chloride solution (0.05 mM) was slowly added (at 100 μL min−1) to an aqueous solution of organic molecules maintained at 20 °C. Free (i.e., unbound) Ca2+ ion concentrations were simultaneously measured using the calcium sensing electrode. Calibration runs were performed by continuous addition of the salt solution to DI water. All titrations were performed in a temperature-controlled reaction vessel equipped with an overhead stirrer.

Surface Characterization. Confocal Raman microscopy (CRM) on Iceland spar crystals was performed using a WITec alpha 300R instrument, equipped with a 532 nm (2.33 eV) excitation laser and operated with a spectral resolution of 2 cm−1 (600 g/mm grating). A 50× objective (Zeiss EC Epiplan, N.A. = 0.75) and a CCD camera (1600 × 200 pixels, 16 μm pixel size, Andor AQ2 Newton) were used. Baseline correction and principal component analysis (PCA) guided denoising algorithms were used to generate distribution maps of calcite and polymeric hydrocarbons (PAHs). Baseline correction eliminates the fluorescence background in the Raman spectra of Iceland spar originating from fluorophores occluded in the mineral structure. Spectral regions of interest were integrated for each pixel: from 1076 to 1095 cm−1 for calcite (z, in-plane bending) and from 1500 to 1650 cm−1 for PAHs (G and D bands).

Using a Bruker Alpha spectrometer, FTIR spectra on calcite powders were acquired in attenuated total reflection (ATR) mode over a range of 400–4000 cm−1. Each spectrum represents the accumulation of 32 scans recorded with a spectral resolution of 2 cm−1. X-ray photoelectron spectroscopy (XPS) was carried out on a Quantera scanning microprobe instrument (Physical Electronics) operated with a monochromatic Al Kz X-ray source (1486.6 eV) and XPS control (Multipak, v.9.8.0.19) software. A Brunauer–Emmett–Teller (BET) surface area analyzer (Micromeritics Tristar II plus) with nitrogen adsorption was used to measure the specific surface area of calcite powder.

For SFG spectroscopy, a home-built spectrometer, described in detail elsewhere, was used. In brief, Spectra Physics (USA) Solstice Ace amplifier system produced 70 fs pulses with an internal beam splitter; ∼3.4 mJ energy pulses are taken to pump a Light Conversion TOPAS Prime optical parametric amplifier (OPA) and a subsequent unit for noncollinear difference-frequency generation of the signal and idler photons from the OPA. This provides mid-IR tunable femtosecond pulses with a bandwidth of >300 cm−1. The visible pulse (VIS) is generated by spectrally narrowing the 70 fs pulses from the Solstice Ace amplifier with an air-spaced etalon (SLS OPTics LTD, FSR 12.4 at 735 nm, R = 94.5%). This provides time-asymmetric pulses with a bandwidth of <5 cm−1 at a wavelength of 804.1 nm. SF photons were collected in a reflection geometry and guided to an Andor Kymera spectograph with 1200 lines/mm grating, where they are spectrally dispersed and subsequently detected with an Andor Newton EMCCD. SFG spectra in the frequency region of interest were acquired by modulating the IR center frequency. The acquisition time for each center frequency was 180 s, and the IR, VIS, and SF beams were set to SSP (S, sum-frequency, S, visible; and P, IR) polarizations.

Contact angles (CAs) of eqCRO droplets were estimated using a goniometer (Dataphysics OCA 20L) via the captive bubble method. The needle of the droplet dispensing module contained eqCRO and was immersed in LSW in a glass cuvette (Hellma Analytics) at RT. On immersing the calcite substrate in the LSW, an aging time of 30 min was given for equilibration. Then a droplet of eqCRO (5 μL) was deposited on the substrate. After 30 min, the oil droplet was infused at a rate of 0.015 μL/min to a final volume of 20 μL, during which the advancing oil contact angle, θadv, was measured. Receding contact angles were generally very low and could not be accurately estimated.

Desorption Studies. In a chromatographic approach, the release of organic sorbents and dissolving ions from eqFW- and eqCRO-aged calcite surfaces under continuous flow of brines was investigated. Iceland spar powder (millimeter-sized particles) was initially packed in a buret (10 mL, borosilicate with PTFE key and glass stopper) to a fixed bed volume (4 mL). Aging steps with eqFW and eqCRO were applied to sealed packed beds at 95 °C. After cooling to RT, toluene injections were applied under gravity to eliminate all unbound (i.e., nonadsorbed) oil. Subsequently, the aged columns were dried via air injections and stored in a fume hood for at least 24 h. In desorption experiments, the aged beds were sequentially eluted with UHSW, HSW, and then LSW (10 mL each (~10 void volumes) at 0.2 mL/min) under gravity flow at RT. Elute fractions (1 mL each) were collected and analyzed with UV–visible absorbance and pH measurements.

Under static conditions (i.e., without active flow), time-dependent mineral changes at the brine–organo–mineral interface were measured with in situ confocal Raman microscopy. An Iceland spar crystal was aged in eqFW and eqCRO at 95 °C and then toluene-washed and air-dried at RT. Next, the aged crystal was incubated in HSW in a glass Petri dish at RT. After 3 h, the high-salinity brine was exchanged with LSW. While the crystal was kept immersed in the brines, CRM was performed using a laser power of 3 mW and integration time of 0.1 s per pixel. In addition, ex situ SFG spectroscopy was performed on the oil-aged and brine-treated air–mineral interfaces, i.e., before and after exposure to HSW and then to LSW for 3 h at RT. Prior to spectra acquisition, samples were gently blown dry in a nitrogen gas stream.

## RESULTS AND DISCUSSION

Formation Water: Source of Surface-Active Molecules. After its geosynthesis in the source rock, crude oil gradually migrates upward through the reservoir. At the same time, water is intrinsic to the rock pores, introduced during or after rock formation and retained by adsorption and capillarity. Therefore, the initial interactions between the migrating oil and rock-confined water could be vital in setting initial reservoir conditions, besides the oil making actual contact with the mineral surface (Figure 1a). To test this notion, we studied the initial interactions between oil-equilibrated formation brine and the carbonate mineral and its subsequent impact on oil–mineral interactions.

First, we estimated the amount of surface-active (i.e., carbonate-binding) organic matter in the oil-equilibrated formation water. For this, the organic contents of eqFW were measured using a total organic content analyzer before and after exposure to calcite powder (1 g/L) at 95 °C for 16 h. The initial organic content of CRO-equilibrated formation brine was about 26 mg/L, which decreased to 23 mg/L after the exposure to calcite. Thus, brine–oil equilibration at high temperature introduced substantial contents of mineral-binding organic molecules into the aqueous phase, producing a formation brine with a “reservoir-pertinent” composition.

We also measured the BET specific surface area of the pristine calcite powder (0.113 m²/g). Assuming homogeneous binding to the mineral surface, the decreased TOC of eqFW reflects a surface coverage by brine-soluble oil components of about 30 μg/cm² on calcite. In literature, the surface coverage of organic molecules deposited from simple brines (i.e., devoid of divalent metal ions) is reported to be much lower (e.g., 0.25
Figure 2. (a) Schematic depiction of different aging conditions applied to calcite (green) at 95 °C: (i) only oil (eqCRO, for 7 days), (ii) formation water (FW, for 16 h) and then FW-equilibrated crude oil (eqCRO, for 7 days), and (iii) oil-equilibrated FW (eqFW, for 16 h) and then eqCRO (7 days). (b) Confocal Raman microscopy-derived false color maps for calcite (green, left) and polyaromatic hydrocarbons (PAH, red, right) across the air–calcite interface after aging in eqFW and eqCRO. Areas were mapped using step sizes of 1 μm in x and z directions. Scale bars represent 10 μm. (c) Corresponding intensity plots of calcite (green) and PAH (red) across the air–calcite interface as a function of depth. (d) Distributions of I_{max} values as an indicator of PAHs deposited on calcite after different aging steps: freshly cleaved and eqCRO-aged (black), FW- and eqCRO-aged (orange), and eqFW- and eqCRO-aged (blue). Box-splitting horizontal dotted lines represent mean values and box range indicates ±1 standard deviation.

Thus, the surface modification and dissolution of carbonates emerge as interconnected chemical reactions involving Ca^{2+}, H^+, and organic ions. Given the heterogeneous organic composition of oil-equilibrated brines, this is likely only one of several mechanisms enabling the organic modifications of reservoir carbonates.

Second, we investigated whether this preconditioning of mineral surfaces with organic and inorganic components of formation brine impact the subsequent interactions of the mineral with CRO. We aged (Iceland spar) calcite pieces in identical crude oil (eqCRO) at 95 °C, however applying distinct initial surface treatments (Figure 2a). In the first condition, freshly cleaved calcite was directly aged in eqCRO for 7 days. In the second and third conditions, the aging in eqCRO was preceded by exposure of the calcite to fresh FW (not equilibrated with CRO) and eqFW (pre-equilibrated with CRO) for 16 h at 95 °C, respectively. Note that while FW presents a purely inorganic composition (Table 1), eqFW is additionally enriched with organic components of which ~12 wt % are surface-active (see above).

Surfaces of the oil-aged calcite were characterized with CRM. Raman spectra of all aged minerals present D1 (1344–1357 cm⁻¹) and G bands (1565–1580 cm⁻¹). These vibrational modes represent the graphic ordering of polyaromatic hydrocarbons (Figure S1), also previously reported for molecular organizations of polyaromatic oil components such as asphaltenes and kerogens. We do not consider the presence of these Raman bands as an absolute determinant of the molecular identity of the surface-active agent but rather defer to solubility testing and other analytical methods (later section). Nonetheless the Raman bands show μg/cm² for cetrimonium bromide, CTAB). To put this in perspective, the surface precipitation of organic acids and divalent metal ions on carbonates produces a multilayer or continuous-type sorption and higher surface coverage (e.g., 10 μg/cm² for calcium ion–protoporphyrin mixtures). Also the formation water that was used to extract the CRO molecules contains divalent metal ions in high abundance (10⁵–10⁷ ppm Ca²⁺ and Mg²⁺ ions). In all, the strong adsorption (in this case, also surface precipitation on calcite) of CRO molecules extracted into formation water thus emerges as a driver of the surface modification of reservoir carbonates.

In this mechanism, Ca²⁺ ion mediated surface deposition of an organic acid (RCOO⁻) on carbonate involves three chemical equilibria:

(a) adsorption of the organic sorbent (RCOO⁻) as a monolayer

>CaCO₃⁰ + 2RCOO⁻ ⇌ >Ca²⁺(RCOO⁻)₂ + CO₃²⁻

(1)

(b) surface precipitation of the organo–calcium salt

>Ca²⁺(RCOO⁻)₂ + 2RCOO⁻ + Ca²⁺

⇌ Ca²⁺(RCOO⁻)₂(s) + >Ca²⁺(RCOO⁻)₂

(2)

(c) dissolution/precipitation of calcium carbonate (related to mineral solubility)

CaCO₃(s) + >CaCO₃ + H⁺ ⇌ >CaCO₃ + Ca²⁺ + HCO₃⁻

(3)

δ = 0.62–0.64

65

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that the primary sorbents in carbonate reservoirs are polycyclic aromatic molecules and exhibit some degree of graphitic ordering on the calcite surface.

To compare the organic modifications of calcite as a consequence of different preconditioning steps, areas were mapped in a plane perpendicular to the calcite–air interface with CRM. Raman maps and corresponding intensity profiles for eqFW- and then eqCRO-aged calcite clearly show the surface deposition of PAHs (Figure 2bc). Relative extents of sorption are estimated from the distributions of Raman intensity ($I_{\text{max}}$) values of PAHs at the carbonate–air interfaces (Figure 2cd). Relative to the freshly cleaved and FW-aged crystals, calcite initially aged in eqFW undergoes a pronounced surface alteration with PAHs on oil contact at 95 °C. This is evident from a 2-fold increase in the mean $I_{\text{max}}$ value for calcite aged in both eqFW and eqCRO (Figure 2d). While the inorganic constituents of formation water such as sulfate ions are known to impact the initial wetting of carbonate rocks by complex oils,\textsuperscript{66} we further reveal that the initial attachment of water-soluble oil components modulates organo–mineral interactions on oil contact. The preconditioning of mineral surfaces in FW could be crucial even in oil displacement, with previous observations showing decreased recovery in imbibition tests of CROs with high contents of water-soluble acids.\textsuperscript{67} The measured intensity ($I_{\text{max}}$) of PAHs at the carbonate–surface interaction indicates the chemical nature of the surface-active asphaltene (Figure 3). To further elucidate the chemical properties of carbonate-binding asphaltene, different analytical methods were applied to the “nonaqueous” and “aqueous” asphaltene extracts. First, FTIR spectra of both sorbent residues (obtained by air-drying) presented similar spectral signatures, however with individual bands of varying intensities (Figure 3). Bands were indexed in accordance with literature values (Table 2). Polar groups such as aromatic carboxylic acid (1705 cm$^{-1}$), diaryl ketone (1615 cm$^{-1}$), aromatic amines or pyridyls (1207 cm$^{-1}$), and also primary (1079 cm$^{-1}$) and secondary alcohols (1150 cm$^{-1}$) were observed. Both spectra also presented a broad band between 3200 and 3750 cm$^{-1}$, indicative of interasphaltene and asphaltene–water hydrogen bonding interactions.\textsuperscript{81} A complex hydrocarbon pattern (2850–2950 cm$^{-1}$) characterized by alkyl and alkene moieties was common to the FTIR spectra, previously reported for shale and carbonate reservoir materials as well as isolated polyaromatic petroleum components such as asphaltene and kerogen.\textsuperscript{82} Overall, the identical spectral features suggest that the distinct solubilities of the carbonate-binding sorbents do not originate from vastly different chemical characteristics.

We also compare the average length of the terminal aliphatic chain (or methyl terminated aliphatic chain, MTAC) of the two sorbent classes by estimating an aliphatic index (R), defined as

$$R = \frac{\text{Abs}_{\text{CH}}}{\text{Abs}_{\text{CH}_3}}$$

where $\text{Abs}_{\text{CH}}$ and $\text{Abs}_{\text{CH}_3}$ denote the respective intensities of asymmetric stretching bands of the CH$_3$ (methylenic chain, ~2927 cm$^{-1}$) and CH$_2$ (methylene chain, ~2950 cm$^{-1}$) (Figure 3b).\textsuperscript{83} This index allows estimating the average molecular weight of the terminal aliphatic chains of asphaltene. The R value of the water-insoluble sorbent (~1.5) was higher than that of the brine-derived sorbents (~1.1), indicating that relatively
longer hydrocarbon side chains contribute to the aqueous insolubility of the major asphaltene fraction as expected. On the basis of systematic studies with structurally defined asphaltenes, this increased R value from the water-soluble to water-insoluble carbonate binders reflects a threshold transition in the average length of terminal alkyl chains from n-propyl to n-butyl.

Second, to characterize elemental compositions and chemical bonding, X-ray photoelectron spectroscopy on air-dried residues of the asphaltic sorbents was performed (survey spectra in Figure S3). Elemental compositions were obtained from element spectra scans. Similar carbon (82.7–82.9%), oxygen (16.4–16.5%), nitrogen (0.3–0.4%), and sulfur (0.4–0.6%) contents are observed for both sorbent classes (Figure 4a,b). With a closer look at the core spectra for carbon and oxygen, we elucidate bonding information for the two sorbent classes (Figure 4c,f). For both water-insoluble and -soluble asphaltenes, two main C 1s peaks were observed with binding energies in the ranges of (i) 284.5–285.8 eV and (ii) 291.9–292.4 eV. These binding energies represent C–C bonding and the characteristic $\pi \rightarrow \pi^*$ transition of aromatic and unsaturated functionalities (shakeup satellite), respectively. In both spectra, the broad, asymmetric tail toward higher binding energies and the satellite features confirm high sp$^2$ carbon concentrations. A minor peak at 285.9–287.5 eV, indicative of O–C–O and C==O groups, is also common to both spectra. However, a distinctive peak for the water-insoluble sorbents appears at 294.2 eV. This is attributed to a $\pi$ plasmon that originates from the long-range organization of carbonate-binding polyaromatic hydrocarbons analogous to graphitic materials. For instance, defects in graphite such as C–N bonds formed via N$^{2+}$ irradiation lead to the disappearance of the $\pi$ plasmon feature. The O 1s core spectra of both sorbent classes exhibit peaks at 529.7–530.8 eV and 531.6–532.5 eV, representing C==O (aromatic) and O–(C==O$^*$)–C (aromatic) bonds, respectively. Together with the FTIR observations (Figure 3), the XPS analyses show that the heteroatom composition and functional groups in the water-soluble and water-insoluble fractions are very similar. This suggests that the different solubilities of the carbonate-binding asphaltenes should primarily be attributed to differences in molar mass rather than chemical composition.

Carbonate dissolution results in an enrichment of calcium and (bi)carbonate ions at the brine–mineral interface. Existence of ionic interactions between asphaltenes and dissolving metal ions could be vital for understanding the surface reactions of underground minerals. Therefore, we third used potentiometric titrations to investigate whether watersoluble asphaltenes bind to calcium ions. In this method, calcium ion contents are continuously measured using an ion-selective electrode while a calcium chloride solution is being added at a constant rate to the reaction vessel. Without any

Table 2. Vibration Frequencies and Their Assignments in IR Spectra for Carbonate-Binding Asphaltenic sorbents*  

| wavenumber (cm$^{-1}$) | functional group/IR band | water-insoluble | water-soluble |
|-----------------------|---------------------------|-----------------|---------------|
| 3320 (broad)          | intermolecular H bonds/O–H group | S               | S             |
| 2949                  | methyl C–H stretching asymmetric | S               | S             |
| 2917                  | methylene C–H stretching asymmetric | S               | S             |
| 2868                  | methyl C–H stretching symmetric | S               | M             |
| 2847                  | methylene C–H stretching symmetric | S               | S             |
| 1705                  | aromatic carboxylic acid/C==O | W               | –             |
| 1615                  | diaryl ketone/C==O | S               | S             |
| 1460                  | methyl C–H bending | S               | M             |
| 1380                  | methyl C–H bending | S               | M             |
| 1207                  | amine or pyridyl C–N stretching | S               | S             |
| 1150                  | secondary alcohol C–O stretching | S               | S             |
| 1079                  | primary alcohol C–O stretching | W               | W             |
| 973                   | trans disubstituted alkene | W               | W             |
| 622                   | alkyne C–H bend | W               | –             |

*Absorption intensities (I) are classified as weak (W, I < 0.01), medium (M, 0.01 < I < 0.02), and strong (S, 0.02 < I).
complexation of calcium ions, a linear development of detected calcium ions is expected as seen for DI water (Figure 5). However, in the presence of asphaltenes (initially dialyzed against deionized water), an initial offset is seen. Also observed for calcium-binding polymers such as poly(acrylic acid), this offset confirms the complexation of calcium ions by water-soluble asphaltenes and supports the notion of surface precipitation of organo-metal complexes on reservoir rocks (1–3).

**Intermediate Discussion: Surface Chemistry of Reservoir Carbonates.** Taken together, the analytical results described in the preceding section provide new insights into how the initial interactions with formation water and buoyantly migrating CRO establish the “prerecovery” or oil-wet surface chemistry of carbonate minerals (Figure 6). Before oil enters the reservoir, pores of water-wet rocks are filled with formation water (Figure 6b). Since a stable brine film prevents direct contact between the oil-brine and brine-mineral interfaces, at first, the gradual dissolution of mineral-binding polyaromatic species from CRO into formation brine occurs. This enables

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**Figure 5.** Developments of free calcium ion contents in deionized water (continuous line) and an aqueous solution of the water-soluble asphaltenic sorbents (0.1 mg/mL, dashed line) during potentiometric titrations.

**Figure 6.** Hierarchical model for the surface modification of reservoir minerals by asphaltenes that are formation water-soluble (red) and interfacially active at the brine-oil junction (black) involving (a) oil migration into formation water containing reservoir pores, (b) transient stability of water films between the mineral and oil at the pore scale, (c) dissolution and surface deposition of organic molecules and metal ions (green dots) from formation water and oil at the microscale, and (d) distinct molecular interactions ([i] aromatic stacking, [ii] ion bridging, and [iii] hydrogen bonding) that consolidate the heterogeneous organo-ionic surface layer, alongside hypothetical molecular average structures for the brine- (red) and oil- (black) derived surface-active asphaltenes.
reservoir rocks to undergo initial modifications with organic (brine-soluble oil components) and inorganic (metal ions) components of formation water via monolayer adsorption and surface precipitation reactions (1–3). Though this modification does not substantially alter the wettability of carbonate surfaces (oil-side contact angles for oil droplets advancing on eqFW-aged calcite range from 110 to 140° and on pristine calcite range from 125 to 145°), it sets the stage for substantial wettability alterations of carbonates on oil contact. Along with its constitution, the thickness of the interfacial formation water layer also can regulate the deposition of asphaltenes from nonaqueous phases.

In this picture, CRO interacts with rock surfaces, primed with surface-active species in formation water, rather than a clean rock surface (Figure 6c). In other words, the surface free energy of the natural rock is not restricted to the intermolecular interactions of surface sites of the mineral alone (e.g., >CO₃ and >Ca⁴⁺ for carbonates) but also encompasses the interactions of already rock-bound aqueous sorbents. To address these interactions, we present hypothetical molecular average structures for the aqueous and nonaqueous asphaltenic sorbents along with their interaction modes (Figure 6d). Aqueous asphaltenes, deposited from eqFW on minerals, contain not only metal-binding (e.g., carboxyls) and hydrogen-bonding (e.g., amines/pyridyls and alcohols) functional groups but also a polyaromatic backbone capable of intermolecular aromatic or π−π-stacking interactions. In comparison, the water-insoluble asphaltenic sorbents, deposited via oil contact, present similar chemical characteristics but conjugated to more aggregation-prone and bulky polycyclic aromatic backbones with longer hydrocarbon termini. Such asphaltenes are known to adsorb and undergo aromatic stacking at the water−oil interface.

At first, we consider the electrostatic interactions between organic groups localized at the oil−brine and brine−mineral interfaces. In an ideal chemical system (close to thermodynamic equilibrium), same-sign charges at the oil−brine and brine−mineral interfaces produce electrostatic repulsion between the two interfaces and stabilization of the intervening brine layer. Our observations reveal that surface-active molecules on minerals and in CRO present similar chemical signatures. In this respect, the adhesion between CRO−brine and brine−mineral interfaces is better explained by the enrichment of divalent metal ions in the brine film. In the pH range of FW (pH 4−9), the carboxylate groups at both interfaces are deprotonated and can participate in ion-bridging interactions with divalent metal ions in the intervening brine film (Figure 6d).

Second, with the polycyclic aromatic nature of asphaltenes, stacking interactions and hydrogen bonding are central to the water-wet to oil-wet transitions of mineral surfaces. Asphaltenene aggregation is driven by stacking interactions between the polycyclic aromatic backbone and water-bridged hydrogen bonding between pyridyl nitrogens of asphaltenes. Low-aromaticity molecules also hydrogen bond and undergo intercalation with asphaltenene aggregates, thereby weakening interactions between the stacked asphaltenenes. Given the asphaltenene nature of both the eqFW- and the eqCRO-derived sorbents, such modes of interactions must also apply for mineral-bound aqueous asphaltenenes interacting with interfacially active asphaltenenes at the brine−oil junction (Figure 6c,d). Graphitic organization or aromatic stacking of carbonate-bound species is indeed shown by the D and G bands in Raman spectra (Figure S1) and the π-plasmon XPS feature (Figure 4). Water molecules further stabilize the surface deposits of asphaltenes, evident by the broad FTIR band at 3200–3750 cm⁻¹ (Figure 3) originating from interasphaltenic and asphaltene−water hydrogen bonding interactions. With the strong association of well-ordered water layers and the solvation dynamics of organic deposits at the water−carbonate interface, we identify water molecules as the third main constituent of the organo−ionic surface layer in addition to asphaltene and metal ion species. With the measured oil-side contact angles for crude oil droplet advancing on eqFW-aged and eqCRO-aged calcite between 138 and 20°, this organo−ionic layer, established via surface reactions of aqueous and nonaqueous asphaltenes, metal ions, and associated solvation underlay the oil-wet nature of reservoir rocks. Thus, a reactive wetting mechanism emerges to have a pivotal role in the wettability transitions of reservoir rocks interacting with complex brines and oils.

In this “reactive wetting” scheme, wetting occurs in conjunction with the formation of a new solid material which spreads at the liquid−solid substrate interface. Our observations suggest that the wettability alterations of reservoir rocks arise from initial brine−oil phase transfer reactions and the precipitation of new organo−ionic material on mineral surfaces. Associative interactions between mineral-bound aqueous asphaltenes and larger asphaltenes at the brine−oil interface further consolidate the organo−ionic surface layer, in consequence altering the wettability characteristics of enveloped rocks via a “reactive” mechanism.

A “layered” or “onionskin” organization of organic molecules has been proposed before for specific oil components on sandstone rocks. Here we report (to the best of our knowledge) for the first time, a layered organization of organic sorbents on carbonate rocks, based on sequential deposition and extraction of mineral-bound asphaltenes. This distinct organization originates from surface alterations of carbonates first in formation brine and then oil. Proximal to the mineral surface, the aqueous (eqFW-derived) asphaltenes contain both mineral-binding acidic groups (1−3) and aromatic backbones that can associate with the larger polyaromatic backbones of asphaltenes at the brine−oil interface (fulfilling the definition of “double-sided-tape” molecules). Even the electron energy loss spectroscopy (EELS) spectrum of grains in carbonate core specimens suggest that the organic layer is bound to the mineral via ionic bonding between Ca²⁺ ions and oxygen (O⁻) groups, that likely are part of the carboxyl group (COO⁻) of certain oil components. An analogous to the intercalation of alkylphenols in asphaltenes, the low-aromaticity aqueous sorbents can also bind to the periphery of asphaltene aggregates via hydrogen bonds and stacking interactions.

With these considerations, we propose a qualitative model for the spatial organization of the heterogeneous organo−ionic material on the mineral surface, based on the functions of “light” asphaltenes in binding to mineral surfaces (zone i or contact zone) as well as intercalating with and capping aggregates of “heavy” asphaltenes (zone ii or hydrophobic zone) (see Figure 7). The contact zone typically involves electrostatic interactions of (presumably partly hydrated) aqueous asphaltenes with the mineral surface and hydrophobic interactions directed toward the bulk solution. Meanwhile the hydrophobic zone involves entropy driven shielding of the hydrophobic polyaromatic backbones of adsorbed asphaltenes from the polar aqueous phase possibly with a second layer of...
aqueous asphaltenes. This organization of asphaltenes on carbonates is analogous to zonal structures (Kleber model) in soil chemistry,106,107 in which an organic coating forms on minerals and only the first layer of molecules is in direct contact with the mineral surface. At the interface between the hydrophobic zone and the brine, a third (kinetic) zone is formed, in which organo−ionic molecules can be extracted into the aqueous phase, depending on the ionic composition of the latter. This zone emerges as crucial for any IOR mechanism.

**Desorption and Mineral Dissolution under Brine Flow.** To investigate the stability of the organo−ionic asphaltene layer in flowing brines, column chromatography of calcite packed beds was performed. Packed beds of calcite particles, aged in both eqFW and eqCRO, were sequentially eluted with brines of decreasing salinities and then the eluted fractions were characterized with UV−visible absorbance and pH measurements (Figure 8a). Absorbance from 290 to 600 nm of the eluted brines shows a gradual release of the carbonate-bound aromatic hydrocarbons (Figure 8b). Molecules that were too strongly bound to desorb were isolated by acid-etching the calcite in the last elution step. Absorbances integrated from 290 to 600 nm, and pH measurements were used to generate desorption profiles (Figure 8c). Desorption efficiencies of the brines are found to be 38 ± 2% (UHSW), 16 ± 6% (HSW), and 20 ± 4% (LSW). While the low-salinity brine leads to some additional release of mineral-attached polyaromatic hydrocarbons even after initial elution with both UHSW and HSW, a significant fraction (26%) of the asphaltene sorbents remains mineral-bound (Figure 8d) even after the third and final elution step. Thus, asphaltene molecules, constituting the heterogeneous sorbent layer, exhibit distinct propensities toward desorption as a function of brine salinity.

The pH developments in Figure 8c, addressing the structural integrity of the organo−ionic surface layer in different brines, are related to (shifts in) several chemical equilibria reactions, involving both organic complexation and calcite dissolution reactions. For the UHSW, the pH decrease from 6.8 to 6.6 suggests that some asphaltenic species with acidic groups are released from the mineral surface:

\[
\text{CaCO}_3(s) + >\text{RCOOH} \rightleftharpoons >\text{CaCO}_3 + \text{RCOO}^- + \text{H}^+ 
\]

Importantly, this minor change in pH also indicates that the residual sorbent layer remains sufficiently intact to suppress carbonate dissolution. In contrast, the eluted fractions of HSW and LSW exhibit gradual increases in pH from pH 7.2 to 7.8 and from pH 7.5 to 8.8, respectively, implying brine access to the mineral surface and subsequent mineral dissolution. Protonation of dissolving carbonate ions then raises the pH:

\[
\text{CaCO}_3(s) + >\text{CaCO}_3 + \text{H}^+ \rightleftharpoons >\text{CaCO}_3 + \text{Ca}^{2+} + \text{HCO}_3^- 
\]
The nonlinear pH rise on injecting HSW reflects the initial exchange of UHSW with HSW, producing, at first, a rapid pH rise of the effluent. Thereafter the simultaneous desorption of acidic sorbents and carbonate dissolution generate a more gradual pH development (5, 6). The mineral dissolution is probably still surface limited due to the passivation by the asphaltene layer. For instance, the dissolution of calcite, after treatment with CRO, occurs at rates about 30% lower than that of pristine calcite.23 In relation, the continuous flow of LSW led to more pronounced pH increase up to pH 8.8 (Figure 8c), indicative of mineral dissolution unrestrained by the sorbent layer.

In all, the desorption profiles show that the release of mineral-bound heterogeneous material not only occurs in incremental steps as a function of brine salinity but also impacts the kinetics of carbonate dissolution. Continuous flow of low-salinity brine is effective at extracting asphaltene sorbents from the carbonate surface and erodes the organo–ionic surface layer enough to achieve a sustained dissolution of the carbonate mineral.

To elucidate this stepwise release of asphaltenes from carbonate surfaces, 1H NMR spectroscopy on the elute fractions was performed. Initial measurements revealed poor solubility of the sorbents in the typical chloroform (CDCl₃) solvent. Therefore, deuterated benzene (C₆D₆), which is a good solvent for asphaltenes,108 was used to solubilize air-dried elute residues. All NMR spectra presented characteristic signals of CHₓ groups (with 0 ≤ x ≤ 3) in aliphatic and aromatic configurations, typical of petroleum components (Figure 9a).

Figure 9. (a) Representative 1H NMR spectrum of asphaltenes released from carbonate surfaces with illustration of α-, β-, and γ-positions relative to aromatic ring. (b) Amounts of aliphatic hydrogens, positioned α, β, and γ to aromatic rings, in asphalteneic sorbents released by sequential elution with UHSW (ultrahigh-salinity water), HSW (high-salinity water), and LSW (low-salinity water) as well as the remaining strongly bound fraction.

Figure 10. (a–c) Representative sum-frequency generation (SFG) spectra of the oil-equilibrated formation water (eqFW) and formation water-equilibrated crude oil (eqCRO) aged and toluene cleaned calcite surface (black) and after its sequential treatment with high-salinity water (HSW, red) and then low-salinity water (LSW, blue) at RT. (d–f) Deconvolution analyses of the spectral regions (shown in panel a) for amorphous (1079 cm⁻¹) and crystalline (1088 cm⁻¹) surface carbonate species. (Note the different vertical scales in panels d–f.)
9b), corresponding to chemical shift ranges of 0.5–1.0, 1.0–1.9, and 1.9–4.5 ppm, respectively.106 While molecules desorbed by UHSW and HSW presented similar ratios of the aliphatic hydrogens in the distinct configurations, the LSW is more effective at displacing asphaltenes enriched in β-position hydrogens from carbonate surfaces. Also, on the basis of the relative reductions in signals of γ-position aliphatic hydrogens, the low-salinity brine is shown to selectively extract smaller polyaromatic sorbents from oil-aged mineral surfaces. In view of our FTIR observations (Figure 3), aqueous asphaltenes with short terminal aliphatic chains emerge more susceptible toward desorption under low-salinity conditions. In contrast, the strongly bound asphaltenes, recalcitrant toward desorption, exhibit high fractions of γ-position aliphatic hydrogens and are more representative of the nonaqueous, bulky asphaltenes (Figure 9b).

**SFG Spectroscopy.** Selective desorption of sorbents from mineral surfaces will impact the composition and the interfacial organization of the bound residue. To investigate this surface phenomenon, we applied SFG spectroscopy, a non-invasive, nonlinear optical spectroscopic method to probe the structural configurations adopted by carbonate ions, asphaltenes, and water molecules on the calcite surface.110,111 Note that the SFG signal intensity is proportional to the number of organized molecules as well as their degree of organization.

SFG spectra were acquired for calcite interfaces in air (Figure 10), obtained by initially aging in eqFW and eqCRO at 95 °C, toluene-washing, and air-drying at RT, followed by sequential exposure to HSW and then LSW for 3 h each. First, on treating the mineral surface with low-salinity brine, the peak at 1085 cm⁻¹ presents about a 60-fold increased intensity relative to the oil-aged and HSW-treated carbonate surfaces (Figure 10a). Attributing the band at 1085 cm⁻¹ to vibrations of surface carbonates of the mineral, the elevated intensity reflects the efficiency of LSW in extracting organic sorbents and generating bare calcite surfaces. This is consistent with increased SFG intensities on LSW exposure at 1360 and 1440 cm⁻¹ (Figure 10b), which can be assigned to asymmetric stretching (νₐ) modes of surface carbonates.112,113 Both signals present red shifts relative to bulk measurements (1392 and 1462 cm⁻¹), caused by chemical bonding or geometric constraints at mineral boundaries.114 Alternatively, these bands might represent CH₂ and CH₃ bending modes (Table 2). However, since only extremely weak symmetric stretching bands (Figure S4) are observed, this is a minor possibility.

Note that the stretching mode (νₐ) of the calcite carbonate at 1085 cm⁻¹ is strictly IR-inactive in the presence of planar structure and symmetry; however, a band at this frequency is often reported for crystal defects and nanoparticles of calcite.112,113,115 On closer inspection of this SFG signal, the peak around 1080 cm⁻¹ can be deconvoluted into two components centered at 1078 and 1088 cm⁻¹ (Figure 10d–f). These components represent two types of surface carbonates: poorly structured and ordered.112 Though structural perturbations of the surface calcium and carbonate units in simple salt solutions were established before by surface X-ray scattering measurements,116,117 our deconvolution analyses reveal the surface deformations of the calcite lattice even in geologically pertinent and chemically heterogeneous brines.

By estimating a surface structure index ($S = \frac{I_{\text{eqCRO}}}{I_{\text{eqFW}}}$, where $I_{\nu}$ is the SFG intensity at wavenumber $\nu$ cm⁻¹), the eqFW- and eqCRO-aged and HSW-treated surface presents $S$ values < 0.4 corresponding to rather poor order of surface carbonates. In contrast, the increased $S$ value of 1.7 after low-salinity brine treatment indicates a relatively well ordered crystal surface. Abundant in both eqFW and HSW, the surface incorporation of Mg²⁺ and SO₄²⁻ ions can contribute to the distortion of surface carbonates via lattice incorporation.118 In addition, the asphaltenic sorbents contain carboxyl groups, which might confine and stabilize amorphous ion clusters against crystallization.119,120 In contrast, LSW is undersaturated with respect to calcite and thereby an effective medium to (i) eliminate surface defects via dissolution alone or dissolution-coupled reprecipitation reactions121,122 and (ii) desorb organic stabilizers of disordered ion clusters.

Second, weak resonances for the asphaltenic sorbents on carbonate surfaces are discernible at 2852 and 2930 cm⁻¹ for the HSW- and LSW-treated mineral surface (Figure S4). Assigned to the symmetric and asymmetric CH₂ stretch vibrations, these intensity developments reflect the reorganization of surface asphaltenes on brine treatment. With LSW selectively extracting aqueous asphaltenes (Figure 9), the residual asphaltenes can reorganize with their polyaromatic backbones parallel and terminal aliphatic chains perpendicular to the mineral surface.123 In contrast, for the oil-aged organo–calcite interface, the absence of distinct spectral features reflects a poorly organized surface assembly of the asphaltenes.

And third, the SFG measurements can address the structural configurations of water molecules at the air–organo–mineral interface (Figure 10c). Signals from the surface hydration of calcite (3000–3600 cm⁻¹) are absent. This is attributed to opposite orientations of the water dipoles constituting the first and second hydration layers124 and for that reason broad O–H stretching bands from H-bonded interfacial water molecules were absent. However, we do observe vibrational bands at 3630 and 3700 cm⁻¹ that are attributable to isolated or non-hydrogen-bonded OH groups. First, similar bands are reported for interfaces between water and hydrophobic media.125 Isolated OH groups could represent the hydrophobicity of a residual asphaltenic fraction strongly bound to the mineral surface. After LSW treatment, the decreased intensities in this spectral regime indicates partial desorption of even insoluble (i.e., well-organized) asphaltenes (likely due to mineral dissolution). This is supported by results of SEM imaging (Figure S5), in which LSW-treated carbonate surfaces specifically exhibit dissolution or etch pits.126 Second, strongly ordered water molecules on carbonate surfaces124 could enhance H-bonding inside the hydration layer and in turn reduce the possibility of H-bonding with external molecules.128 In this scenario, the increased intensities of bands at 3630 and 3700 cm⁻¹ on brine exposures also reflect the generation of asphaltene-free calcite surfaces but rather explained with the inability of the atmospheric water molecules to H-bond with the surface hydration layer of pristine calcite. Nonetheless, both explanations concur in the effectiveness of HSW and LSW at desorbing asphaltenes from carbonate surfaces.

To ascertain the precise origin of these isolated or non-hydrogen-bonded OH groups, SFG spectra were acquired for clean calcite surfaces. Vibrational bands for both hydrogen-bonded and isolated OH groups were absent for the freshly cleaved mineral surface. On wetting with ultrapure water, a major band at 3630 cm⁻¹ (Figure S6) confirms the presence of a water layer that cannot H-bond with the well-structured
surface hydration of calcite.\textsuperscript{116,124} This nicely demonstrates the phenomenology of “ordered water that does not completely wet water”\textsuperscript{128} operating on the surface of a ubiquitous mineral under ambient conditions. We also observe a minor band at 3460 cm\textsuperscript{−1}, which likely arises due to small contents of adventitious carbon and natural fluorophores on surfaces of Iceland spar that H-bond with water molecules.\textsuperscript{26,129} Thus, for asphaltenes desorbing from carbonate surfaces, the increased contents of non-hydrogen-bonded OH groups (Figure 10c) are better elucidated by the failure of water molecules to effectively H-bond with the surface hydration of pristine (i.e., asphaltene-free) calcite.

Confocal Raman Microscopy. Confocal Raman microscopy is an established method to characterize the molecular organizations of graphitic materials such as asphaltenes.\textsuperscript{63,64,130−132} Here we apply CRM to elucidate the low-salinity effect, investigating the desorption and structural transitions of the surface-active asphaltene assemblies in various brine compositions (Figure 11a).

Although Raman spectroscopy is considered as a non-invasive or non-destructive analytical tool, caution is needed with sensitive samples. To optimize the laser output, initial independent single-point Raman measurements were performed at the organo–calcite interface in HSW at 30, 3, and 0.3 mW and integration time of 0.1 s. The intermediate laser power was optimal, at which the spectral intensities did not decrease over time and the Raman signals for calcite were distinct in the raw spectrum (Figure S7).

To study the stability of surface asphaltenes, the brine–calcite interface was monitored with Raman microscopy for 3 h in HSW, followed by a slow exchange to LSW and monitoring for another 3 h. Large area scans were performed in a plane perpendicular to the calcite–brine interface and spectral regions of interest were integrated for each pixel (1500–1650 cm\textsuperscript{−1} for G and D2 bands) to generate PAH, viz., asphaltene maps (Figure 11d). Though the false-color maps show pronounced desorption of asphaltenes from the mineral surface in LSW, a closer inspection of corresponding intensity profiles reveals gradual desorption already in HSW, too (Figure 11b,c). The low-salinity brine eventually generates mineral surfaces that are devoid of asphaltenes (arrows, Figure 11d). In a replicate experiment, we observed microscopic asphaltene aggregates in the ambient LSW, however after 6 h (Figure S8). Hence the desorption of heterogeneous organo–ionic surface layer emerges comprised of two regimes: the initial gradual solubilization and subsequent detachment of asphaltene assemblies from the dissolving mineral (shown by elevated pH in packed bed chromatography, Figure 8).

Figure 11. (a) Experimental scheme of confocal Raman microscopy on organo–calcite interfaces in ambient brines at room temperature. Aging time-dependent intensity profiles of asphaltene sorbents across the brine–organo–calcite interface as a function of depth in (b) high-salinity water (HSW) and (c) subsequently low-salinity water (LSW). Corresponding distributions maps of (d) asphaltenes (red) and (e) their degree of organization (\(L_a\)) at the brine–mineral interface in the x–z plane. High–top row and low–bottom row) salinity conditions at 0, 0.5, and 3 h of brine exposure are shown. Arrows in panel d indicate locations where the mineral surface is devoid of asphaltenes, while in panel e they indicate pore formation.
First, the gradual emergence of asphaltene assemblies with high \( L_a \) is explained by the selective extraction of aqueous species by HSW and LSW (Figure 8), eliminating “defects” in stacked organizations of larger asphaltenes. The prevalence of this high \( L_a \) state proximal to the organo–calcite interface in HSW after 3 h is accompanied with some lateral discontinuity within the organo–ionic sorbent material, possibly via the development of pores over time (arrow, Figure 11e). In contrast, brine access to the organo–mineral junction is clear in LSW (arrows, Figure 11d). One explanation for the gradual pore formation in the surface organo–ionic layer is an increased density or decreased free volume of the mineral-bound asphaltenes on the removal of smaller sorbent molecules. Such instabilities could generate pores in the asphaltene layer and allow the brine to creep underneath the sorbent layer.

Second, retention of the low \( L_a \) or poorly organized asphaltene subset toward the interior of the sorbent layer (Figure 11e and Figure S12) is attributed to water-impermeable barriers at the brine–organo and organo–mineral interfaces. Established by the enrichment of bulky asphaltene species from the surface layer. In this manner, our observations in Figure 11 are explained by the selective desorption or extraction of aqueous asphaltenes and the reorganization of the residual mineral-bound asphaltenes. While such processes are mentioned in studies on simple brine–CRO systems, our in situ Raman observations reveal the interfacial reorganization of asphaltene at the brine–organomineral interface as a key phenomenon in the low-salinity waterflooding of carbonate reservoirs.

To further verify this mechanism, we measured advancing contact angles of eqCRO droplets on calcite substrates as a measure of surface wettability in LSW-containing cuvettes at RT (Figure S13). Alongside previous measurements that established a wettability alteration toward oil-wet (oil-side contact angles for oil droplets advancing range from 50 to 130°) on aging calcite in eqFW and eqCRO, we now report recovery of more water-wet characteristics of calcite in the low-salinity brine with oil-side contact angles between 100 and 150°. On completion of these contact angle measurements, the LSW showed the presence of asphaltene-rich and brine-insoluble organic flakes (Figure S13). This is consistent with our proposed two-stage mechanism of organo–ionic layers desorbing from carbonate surfaces, underpinning its mecha-

\[
L_a = \frac{560}{E_l} \left( \frac{A_G}{A_D} \right) \tag{7}
\]

where \( E_l \) is the excitation laser energy (eV) and \( A_G \) and \( A_D \) are the integrated areas of the D and G bands, respectively. Previous studies show that \( L_a \) correlates with aromatic sheet diameter and number of sheets in an asphaltene stack. \( L_a \) is also reported to inversely scale with the hydrogen-bonding capability of asphaltenes. Considering the chemical heterogeneity of the carbonate-bound asphaltene material, we utilize \( L_a \) distributions only as a qualitative probe for the structural (re)organization of mineral-attached asphaltenes under different salinity conditions.

Lorentzian peak fits and integrals of the D and G bands (Figures S9 and S10) were used to generate maps of \( L_a \) values (Figure 11e). After 3 h in HSW and subsequently 0.5 h in LSW, asphaltene assemblies on calcite surfaces undergo a remarkable reorganization. Asphaltenes localized at the brine–organo and organo–carbonate interfaces show gradually increasing \( L_a \) values, indicative of more efficient stacking interactions. This is also evident in the histogram analyses (Figure S11). On initial contact with HSW and LSW, the asphaltenic sorbents present a wide but monomodal distribution of \( L_a \). This reflects a homogeneous supramolecular organization of asphaltenes, encompassing stacking and hydrogen bonding interactions between aqueous and nonaqueous species. In both brines (faster in LSW), bimodal \( L_a \) distributions emerge over time. Two distinct supramolecular domains of asphaltenes are also reflected in relative changes in the intensities of D and G bands in the Raman spectra (Figure S12). On brine exchange from HSW to LSW, the initial transition from a bi- to monomodal distribution highlights the reversibility of the structural dynamics of surface asphaltenes.

First, the gradual emergence of asphaltene assemblies with high \( L_a \) is explained by the selective extraction of aqueous species by HSW and LSW (Figure 8), eliminating “defects” in stacked organizations of larger asphaltenes. The prevalence of this high \( L_a \) state proximal to the organo–calcite interface in HSW after 3 h is accompanied with some lateral discontinuity involving (i) release of soluble sorbents (white arrows), (ii) reorganization of nonaqueous surface asphaltenes, and (iii) delamination of the residual sorbent layer driven by dissolution of the carbonate substrate (green arrows). Area designated with dotted box is magnified in panel b.
nistic relevance in the low-salinity waterflooding of oil reservoirs.

**Discussion: Low-Salinity Effect at the Nanoscale.**
Reservoir minerals, brines, and oils present enormous chemical heterogeneity and structural dynamism that are challenging to represent by a single-point measurement or analytical method. However, by integrating our observations with packed bed chromatography and multiple spectroscopic methods, we converge to a clear picture for microscopic reactions at the brine−organo−mineral interfaces during low-salinity waterflooding of carbonate reservoirs (Figure 12). On account of the surface passivation by asphaltenes, the equilibration of injected brines with the carbonate mineral is not instantaneous and entails desorption of a multicomponent and polyaromatic sorbent layer. Nanoscale observations with in situ atomic force microscopy also confirm that mineral dissolution occurs after the desorption of bound asphaltenes.103

Our results show that the chemically heterogeneous sorbent layer indeed dissolves in low-salinity brines through a process that encompasses two stages. At first, the water-soluble asphaltenes are extracted by the brine enhancing the stacking interactions between residual less polar asphaltenes. This selective extraction of asphaltenes by moderate- to low-salinity brines is attributed to (i) a salting-out or dilution effect, wherein increased water activity enhances the solubility of lighter asphaltenes,103,138 (ii) the dissociation and dissolution of organo−metal complexes/salts under low-salinity conditions (undersaturated with respect to organo−metal phases),25,34 and (iii) relatively poor hydrophobic attraction between asphaltenes at low ionic strength.139,140 Second, this selective extraction or fractional desorption leads to the relative enrichment of nonaqueous bulky asphaltenes at the brine−mineral interface, which undergo efficient stacking interactions and present organized alkyl terminal groups toward the brine and possibly attain high packing densities.25 While restructuring of asphaltenes toward more organized assemblies on the mineral surface are anticipated to yield more oil-wet conditions, the gradual depletion of aqueous or double-sided-tape51 asphaltenes plays a pivotal role in the overall wettability alteration. In the absence of metal- or mineral-binding asphaltenes, the ionic interactions between the mineral surface and residual asphaltene assemblies are compromised (Figure 12). Eventual brine access to the carbonate leads to delamination of asphaltene layer as flakes from the dissolving mineral surface.25 Thus, the selective extraction and structural reorganization of surface-active asphaltenes coupled with mineral dissolution emerge as the main drivers of the low-salinity effect in carbonate reservoirs. In terms of the zonal structure of asphaltenes on the mineral surface (Figure 7), the low-salinity effect is driven by the gradual erosion of the contact zone and expansion of the kinetic zone coupled with mineral dissolution under low-salinity conditions (Figure 12).

Complex bio-macromolecules such as proteins are often considered structurally analogous to asphaltenes due to common molecular configurations involving both hydrophilic polar and hydrophobic components.81,123,141 With the enormous chemical complexity of biological and geological systems, the rich interconnectivity between distinct asphaltene types emerges analogous to the interactions and networks linking different bio-macromolecules. In this respect, even though surface phenomenology in natural environments involve adsorbate mixtures, addressing competitive and synergistic adsorbate−adsorbate and adsorbate−adsorbent interactions remains challenging.

Our study addresses the surface reactions of reservoir carbonates with complex brines and oil at the nano- and microscales, elucidating the synergistic contributions of brine−oil phase transfer, mineral interactions with distinct asphaltenes, types, and multistage desorption events. This represents only the smallest level in the hierarchical structure112 of oil reservoirs, with key phenomenology even operating at larger scales, from the pore and Darcy levels to the entire kilometer scale reservoir system,145,146 as illustrated in Figure 6. Since multiple mechanisms operating across distinct spatial and time scales ultimately govern wettability and oil recovery, not only the physical chemistry of individual mechanisms but also their interplay and scaling require attention.145 Advancing toward this governing model becomes the key to successfully upscaling the interface reactions from pore level phenomenology, which will require robust, quantitative knowledge of mechanisms operating at each level in the hierarchical structure of oil recovery.

**CONCLUSIONS**
We provide a conceptual picture of the microscopic modifications of geological carbonates with natural sorbents (asphaltenes) in complex brines and oils and its reversal under low-salinity conditions. First, aqueous and nonaqueous asphaltenes, metal ions, and water molecules establish a heterogeneous yet layered sorbent material on the mineral, resulting in "oil-wet" surfaces via reactive wetting mechanisms. Initial preconditioning of carbonate surfaces with organo−ionic sorbents (involving water-soluble asphaltenes) enhances the surface deposition of bulky and less polar asphaltenes on oil contact. Deposition of this heterogeneous organic−ionic material on the carbonate mineral produces a "hard−soft" interface, which is central in determining the dissolution and wettability of reservoir rocks. Spatially categorized into three zones: contact, hydrophobic, and kinetic (from the mineral to the bulk fluid), the perturbation or destabilization of this organo−mineral interface layer emerges as a pivotal step in altering wettability and improving oil recovery. Second, by replicating waterflooding conditions, we show that the "low-salinity effect" is driven by the two-stage desorption of the asphaltene adlayer: at first, the solubilization or selective extraction of lighter asphaltenes from organo−mineral surfaces and subsequent delamination of the residual, well-organized asphaltene assemblies from the dissolving mineral surface. In both initial deposition and subsequent release of mineral-bound asphaltenes, the ionic interactions of asphaltenes with divalent metal ions and mineral surfaces, stacking interactions and hydrogen bonding in mineral-attached asphaltene assemblies as well as interfacial hydration have key contributions. Uncovering the dynamics of supramolecular asphaltene assemblies and the nanoscale reorganization of distinct surface species, these analytical results represent a major step forward in understanding key interfacial phenomenology of geological minerals and synergistically functioning adsorbates. While demonstrated here for a specific type of crude oil, preliminary experiments with several other types suggest that the principles discussed throughout this work are of broader relevance and applicability. Future work on the formation and mobilization of these organo−ionic sorbent layers in response to the fine chemistry of oils and injection fluids and elevated temperature...
and pressure conditions will aid the development and deployment of IOR technologies.

■ ASSOCIATED CONTENT

+ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c01117.

Chemical analysis of dead crude oil; Raman spectroscopy; SEM imaging and solvent extraction; XPS spectroscopy; time-dependent Raman spectroscopy and analyses of spectral data sets; contact angle goniometry (PDF)

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Notes

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