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Research Article

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Posted Date: October 14th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11077305/v1>

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Additional Declarations: No competing interests reported.

Optothermal Raman thermometry resolves grain-scale conductivity and aromatic ordering across the coal rank series

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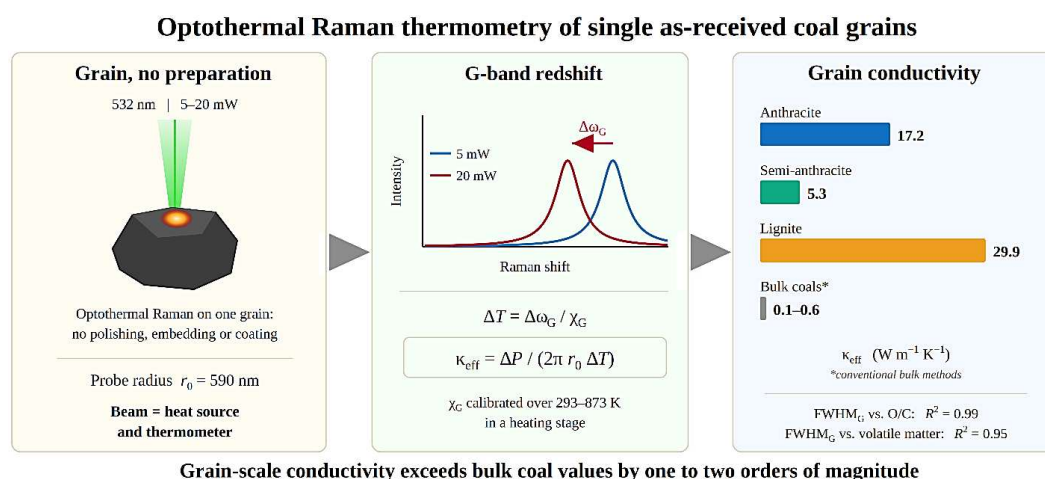
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Highlights

- Optothermal Raman gives grain-level thermal conductivity of coal, unprepared.
- Grain conductivity: 17.2 (anthracite) and 5.3 W m⁻¹ K⁻¹ (semi-anthracite).
- G-band width scales linearly with EDS O/C ratio and with bulk volatile matter.
- Contact-potential spread widens from 50.9 μV to 369 mV with aromatic ordering.
- Grain values exceed bulk coal conductivity by one to two orders of magnitude.

Graphical abstract



Abstract

Thermal transport in coal governs conversion efficiency in gasification, coking and combustion, yet established methods need machined or compacted specimens and return bulk values in which intrinsic conduction, porosity and contact resistance are inseparable. Here, optothermal Raman (OTR) thermometry is applied to individual as-received grains of anthracite, semi-anthracite and lignite, combined on the same grains with five-band micro-Raman deconvolution, SEM-EDS and AFM surface and nanomechanical mapping; bulk proximate analysis and the ASTM D388 rank classification give an independent reference. The G-band temperature coefficient, calibrated between 293 and 873 K, was $\chi_G = -0.0328 \pm 0.0033$, -0.0098 ± 0.0033 and -0.0333 ± 0.0033 cm⁻¹ K⁻¹, and a power ramp from 5 to 20 mW (to 15 mW for lignite) gave $\Delta\omega_G/\Delta P = -0.514 \pm 0.099$, -0.500 ± 0.041 and -0.300 ± 0.058 cm⁻¹ mW⁻¹. A steady-state solution for a 590 nm source on a semi-infinite absorbing solid gave effective grain conductivities of 17.2 ± 3.7 , 5.3 ± 1.8 and 29.9 ± 6.5 W m⁻¹ K⁻¹, one to two

orders of magnitude above bulk coal values and within the optothermal-Raman range for low-ordered carbon fibers. Across the series the G-band width narrowed from 69.24 to 53.11 cm^{-1} , the O/C ratio fell from 0.343 to 0.066 and dry, mineral-matter-free fixed carbon from 96.60 to 51.37 %. The G-band width varied linearly with both surface O/C and bulk volatile matter, and contact-potential dispersion widened from 50.9 μV to 369 mV. The protocol yields preparation-free, spatially resolved thermal and structural descriptors of carbonaceous fuels.

Keywords: Coal rank; Effective thermal conductivity; Nanomechanical mapping; Optothermal Raman thermometry; Raman deconvolution; Scanning Kelvin probe microscopy

1. Introduction

Coal remains one of the largest primary energy carriers worldwide and, increasingly, a feedstock for engineered carbons: coal-derived hard carbons and graphene are now competitive anode precursors for sodium-ion batteries, and the rank of the parent coal is a principal variable governing the sodium-storage capacity of the derived carbon [1], [2]. Whether coal is burned, gasified, coked or converted into a carbon material, heat has to be delivered into and removed from a particulate solid, so thermal transport governs reactor temperature gradients, the propagation of the reaction front in underground gasification, the coking profile in the oven charge and the onset of self-heating during stockpile storage; the structural transformations that accompany these conversions have been followed in situ by Raman spectroscopy [3]. Thermal conductivity is therefore not an incidental property of coal but a direct determinant of how efficiently its chemical energy can be released and how safely it can be stored.

The measurement of that property, however, has remained tied to the bulk scale. A recent systematic review of the field identifies six mainstream techniques — steady-state guarded hot plate and comparative methods, and transient hot wire, hot disk, laser flash and 3ω methods — all of which require a machined, pressed or otherwise geometrically defined specimen [4]. The values they return for coals cluster between roughly 0.1 and 0.6 $\text{W m}^{-1} \text{K}^{-1}$ [5], and are effective quantities in which the intrinsic conduction of the organic matrix, the volume fraction and topology of the pore network, the mineral inclusions and, for compacted specimens, the inter-particle contact resistance are convolved and cannot be separated. Correlations between chemical structure and thermal conductivity across Chinese coals have shown that the aromatic fraction and the degree of condensation are the dominant molecular controls [6], but such correlations are established on bulk averages and therefore cannot address the maceral-scale heterogeneity that petrographic analysis shows to exist within a single particle. The same constraint applies to the descriptors on which the industry actually trades coal quality: proximate analysis, which apportions an analysis sample into moisture, ash, volatile matter and fixed carbon [7], and the rank classification built on its dry, mineral-matter-free values [8], are determinations on gram-scale bulk material and therefore return a single figure for a population of grains of differing maceral composition. No established method delivers a thermal descriptor at the scale of the individual maceral domain, which is precisely the scale at which the aromatic architecture responsible for phonon transport is organized.

Raman spectroscopy addresses the structural half of this problem with well-developed protocols. In the first-order region between 1000 and 2000 cm^{-1} , disordered carbons display an

envelope that the five-band procedure of Sadezky et al. resolves into the G band near 1590 cm^{-1} (in-plane E_{2g} stretching of sp^2 carbon), the defect-activated D1 band near 1350 cm^{-1} , the D2 shoulder near 1610 cm^{-1} , the amorphous D3 band near 1500 cm^{-1} and the D4 band near 1200 cm^{-1} associated with sp^3 and hydroaromatic linkages [9]. Within the three-stage amorphization trajectory of Ferrari and Robertson [10], [11], the derived descriptors — the D1-to-G area ratio, the G–D1 separation and the G-band width — report on aromatic cluster size and bond-angle disorder, and the general relation between the D-to-G intensity ratio and the in-plane crystallite size L_a makes that interpretation quantitative [12]; a recent critical compilation of the empirical correlations available for disordered and amorphous carbons sets out both their reach and their conditions of validity [13]. These descriptors have been applied to functional-group evolution across rank [14], to coking-coal quality [15], to coke and char formation [3], and to the structural heterogeneity of low-rank coal and its pyrolysed char, where multi-point mapping showed that within-grain variation can rival between-rank variation [16]. The field is not uncritical of itself: a detailed reassessment has argued that Raman parameters map onto conventional maturity indices only within restricted maturity windows and with a strong dependence on acquisition and fitting conventions [17]. Any new use of Raman descriptors as rank proxies must therefore be validated against an independent modality rather than asserted.

Raman also provides a thermometer. Phonon anharmonicity shifts the G band to lower wavenumber as temperature rises, a dependence first quantified for graphene and its multilayers [18] and then exploited by Balandin and co-workers, who used a focused laser simultaneously as a localized heat source and as a temperature probe to obtain the intrinsic conductivity of suspended single-layer graphene [19]. The optothermal Raman (OTR) method that grew out of that work is now a recognized nanoscale thermal metrology [20], [21], and it has been extended to few-layer transition metal dichalcogenides [22], to MoTe_2 thin films where in-plane conductivity and interfacial conductance were extracted together [23], and, in the case closest to the present study, to low-ordered carbon fibers, for which longitudinal conductivities of $13\text{--}37\text{ W m}^{-1}\text{ K}^{-1}$ were obtained and shown to correlate with Raman structural order rather than with fiber diameter [24]. The accuracy of the technique has been scrutinized in parallel: the modeling assumptions behind Raman thermometry have been revisited and shown to introduce errors of up to 30 % when substrate conduction is neglected [25], and a recent analytical treatment now accounts explicitly for convective, radiative and substrate-conductive losses, extending the method to supported and thick specimens [26]. What unites every one of these applications is that the specimen is a two-dimensional, thin or fibrous carbon of controlled geometry. The method has not been applied to a bulk, opaque, chemically heterogeneous natural solid.

Two further modalities complete the description of a coal surface. Scanning Kelvin probe microscopy (SKPM) maps the contact potential difference and thus the local work function [27]; in carbonaceous solids the signal is governed by the balance between condensed aromatic $\text{C}=\text{C}$ domains, which accumulate π -electron density, and oxygen-bearing groups, which impose opposing surface dipoles, so that the potential distribution shifts systematically with rank and oxidation state [28]. Mild air oxidation of semi-anthracite has been shown to alter surface energy and functional-group distribution in ways that AFM-based potential mapping detects [29], and the sensitivity of the measurement to sample preparation was recognized early in the

AFM study of coal macerals [30]. Nanomechanical mapping, in turn, resolves the mechanical consequences of the macromolecular architecture: modulus and pore-scale properties differ systematically between ranks [31], the electro-mechanical response of coal is heterogeneous at the micro- and nanoscale [32], and force-curve hysteresis quantifies viscoelastic dissipation provided that tip geometry and contact model are controlled [33]–[36].

Three gaps follow from this state of the art. First, optothermal Raman thermometry has been developed and validated exclusively on specimens of controlled geometry — suspended two-dimensional crystals, thin films and fibers [19]–[24] — and has never been applied to a bulk, opaque, chemically heterogeneous natural solid, so no grain-level thermal descriptor exists for the material whose bulk conductivity is routinely used in process models. Second, although micro-Raman deconvolution, SEM-EDS, scanning Kelvin probe microscopy and nanomechanical mapping have each been applied to coal separately, they have not been acquired on the same as-received grains of a rank-spanning series, nor referred to the proximate composition and the standardized rank assignment of the very same coals, so the mechanistic chain that connects aromatic ordering to phonon transport, surface electrostatics and viscoelastic response has not been assembled on one specimen. Third, and consequently, the Raman descriptors proposed as rank proxies have not been validated against an independent compositional measurement made on the same material, which is the specific weakness identified in the critical literature [17]. The novelty of the present work lies in closing these three gaps simultaneously: it transfers optothermal Raman thermometry from engineered low-dimensional carbons to natural coal grains measured without any preparation; it acquires five independent modalities on those same grains; and it validates the micro-Raman descriptor against one surface and one bulk measurement of composition determined on the same coals. The specific objectives are: (i) to implement a two-step optothermal Raman protocol on as-received grains of anthracite, semi-anthracite and lignite and to extract χ_G , $\Delta\omega_G/\Delta P$ and the effective grain conductivity κ_{eff} with propagated uncertainties; (ii) to determine the five-band Raman structural descriptors of the same grains; (iii) to quantify elemental composition, minor inorganic constituents and pore morphology by SEM-EDS; (iv) to map contact potential, elastic modulus and dissipation energy by AFM-SKPM and PinPoint nanomechanical mode on the anthracite and semi-anthracite grains, whose as-received relief lies within the vertical range of the scanner; (v) to refer all of these grain-scale descriptors to the bulk proximate composition and the standardized rank assignment of the same coals; and (vi) to test the convergence of the modalities and to benchmark the resulting κ_{eff} against the optothermal-Raman literature on carbon materials and against bulk coal conductivities obtained by conventional methods.

2. Materials and methods

2.1. Coal specimens

Three natural coals spanning the rank continuum were studied: anthracite (high rank), semi-anthracite (medium rank) and lignite (low rank). Specimens were subjected exclusively to primary mechanical extraction and were analyzed as received, without polishing, epoxy embedding, conductive coating or chemical treatment. This choice is intrinsic to the method rather than incidental to it: embedding and polishing modify surface chemistry and functional-group population, which are exactly the quantities probed by SKPM, alter the grain geometry

that enters the thermal analysis, and introduce fluorescent resin backgrounds into the Raman spectra. Three grains of each coal were selected with dimensions as closely matched as the natural habit allowed; the anthracite and lignite grains presented euhedral to subhedral habits while the semi-anthracite grains were anhedral and closer to equant. Grain width and height were measured optically with the HORIBA LabSpec 6 imaging module before each thermal measurement, giving mean cross-sectional areas $S = h \times w$ of 15.0, 0.40 and 4.5 mm² for anthracite, semi-anthracite and lignite respectively. All Raman, SEM-EDS and AFM measurements were performed on these same grains. The ASTM D388 class name is spelled “semianthracite”; the hyphenated form “semi-anthracite” is used throughout when referring to the specimen itself.

2.2. Proximate analysis and rank classification

Representative bulk material of each coal was reduced to an analysis sample and characterized by proximate analysis on an as-received basis following the standard practice of ASTM D3172 [7], which partitions the sample into moisture, ash, volatile matter and fixed carbon, the last obtained by difference. Total sulfur was determined on the same analysis sample by high-temperature tube-furnace combustion [37]. Rank was then assigned according to ASTM D388 [8] from the fixed carbon and volatile matter recalculated to a dry, mineral-matter-free basis, so that the classification rests on a standardized bulk determination and is independent of every spectroscopic or microscopic criterion used elsewhere in this work. The semi-anthracite ash, volatile matter and fixed carbon were determined on a dry basis (10.62, 12.06 and 77.32 %) and are converted using the measured moisture; the Parr formulae of ASTM D388 return the same dry, mineral-matter-free values from either basis. These bulk values provide the reference against which the grain-scale descriptors are assessed.

2.3. Optothermal Raman thermometry

Raman measurements were made on a HORIBA LabSpec 6 spectrometer with a 532 nm continuous-wave diode-pumped solid-state source (Laser Quantum Torus 532) focused through a 50× long-working-distance objective (NA = 0.55). The diffraction-limited spot diameter, $d = 1.22 \lambda/\text{NA}$, is 1.18 μm, so the characteristic source radius used throughout is $r_0 = 0.61 \lambda/\text{NA} = 590$ nm and the lateral resolution is 0.59 μm. Because κ_{eff} scales as $1/r_0$, a ±10 % uncertainty in the effective source radius propagates as ±10 % in the reported conductivities; this is the dominant systematic contribution and is not included in the statistical uncertainties quoted in Section 3.3. Incident power at the specimen was verified with a Coherent FieldMaxII meter before each session. A 600 grooves mm⁻¹ grating and a Synapse CCD gave a spectral resolution near 1 cm⁻¹ over 200–3500 cm⁻¹.

In the first step, each grain was mounted on a borosilicate slide inside a Linkam THMS600 stage and spectra were acquired at 293, 573, 673, 773 and 873 K at an incident power below 0.5 mW. At that power the residual self-heating shift predicted from $\Delta\omega_G/\Delta P$ is ≤ 0.26 cm⁻¹, below the 1 cm⁻¹ spectral resolution of the instrument, so no measurable self-heating contribution to the G-band position is expected. Five spectra of 20 s were averaged at each set point and ω_G was obtained by a single Lorentzian fit over 1560–1640 cm⁻¹. The temperature coefficient follows from the linear regression of ω_G against absolute temperature,

$$\omega_G(T) = \omega_{G,0} + \chi_G \cdot T, \quad \chi_G = d\omega_G/dT \quad (\text{cm}^{-1} \text{ K}^{-1}) \quad (1)$$

which converts any subsequent G-band shift into a local temperature rise:

$$\Delta T = \Delta\omega_G / \chi_G \quad (2)$$

In the second step the stage was removed, the grain was returned to a plain slide at ambient temperature, and the incident power was increased stepwise from 5 to 20 mW using the spectrometer attenuator, except for lignite, whose ramp ended at 15 mW. Three power levels were used for anthracite (5, 10 and 20 mW) and for lignite (5, 10 and 15 mW) and four for semi-anthracite (5, 10, 15 and 20 mW), as plotted in Fig. 1b; the standard error of each slope was computed from the number of levels actually regressed, so the semi-anthracite slope carries two degrees of freedom and the other two carry one. Each level was held for 10 min before acquisition to allow the mechanical and thermal drift of the stage to settle; the thermal steady state itself is established on a sub-microsecond timescale for a probe volume of this size. The slope $\Delta\omega_G/\Delta P$ was obtained by linear regression over those levels. The power that enters the thermal balance is the absorbed power, $P_{\text{abs}} = (1 - R) \cdot P_{\text{inc}}$, where R is the specular reflectance of the grain at 532 nm; coals are strongly absorbing at this wavelength, and taking $R \leq 0.10$ for all three specimens gives $P_{\text{abs}} \geq 0.90 \cdot P_{\text{inc}}$. Because the same bound applies to the three coals, the ratios between them are unaffected. P denotes the incident power in Eqs. (3) and (4), so the conductivities reported below are lower bounds that would rise by at most 10 % if the absorbed power were used instead. Because a coal grain is opaque and thick relative to both the beam radius and the optical penetration depth of a 532 nm beam in a carbonaceous solid, the heated volume is approximated as a hemispherical isothermal source of radius $r_0 = 590$ nm at the surface of a semi-infinite medium rather than as a surface disc, since absorption occurs over a depth comparable to the beam radius and not over a two-dimensional footprint. For that geometry the steady-state solution of Fourier's law, $q = -\kappa \nabla T$, is

$$\Delta T = P / (2\pi \cdot \kappa_{\text{eff}} \cdot r_0) \quad (3)$$

so that, substituting Eq. (2), the operative expression is

$$\kappa_{\text{eff}} = \Delta P / (2\pi r_0 \Delta T) = (|\chi_G| / 2\pi r_0) \cdot (\Delta P / |\Delta\omega_G|) \quad (4)$$

Both χ_G and $\Delta\omega_G/\Delta P$ are negative, so their quotient is positive; absolute values are used in Eq. (4) to make this explicit. The quantity obtained is an effective conductivity referred to the source radius: it describes the rate at which the grain removes heat deposited in a volume of that scale, and it is the correct basis for comparing grains measured under identical optical conditions. The choice of source geometry sets a fixed multiplicative factor on κ_{eff} . Adopting instead the isothermal-disc solution, $\Delta T = P / (4\kappa r_0)$, would scale every reported conductivity by $2\pi/4 = 1.571$ without altering the ordering of the three coals or any of the correlations reported below; the hemispherical form is retained for the reason given above, and the absolute scale is therefore referred explicitly to this geometric convention. Two model-independent descriptors are reported alongside it, the thermal resistance and conductance of the heated volume,

$$R_{\text{th}} = \Delta T / \Delta P \quad (\text{K W}^{-1}), \quad G_{\text{th}} = 1/R_{\text{th}} = \Delta P / \Delta T \quad (\text{W K}^{-1}) \quad (5)$$

which depend only on the two measured slopes. Uncertainties in κ_{eff} were propagated from the standard errors of the two regressions as $(\sigma_{\kappa}/\kappa)^2 = (\sigma_{\chi}/\chi)^2 + (\sigma_s/s)^2$, where $s = \Delta\omega_G/\Delta P$. All

reported thermal quantities are means over three grains per coal. χ_G and $\Delta\omega_G/\Delta P$ are the regression slopes of Fig. 1a and 1b, quoted with their standard errors, and $\Delta T/\Delta P$, κ_{eff} , R_{th} and G_{th} follow from Eqs. (2), (4) and (5) with $r_0 = 590$ nm. The mean grain cross-section S given in Section 2.1 is reported to show that every grain dimension exceeds the source radius by more than three orders of magnitude, which is the condition under which the semi-infinite approximation of Eq. (3) holds. The maximum temperature rise reached at the highest power applied to each coal, obtained from Eq. (2), was 314 K for anthracite and 1020 K for semi-anthracite at 20 mW and 135 K for lignite at 15 mW. For anthracite and lignite the derived temperatures lie inside the 293–873 K interval over which χ_G was calibrated; for semi-anthracite the upper end of the ramp extrapolates beyond it, and the linearity of $\omega_G(T)$ verified to 873 K (Fig. 1a) is therefore assumed to persist. The extrapolation affects the derived ΔT but not the slope $\Delta\omega_G/\Delta P$, which enters Eq. (4) together with χ_G . Spectra recorded at the lowest power immediately before and immediately after each ramp were compared for every grain to confirm that the measurement left the probed volume unaltered.

2.4. Micro-Raman structural analysis

Structural spectra were acquired at incident powers below 0.3 mW, at which ω_G was invariant within 0.1 cm^{-1} between 0.1 and 0.3 mW, using three accumulations of 30 s. The 1000–2000 cm^{-1} region was deconvolved in OriginPro 2019 following the five-band procedure of Sadezky et al. [9]: Lorentzian profiles for D1 ($\sim 1350 \text{ cm}^{-1}$), D2 ($\sim 1610 \text{ cm}^{-1}$), D4 ($\sim 1200 \text{ cm}^{-1}$) and G ($\sim 1590 \text{ cm}^{-1}$), and a Gaussian profile for D3 ($\sim 1500 \text{ cm}^{-1}$). Three descriptors were extracted: the area ratio A_{D1}/A_G , an index of defect density and aromatic domain connectivity; the G–D1 separation, a proxy for aromatic cluster size; and the G-band full width at half maximum, FWHM_G , which responds to bond length and angle disorder. A linear baseline was subtracted over 1000–2000 cm^{-1} prior to deconvolution and the fit was constrained to non-negative amplitudes; coefficients of determination are reported over that window only. Three spectra per grain and three grains per coal were analyzed ($n = 9$ per coal), and the complete set of fitted band centers, widths and areas is available from the corresponding author.

2.5. SEM-EDS

Morphological and elemental analysis used a Carl Zeiss EVO MA 10 scanning electron microscope under high vacuum, with specimens uncoated and in the as-received condition. Secondary-electron imaging was performed at an accelerating voltage of 15 kV and a working distance of 8.5 mm; field sizes are given by the scale bars of Fig. 3 rather than by nominal magnifications, which depend on the reproduction size. Elemental quantification used an Oxford Instruments X-act silicon drift detector of 10 mm^2 nominal active area, with acquisition and ZAF quantification in INCA Suite 5.05. Four-point analyses (p1–p4) were made per grain, and full elemental maps of C, O, Al, Si, S and Fe were collected over the same fields and used to verify that the four point analyses are representative of the mapped area; the concentrations quoted below are the point-analysis means, and no compositional domain resolved in the maps departed from them by more than one standard deviation. Pore equivalent diameters and circularity were measured from the secondary-electron images using the Analyze Particles routine of ImageJ 1.53.

2.6. AFM-SKPM and PinPoint nanomechanical mapping

Surface topography, phase and contact potential difference were measured on a Park Systems NX-10 atomic force microscope in two-pass electrostatic-force / scanning Kelvin probe mode. Topography was acquired in non-contact mode in the first pass; in the second pass, at a lift height of 15 nm, an AC bias of 2 V was applied and a feedback loop adjusted the DC bias to null the first-harmonic electrostatic force, yielding $CPD = (\Phi_{\text{tip}} - \Phi_{\text{sample}})/e$. A Multi75E-G probe (Cr/Pt coating, tip radius ≈ 25 nm, resonance 75 kHz, spring constant $1\text{--}7$ N m $^{-1}$) was used, calibrated against freshly cleaved HOPG, for which $\Phi(\text{HOPG}) = 4.60$ eV was adopted. Scans covered 5×5 μm at 256×256 pixels and 0.25 Hz. Images were processed in XEI (Park Systems) with second-order line flattening and no interpolation; CPD histograms were fitted with a single Gaussian to extract the mean and standard deviation. Grains were seated in modeling clay and leveled to within 1° of the cantilever axis; the clay contacts only the underside of the grain and leaves the scanned surface untouched. Nanomechanical mapping was performed on the same instrument in PinPoint mode with an NSC14 probe (Si, Al back coating, resonance 130–220 kHz, spring constant $5\text{--}13$ N m $^{-1}$, tip radius ≈ 35 nm), the spring constant being calibrated by the thermal method in SmartScan and the sensitivity on a clean Si wafer. Force–distance curves were collected at 256×256 pixels over 5×5 μm at a z-ramp rate of 0.3 $\mu\text{m s}^{-1}$. The elastic modulus was obtained by fitting the retract branch with the Hertz spherical model,

$$F = (4/3) \cdot E^* \cdot \sqrt{r} \cdot \delta^{3/2} \quad (6)$$

with $1/E^* = (1 - \nu_s^2)/E_s + (1 - \nu_{\text{tip}}^2)/E_{\text{tip}}$, $\nu_s = 0.25$ and $\nu_{\text{tip}} = 0.27$; the retract branch was fitted over the repulsive portion above the adhesion minimum, where the Hertz assumption of negligible adhesion holds. The dissipation energy E_{dis} was taken as the area of the loading–unloading hysteresis loop at each pixel. Modulus maps are displayed on a logarithmic color scale clipped to 0.1–100 GPa; pixels whose force curves failed to converge were excluded rather than clipped. Surface and nanomechanical mapping were carried out on the anthracite and semi-anthracite grains, for which the as-received surface relief lay within the vertical range of the scanner.

3. Results

3.1. Proximate composition and rank assignment

Table 1 gives the proximate composition, the total sulfur content and the rank assignment of the three coals.

Volatile matter rises steeply with decreasing rank, from 3.93 % in anthracite through 11.09 % in semi-anthracite to 36.60 % in lignite, a factor of 9.3 between the extremes on an as-received basis and of 14.3 once recalculated to a dry, mineral-matter-free basis. Fixed carbon moves in the opposite sense, from 83.17 % through 71.11 % to 35.00 %. Ash is lowest in anthracite (9.37 %) and highest in lignite (21.50 %), and total sulfur follows the same order, rising from 0.64 % in anthracite and 0.76 % in semi-anthracite to 6.78 % in lignite. Moisture does not order with rank: semi-anthracite holds the most (8.03 %) and anthracite the least (3.54 %).

Table 1. Proximate analysis, total sulfur and ASTM D388 rank assignment of the three coals, on an as-received basis and recalculated to a dry, mineral-matter-free (dmmf) basis.

Parameter	Anthracite	Semi-anthracite	Lignite
Proximate analysis (as-received basis)			
Moisture (%)	3.54	8.03	6.90
Ash (%)	9.37	9.77	21.50
Volatile matter (%)	3.93	11.09	36.60
Fixed carbon (%)	83.17	71.11	35.00
Total sulfur (%)	0.64	0.76	6.78
Dry, mineral-matter-free basis (dmmf)			
Fixed carbon, dmmf (%)	96.60	87.65	51.37
Volatile matter, dmmf (%)	3.40	12.35	48.63

Recalculated to a dry, mineral-matter-free basis, the fixed carbon of the three specimens is 96.60 %, 87.65 % and 51.37 %. These values place the first specimen in the anthracite class of ASTM D388 (92–98 % fixed carbon, dmmf), the second in the semianthracite class (86–92 %) and the third, whose volatile matter reaches 48.63 % on the same basis, among the low-rank coals, so the rank labels used throughout this work rest on a standardized bulk determination rather than on any of the spectroscopic or microscopic criteria applied below.

3.2. Raman thermometry and power response

Fig. 1 shows the two regressions on which every thermal quantity in this work rests.

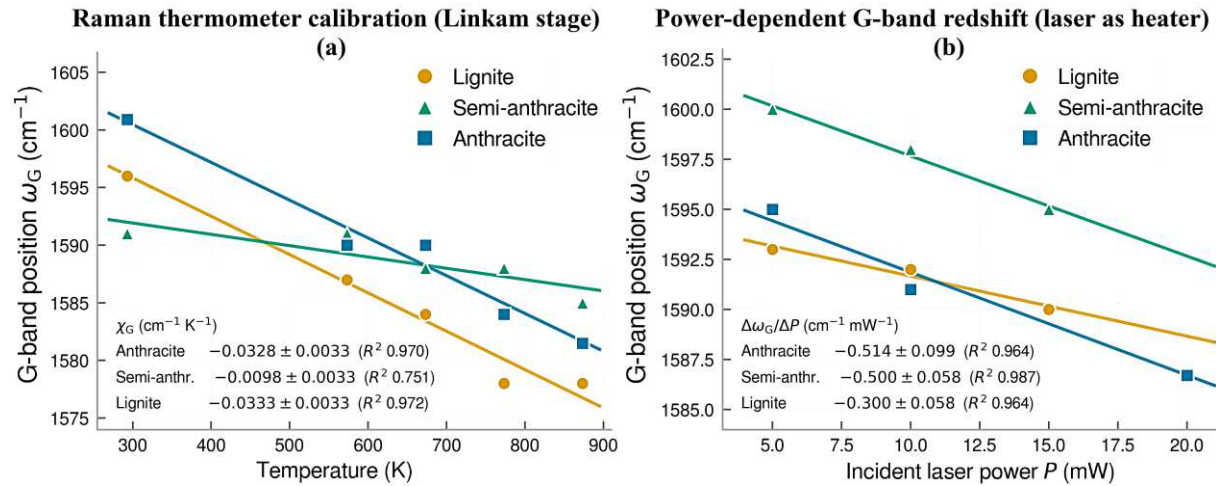


Fig. 1. Optothermal Raman thermometry of as-received coal grains. (a) G-band position ω_G against absolute temperature in the heating stage; (b) G-band position against incident laser power at ambient temperature.

In Fig. 1a the G-band position is plotted against absolute temperature, measured in a Linkam THMS600 stage at an incident power below 0.5 mW; the slope of each line is the Raman thermometer coefficient χ_G of Eqs. (2) and (4). In Fig. 1b the same grains are plotted against incident laser power at ambient temperature, with the beam acting as both heat source and

probe; the slope $\Delta\omega_G/\Delta P$ converts power into temperature rise. Symbols distinguish the three rank classes and solid lines are least-squares fits. Panels (a) and (b) were acquired in separate sessions and, in (b), at a different point on each grain, so the absolute band positions are not comparable between panels; only the regression slopes enter Eqs. (2)–(4).

Regression gives temperature coefficients of $-0.0328 \pm 0.0033 \text{ cm}^{-1} \text{ K}^{-1}$ for anthracite ($R^2 = 0.970$), $-0.0098 \pm 0.0033 \text{ cm}^{-1} \text{ K}^{-1}$ for semi-anthracite ($R^2 = 0.751$) and $-0.0333 \pm 0.0033 \text{ cm}^{-1} \text{ K}^{-1}$ for lignite ($R^2 = 0.972$). The anthracite and lignite coefficients agree with each other to within their standard errors, whereas the semi-anthracite coefficient is smaller by a factor of about three and its regression is correspondingly less well determined; that difference propagates directly into the thermal quantities derived below.

The G band redshifts linearly with incident power in every case, with slopes of $-0.514 \pm 0.099 \text{ cm}^{-1} \text{ mW}^{-1}$ for anthracite ($R^2 = 0.964$), $-0.500 \pm 0.041 \text{ cm}^{-1} \text{ mW}^{-1}$ for semi-anthracite ($R^2 = 0.987$) and $-0.300 \pm 0.058 \text{ cm}^{-1} \text{ mW}^{-1}$ for lignite ($R^2 = 0.964$). The linearity over the whole ramp confirms that laser-induced heating, rather than any other power-dependent spectral process, dominates the observed shift.

3.3. Effective thermal conductivity

The two slopes of Fig. 1 convert directly into the thermal descriptors of the grain through Eqs. (2), (4) and (5). The thermal response of the heated volume, $\Delta T/\Delta P$, is 15.7 K mW^{-1} for anthracite, 51.0 K mW^{-1} for semi-anthracite and 9.0 K mW^{-1} for lignite; these are numerically the thermal resistances R_{th} of the probed volume in units of 10^3 K W^{-1} , and the corresponding thermal conductances G_{th} are 6.37 , 1.96 and $11.09 \times 10^{-5} \text{ W K}^{-1}$. The effective conductivities that follow, plotted against rank in Fig. 6a, are 17.2 ± 3.7 , 5.3 ± 1.8 and $29.9 \pm 6.5 \text{ W m}^{-1} \text{ K}^{-1}$. Anthracite therefore dissipates heat about three times more efficiently than semi-anthracite, while lignite returns the highest value of the series. The three values are separated by more than their propagated uncertainties, which range from 22 % for anthracite and lignite to 35 % for semi-anthracite; the larger figure reflects the lower precision of the semi-anthracite calibration in Fig. 1a rather than of its power ramp, which is the best determined of the three.

3.4. Raman structural descriptors

Fig. 2a–c show the five-band deconvolution of the first-order region for anthracite, semi-anthracite and lignite, with the individual components, the cumulative fit and its coefficient of determination; spectra were acquired at 532 nm below 0.3 mW through the 50× objective in three accumulations of 30 s. Fig. 2d gives the G-band width FWHM_G , Fig. 2e the D1-to-G area ratio A_{D1}/A_G and Fig. 2f the G–D1 separation, all ordered by increasing rank. Error bars in Fig. 2d are one standard deviation over the $n = 9$ spectra acquired per coal; in Fig. 2e and 2f the descriptors are derived from the cumulative fit of the averaged spectrum of each coal, so a within-rank dispersion is not defined for them.

Cumulative fits reproduce the measured envelopes over the $1000\text{--}2000 \text{ cm}^{-1}$ window with coefficients of determination of 0.9895, 0.9769 and 0.9271 for anthracite, semi-anthracite and lignite. The fitted band centers are 1177 (D4), 1243 (D3), 1351 (D1) and 1594 cm^{-1} (G) for anthracite; 1123 (D4), 1233 (D3), 1354 (D1) and 1594 cm^{-1} (G) for semi-anthracite; and 1176 (D4), 1296 (D3), 1357 (D1) and 1591 cm^{-1} (G) for lignite. The D2 shoulder near 1610 cm^{-1}

was resolved as an independent component only in the two high-rank coals; in lignite the G band is broad enough to subsume it, so that envelope was described by four components. That is itself a structural result, because a resolvable D2 requires the ordered graphitic domains that lignite does not possess. The D4 band between 1123 and 1177 cm^{-1} is present in all three coals, so aliphatic and oxygenated bridging groups persist even in the most ordered member of the series, and the D1 position shifts from 1357 cm^{-1} in lignite to 1351 cm^{-1} in anthracite.

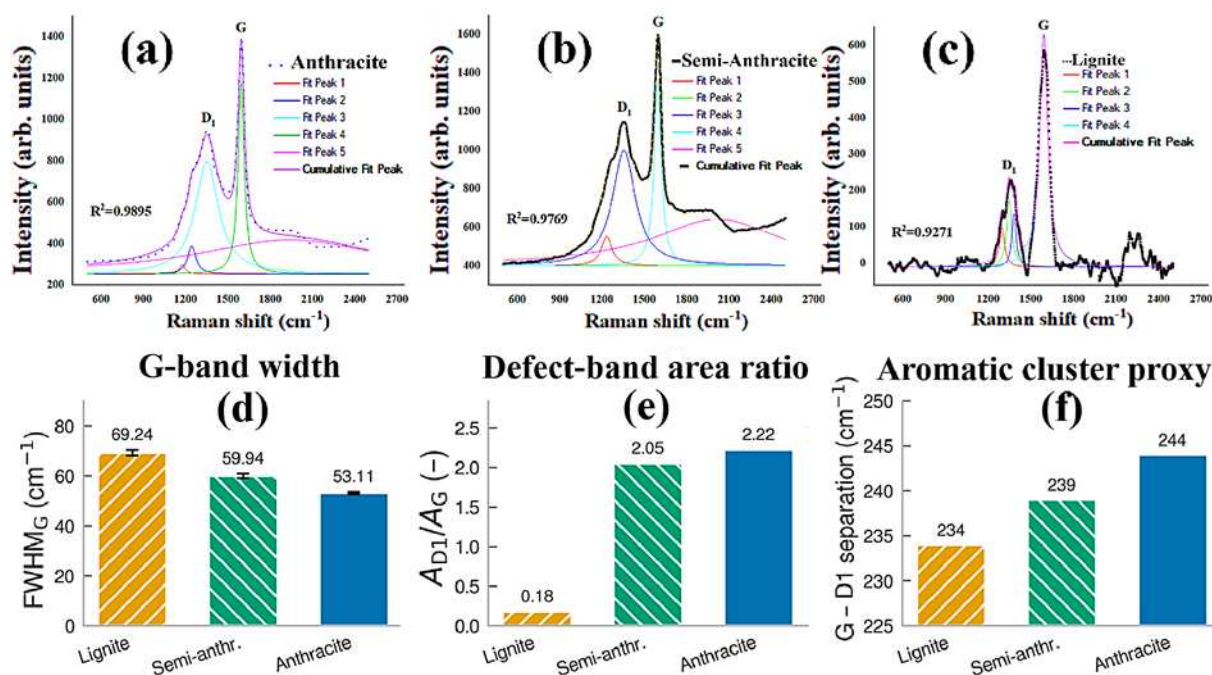


Fig. 2. Micro-Raman structure of the same grains. (a–c) Five-band deconvolution of the first-order region for anthracite, semi-anthracite and lignite; (d) G-band width FWHM_G ; (e) D1-to-G area ratio A_{D1}/A_G ; (f) G–D1 separation.

The three quantitative descriptors order the series consistently. FWHM_G narrows monotonically from $69.24 \pm 1.16 \text{ cm}^{-1}$ in lignite through $59.94 \pm 0.94 \text{ cm}^{-1}$ in semi-anthracite to $53.11 \pm 0.56 \text{ cm}^{-1}$ in anthracite (Fig. 2d), a spread of 16.1 cm^{-1} that is more than an order of magnitude larger than the within-rank standard deviations. The A_{D1}/A_G ratio rises from 0.18 in lignite to 2.05 in semi-anthracite and 2.22 in anthracite (Fig. 2e), the step between lignite and the two high-rank coals being far larger than that between the high-rank coals themselves. The G–D1 separation widens uniformly from 234 to 239 to 244 cm^{-1} (Fig. 2f).

3.5. Composition and pore morphology

Fig. 3a and 3b show the secondary-electron morphology of anthracite, Fig. 3c and 3d that of semi-anthracite and Fig. 3e and 3f that of lignite, each at two field sizes (15 kV, uncoated); the red frames mark the magnified fields and the yellow ellipses the pores measured by image analysis.

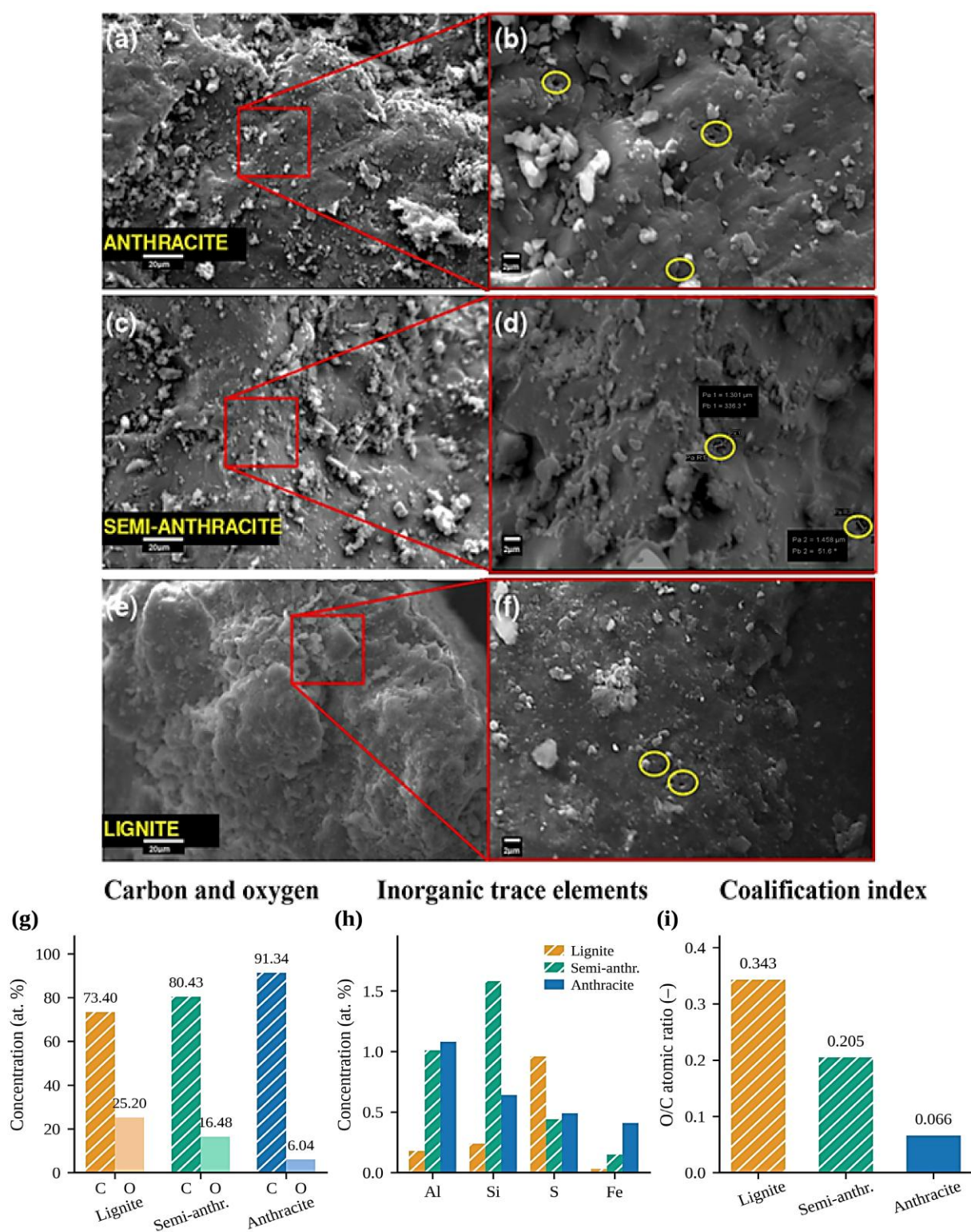


Fig. 3. Morphology and composition of the as-received grains. (a, b) Anthracite, (c, d) semi-anthracite and (e, f) lignite imaged in secondary electrons at two field sizes; (g) carbon and oxygen atomic concentrations; (h) minor inorganic constituents; (i) O/C atomic ratio.

Fig. 3g gives the carbon and oxygen atomic concentrations from the four-point EDS analyses, Fig. 3h the minor inorganic constituents and Fig. 3i the resulting O/C atomic ratio. Carbon rises monotonically with rank, from 73.40 at. % in lignite through 80.43 at. % in semi-anthracite to

91.34 at. % in anthracite, while oxygen falls from 25.20 to 16.48 to 6.04 at. % (Fig. 3g). The resulting O/C atomic ratio decreases by a factor of 5.2 across the series, from 0.343 to 0.205 to 0.066 (Fig. 3i). Aluminum, silicon, sulfur and iron are present as minor constituents in all three coals but with distinct distributions (Fig. 3h): aluminum and silicon are an order of magnitude more abundant in the two high-rank coals (1.01–1.08 at. % Al, 0.64–1.58 at. % Si) than in lignite (0.18 at. % Al, 0.24 at. % Si), whereas sulfur is highest in lignite (0.96 at. %, against 0.44 at. % in semi-anthracite and 0.49 at. % in anthracite) and iron is highest in anthracite (0.41 at. %), intermediate in semi-anthracite (0.15 at. %) and lowest in lignite (0.03 at. %).

The micrographs resolve a systematic change in pore habit. Anthracite (Fig. 3a, b) presents well-defined, near-circular sub-micrometer pores of about 739 nm equivalent diameter, circularity 0.87, distributed over a smooth surface carrying a network of micro-fractures and small angular agglomerates. Semi-anthracite (Fig. 3c, d) shows elongated, cleat-like pores of about 1.3 μm and circularity 0.61 within a more irregular, anhedral relief. Lignite (Fig. 3e, f) shows irregular pores of about 401 nm and circularity 0.42, largely masked by extensive surface agglomerates of rounded habit and considerably larger size than those of the higher-rank coals; the same agglomerates dominate the as-received relief of this coal.

3.6. Surface topography and contact potential

Fig. 4a–c show the topography, phase and surface potential of anthracite and Fig. 4d its contact-potential histogram; Fig. 4e–g show the same three channels for semi-anthracite and Fig. 4h its histogram.

All maps cover $5 \times 5 \mu\text{m}$ at 256×256 pixels and were acquired with a Multi75E-G Cr/Pt probe at 75 kHz with $V_{\text{AC}} = 2 \text{ V}$ and a 15 nm lift height. Green frames mark positive-potential domains and red frames negative-potential domains. The potential scales differ between the two coals — millivolts for anthracite, microvolts for semi-anthracite — which is itself the principal result of the figure.

The two coals differ by more than three orders of magnitude in potential dispersion. Semi-anthracite gives a narrow distribution with a mean of $-7.7 \mu\text{V}$ and a standard deviation of $50.9 \mu\text{V}$, spanning roughly -100 to $+110 \mu\text{V}$; anthracite gives a distribution centered at -12.5 mV with a standard deviation of 369 mV , spanning approximately $\pm 700 \text{ mV}$, the map itself resolving domains between -500 and $+500 \text{ mV}$. Both distributions are unimodal. The anthracite histogram is well described by a single Gaussian; the semi-anthracite histogram is negatively skewed, with a sharp low-potential edge near $-40 \mu\text{V}$ and an extended positive tail, so its Gaussian parameters are reported for the central tendency only. In both maps the bright, positive-potential domains marked by green frames and the dark, negative-potential domains marked by red frames occur on a lateral scale of roughly $0.5\text{--}2 \mu\text{m}$, comparable to the size of individual maceral components, and their contrast is far stronger in anthracite than in semi-anthracite. In anthracite the phase channel reproduces the same domain structure as the potential map, indicating that the contrast originates in genuine material heterogeneity rather than in topographic crosstalk. In semi-anthracite the phase channel is featureless at the same scale, consistent with the chemically and mechanically uniform surface that its narrow potential distribution also indicates.

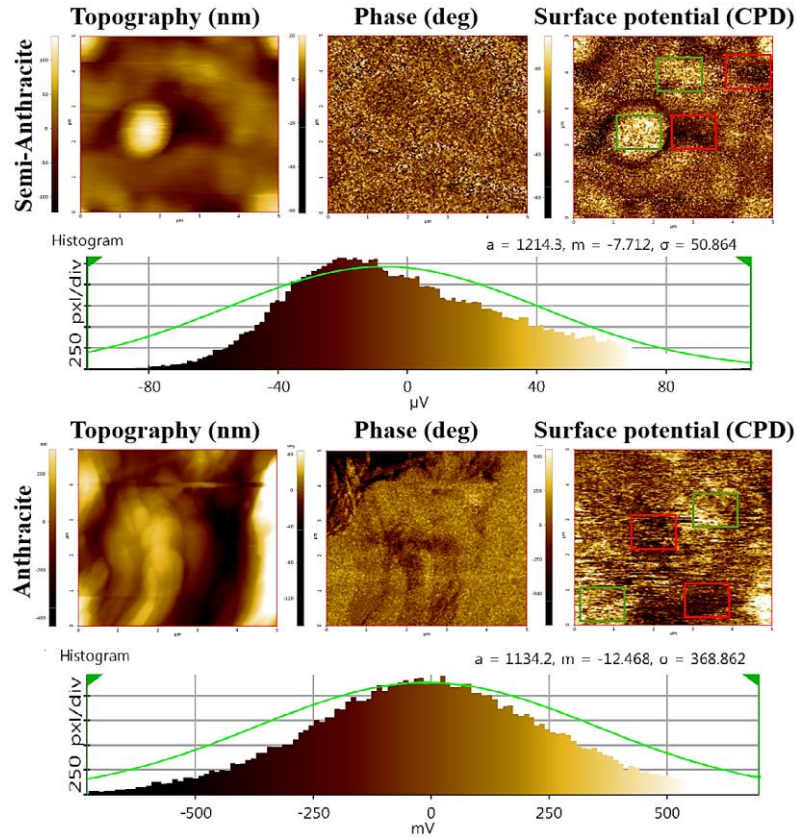


Fig. 4. AFM electrostatic-force and scanning Kelvin probe mapping. (a–c) Topography, phase and surface potential of anthracite and (d) its contact-potential histogram; (e–g) the same three channels for semi-anthracite and (h) its contact-potential histogram.

3.7. Nanomechanical response

Fig. 5a–d show the height, elastic modulus, deformation force and dissipation energy of anthracite and Fig. 5e the corresponding line profiles; Fig. 5f–i show the same four channels for semi-anthracite and Fig. 5j its profiles.

All maps cover $5 \times 5 \mu\text{m}$ at 256×256 pixels and were acquired with an NSC14 probe ($k = 5\text{--}13 \text{ N m}^{-1}$, tip radius $\approx 35 \text{ nm}$) and reduced with the Hertz model. In the profiles, red is height, green modulus, blue deformation force and magenta dissipation energy; a three-dimensional rendering of each scanned field accompanies them. Color scales for the modulus maps are logarithmic and scale bars are $1 \mu\text{m}$.

Height profiles give a relief of about 150 nm for anthracite and 125 nm for semi-anthracite, with arithmetic mean roughness of 76.45 and 30.76 nm respectively. Within a single $5 \times 5 \mu\text{m}$ field the elastic modulus spans 0.4 to 50 GPa in anthracite and 0.25 to 12.5 GPa in semi-anthracite; the softest regions, near $0.25\text{--}0.4 \text{ GPa}$, occupy most of the field, while bright, high-modulus features above 10 GPa are confined to narrow elongated domains whose size and habit are consistent with the aluminosilicate and iron-bearing inclusions detected by EDS.

At the constant peak force of the PinPoint cycle the deformation-force channel varies by less than 8 nN across the field, and the indentation depth derived from it is anti-correlated with the modulus, as expected for a stiffer material accommodating a smaller deformation at constant

load. The anti-correlation is not exact: a lateral offset of about 80 nm persists between the modulus maximum and the depth minimum. Dissipation energy ranges from 1 to 5 fJ in anthracite and from 0.5 to 1.75 fJ in semi-anthracite, and the bright, high-dissipation regions of the E_{dis} maps correspond to the lower-modulus regions of the modulus maps.

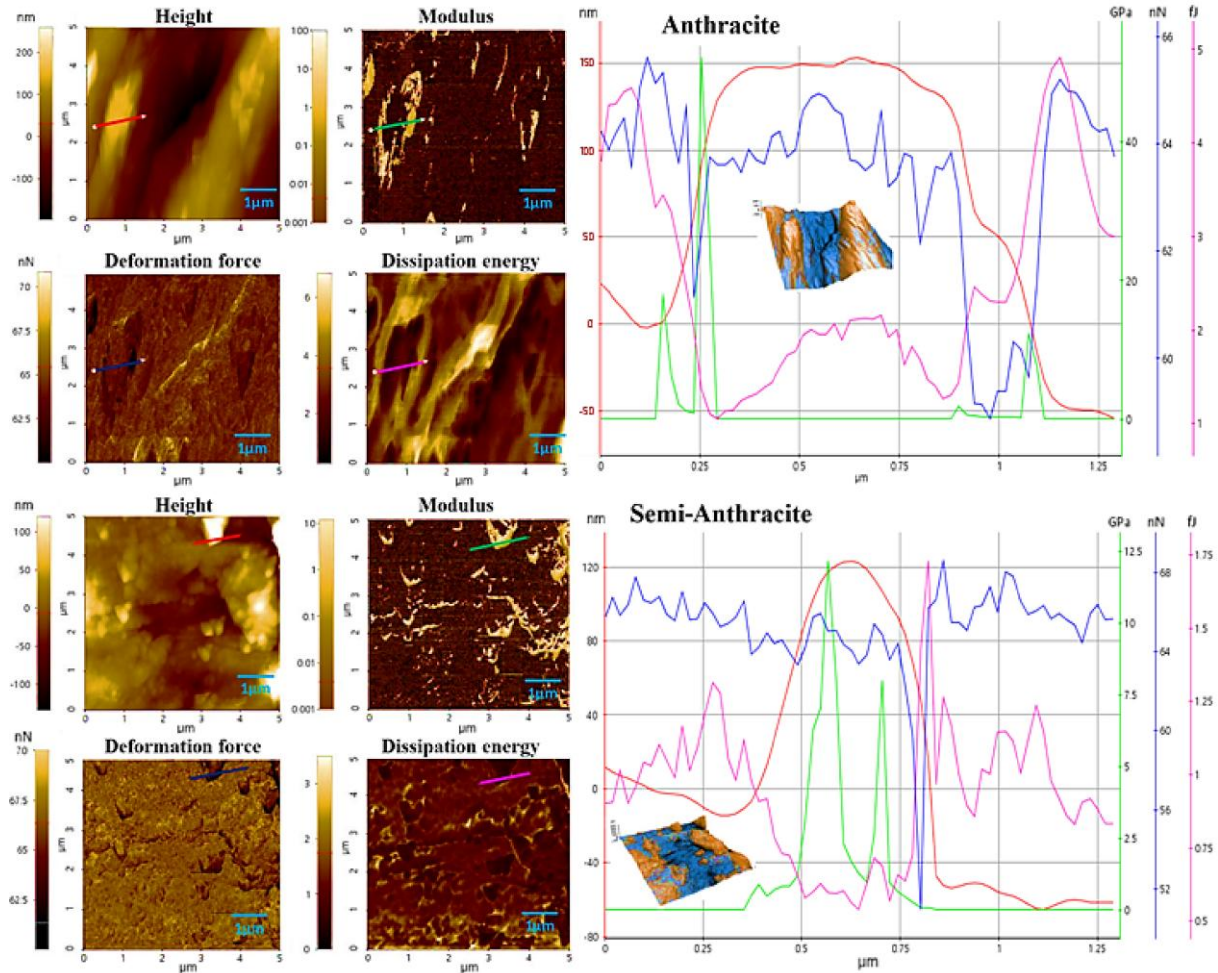


Fig. 5. AFM PinPoint nanomechanical mapping of the two high-rank coals. (a–d) Height, elastic modulus, deformation force and dissipation energy of anthracite and (e) the corresponding line profiles; (f–i) the same four channels for semi-anthracite and (j) its line profiles.

3.8. Cross-technique relations

Fig. 6 assembles the five modalities on a common rank axis.

Fig. 6a gives the effective thermal conductivity, Fig. 6b the G-band width, Fig. 6c the O/C atomic ratio, Fig. 6d the as-received volatile matter and Fig. 6e the dissipation energy; error bars are one propagated standard deviation in (a) and (b) and the measured interval in (e), whose bars are the midpoints of that interval. Fig. 6e contains two rank classes because lignite was not mapped by AFM. Fig. 6f and 6g cross-validate the micro-Raman descriptor against one surface and one bulk measurement of composition, with the least-squares lines and their coefficients of determination. Fig. 6h places the measured conductivities on a logarithmic scale against published optothermal-Raman values for suspended monolayer graphene [19], graphene

laminates [38] and low-ordered carbon fibers [24], and against the range reported for bulk coals by steady-state and transient methods [4], [5].

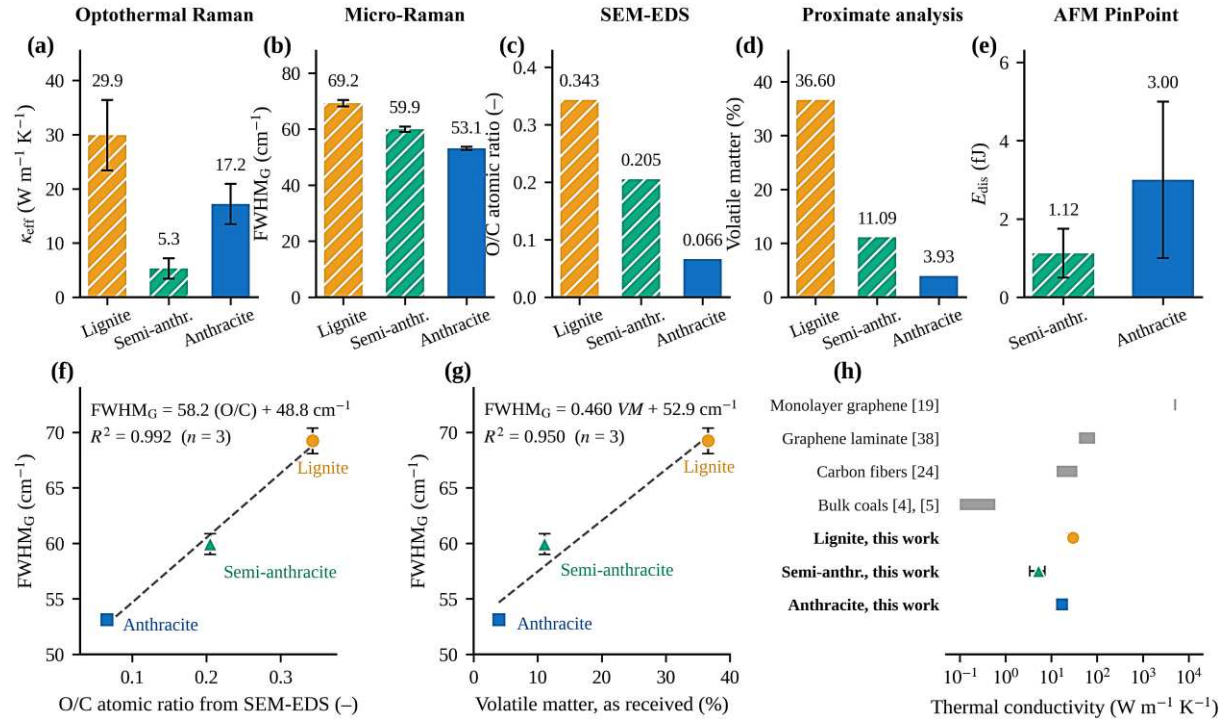


Fig. 6. Rank dependence of the five modalities and cross-technique validation. (a) Effective thermal conductivity; (b) G-band width; (c) O/C atomic ratio; (d) as-received volatile matter; (e) dissipation energy; (f, g) G-band width against the surface and the bulk composition; (h) benchmark against the optothermal-Raman literature and against bulk coal values.

Five of the observables vary monotonically with rank: FWHM_G falls (Fig. 6b), the O/C ratio falls (Fig. 6c), the volatile-matter content falls (Fig. 6d), the dissipation energy rises (Fig. 6e), and, from Fig. 2, A_{D1}/A_G and the G–D1 separation rise. The effective thermal conductivity does not (Fig. 6a): it increases from semi-anthracite to anthracite as the structural descriptors would predict, but lignite returns the highest value of the three. Fig. 6f and 6g plot the G-band width against the two independent compositional measurements and find linear relations in both cases: $\text{FWHM}_G = 58.2 \cdot (\text{O/C}) + 48.8 \text{ cm}^{-1}$ with $R^2 = 0.992$ against the surface oxygen-to-carbon ratio, and $\text{FWHM}_G = 0.460 \cdot \text{VM} + 52.9 \text{ cm}^{-1}$ with $R^2 = 0.950$ against the as-received volatile matter VM expressed in per cent. Fig. 6h places the measured conductivities on the scale of published optothermal-Raman results and of bulk coal conductivities obtained by conventional methods.

4. Discussion

The results above support a single interpretation, which is stated here before being defended: every observable measured in this work is a different projection of one structural variable, the size and connectivity of the condensed aromatic domain built up during coalification, and the optothermal Raman measurement adds to that set the one projection that had been missing, a thermal descriptor obtained at the scale on which the domains themselves are organized.

The clearest evidence is the relation of Fig. 6f. The G-band width and the EDS oxygen-to-carbon ratio are measured by physically unrelated processes — inelastic photon scattering from lattice vibrations in one case, characteristic X-ray emission following core-level ionization in the other — and yet across the three ranks they are linearly related with $R^2 = 0.992$. That relation is the direct experimental answer to the objection raised by Cheng et al. [17], who argued that Raman descriptors map onto conventional maturity indices only within restricted windows and with a strong dependence on acquisition and fitting conventions. The present data do not refute that argument as a general caution, and they should not be read as doing so; what they establish is that when the Raman descriptor and the independent compositional measurement are acquired on the same as-received grain under a fixed acquisition protocol, the correspondence is quantitative. The point is strengthened by the second relation of Fig. 6g, because there the G-band width is matched not against another surface measurement but against the bulk volatile matter of the same coal, determined on a gram-scale analysis sample by a standardized combustion procedure [7]. That a micrometer-sized probe volume on one grain should predict a bulk proximate quantity to $R^2 = 0.950$ is not self-evident, given the maceral heterogeneity that the maps of Figs. 4 and 5 document within that same grain, and it places the empirical Raman correlations compiled for disordered carbons [13] on a footing that is directly usable for fuel assessment. Both relations rest on three rank classes and therefore on a single degree of freedom, so the coefficients of determination quantify how closely the three points fall on a line rather than establish statistical significance; they are reported as an internal consistency check between independent modalities, not as a calibration, and extending them to a wider rank population is identified below as the necessary next step. The rank labels themselves are secured independently: the dry, mineral-matter-free fixed carbon of Table 1 assigns the specimens to the anthracite and semianthracite classes of ASTM D388 [8] and to the low-rank field, without recourse to any spectroscopic criterion, so the ordering against which every trend in this work is read is not itself inferred from the measurements being interpreted. The mechanism is straightforward: the ether, hydroxyl, carbonyl and carboxyl groups counted as oxygen by EDS are precisely the groups that interrupt aromatic conjugation and impose the bond-length and bond-angle disorder that broadens the G band. Removing them by dehydration and decarboxylation, as coalification does, simultaneously lowers O/C and narrows FWHM_G . This is consistent with the FTIR and Raman correlation established across rank by He et al. [14], with the coking-coal correlations of Morga et al. [15], and with the classical description of carbonization and graphitization [39], and it extends those bulk correlations to the single-grain scale.

The A_{D1}/A_G ratio requires a more careful reading than the other descriptors, and the present data show why. The ratio rises steeply between lignite (0.18) and semi-anthracite (2.05) and then almost saturates toward anthracite (2.22), whereas FWHM_G and the G–D1 separation continue to change uniformly across the whole series. That non-uniformity is the expected behavior within the amorphization trajectory of Ferrari and Robertson [10]: the D1 band is activated by defects in a medium-range-ordered aromatic network, so its intensity grows as ordered domains appear but collapses in the amorphous limit where no such domains exist and the activation mechanism itself breaks down. Lignite sits at that limit. Reading A_{D1}/A_G as a monotonic rank index, as is sometimes done, therefore inverts the physics at the low-rank end,

and the general relation between the D-to-G ratio and in-plane crystallite size [12], [40] is applicable only above it. FWHM_G and the G–D1 separation, which respond to disorder rather than to defect activation, do not suffer this reversal and are the descriptors that should be preferred when a rank series spans the amorphous limit — a practical conclusion that follows from the data of Fig. 2 rather than from assumption.

The thermal results must be discussed on two levels, the absolute scale and the ordering, because they carry different information. On the absolute scale, the values of 5.3 to 29.9 W m⁻¹ K⁻¹ lie one to two orders of magnitude above the 0.1–0.6 W m⁻¹ K⁻¹ that steady-state and transient methods return for coals [4], [5]. This is not a discrepancy to be explained away; it is the physically expected consequence of what each method measures. A hot-disk or laser-flash measurement is made on a pressed pellet or a machined block, so its result is an effective conductivity of a two-phase medium in which the pore network and, for compacted specimens, the inter-particle contact resistances dominate the heat path; the reviews of determination methods and of the structure–conductivity relation make exactly this point, identifying porosity and moisture as first-order controls on the bulk value [4], [6]. The optothermal measurement, by contrast, deposits its heat inside a single grain within a volume of the order of a cubic micrometer and follows its removal through continuous solid material. The proximate data of Table 1 make that separation concrete from a second direction. Moisture is the one proximate variable that does not order with rank, and it is highest in the semi-anthracite (8.03 %) that returns the lowest κ_{eff} of the series; if the grain-scale measurement responded to the same variables as a bulk one, that specimen ought to conduct best rather than worst, since the conductivity of water exceeds that of dry coal. It does not, because over a ten-minute hold at a temperature rise of several hundred kelvin the micrometer-scale probe volume is dry whatever moisture the surrounding bulk holds; the optothermal measurement is simply not sensitive to a variable that is first-order for the bulk value. That the two differ by one to two orders of magnitude is a quantitative statement of how much of the bulk thermal resistance of a coal bed resides in its architecture rather than in its substance — and it is a statement that could not be made before, because no grain-scale measurement existed. The independent support for the absolute scale comes from Fig. 6h: the anthracite value of 17.2 ± 3.7 W m⁻¹ K⁻¹ falls within the 13–37 W m⁻¹ K⁻¹ that Kumar et al. [24] obtained for low-ordered carbon fibers by the same optothermal technique, albeit with the heat-diffusion problem solved for the cylindrical geometry of a fiber rather than for a semi-infinite solid, and the whole series lies below graphene laminate [38] and suspended monolayer graphene [19], exactly where a poorly ordered but genuinely sp²-bonded carbon should sit. The agreement is the more meaningful because Kumar et al. also found that the conductivity of their fibers correlated with Raman structural order rather than with specimen dimensions, which is the same coupling reported here.

On the ordering, anthracite conducts about three times better than semi-anthracite, and this is straightforward: within the Debye–Callaway picture the conductivity is a sum over modes of heat capacity, group velocity and mean free path, and both the velocity and the mean free path grow as aromatic ordering reduces boundary and defect scattering [20], [41], [42]. The G-band width, which measures the spread of bond lengths and angles and therefore the width of the phonon dispersion, is the descriptor most directly tied to that mean free path, and the ordering

of κ_{eff} between the two high-rank coals follows the ordering of FWHM_G exactly. The same structural argument explains the thermometer coefficients themselves: the larger $|\chi_G|$ of anthracite reflects stronger phonon–phonon anharmonicity in a more graphite-like network, and the small $|\chi_G|$ of semi-anthracite means that a given temperature rise produces a smaller measurable shift, which is why its calibration in Fig. 1a is the least precise of the three and why its propagated uncertainty is the largest of the three (Fig. 6a). This coupling between thermometric sensitivity and structural state is a practical constraint on the method that the graphene and dichalcogenide literature [18], [22], [23] has had no reason to encounter, because those materials are structurally uniform; it becomes a design consideration as soon as the technique is applied to natural carbons.

Lignite is the informative exception, and it should be read as such rather than smoothed over. Its aromatic order is the lowest of the three by every structural measure, yet it returns the highest effective conductivity. Two features of the same specimen account for this, and the proximate analysis now quantifies the first of them. Lignite carries 36.60 % volatile matter as received, 48.63 % on a dry, mineral-matter-free basis, against 3.93 % and 3.40 % for anthracite — a factor of 9.3 and 14.3 respectively (Table 1). The surface of this coal is correspondingly dominated by large rounded agglomerates of that volatile-rich material (Fig. 3e, f), so the volume that receives the laser energy is not the compact aromatic solid probed in the higher-rank grains but a loosely bound assemblage in which roughly half the mass, on a mineral-free basis, consists of species mobile at the temperatures reached under the beam and able to redistribute energy by routes that are not phononic. The second feature is that the pore habit of lignite is irregular and of low circularity, and its macroscopic void network is correspondingly interconnected [43], so radiative and convective transfer across pores contributes to the measured heat removal in a way that it cannot in the compact anthracite. Both mechanisms inflate the effective conductivity without implying superior phonon transport, and both are precisely the contributions that the recent analytical treatment of Vallin et al. [26] was formulated to separate for supported and thick specimens, and that Jaramillo-Fernandez et al. [25] identified as the source of errors up to 30 % when neglected. The lignite point therefore does not weaken the structural interpretation of the anthracite–semi-anthracite pair; it marks the boundary of the regime in which a single-channel phonon reading of κ_{eff} is admissible, and it identifies volatile content and pore topology as the variables that must be measured alongside it at the low-rank end.

The surface and mechanical measurements close the chain from the same direction. The contact-potential dispersion of anthracite exceeds that of semi-anthracite by more than three orders of magnitude — 369 mV against 50.9 μV — and this is the electrostatic signature of the same aromatic condensation. Condensed polycyclic domains accumulate π -electron density and generate strong local surface dipoles, whereas the oxygen-bearing groups that populate the periphery of small aromatic clusters impose weaker and more uniform dipoles of opposite sense; a surface with large, well-separated aromatic domains therefore presents strong potential contrast between domains, while a chemically more uniform, more oxidized surface presents a narrow distribution. This is consistent in mechanism with the rank and oxidation dependence reported by He et al. [28], with the surface-potential behavior of coal in electrolyte described by Hamieh and Siffert [44], and with the oxidation-induced surface energy changes observed

by Mursito et al. [29], but it differs from those studies in an important respect that is worth making explicit rather than leaving implicit. The studies of He et al. [28] and Mursito et al. [29] were performed on polished and embedded specimens and reported potential ranges two to three orders of magnitude narrower than those measured here. The comparison suggests that mechanical preparation homogenizes the very surface chemistry the measurement is intended to resolve, which is the strongest available argument for the as-received protocol adopted in this work and an early concern of Bruening and Cohen [30] that the present data quantify. The mineral matter completes the picture, and there the bulk and surface determinations prove complementary rather than redundant. Lignite carries the largest ash yield of the series (21.50 %) yet the smallest surface aluminum and silicon signal (0.42 at. % combined), whereas anthracite carries the smallest ash yield (9.37 %) and the largest surface aluminosilicate and iron signal (1.72 and 0.41 at. %). Ash is a bulk quantity and EDS a surface one, so read together they indicate that the mineral matter of lignite is finely disseminated through the organic matrix rather than concentrated as discrete phases at the exposed surface, while that of anthracite occurs as inclusions large enough to be resolved by a micrometer-scale probe. Total sulfur runs the other way, rising to 6.78 % in lignite against 0.64 % in anthracite (Table 1), in the same sense as the surface sulfur measured by EDS, so that element is present in both the bulk and the surface of the low-rank coal. The nanomechanical maps add the final leg, and they corroborate the spatial argument: the modulus range of 0.4–50 GPa within one anthracite field spans the compliant organic matrix, the stiffer inertinitic material and the mineral inclusions independently identified by EDS, a within-grain heterogeneity invisible to any bulk mechanical test and consistent with the rank-resolved nanomechanical differences reported by Zhang et al. [31] and with the micro- to nanoscale heterogeneity documented by Tian et al. [32]. The higher dissipation energy of anthracite, and the ~80 nm lag between the modulus maximum and the indentation-depth minimum, indicate a relaxation time comparable to the approach–retract cycle: a denser covalent cross-link network stores more strain energy per indentation and also loses more of it per cycle, the behavior expected of the viscoelastic response measured by force-curve hysteresis [33]–[36].

Taken together, these strands define what is new here. The methodological contribution is the demonstration that optothermal Raman thermometry, developed for suspended two-dimensional crystals and thin films [19]–[23] and until now confined to specimens of controlled geometry, transfers to an opaque, porous, chemically heterogeneous natural solid measured in its as-received state, and that it does so within a protocol that adds only a calibration run and a power ramp to a standard micro-Raman session and requires no polishing, embedding, coating or compaction. The scientific contribution is the closure of the mechanistic chain on one specimen: thermal transport, aromatic ordering, elemental composition, surface electrostatics and viscoelastic response were measured on the same as-received grains and shown to be governed by one variable, with the cross-validations of Fig. 6f and 6g providing the internal consistency check that the critical Raman literature [17] has called for; the electrostatic and viscoelastic legs of that chain are established on the two high-rank coals, for which the as-received relief lies within the vertical range of the scanner. A third element follows from the proximate data: because the grain-scale descriptors are referred to a standardized bulk determination made on the same coals, the rank assignment is independent of the measurements

being interpreted and the micro-Raman descriptor is calibrated against the quantity — volatile matter — on which fuel specifications are actually written. The consequence for the assessment of energetic quality is direct. The properties that determine how much energy a coal contains and how readily it can be released — aromaticity, volatile content, oxygen functionality, mineral load and the thermal resistance of the solid itself — are read here from a single grain, in one session, as a set of mutually consistent numbers: FWHM_G and the G–D1 separation for aromatic ordering, A_{D1}/A_G for medium-range order above the amorphous limit, O/C for the oxygen functionality that dilutes calorific value, the EDS minor-element budget for the spatial distribution of the mineral matter that reports as ash, and κ_{eff} together with R_{th} for the thermal behavior of the grain. The calibration of FWHM_G against volatile matter in Fig. 6g converts the first of these from a structural descriptor into a fuel descriptor, since volatile matter governs ignition behavior, flame stability and coking propensity and enters the ASTM D388 classification directly [8]. Because the structure–conductivity relation established for bulk coals [6] is reproduced here at the grain scale and with the pore and contact contributions excluded, these descriptors provide the missing link between molecular structure and the effective conductivities used in combustion, gasification and coking models — and the same descriptors govern the suitability of a given rank as a precursor for coal-derived carbons, where the parent aromatic architecture controls the performance of the derived material [1], [2]. Three directions follow. The absolute scale of κ_{eff} should be established against a reference specimen of known conductivity measured under identical optics, so that the spot-referenced value can be converted into an intrinsic one; the low-rank regime should be resolved by combining time-resolved optothermal acquisition with the loss model of Vallin et al. [26] and with a grain-resolved measure of the agglomerate coverage, so that the phononic and non-phononic contributions identified above can be separated quantitatively; and the protocol should be applied to a larger rank population with paired vitrinite reflectance and calorific value, since the correlation between FWHM_G and volatile matter established here on three coals needs both the statistical weight of a wider population and a direct link to heating value before the descriptor set demonstrated here becomes a calibrated quality index.

5. Conclusions

Optothermal Raman thermometry has been applied for the first time to individual, as-received grains of anthracite, semi-anthracite and lignite and combined, on those same grains, with five-band micro-Raman deconvolution, SEM-EDS and AFM-based surface and nanomechanical mapping, the bulk proximate composition and the ASTM D388 rank assignment of the same coals providing an independent reference. Calibration of the G-band thermometer between 293 and 873 K and a stepwise power ramp (Fig. 1) yielded effective grain conductivities of 17.2 ± 3.7 , 5.3 ± 1.8 and $29.9 \pm 6.5 \text{ W m}^{-1} \text{ K}^{-1}$ (Fig. 6a): anthracite conducts about three times better than semi-anthracite, in the order predicted by its narrower G band, while lignite returns the highest value of the series because its 36.60 % volatile matter, borne on the surface as rounded agglomerates, together with an open, low-circularity pore network, opens non-phononic channels for heat removal. Across the series the G-band width narrows from 69.24 to 53.11 cm^{-1} and the G–D1 separation widens from 234 to 244 cm^{-1} (Fig. 2), the O/C atomic ratio falls from 0.343 to 0.066 (Fig. 3i), the contact-potential dispersion widens from 50.9 μV to 369 mV (Fig. 4) and the dissipation energy rises from 0.5–1.75 to 1–5 fJ (Fig. 5), so that a single variable

— the growth of the condensed aromatic domain during coalification — accounts for the thermal, structural, compositional, electrostatic and mechanical behavior of the same material; the linear relations between the G-band width and two independent compositional measurements, the EDS oxygen-to-carbon ratio of the surface and the proximate volatile matter of the bulk (Fig. 6f, g), provide the internal cross-validation of that claim, and the coincidence of the measured conductivities with the optothermal-Raman range of low-ordered carbon fibers (Fig. 6h) sets the thermal scale. The impact of the work is that it supplies a preparation-free, spatially resolved thermal descriptor of coal at the scale on which its aromatic architecture is organized, one to two orders of magnitude above the values that conventional bulk methods return, which quantifies how much of the thermal resistance of a coal bed belongs to its architecture rather than to its substance and, through the calibration of the G-band width against volatile matter, connects molecular structure to the descriptor on which fuel specifications are written. The scope of the demonstration is defined by three boundaries: the reported conductivity is referred to the source radius and is therefore a comparative measure between grains examined under identical optics rather than an absolute intrinsic value; the electrostatic and nanomechanical maps cover the two high-rank coals; and three rank classes establish the internal consistency of the descriptor set without calibrating a continuous quality index. Future work should therefore anchor the absolute scale against a reference material of known conductivity measured under identical optics, resolve the low-rank regime by combining time-resolved optothermal acquisition with an explicit loss model and a grain-resolved measure of agglomerate coverage, and extend the protocol to a rank population large enough, with paired vitrinite reflectance and calorific value, to convert the descriptor set demonstrated here into a calibrated index of the energetic quality of solid carbonaceous fuels.

CRedit authorship contribution statement

H. A. Estupiñán Durán: Conceptualization, Methodology, Formal analysis, Supervision, writing – original draft, Writing – review & editing, Funding acquisition. J. J. Rosero Romo: Investigation, Formal analysis, Visualization, Writing – original draft. G. Neira Arenas: Resources, Investigation, Writing – review & editing.

Funding

This work was supported by the Universidad Nacional de Colombia.

Data availability

The Raman spectra, force–distance curves, AFM images and proximate analysis data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of competing interest

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

Acknowledgements

The authors acknowledge the Facultad de Minas, Universidad Nacional de Colombia, Medellín, and the Laboratorio de Biomateriales for technical support.

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